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PhD Thesis

Rehabilitation of contaminated soils and water using "tailor-made" Technosols

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TESIS DE DOCTORADO

REHABILITATION OF CONTAMINATED SOILS AND WATER USING “TAILOR-MADE” TECHNOSOLS

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D./Dna. **Maria João Cerveira Fernandes**

Título da tese: **Rehabilitation of contaminated soils and water using “tailor-made” Technosols**

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Rehabilitation of contaminated soils and water using "tailor-made" Technosols

D. Juan Manuel Lema Rodicio

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Rehabilitation of contaminated soils and water using "tailor-made" Technosols

D./Dna. Felipe Macias Vazquez
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En Santiago de Compostela, 3 de Abril de 2023

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RESUMO

A contaminación ambiental, a alteración dos procesos ambientais naturais que afectan tanto aos compoñentes físicos como biolóxicos do sistema Terra/atmosfera, representa un problema grave e actual para a sociedade moderna. O notable crecemento da poboación provocou cambios profundos nos patróns de consumo, incluíndo as necesidades alimentarias e sanitarias, e o conseguinte uso excesivo de substancias como pesticidas (produción de alimentos) e farmacéuticos (saúde humana e animal). Tanto os produtos farmacéuticos como os pesticidas considéranse cada vez máis produtos químicos de preocupación emerxente, con efectos negativos coñecidos sobre as especies do solo e acuáticas e os seus respectivos ecosistemas, así como efectos potenciais sobre a saúde humana.

A fluoxetina é un antidepresivo moi utilizado para tratar a depresión. Como ocorre con outros produtos farmacéuticos, só unha parte deste composto é metabolizada polo corpo humano, mentres que o resto, así como os seus metabolitos, son excretados, chegando finalmente aos sistemas de augas residuais e potencialmente ao medio ambiente.

O glifosato e o glufosinato, dous herbicidas organofosforados non selectivos de amplo espectro, e o ácido aminometilfosfónico (AMPA), o principal metabolito do glifosato, tamén son tres compostos de interese. O nivel de exposición de humanos e animais e os efectos nocivos destes compostos están amplamente documentados.

Ademais doutros contaminantes emerxentes, a contaminación ambiental por fluoxetina, glifosato, glufosinato e AMPA require de medidas correctoras, impoñendo o desenvolvemento de tecnoloxías de remediación para a rehabilitación das zonas afectadas.

Estudáronse e desenvolvéronse diversas tecnoloxías de remediación para facer fronte ás contaminacións ambientais. Unha destas tecnoloxías de remediación é a adsorción, un método no que as moléculas ou partículas dunha substancia son retidas na superficie dun material sólido ou líquido a través de diversos mecanismos, como a atracción electrostática, forzas de *Van der Waals* ou enlaces químicos. Úsase habitualmente en procesos industriais para eliminar impurezas de líquidos ou gases, así como na rehabilitación de solos, tratamento de augas residuais e depuración de auga potable. Ademais, é un proceso que se produce de forma espontánea en diversos sistemas naturais, como no solo, beneficiando a absorción de nutrientes por parte das plantas ou a adsorción de gases da atmosfera polas partículas do solo. A adsorción inflúe significativamente na transferencia e dispoñibilidade de pesticidas no solo, sendo un dos principais procesos para controlar a lixiviación dos pesticidas e reducir a

súa migración e o potencial de contaminación das augas superficiais ou subterráneas. Dado que é moi utilizado no tratamento de augas residuais a gran escala, pola súa estrutura sinxela, a súa alta eficiencia e a posibilidade de utilizar adsorbentes non tóxicos e de baixo custo, pódese optimizar e aplicar para a eliminación de produtos farmacéuticos e pesticidas. Para estudar a adsorción de diferentes tipos de substancias como fluoxetina, glifosato, AMPA e glufosinato, é fundamental avaliar a utilización dunha gran variedade de materiais adsorbentes e as súas propiedades fisicoquímicas. A súa selección é de gran importancia, e características como o baixo custo, a sustentabilidade, a non toxicidade e a alta capacidade de absorción son atributos importantes a ter en conta.

O biochar é un material poroso sólido e estable cun alto contido en carbono, producido mediante a pirólise/carbonización da biomasa nun ambiente de osíxeno limitado ou nulo e condicións de temperatura moderadas. É un material atractivo para ser usado como adsorbente para reter e eliminar contaminantes de ambientes acuosos. O seu uso preséntase como unha ferramenta de xestión ambiental, actuando na mellora do solo, no tratamento de residuos, na mitigación do cambio climático e na produción de enerxía. Ademais de ser economicamente atractivo, o biochar utilízase amplamente como adsorbente debido á súa alta capacidade de retención de diferentes contaminantes asociados á súa elevada superficie específica e porosidade, capacidade de intercambio iónico e pH. A selección da materia prima pode influír en gran medida nas súas propiedades, así como nas condicións do proceso de produción, a saber, a temperatura, a velocidade de calefacción, a presión e o tempo de residencia.

Outra tecnoloxía innovadora de remediación é o uso de Tecnosoles "á carta". Os Tecnosoles son un grupo de solos de referencia definidos na World Reference Base para os recursos do solo (da Organización das Nacións Unidas para a Agricultura e a Alimentación e a Unión Internacional de Ciencias do Solo) como unha combinación de solos "*cuxas propiedades e pedoxénese están dominadas pola súa orixe técnica*". Estes solos están significativamente dominados ou fortemente influenciados por material feito polo home, fortemente alterado (denominados artefactos como materiais de refugallo, a saber, ladrillos, vidro, residuos domésticos, residuos mineiros, lodos, etc.) ou extraídos de maiores profundidades. Atópanse frecuentemente en zonas urbanas e industriais. Os Tecnosoles "á carta" son solos artificiais creados pola combinación de solo natural con materiais antropoxénicos, derivados das actividades humanas, con outros aditivos para obter as características desexadas. Replican as funcións do solo natural e pódense utilizar para proporcionar varias funcións do solo e servizos ecosistémicos, como condicións adecuadas para o crecemento/produción de plantas (alimentos e biomasa), a remediación do solo, o secuestro de carbono, a restauración de masas de auga e áreas degradadas ou contaminadas, recarga de augas subterráneas e biodiversidade do ecosistema. O biochar é un dos materiais que se poden incorporar á produción de Tecnosoles "á carta".

Así, como primeira aproximación aos problemas abordados neste traballo, realizouse o seguimento de antibióticos e antidepresivos nas augas e sedimentos de dous ríos do norte de Portugal. Recolléronse mostras de sedimentos de dúas capas, a capa superior, de entre 0 e 2 cm de profundidade, e a capa inferior, de entre 2 e 10 cm. O presente estudo incluíu a caracterización e análise de mostras de dezasete antibióticos e dez antidepresivos. A comparación das concentracións de fármacos en mostras do río Leça e do río Douro revelou niveis máis altos no río Leça. Nas mostras de auga do Douro só se detectaron carbamazepina e fluoxetina, mentres que as de Leça contiñan trece dos vinte e sete produtos farmacéuticos, entre eles seis antibióticos e sete psiquiátricos. En particular, a azitromicina atopouse na maior concentración (2.82 µg/L) en mostras do río Leça, especialmente preto dun punto de vertido de efluentes dunha estación depuradora de augas residuais. A fluoxetina presentou a maior frecuencia de detección nas mostras de auga. A presenza de carbamazepina e venlafaxina na auga do río Leça revelou posibles riscos para as algas. Nas mostras de sedimentos atopouse sulfametoxipiridazina no sedimento do Douro, mentres que no sedimento de Leça detectouse azitromicina, ambos principalmente na capa superior do sedimento. Tamén se detectaron fármacos psiquiátricas, catro no sedimento do Douro e seis en Leça. Unha comparación entre as capas superior e inferior do sedimento en cada punto de mostraxe mostrou que a venlafaxina, o único fármaco cuantificado no río Douro, tiña unha maior concentración na zona baixa, potencialmente relacionada coa migración do solo. Nos sedimentos de Leça observáronse maiores concentracións na capa superior, probablemente asociadas a episodios recentes de contaminación da zona. Unha revisión dos estudos de seguimento informados na literatura revelou unha inclusión reducida das análises de sedimentos, coa maioría dos estudos centrándose unicamente en mostras de auga (especialmente para fármacos psiquiátricos). Polo tanto, non foi posible identificar un patrón de contaminación consistente nin establecer un vínculo claro entre a contaminación dos sedimentos e a migración de contaminantes da auga, a partir dos resultados obtidos e das comparacións da literatura. Non obstante, observáronse de forma consistente concentracións máis elevadas de contaminantes nos lugares de mostraxe augas abaixo dos vertidos das estacións de tratamento de augas residuais.

Ademais, realizouse unha revisión da literatura sobre a contaminación de auga e sedimentos por glifosato, AMPA e glufosinato en todo o mundo. O obxectivo foi investigar a contaminación e mobilidade das referidas substancias en ambientes acuáticos, con especial atención ás mostras de auga e sedimentos. A investigación incluíu unha exhaustiva revisión bibliográfica para analizar os estudos publicados nos últimos cinco anos que monitorizaron as concentracións destes compostos nas augas (tanto superficiais como subterráneas) e nos sedimentos. A análise da lexislación aplicable revelou variacións significativas nos valores límite destes contaminantes nos diferentes países. Por exemplo, a Unión Europea estableceu o límite legal máis baixo para os residuos de glifosato na auga potable en 0.1 µg/L, mentres que Xapón estableceu o límite máis alto en 2 000 µg/L. Os métodos de detección máis utilizados nos estudos analizados foron a cromatografía líquida de alta resolución (HPLC) con espectrometría de masas en tándem (MS/MS). Non obstante, comprobouse que só o 40% dos estudos revisados informaron límites de detección inferiores ao valor máximo permitido da Unión Europea para a contaminación da auga por pesticidas individuais (0.1 µg/L). O seguimento da investigación do glifosato na auga e nos sedimentos revelou tendencias interesantes. Francia resultou ser o país con maior proporción mostras/publicación, seguido de Xapón e Italia. Arxentina, pola súa banda, presentou unha maior frecuencia de publicacións de estudos, pero unha menor proporción mostra/publicación. En particular, os países europeos que realizaron un maior número de análises de niveis de glifosato tenden a corresponder a unha maior taxa de aplicación de glifosato. En canto ao seguimento da AMPA, Arxentina presentou unha maior frecuencia de estudos, mentres que Francia mantivo a súa posición como o país con maior ratio mostras/publicación, seguido de Estados Unidos, Suecia e Italia. China destacou cun número significativamente maior de mostras monitorizadas para glufosinato en comparación con outros países con publicacións sobre este composto. As concentracións máximas de contaminantes variaron en función da matriz ambiental. Nas augas superficiais atopáronse as concentracións máis altas para o AMPA (6 872 µg/L), seguido do glifosato (5 750 µg/L) e o glufosinato (13.15 µg/L). Nas augas subterráneas, os valores máximos foron 8 700 µg/L para o glifosato, 233 µg/L para o AMPA e 0.03 µg/L para o glufosinato. Os sedimentos mostraron as concentracións máis altas de glufosinato detectadas (14.9 µg/kg), mentres que o glifosato e o AMPA alcanzaron concentracións máximas de 1 882 µg/kg e 4 033 µg/kg, respectivamente. Contrariamente ás expectativas, a concentración máxima de glifosato foi maior nas augas subterráneas que nas superficiais. Non obstante, a frecuencia de detección foi significativamente maior nas augas superficiais (70%) en comparación coas augas subterráneas (18%). No que respecta a AMPA e glufosinato, a frecuencia de detección nas augas superficiais foi do 87% e do 6%, respectivamente, mentres

que nas subterráneas foi do 16% e do 0.7%. Os países sudamericanos presentaron os valores máis altos de concentración máxima detectada para glifosato e AMPA, mentres que os sedimentos foron a matriz ambiental con maior concentración de glufosinato. Francia tivo as concentracións máximas máis altas de glifosato nas augas superficiais, seguida de Italia e Alemaña. Nas augas subterráneas, Suecia tivo as concentracións máis altas de glifosato, seguida de Italia. Alemaña e Croacia presentaron os niveis máximos de concentración nos sedimentos. Identificáronse varios factores como impulsores da dispersión destes compostos nas augas superficiais, sedimentos e subterráneas. Estes factores incluíron a sobrepulverización, a deriva da pulverización, a escorrentía superficial, as capas freáticas pouco profundas, a baixa condutividade hidráulica dos acuíferos, o baixo gradiente hidráulico, a velocidade de fluxo moi baixa, o tipo de solo e a constitución química. Identificáronse como fontes potenciais de contaminación a aplicación persistente e crecente destes compostos en actividades agrícolas e domésticas, o uso inadecuado e as depuradoras de augas residuais. Esta revisión aclarou o problema da contaminación e a mobilidade do glifosato, AMPA e glufosinato na auga e nos sedimentos. Os resultados subliñaron a necesidade dun seguimento e desenvolvemento continuos de estratexias de remediación para mitigar o impacto ambiental destes compostos. Os resultados tamén destacaron a importancia da lexislación harmonizada e dos valores límite unificados en todos os países para garantir a protección.

Tendo en conta a contaminación documentada asociada aos compostos investigados, é fundamental identificar tecnoloxías de remediación que non só abordan os lugares contaminados, senón que tamén reducen a mobilidade destes compostos. Estas tecnoloxías poden evitar a contaminación da auga e do solo e minimizar os problemas de saúde asociados á inxestión destes compostos. En consecuencia, esta investigación centrouse no estudo da adsorción de fluoxetina, glifosato, AMPA e glufosinato sobre diversos materiais, de diferentes características, co fin de comprender e optimizar a súa adsorción. Para iso, desenvolvéronse estudos de adsorción, concretamente ensaios de equilibrio, cinética e influencia do pH, para estudar a adsorción dos catro compostos ensaiados. Probáronse diferentes adsorbentes con diferentes características para atopar os materiais e características máis idóneas para integrar a composición dun Technosol "á carta". Se se aplica á produción dun Technosol "á carta", os resultados permitirán desenvolver unha solución innovadora e integrada que contribúa a mellorar a calidade dos recursos naturais, a sustentabilidade, a redución da produción de residuos e a restauración de zonas contaminadas.

Na primeira fase do estudo probáronse doce biochars derivados de diferentes residuos forestais e agroalimentarios (podas de *Quercus ilex*, Eu*calyptus grandis, Pinus pinaster,* *Quercus suber, Malus pumila, Prunus spinosa, Cydonia oblonga, Eriobotrya japonica, Juglans regia). , Actinidia deliciosa, Citrus sinensis* e *Vitis vinifera*) como potenciais adsorbentes de baixo custo e renovables para a eliminación da fluoxetina da auga. Os experimentos de adsorción preliminares permitiron seleccionar os adsorbentes máis prometedores, material de poda de *Quercus ilex* (aciñeira), *Cydonia oblonga* (marmelo), *Eucalyptus, Juglans regia* (nogueira) e *Vitis vinifera* (vide). Caracterizáronse por análise proximal, elemental e mineral, análise termogravimétrica, espectroscopia infravermella por transformada de Fourier, determinación da superficie específica e pH no punto de carga cero (pH_{PZC}). Realizáronse estudos de lotes e de equilibrio, e avaliouse a influencia do pH. Determináronse as capacidades de adsorción dos biochars seleccionados, con valores que oscilan entre 2.21 e 6.41 mg/g segundo o modelo de Langmuir. Entre os biochars probados, o biochar de eucalipto mostrou a maior capacidade de adsorción, seguido dos biochars de aciñeira, vide, nogueira e marmelo. A cinética de adsorción foi rápida, a adsorción completa produciuse en menos de 15 minutos. Os experimentos de adsorción en columna realizados con biochar de eucalipto demostraron a súa eficacia en modo continuo, presentando unha taxa de eliminación do 50% aos 90 minutos, o que suxire o seu potencial como alternativa renovable para a eliminación da fluoxetina.

A seguinte fase da investigación centrouse en investigar a adsorción de glifosato, AMPA e glufosinato en corenta e un materiais diferentes, incluíndo biochar, solos e Tecnosoles "á carta" (TMT). Os biochars probados foron producidos a partir de troncos de acacia (*Acacia melanoxylon*) divididos en albura (BAcSw-3) e duramen (BAcHw-2), ramas de eucalipto (BEu-2), serrín de piñeiro (BSd-1), casca de piñeiro (BPb), compost de orujo de oliva (BOpc), casca de arroz (BRh), mazorca de millo (BCc1 e BCc-2) e virutas de madeira trituradas alemás (BSdG). As oito mostras de solo analizadas foron Umbrisois Aluminicos (S4A, 11B, 13A), Ferrasois derivados de Anfibolitas (S9B), Umbrisois Háplicos (1Ah e 2Ah) e Leptosois Andicos e Ferralicos. En relación ao Technosol "á carta" (TMT), os materiais ensaiados clasificáronse como Tecnosol cálcico-arénico (TMT 1), Tecnosoles aluándicos (TMT 2), Tecnosoles ándicos éutricos (TMT 3, G, I, J, K, L, M, Q, R e S), Tecnosoles éutricos reductores (TMT 4 e A), Tecnosoles dístricos (TMT B e D), Tecnosoles cálcicos (TMT C), Tecnosoles andicos (TMT E e F), Tecnosoles eutricos (TMT H e O), Tecnosoles férricos (TMT N) e Tecnosoles andicos reductores (TMT P). Estes TMT producíronse a partir de residuos industriais e agroindustriais, é dicir, sedimentos da mina, biomasa de serrín, lodos de tratamento de augas residuais, compost orgánico, cinzas e area. Os resultados indicaron que os tres compostos foron mal adsorbidos pola maioría das mostras de biochar, con taxas máximas de eliminación do 25% para o glifosato, o 12% para o AMPA e o 4% para o glufosinato. Estes resultados atribuíronse principalmente á temperatura de produción do biochar. Pola contra, os solos ensaiados mostraron altas capacidades de adsorción de glifosato e AMPA, con taxas máximas de eliminación do 94% e do 91% en probas preliminares, respectivamente. Non obstante, a adsorción de glufosinato foi limitada, con taxas de eliminación non superiores ao 6%. Os TMT tamén mostraron capacidades de adsorción significativas durante as probas preliminares, con taxas máximas de eliminación do 79% para o glifosato e do 83% para o AMPA. Unha vez máis, o glufosinato mostrou baixos valores de adsorción, cunha taxa de eliminación máxima de só un 3%. Ademais, descubriuse que tamaños de grans máis pequenos melloran o rendemento de adsorción en comparación cos solos ou TMT con tamaños de grans maiores. O tempo de equilibrio para a adsorción variou, producíndose a adsorción total en 14 horas para os solos e 72 horas para os TMT, de acordo cos achados anteriores na literatura. As capacidades máximas de adsorción, segundo o modelo de Langmuir, determináronse en 10.84 mg/g para glifosato (solo S9B) e 15.08 mg/g para AMPA (TMT 1). En canto á influencia do pH no proceso de adsorción, o glifosato e o AMPA presentan diferentes comportamentos de carga. Analizando o impacto do pH no proceso de adsorción cos adsorbentes ensaiados, que teñen un pH_{PZC} de aproximadamente 4,9, a adsorción de glifosato e AMPA mostrou un comportamento dependente do pH. A adsorción aumentou entre pH 1 e pH 3, correspondente á perda de protóns asociada ao grupo carboxilo do glifosato (pKa_2) e ao grupo fosfónico do AMPA (pKa_1) en presenza dunha superficie adsorbente predominantemente cargada positivamente. Posteriormente, produciuse unha diminución gradual da adsorción entre pH 3 e pH 6, máis acusada para o glifosato que para o AMPA. Entre pH 6 e 10, a adsorción de glifosato nos adsorbentes probados diminuíu significativamente, excepto no caso de TMT 1, que só mostrou unha reducida adsorción a pH superior a 10, achegándose a valores próximos a cero. No caso de AMPA, a redución da adsorción por TMT produciuse de forma máis destacada a partir de valores de pH superiores a 9, observándose unha adsorción relativamente constante entre pH 6 e 10 para o resto de adsorbentes. Para todos os adsorbentes, houbo unha notable diminución da adsorción a valores próximos a cero entre pH 10 e 12, agás a adsorción de glifosato en solo S4A, que mostrou unha adsorción lixeiramente maior a pH 12 en comparación cos outros adsorbentes. En xeral, a maior adsorción de glifosato e AMPA aos solos e TMT produciuse dentro do intervalo de pH de 2 a 5, coas superficies adsorbentes predominantemente cargadas positivamente, e aínda que a principal forma iónica de AMPA dentro deste intervalo de pH é neutra. Estes achados demostran que os solos naturais e os TMT poden servir como adsorbentes eficaces, de baixo custo e sostibles para eliminar o glifosato e o AMPA das solucións acuosas. Ademais, para a produción de TMT, débense seleccionar materiais con pH relativamente baixo e alto contido de óxidos de aluminio e ferro, arxila e materia orgánica. O desenvolvemento de Tecnosoles “a la carta” ofrece unha solución innovadora e integrada que contribúe a mellorar a calidade dos recursos naturais, promovendo a sustentabilidade, reducindo a produción de residuos e restaurando zonas contaminadas.

En xeral, os coñecementos adquiridos permiten coñecer mellor o estado actual de contaminación ambiental por produtos farmacéuticos e praguicidas, xa que demostra que a contaminación non só chega aos cursos de auga, senón que tamén afecta aos sedimentos e ás augas subterráneas. Esta investigación proporciona datos valiosos sobre a adsorción de fluoxetina, glifosato, AMPA e glufosinato en diferentes materiais. Os estudos de adsorción mostraron, entre outros resultados, que os materiais biochar probados xurdiron como excelentes materiais adsorbentes de fluoxetina pero, pola contra, non teñen unha boa capacidade de retención de compostos como o glifosato, o AMPA e, especialmente, o glufosinato. Por outra banda, os solos e Tecnosoles mostraron unha alta capacidade de retención de glifosato e AMPA. O glufosinato non tendeu a adsorbirse a ningún dos materiais ensaiados.

Os resultados apoian o desenvolvemento de tecnoloxías de remediación destinadas a mitigar o impacto ambiental destes compostos, previr a contaminación e salvagardar a saúde pública. Ademais, propoñen o uso do biochar como compoñente dos tecnosoles producidos para reter a fluoxetina. Tamén destaca algunhas das características fundamentais que se requiren dos constituíntes do tecnosol para a correcta adsorción do glifosato e do AMPA.

RESUMEN

La contaminación ambiental, la alteración de los procesos ambientales naturales que afectan tanto a los componentes físicos como biológicos del sistema Tierra/atmósfera, representa un problema grave y actual para la sociedad moderna. El notable crecimiento demográfico ha provocado profundas alteraciones en los patrones de consumo, incluyendo las necesidades alimentarias y sanitarias, y el consiguiente uso excesivo de sustancias como los plaguicidas (producción de alimentos) y los productos farmacéuticos (salud humana y animal). Tanto los productos farmacéuticos como los plaguicidas se consideran cada vez más sustancias químicas de preocupación emergente, con efectos negativos conocidos sobre el suelo y las especies acuáticas y sus respectivos ecosistemas, así como efectos potenciales sobre la salud humana.

La fluoxetina es un antidepresivo ampliamente utilizado para tratar la depresión. Como ocurre con otros productos farmacéuticos, sólo una parte de este compuesto es metabolizada por el cuerpo humano, mientras que el resto, así como sus metabolitos, son excretados, alcanzando eventualmente los sistemas de aguas residuales y potencialmente el medio ambiente.

El glifosato y el glufosinato, dos herbicidas organofosforados no selectivos de amplio espectro, y el ácido aminometilfosfónico (AMPA), metabolito principal del glifosato, son también tres compuestos de interés. El nivel de exposición de humanos y animales y los efectos nocivos de estos compuestos están ampliamente documentados.

Así como otros contaminantes emergentes, la contaminación ambiental por fluoxetina, glifosato, glufosinato y AMPA, requiere medidas correctoras, imponiéndose el desarrollo de tecnologías de remediación para la rehabilitación de las zonas afectadas.

Se han estudiado y desarrollado varias tecnologías de remediación para tratar las contaminaciones medioambientales. Una de estas tecnologías de remediación es la adsorción, un método en el que las moléculas o partículas de una sustancia son retenidas en la superficie de un material sólido o líquido a través de distintos mecanismos, como la atracción electrostática, las fuerzas de Van der Waals o los enlaces químicos. Se utiliza habitualmente en procesos industriales para eliminar impurezas de líquidos o gases, así como en la rehabilitación de suelos, en el tratamiento de aguas residuales y en la purificación de agua potable. Además, es un proceso que ocurre espontáneamente en diversos sistemas naturales, como en el suelo, beneficiando la absorción de nutrientes por las plantas o la adsorción de gases de la atmósfera por las partículas del suelo. La adsorción influye significativamente en

la transferencia y disponibilidad de los plaguicidas en el suelo, siendo uno de los principales procesos de control de la lixiviación de plaguicidas y reduciendo su migración y el potencial de contaminación de las aguas superficiales o subterráneas. Dado que se utiliza ampliamente en tratamientos de aguas residuales a larga escala, debido a su sencilla estructura, su alta eficiencia y la posibilidad de utilizar adsorbentes de bajo coste y no tóxicos, puede optimizarse y aplicarse a la eliminación de productos farmacéuticos y plaguicidas. Para estudiar la adsorción de diferentes tipos de sustancias como la fluoxetina, el glifosato, el AMPA y el glufosinato, es esencial evaluar el uso de una amplia variedad de materiales adsorbentes y sus propiedades fisicoquímicas. Su selección es de gran importancia, y características como el bajo coste, la sostenibilidad, la no toxicidad y la alta capacidad de sorción son atributos significativos a tener en cuenta.

El biochar es un material poroso sólido y estable con alto contenido en carbono, producido a través de la pirólisis/carbonización de biomasa en un entorno de oxígeno limitado o ausente y en condiciones de temperatura moderada. Es un material atractivo para ser implementado como adsorbente para retener y eliminar contaminantes de ambientes sólidos y acuosos. Su uso se presenta como una herramienta para la gestión medioambiental, actuando en la mejora de la calidad de los suelos, en el tratamiento de residuos, en la mitigación del cambio climático y en la producción de energía. Además de ser económicamente atractivos, los biochar se utilizan en gran medida como adsorbentes debido a su alta capacidad de retención de distintos contaminantes asociada a su elevada superficie específica y porosidad, capacidad de intercambio iónico y pH. La selección de la materia prima puede influenciar ampliamente sus propiedades, así como las condiciones del proceso de producción, es decir, la temperatura, la rapidez de calentamiento, la presión y el tiempo de residencia.

Otra tecnología innovadora de remediación es el uso de Tecnosoles “a la carta”. Los Tecnosoles son un grupo de suelos de referencia definido en la World Reference Base para los recursos edáficos (de la Organización de las Naciones Unidas para la Agricultura y la Alimentación y la Unión Internacional de Ciencias del Suelo) como una combinación de suelos "*cuyas propiedades y pedogénesis están dominadas por su origen técnico*". Estos suelos, dominados o fuertemente afectados por materiales fabricados por el hombre y fuertemente modificados (denominados artefactos, como residuos de materiales como ladrillos, vidrio, residuos domésticos, residuos de minas, lodos, entre otros) o extraídos de grandes profundidades, se encuentran con frecuencia en zonas urbanas e industriales. Los Tecnosoles "a la carta" son suelos artificiales creados mediante la combinación de suelo natural con materiales antropogénicos, derivados de actividades humanas, con otros aditivos para obtener las características deseadas. Replican las funciones del suelo natural y pueden utilizarse para proporcionar varias funciones del suelo y servicios ecosistémicos, como condiciones adecuadas para el crecimiento/producción de plantas (alimentos y biomasa), la recuperación del suelo, el secuestro de carbono, la restauración de masas de agua y zonas degradadas o contaminadas, la reposición de aguas subterráneas y la biodiversidad de los ecosistemas. El biochar es uno de los materiales que pueden incorporarse en la producción de Tecnosoles "a la carta".

Así, como una primera aproximación a los problemas abordados en este trabajo, se llevó a cabo el monitoreo de antibióticos y antidepresivos en las aguas y sedimentos de dos ríos del norte de Portugal. Se recogieron muestras de sedimentos de dos camadas, la camada superior, entre 0 y 2 cm de profundidad, y la camada inferior, entre 2 y 10 cm. El presente estudio incluyó la caracterización y el análisis de muestras para diecisiete antibióticos y diez antidepresivos. La comparación de las concentraciones de fármacos en las muestras del río Leça y del río Douro reveló niveles más elevados en el río Leça. Sólo se detectaron carbamazepina y fluoxetina en las muestras de agua del Douro, mientras que las muestras de agua de Leça contenían trece de los veintisiete productos farmacéuticos, incluidos seis antibióticos y siete fármacos psiquiátricos. En particular, la azitromicina se encontró en la concentración más alta (2.82 µg/L) en las muestras del río Leça, especialmente cerca de un punto de descarga de efluentes de una planta de tratamiento de aguas residuales. La fluoxetina presentó la mayor frecuencia de detección en las muestras de agua. La presencia de carbamazepina y venlafaxina en el agua del río Leça fue reveladora de riesgos potenciales para las algas. En las muestras de sedimentos, se encontró sulfametoxipiridazina en el sedimento del Douro, mientras que se detectó azitromicina en el sedimento de Leça, ambas principalmente en la camada superior del sedimento. También se detectaron fármacos psiquiátricos, cuatro en el sedimento de Douro y seis en el de Leça. Una comparación entre las camadas superior e inferior del sedimento en cada punto de muestreo mostró que la venlafaxina, el único fármaco cuantificado en el río Douro, presentaba una mayor concentración en la zona inferior, potencialmente relacionada con la migración del suelo. En los sedimentos de Leça, se observaron concentraciones más elevadas en la camada superior, probablemente asociadas a episodios recientes de contaminación en la zona. Una revisión de los estudios de monitorización reportados en la literatura reveló una inclusión reducida de análisis de sedimentos, centrándose la mayoría de los estudios únicamente en muestras de agua (especialmente para drogas psiquiátricas). Por lo tanto, no fue posible identificar un patrón de contaminación consistente ni establecer un vínculo claro entre la contaminación de los sedimentos y la migración de contaminantes del agua, basándose en los resultados obtenidos y en las comparaciones bibliográficas. Sin embargo, se observaron sistemáticamente concentraciones más elevadas de contaminantes en los lugares de muestreo situados aguas abajo de los vertidos de las plantas de tratamiento de aguas residuales.

Además, se realizó una revisión bibliográfica de la contaminación del agua y los sedimentos por glifosato, AMPA y glufosinato en todo el mundo. El objetivo fue investigar la contaminación y la movilidad de las sustancias referidas en los medios acuáticos, con especial atención a las muestras de agua y sedimentos. La investigación incluyó una exhaustiva revisión bibliográfica para analizar los estudios publicados en los últimos cinco años que monitorizaron las concentraciones de estos compuestos en agua (tanto superficial como subterránea) y sedimentos. El análisis de la legislación aplicable reveló variaciones significativas en los valores límite de estos contaminantes en los distintos países. Por ejemplo, la Unión Europea estableció el límite legal más bajo para los residuos de glifosato en el agua destinada al consumo humano, con un límite de 0.1 µg/L, mientras que Japón estableció el límite más alto en 2 000 µg/L. Los métodos de detección más utilizados en los estudios analizados fueron la cromatografía líquida de alta resolución (HPLC) en tándem con la espectrometría de masas (MS/MS). Sin embargo, se encontró que sólo el 40% de los estudios revisados reportaron límites de detección por debajo del valor máximo permisible de la Unión Europea para la contaminación del agua por plaguicidas individuales (0.1 µg/L). La investigación del monitoreo del glifosato en el agua y los sedimentos reveló tendencias interesantes. Francia resultó ser el país con la mayor relación muestras/publicaciones, seguido de Japón e Italia. Argentina, por su parte, presentó una mayor frecuencia de publicaciones de estudios, pero una menor relación muestras/publicaciones. En particular, los países europeos que realizaron un mayor número de análisis del nivel de glifosato tendieron a corresponderse con una mayor tasa de aplicación de glifosato. En cuanto al seguimiento de AMPA, Argentina presentó una mayor frecuencia de estudios, mientras que Francia mantuvo su posición como país con la mayor relación muestras/publicación, seguida de Estados Unidos, Suecia e Italia. China se destacó con un número significativamente mayor de muestras monitoreadas para glufosinato en comparación con otros países con publicaciones sobre este compuesto. Las concentraciones máximas de contaminantes variaron en función de la matriz ambiental. En aguas superficiales, las concentraciones más altas se encontraron para el AMPA (6 872 µg/L), seguido del glifosato (5 750 µg/L) y el glufosinato (13.15 µg/L). En las aguas subterráneas, los valores máximos fueron de 8 700 µg/L para el glifosato, 233 µg/L para el AMPA y 0.03 µg/L para el glufosinato. Los sedimentos mostraron las mayores concentraciones detectadas de glufosinato (14.9

µg/kg), mientras que el glifosato y el AMPA alcanzaron concentraciones máximas de 1 882 µg/kg y 4 033 µg/kg, respectivamente. Contrariamente a lo esperado, la concentración máxima de glifosato fue mayor en las aguas subterráneas que en las superficiales. Sin embargo, la frecuencia de detección fue significativamente mayor en las aguas superficiales (70%) en comparación con las subterráneas (18%). En cuanto al AMPA y al glufosinato, la frecuencia de detección en las aguas superficiales fue del 87% y del 6%, respectivamente, mientras que en las aguas subterráneas fue del 16% y del 0.7%. Los países sudamericanos presentaron los valores más altos de concentración máxima detectada para el glifosato y el AMPA, mientras que los sedimentos fueron la matriz ambiental con mayor concentración de glufosinato. Francia presentó las mayores concentraciones máximas de glifosato en aguas superficiales, seguida de Italia y Alemania. En las aguas subterráneas, Suecia presentó las concentraciones máximas de glifosato, seguida de Italia. Alemania y Croacia presentaron los niveles máximos de concentración en sedimentos. Se identificaron varios factores como impulsores de la dispersión de estos compuestos en aguas superficiales, sedimentos y aguas subterráneas. Estos factores incluían el exceso de pulverización, la deriva de la pulverización, las escorrentías superficiales, los niveles freáticos poco profundos, la baja conductividad hidráulica de los acuíferos, el bajo gradiente hidráulico, la velocidad muy baja del flujo, el tipo de suelo y la constitución química. La aplicación persistente y creciente de estos compuestos en actividades agrícolas y domésticas, el uso inadecuado y las plantas de tratamiento de aguas residuales se identificaron como fuentes potenciales de contaminación. Esta revisión aclaró el problema de la contaminación y la movilidad del glifosato, el AMPA y el glufosinato en el agua y los sedimentos. Los resultados subrayaron la necesidad de llevar a cabo un seguimiento continuo y de desarrollar estrategias de remediación para mitigar el impacto ambiental de estos compuestos. Los resultados también pusieron en relieve la importancia de una legislación armonizada y unos valores límite unificados en todos los países para garantizar una protección eficaz de los recursos hídricos.

A la vista de la contaminación documentada asociada a los compuestos investigados, es crucial identificar tecnologías de remediación que no sólo se ocupen de los lugares contaminados, sino que también reduzcan la movilidad de estos compuestos. Estas tecnologías pueden evitar la contaminación del agua y del suelo y minimizar los problemas de salud asociados a la ingestión de estos compuestos. En consecuencia, esta investigación se centró en el estudio de la adsorción de fluoxetina, glifosato, AMPA y glufosinato sobre diversos materiales, con diferentes características, con el fin de comprender y optimizar su adsorción. Con este fin, se desarrollaron estudios de adsorción, a saber, ensayos de equilibrio, cinéticos y de influencia del pH, para estudiar la adsorción de los cuatro compuestos analizados. Se ensayaron diferentes adsorbentes con características distintas para encontrar los materiales y características más adecuados para integrar la composición de un Technosol "a la carta". Si se aplican a la producción de un Technosol "a la carta”, los resultados permitirán desarrollar una solución innovadora e integrada que contribuya a mejorar la calidad de los recursos naturales, la sostenibilidad, la reducción de la producción de residuos y la restauración de zonas contaminadas.

En la primera fase del estudio se ensayaron doce biochars derivados de diferentes residuos forestales y agroalimentarios (podas de *Quercus ilex*, *Eucalyptus grandis*, *Pinus pinaster*, *Quercus suber*, *Malus pumila*, *Prunus spinosa*, *Cydonia oblonga*, *Eriobotrya japonica*, *Juglans regia*, *Actinidia deliciosa*, *Citrus sinensis* y *Vitis vinifera*) como adsorbentes potenciales, de bajo coste y renovables, para la eliminación de la fluoxetina del agua. Los experimentos preliminares de adsorción permitieron seleccionar los adsorbentes más prometedores, *Quercus ilex* (encina), *Cydonia oblonga* (membrillo), *Eucalyptus, Juglans regia* (nogal) y material de poda de *Vitis vinifera* (vid). Se caracterizaron mediante análisis proximal, elemental y mineral, análisis termogravimétrico, espectroscopia infrarroja por transformada de Fourier, determinación de la superficie específica y pH en el punto de carga cero (pH_{PZC}). Se realizaron estudios por *batch* y de equilibrio, y se evaluó la influencia del pH. Se determinaron las capacidades de adsorción de los biochars seleccionados, con valores que oscilaban entre 2.21 y 6.41 mg/g según el modelo de Langmuir. Entre los biochars ensayados, el biochar de eucalipto mostró la mayor capacidad de adsorción, seguido de los biochars de encina, vid, nogal y membrillo. La cinética de adsorción fue rápida, produciéndose la adsorción completa en menos de 15 minutos. Los experimentos de adsorción en columna realizados con biochar de eucalipto demostraron su eficacia en modo continuo, presentando un avance del 50% de eliminación a los 90 minutos, lo que sugiere su potencial como alternativa renovable para la eliminación de fluoxetina.

La siguiente fase de la investigación se centró en investigar la adsorción de glifosato, AMPA y glufosinato en cuarenta y un materiales diferentes, incluidos biochars, suelos y Tecnosoles "a la carta" (TMT). Los biochars ensayados se produjeron a partir de troncos de acacia (*Acacia melanoxylon*) divididos en albura (BAcSw-3) y duramen (BAcHw-2), ramas de eucalipto (BEu-2), serrín de pino (BSd-1), corteza de pino (BPb), compost de orujo de oliva (BOpc), cascarilla de arroz (BRh), mazorca de maíz (BCc1 y BCc-2), y astillas de madera trituradas alemanas (BSdG). Las ocho muestras de suelo analizadas eran Umbrisoles alumínicos (S4A, 11B, 13A), Ferrasoles derivados de anfibolitas (S9B), Umbrisoles Háplicos (1Ah y 2Ah) y Leptosoles Ándicos y Ferrálicos. En relación con el TMT, los materiales ensayados se clasificaron como Tecnosoles arénicos cálcicos (TMT 1), Tecnosoles aluándicos (TMT 2), Tecnosoles ándicos eútricos (TMT 3, G, I, J, K, L, M, Q, R y S), Tecnosoles eútrico reductores (TMT 4 y A), Tecnosoles dístricos (TMT B y D), Tecnosoles cálcicos (TMT C), Tecnosoles ándicos (TMT E y F), Tecnosoles eútricos (TMT H y O), Tecnosol férrico (TMT N) y Tecnosoles ándicos reductores (TMT P). Estos TMT se produjeron a partir de residuos industriales y agroindustriales, a saber, sedimentos de mina, biomasa de serrín, lodos del tratamiento de aguas residuales, compost orgánico, cenizas y arena. Los resultados indicaron que los tres compuestos fueron pobremente adsorbidos por la mayoría de las muestras de biochar, con tasas máximas de eliminación del 25% para el glifosato, 12% para el AMPA, y 4% para el glufosinato. Estos resultados se atribuyeron principalmente a la temperatura de producción de los biochar. Por el contrario, los suelos ensayados mostraron altas capacidades de adsorción para glifosato y AMPA, con tasas máximas de eliminación del 94% y 91% en los ensayos preliminares, respectivamente. Sin embargo, la adsorción de glufosinato fue limitada, con tasas de eliminación que no superaron el 6%. Los TMT también mostraron capacidades de adsorción significativas durante los ensayos preliminares, con tasas de eliminación máximas del 79% para el glifosato y del 83% para el AMPA. Una vez más, el glufosinato mostró valores de adsorción bajos, con una tasa de eliminación máxima de sólo el 3%. Además, se observó que los tamaños de grano más pequeños mejoraban el rendimiento de la adsorción en comparación con los suelos o TMT con tamaños de grano más grandes. El tiempo de equilibrio para la adsorción varió, produciéndose la adsorción total en 14 horas en el caso de los suelos y en 72 horas en el de los TMT, lo que concuerda con hallazgos anteriores en la bibliografía. Las capacidades máximas de adsorción, según el modelo de Langmuir, se determinaron en 10.84 mg/g para el glifosato (suelo S9B) y 15.08 mg/g para el AMPA (TMT 1). En cuanto a la influencia del pH en el proceso de adsorción, el glifosato y el ácido aminometilfosfónico (AMPA) presentan comportamientos de carga distintos. Analizando el impacto del pH en el proceso de adsorción con los adsorbentes ensayados, que tienen un pHPZC de aproximadamente 4.9, la adsorción de glifosato y AMPA exhibió un comportamiento dependiente del pH. La adsorción aumentó entre pH 1 y pH 3, correspondiendo a la pérdida de protones asociada al grupo carboxilo del glifosato (pKa_2) y al grupo fosfónico del AMPA (pKa_1) en presencia de una superficie adsorbente predominantemente cargada positivamente. Posteriormente, se produjo una disminución gradual de la adsorción entre pH 3 y pH 6, más pronunciada para el glifosato que para el AMPA. Entre pH 6 y 10, la adsorción de glifosato en los adsorbentes ensayados disminuyó significativamente, excepto en el caso de TMT 1, que sólo mostró una adsorción reducida a pH superiores a 10, acercándose a valores próximos a cero. En el caso del AMPA, la reducción

de la adsorción por los TMT se produjo de forma más destacada a partir de valores de pH superiores a 9, observándose una adsorción relativamente constante entre pH 6 y 10 para el resto de adsorbentes. Para todos los adsorbentes, se produjo una notable disminución de la adsorción hasta valores cercanos a cero entre pH 10 y 12, excepto para la adsorción de glifosato en el suelo S4A, que mostró una adsorción ligeramente superior a pH 12 en comparación con los otros adsorbentes. En general, la mayor adsorción de glifosato y AMPA en suelos y TMTs ocurrió dentro del rango de pH de 2 a 5, con las superficies de los adsorbentes predominantemente cargadas positivamente, y aunque la principal forma iónica del AMPA dentro de este rango de pH es neutra. Estos hallazgos demuestran que los suelos naturales y los TMT pueden servir como adsorbentes eficaces, de bajo coste y sostenibles para eliminar el glifosato y el AMPA de soluciones acuosas. Además, para la producción de TMT deberían seleccionarse materiales con pH relativamente bajo y alto contenido en óxidos de aluminio y hierro, arcilla y materia orgánica. El desarrollo de Tecnosoles a medida ofrece una solución innovadora e integrada que contribuye a mejorar la calidad de los recursos naturales, promover la sostenibilidad, reducir la producción de residuos y restaurar las zonas contaminadas.

En general, los conocimientos adquiridos permiten comprender mejor el estado actual de la contaminación ambiental por productos farmacéuticos y plaguicidas, pues demuestran que la contaminación no sólo llega a los cursos de agua, sino que también afecta a los sedimentos y las aguas subterráneas. Esta investigación aporta valiosos datos sobre la adsorción de fluoxetina, glifosato, AMPA y glufosinato en distintos materiales. Los estudios de adsorción mostraron, entre otros resultados, que los materiales de biochar ensayados se erigieron como excelentes materiales adsorbentes de fluoxetina pero, por el contrario, no presentan una buena capacidad de retención a compuestos como glifosato, AMPA y, especialmente, glufosinato. Por otro lado, los suelos y los Technosols han mostrado una alta capacidad de retención para el glifosato y el AMPA. El glufosinato no tendió a adsorberse en ninguno de los materiales ensayados.

Los resultados apoyan el desarrollo de tecnologías de remediación destinadas a mitigar el impacto ambiental de estos compuestos, prevenir la contaminación y salvaguardar la salud pública. Además, proponen el uso de biochar como componente de Tecnosoles producidos para retener la fluoxetina. También destaca algunas de las características clave que se requieren de los constituyentes del Tecnosol para una adsorción adecuada del glifosato y el AMPA.

ABSTRACT

Environmental pollution, the disturbance of natural environmental processes that affect both the physical and biological components of the earth/atmosphere system, represents a serious and current problem for modern society. The substantial population growth has led to remarkable alterations in consumption patterns, including food and health necessities and consequent overuse of substances such as pesticides (food production) and pharmaceuticals (human and animal health). Both pharmaceuticals and pesticides are increasingly acknowledged as chemicals of emerging concern, with known negative impacts on soil and aquatic species and respective ecosystems and potential effects on human health.

Fluoxetine is an anti-depressant pharmaceutical widely used to treat depression. As with other pharmaceuticals, only a part of this compound is metabolized by the human body, while the rest, as well as its metabolites, are excreted, eventually reaching the wastewater systems and potentially the environment.

Glyphosate and glufosinate, two broad-spectrum, non-selective, organophosphorus herbicides, and aminomethylphosphonic acid (AMPA), the primary metabolite of glyphosate, are also three compounds of concern. The exposure level of humans and animals and the harmful effects of these compounds is largely documented.

As well as other emerging pollutants, environmental contamination by fluoxetine, glyphosate, glufosinate, and AMPA, require corrective measures, imposing the development of remediation techniques for the rehabilitation of the affected areas.

Several remediation technologies have been studied and developed to treat environmental contaminations. One of these remediation technologies is adsorption, a method in which molecules or particles of a substance are retained on the surface of a solid or liquid material through various mechanisms, such as electrostatic attraction, van der Waals forces, or chemical bonding. It is commonly used in industrial processes to remove impurities from liquids or gases, as well as in soil remediation, wastewater treatment, and drinking water purification. Also, it is a process that spontaneously occurs in many natural systems, such as in soil, benefiting the uptake of nutrients by plants or the adsorption of gases in the atmosphere by soil particles. Adsorption significantly affects the transfer and availability of pesticides in soil, being one of the main processes of controlling pesticide leaching and reducing their migration and the potential to contaminate surface waters or groundwater. As it is extensively used in large-scale wastewater treatments, due to its simple layout, high efficiency, and the possibility of using low-cost and non-toxic adsorbents, it can be optimized and applied to pharmaceutical and pesticide removal. To study the adsorption of different types of substances such as fluoxetine, glyphosate, AMPA, and glufosinate, evaluating the use of a wide variety of adsorbent materials and their physical-chemical properties is essential. Their selection is of great concern, and characteristics such as low cost, sustainability, non-toxic, and high sorption capacity are significant attributes to be considered.

Biochar is a solid and stable porous material with high carbon content manufactured through pyrolysis/carbonization of biomass under a limited or absent oxygen environment and moderate temperature conditions. It is an attractive material to be implemented as an adsorbent to retain and remove pollutants from aqueous environments. Its use presents itself as a tool for environmental management, acting in soil improvement, waste treatment, climate change mitigation, and energy production. Besides being economically attractive, biochars are largely used as adsorbents due to their high retention capacity for distinct contaminants associated with their high specific surface and porosity, ion exchange capacity, and pH. The feedstock selection can largely influence its properties, as well as the production process conditions, namely temperature range, heating rate, pressure, and residence time.

Another innovative remediation technology is the use of tailor-made Technosols. Technosols are a reference soil group defined in the World reference base for soil resources (by the Food and Agriculture Organization of the United Nations and International Union of Soil Sciences) as a combination of soils "*whose properties and pedogenesis are dominated by their technical origin".* Significantly dominated or strongly influenced by human-made, strongly altered material (referred to as *artifacts* such as waste materials namely bricks, glass, household waste, mine waste, sludge, etc.) or extracted from greater depths, these soils are frequently found in urban and industrial areas. Tailor-made Technosols (TMTs) are engineered soils created by the combination of natural soil with anthropogenic materials derived from human activities with other additives to obtain the desired characteristics. They replicate functions of natural soil and can be used to provide several soil functions and ecosystem services, such as suitable conditions for plant growth/production (food and biomass), soil remediation, carbon sequestration, restoring water bodies and degraded or polluted areas, groundwater recharge, and ecosystem biodiversity. Biochar is one of the materials that can be incorporated into the production of tailor-made Technosols.

Thus, as a first approach to the problems addressed in this work, monitoring antibiotics and anti-depressants in the waters and sediments along two rivers in northern Portugal was carried out. Sediment samples were collected from two layers, the top layer, within 0 and 2

cm depth, and bottom layer within 2 and 10 cm. The present study involved the characterization and analysis of samples for seventeen antibiotics and ten antidepressants. A comparison of pharmaceutical concentrations in samples from the Leça River and the Douro River revealed higher levels in the Leça River. Only carbamazepine and fluoxetine were detected in the Douro water samples, whereas the Leça water samples contained thirteen out of twenty-seven pharmaceuticals, including six antibiotics and seven psychiatric drugs. Notably, azithromycin was found at the highest concentration (2.82 µg/L) in the Leça River samples, particularly near a wastewater treatment plant effluent discharge point. Fluoxetine exhibited the highest detection frequency in water samples. The presence of carbamazepine and venlafaxine in Leça River water indicated potential risks to algae. In sediment samples, sulfamethoxypyridazine was found in Douro sediment, while azithromycin was detected in Leça sediment, both primarily in the top sediment layer. Psychiatric drugs were also detected, with four found in Douro sediment and six in Leça sediment. A comparison between the top and bottom sediment layers at each sampling point showed that venlafaxine, the only quantified pharmaceutical in the Douro River, exhibited a higher concentration in the bottom zone, potentially related to soil migration. In Leça sediments, higher concentrations were observed in the top layer, likely associated with recent pollution events in the area. A review of monitoring studies reported in the literature revealed a reduced inclusion of sediment analysis, with most studies focusing solely on water samples (especially for psychiatric drugs). Therefore, it was not possible to identify a consistent contamination pattern or establish a clear link between sediment contamination and the migration of contaminants from water, based on the obtained results and literature comparisons. However, higher concentrations of contaminants were consistently observed at sampling locations downstream of wastewater treatment plant discharges.

Additionally, a literature review of glyphosate, AMPA, and glufosinate contamination of water and sediment worldwide was performed. The aim was to investigate the contamination and mobility of the referred substances in aquatic environments, with a specific focus on water and sediment samples. The research included a comprehensive literature search to analyze studies published within the last five years that monitored the concentrations of these compounds in water (both surface and groundwater) and sediments. The analysis of applicable legislation revealed significant variations in limit values for these pollutants across different countries. For instance, European Union set the lowest legal limit for glyphosate residues in water intended for human consumption, with a threshold of 0.1 µg/L, while Japan established the highest limit at 2 000 µg/L. The most commonly used detection methods in the analyzed studies were high-performance liquid chromatography (HPLC) tandem mass

spectrometry (MS/MS). However, it was found that only 40% of the reviewed studies reported detection limits below the European Union's maximum permissible value for individual pesticide water contamination (0.1 µg/L). The investigation of glyphosate monitoring in water and sediments revealed interesting trends. France emerged as the country with the highest samples/publication ratio, followed by Japan and Italy. Argentina, on the other hand, had a higher frequency of study publications but a lower samples/publication ratio. Notably, the European countries that conducted a higher number of glyphosate level analyses tended to correspond with an increased rate of glyphosate application. As for AMPA monitoring, Argentina had a higher frequency of studies, while France maintained its position as the country with the highest samples/publication ratio, followed by the USA, Sweden, and Italy. China stood out with a significantly larger number of samples monitored for glufosinate compared to other countries with publications on this compound. Maximum contaminant concentrations varied depending on the environmental matrix. In surface water, the highest concentrations were found for AMPA (6 872 µg/L), followed by glyphosate (5 750 µg/L) and glufosinate (13.15 µg/L). In groundwater, the maximum values were 8 700 µg/L for glyphosate, 233 µg/L for AMPA, and 0.03 µg/L for glufosinate. Sediments displayed the highest detected concentrations of glufosinate (14.9 µg/kg), while glyphosate and AMPA reached maximum concentrations of 1 882 µg/kg and 4 033 µg/kg, respectively. Contrary to expectations, the maximum glyphosate concentration was higher in groundwater than in surface water. However, the frequency of detection was significantly higher in surface water (70%) compared to groundwater (18%). As for AMPA and glufosinate, the detection frequency in surface water was 87% and 6%, respectively, while in groundwater, it was 16% and 0.7%. South American countries presented the highest values of maximum detected concentration for glyphosate and AMPA, while sediments were the environmental matrix with the highest concentration of glufosinate. France had the highest maximum concentrations of glyphosate in surface waters, followed by Italy and Germany. In groundwater, Sweden exhibited the highest glyphosate concentrations, followed by Italy. Germany and Croatia presented the maximum concentration levels in sediments. Several factors were identified as drivers for the dispersion of these compounds in surface water, sediments, and groundwater. These factors included overspray, spray drift, surface run-off, shallow water tables, low hydraulic conductivity in aquifers, low hydraulic gradient, very low flow velocity, soil type, and chemical constitution. The persistent and escalating application of these compounds in agricultural and domestic activities, improper use, and wastewater treatment plants were identified as potential sources of contamination. This review shed light on the contamination and mobility of glyphosate, AMPA, and glufosinate in water and sediments. The findings emphasized the need for ongoing

monitoring efforts and for the development of remediation strategies to mitigate the environmental impact of these compounds. The results also highlighted the importance of harmonized legislation and unified limit values across countries to ensure effective protection of water resources.

In light of the documented contamination associated with the compounds under investigation, it is crucial to identify remediation technologies that not only address contaminated sites but also reduce the mobility of these compounds. Such technologies can prevent water and soil contamination and minimize the associated health problems resulting from the ingestion of these compounds. Consequently, this research focused on studying the adsorption of fluoxetine, glyphosate, AMPA, and glufosinate onto various materials, with different characteristics, in order to understand and optimize their adsorption. To this end, adsorption studies, namely equilibria, kinetics, and pH influence assays, were developed to study the adsorption of the four compounds under analysis. Different adsorbents with distinct characteristics were tested to find the most suitable materials and characteristics to integrate the composition of a tailor-made Technosol. If applied to a tailor-made Technosol production, the results will allow the development of an innovative and integrated solution that contributes to improving the quality of natural resources, sustainability, reducing waste production, and restoring contaminated areas.

The first phase of the study involved testing twelve biochars derived from different forest and agri-food wastes (pruning of *Quercus ilex, Eucalyptus grandis, Pinus pinaster, Quercus suber, Malus pumila, Prunus spinosa, Cydonia oblonga, Eriobotrya japonica, Juglans regia, Actinidia deliciosa, Citrus sinensis* and *Vitis vinifera*) as potential low-cost and renewable adsorbents for fluoxetine removal from water. Preliminary adsorption experiments allowed to select the most promising adsorbents, *Quercus ilex* (hollow tree), *Cydonia oblonga* (quince), *Eucalyptus*, *Juglans regia* (walnut tree) and *Vitis vinifera* (vine) pruning material. They were characterized by proximate, elemental and mineral analysis, thermogravimetric analysis, Fourier transform infrared spectroscopy, determination of specific surface area and pH at the point of zero charge (pH_{PZC}). Batch and equilibrium studies were performed, and the influence of pH was evaluated. The adsorption capacities of the selected biochars were determined, with values ranging from 2.21 to 6.41 mg/g according to the Langmuir model. Among the biochars tested, eucalyptus biochar exhibited the highest adsorption capacity, followed by hollow tree, vine, walnut tree, and quince biochars. The adsorption kinetics were rapid, with complete adsorption occurring in less than 15 minutes. Column adsorption experiments conducted with eucalyptus biochar demonstrated its effectiveness in continuous mode,

presenting a breakthrough for 50% removal at 90 minutes, suggesting its potential as a renewable alternative for fluoxetine removal.

The following phase of the research focused on investigating the adsorption of glyphosate, AMPA, and glufosinate onto forty-one different materials, including biochars, soils, and tailor-made Technosols (TMTs). Tested biochars were produced from acacia (*Acacia melanoxylon*) trunk divided in sapwood (BAcSw-3) and heartwood (BAcHw-2), eucalyptus branches (BEu-2), pine sawdust (BSd-1), pine bark (BPb), olive pomace compost (BOpc), rice husk (BRh), corncob (BCc1 and BCc-2), and German crushed wood chips (BSdG). The eight tested soil samples were Aluminic Umbrisols (S4A, 11B, 13A), Ferrasols derived from amphibolites (S9B), Háplic Umbrisols (1Ah and 2Ah) and Andic and Ferralic Leptosols (referred as Andic and Ferralic). Relatively to TMT, the tested materials were classified as Arenic Calcic Technosol (TMT 1), Aluandic Technosol (TMT 2), Andic Eutric Technosol (TMT 3, G, I, J, K, L, M, Q, R and S), Reductic Eutric Technosol (TMT 4 and A), Dystric Technosol (TMT B and D), Calcic Technosol (TMT C), Andic Technosol (TMT E and F), Eutric Technosol (TMT H and O), Ferric Technosol (TMT N) and Reductic Andic Technosol (TMT P). These TMTs were produced from industrial and agro-industrial waste, namely mine sediment, sawdust biomass, sludge from wastewater treatment, organic compost, ash, and sand. The results indicated that the three compounds were poorly adsorbed by most of the biochar samples, with maximum removal rates of 25% for glyphosate, 12% for AMPA, and 4% for glufosinate. These results were primarily attributed to the production temperature of the biochars. In contrast, the tested soils exhibited high adsorption capacities for glyphosate and AMPA, with maximum removal rates of 94% and 91% in the preliminary assays, respectively. However, the adsorption of glufosinate was limited, with removal rates not exceeding 6%. The TMTs also showed significant adsorption capacities during preliminary assays, with maximum removal rates of 79% for glyphosate and 83% for AMPA. Once again, glufosinate exhibited low adsorption values, with a maximum removal rate of only 3%. Additionally, smaller grain sizes were found to enhance adsorption performance compared to soils or TMTs with larger grain sizes. The equilibrium time for adsorption varied, with total adsorption occurring in 14 hours for soils and 72 hours for TMTs, which is consistent with previous findings in the literature. The maximum adsorption capacities, according to the Langmuir model, were determined to be 10.84 mg/g for glyphosate (soil S9B) and 15.08 mg/g for AMPA (TMT 1). In terms of pH influence on the adsorption process, glyphosate and aminomethylphosphonic acid (AMPA) exhibit distinct charge behaviors. Analyzing de pH impact in the adsorption process with the tested adsorbents, which have a pH_{PZC} of approximately 4.9, the adsorption of glyphosate and AMPA exhibited pH-dependent behavior. The adsorption increased between pH 1 and pH 3,

corresponding to the protons loss associated with the carboxyl group of glyphosate (pKa_2) and the phosphonic group of AMPA (pKa_1) in the presence of a predominantly positively charged adsorbent surface. Subsequently, there was a gradual decrease in adsorption between pH 3 and pH 6, more pronounced for glyphosate than for AMPA. Between pH 6 and 10, the adsorption of glyphosate onto the tested adsorbents significantly decreased, except for TMT 1, which only exhibited reduced adsorption at pH higher than 10, approaching values close to zero. In the case of AMPA, the reduction in adsorption by TMTs occurred more prominently from pH values higher than 9, with relatively constant adsorption observed between pH 6 and 10 for the other adsorbents. For all adsorbents, there was a notable decrease in adsorption to values close to zero between pH 10 and 12, except for glyphosate adsorption onto soil S4A, which exhibited slightly higher adsorption at pH 12 compared to the other adsorbents. Overall, higher adsorption of glyphosate and AMPA onto soils and TMTs occurred within the pH range of 2 to 5, with the adsorbents surfaces predominantly positively charged, and although the main ionic form of AMPA within this pH range is neutral. These findings demonstrate that natural soils and TMTs can serve as effective, low-cost, and sustainable adsorbents for removing glyphosate and AMPA from aqueous solutions. Moreover, materials with relatively low pH and high aluminum and iron oxides, clay content, and organic matter should be selected for TMT production. The development of tailor-made Technosols offers an innovative and integrated solution that contributes to improving the quality of natural resources, promoting sustainability, reducing waste production, and restoring contaminated areas.

Overall, the knowledge acquired leads to a better understanding of the current state of environmental contamination by pharmaceuticals and pesticides, showing that pollution not only reaches the watercourses but also sediments and groundwater are affected. This research provides valuable insights into the adsorption of fluoxetine, glyphosate, AMPA, and glufosinate onto different materials. The adsorption studies showed, among other results, that the tested biochar materials stood as excellent adsorbent materials of fluoxetine but, on the contrary, do not present a good retention capacity to compounds such as glyphosate, AMPA, and especially glufosinate. On the other hand, soils and Technosols have shown a high retention capacity for glyphosate and AMPA. Glufosinate did not tend to adsorb to any of the tested materials.

The findings support the development of remediation technologies aimed at mitigating the environmental impact of these compounds, preventing contamination, and safeguarding public health. Additionally, propose the use of biochar as components of Technosols produced

to retain fluoxetine. It also highlights some of the key characteristics required from the Technosol constituents for adequate adsorption of glyphosate and AMPA.

INDICE

LIST OF ABBREVIATIONS

AA	Aceticacidanhydride
ACN	Acetonitrile
AOP	Advanced oxidation process
EC	Electrical conductivity
CEC	Chemicals of emerging concern
CE-MS	Capillary electrophoresis-mass spectrometry
DAD	Diode array detector
EBS	effective base saturation
ECD	Electrochemical detection
EFSA	European Food Safety Authority
ELISA	Enzyme-linked immunosorbent assay
ESI-MS/MS	Electrospray ionisation tandem mass spectrometry
FAO	Food and Agriculture Organization of the United Nations
FLD	Fluorescence detection
FLX	Fluoxetine
FMOC-Cl	9-fluorenylmethylchloroformate
GBH	Glyphosate based herbicides
GC	Gas chromatography
HFB	Heptafluorobutanol
HPAEC	High-performance anion-exchange chromatography
IC	Ion chromatography with suppressed conductivity detection
IC-HESI-MS/MS	Ion chromatography hyphenated to electrospray tandem mass spectrometry
ICP-MS/MS	Inductively coupled plasma tandem mass spectrometry
LC	Liquid Chromatography

LOD	Limit of detection
LOQ	Limit of quantification
MDL	Method detection limit
MKP, KH_2PO_4	Monopotassium phosphate
MQL	Method quantification limit
MS	Mass spectrometry
NSAIDs	Non-Steroidal Anti-Inflammatory Drugs
NBD-Cl	4-chloro-7-nitrobenzofurazan
NPD	Nitrogen-phosphorous detection
OM	Organic matter
OPA-MCE	o-phthalaldehyde-2-mercaptoethanol
PAD	Pulsed amperometric detection
PFAS	Per-fluoroalkyl and polyfluoroalkyl substances
PTFE	Polytetrafluoroethylene
Q-TOF-MS	Quadrupole Time-of-Flight Mass Spectrometry
RP-HPLC	Reverse phase high-performance liquid chromatography
SIC	Sequential injection chromatography
SIM	Selected ion monitoring
SM-FIA	Spectrophotometric method - standard flow injection analysis
SSRI	Selective serotonin reuptake inhibitor
SWV	Square-wave voltammetry
UHPLC-HRMS	Ultra-performance liquid chromatography high-resolution mass spectrometry
UPLC-MS/MS	Ultra-performance liquid chromatography Mass spectrometer
UV	Ultraviolet detection
UV-Vis	Ultraviolet–visible spectrophotometry
VDP	Differential pulse voltammetry
WHO	World Health Organization

CHAPTER 1 INTRODUCTION

1.1 General background

Environmental contamination is an issue of growing concern worldwide. Due to the known and unknown possible impact on the environment, Human and wildlife health, emerging contaminants have raised alarms among the scientific community and official environmental agencies. Emerging contaminants are newly developed or categorized as contaminants or known compounds freshly identified in the environment (frequently associated with analytical developments) and cause known or suspected adverse ecological and/or human health effects. They incorporate a wide variety of substances such as personal care products, pharmaceutical products, pesticides, veterinary products, heavy metals, microplastics, industrial by-products, engineered nanomaterials, food additives, and natural and synthetic hormones. Their metabolites and transformation products are also included (X. Li *et al*., 2022; Puri *et al*., 2023). After their entrance into the environment, they present several possible biogeochemical behaviors. The most common and impacting are transformation, transfer, and accumulation along the food chain, altering some properties and possibly turning their detection into a challenging process. Additionally, these changes and wide-spread can result in distinct and unknown impacts on environmental health (X. Li *et al*., 2022).

Anthropogenic activities are the major sources of emerging contaminants’ introduction into the environment. Wastewater treatment plants (WWTPs) are one of the main entry channels of these compounds in the soil and water environmental compartment, as they receive wastewater from several sources (e.g. households, hospitals, industries) and are unable to entirely degrade emerging contaminant’s using conventional treatments (e.g. activated sludge, filtration, and disinfection) (Mukhopadhyay *et al*., 2022; Puri *et al*., 2023; Terpenning & Öberg, 2017). Additionally, according to World Health Organization (WHO), in 2020, nearly 22% of the global population (1.7 billion people) still did not have basic sanitation services, and 45% of the household wastewater globally generated was discharged without safe treatment, increasing the potential for effluents with high concentrations of these contaminants to be released into water bodies (World Health Organization & United Nations Children’s Fund, 2020).

Pesticides are chemicals used to control plagues and diseases in agriculture, while pharmaceuticals are drugs used to treat or prevent diseases in humans and animals. Even though these substances have brought significant benefits to society, their widespread use has also led to unintended consequences, such as soil, water, and air pollution (Sousa *et al*., 2018). Both pesticides and pharmaceuticals are considered emerging contaminants of concern because their impact on the environment is complex and multifaceted, and their effects on ecosystems can be subtle and challenging to predict, leading to long-term ecological and economic consequences.

Due to the continuous introduction of human-made and natural organic substances into the environment, it is crucial to understand better the chemical status of the Earth's surface water and soils. To reduce and prevent water and soil pollution, it is essential to invest in infrastructure and technology to improve wastewater treatment and reduce the discharge of pollutants into water sources. Promoting sustainable practices in agriculture and industry is also crucial, as increasing public awareness of the importance of protecting our water resources.

This work address and explore the presence, potential sources, pathways, and impacts of environmental contamination by emergent pollutants, focusing on four significant substances: glyphosate and its primary degradation product (AMPA) and glufosinate, pesticides from herbicides family and fluoxetine, a pharmaceutical belong to antidepressant group. Also, examine some of the strategies and technologies used to mitigate this problem proposing and assessing adsorption as one of the technologies applied to treat these contaminants in water or directly in soils, preventing them from flowing into water bodies.

1.2 Objectives and structure

1.2.1 Main objective

This work aimed, firstly, to improve knowledge within the scope of new contamination trends as well as the primary sources of contamination and their pathways to reach the environmental compartments. Glyphosate, its major degradation product AMPA, glufosinate and fluoxetine were selected to represent two different families of compounds: herbicides and pharmaceuticals. Thus, also intend to fill in the gaps in the existing knowledge on glyphosate, AMPA, glufosinate and fluoxetine environmental contamination and to propose a low-cost and sustainable remediation technique to prevent their spread and consequent contamination of soils, and water resources, namely the application of tailor-made Technosol. Secondly, it sought to search for inexpensive and sustainable material with high glyphosate, AMPA, glufosinate and fluoxetine adsorption capability that could be incorporated as a tailor-made Technosol component.

Figure 1.1 presents a flow chart of the several steps through the subject's approach with a focus on the main objectives of the work.

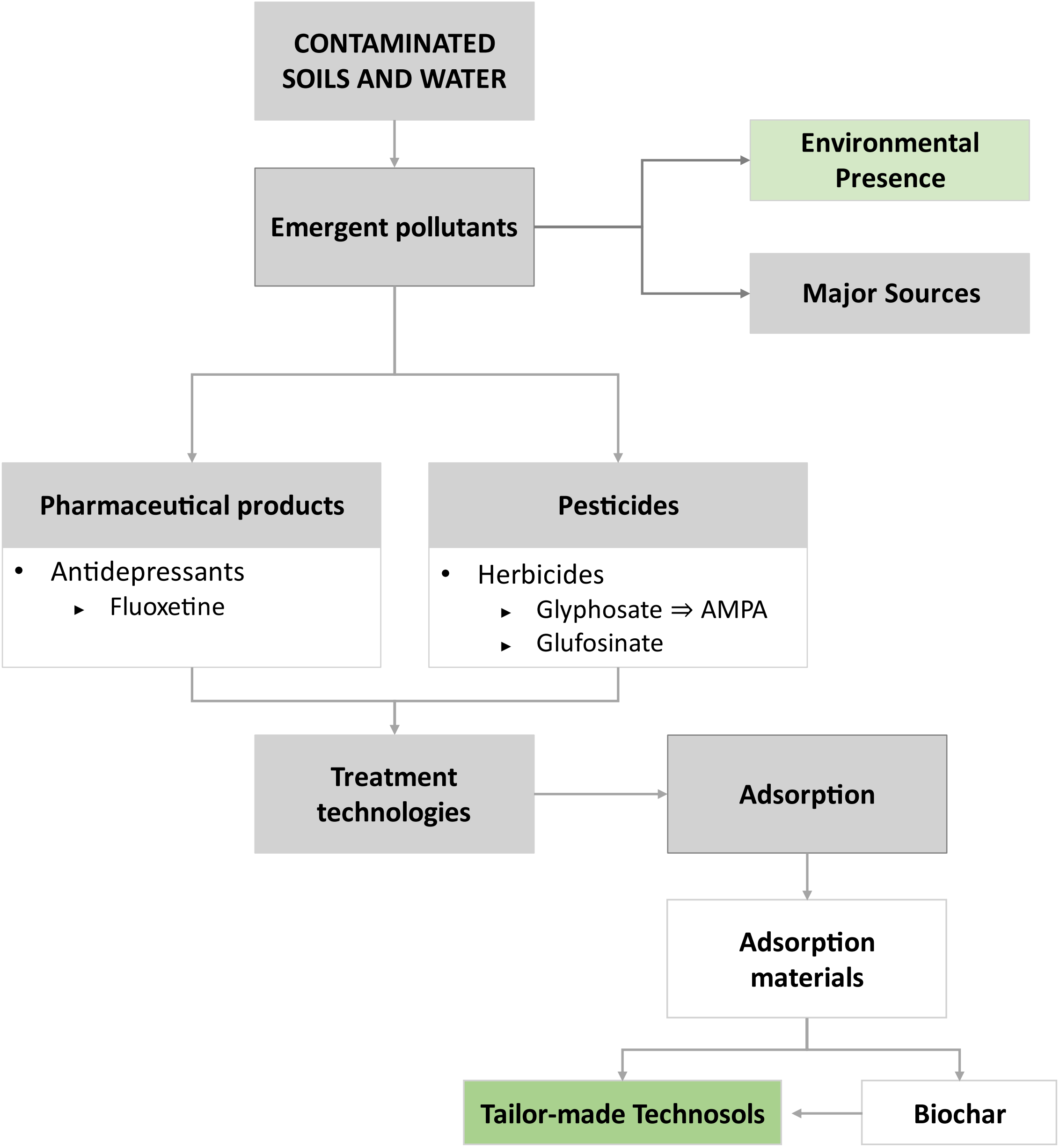


Figure 1.1 - Flow chart of the topics approached throughout the thesis to reach the objectives.

1.2.2 Specific objectives

1. To monitor sites contaminated with pharmaceuticals and pesticides, namely fluoxetine, glyphosate, AMPA and glufosinate in Portugal and in the World;
2. To discover sustainable material to use as adsorbents. Additionally, to understand the characteristics that make them more favorable to the adsorption of the target compounds;

3. To test several different materials with possibility to be incorporated in a tailor-made Technosol with purpose of retention/elimination by adsorption/reaction of fluoxetine, glyphosate, AMPA and glufosinate from contaminated waters and soils.

To achieve the general objectives, the specific objectives are described:

a. Access analytical methodologies for measuring fluoxetine, glyphosate, AMPA and glufosinate in water and soils, using liquid chromatography with after previous sample extraction;
b. To value waste materials by promoting a sustainable final destination;
c. To characterize and test the selected materials;
d. To assess the efficiency of each material application in contaminated soils and waters;

1.2.3 Thesis outline

The thesis organization and structure aim to sequence address the main themes and include seven chapters. **Chapter 1** (this chapter) introduces the thesis theme and describes general background information. This chapter also reveals the main and specific objectives of the present work and its planification.

Chapter 2 addresses a literature review to provide an overview of the problem of environmental pollution, converging in pharmaceutical products and pesticides. Also address the importance of the study of glyphosate, AMPA, glufosinate and fluoxetine as emergent contaminants, focusing on (i) their worldwide use, (ii) chemical and physical properties, (iii) their degradation and dissipation paths, and (iv) analytical methodologies for detection in environmental matrixes. Additionally, outline innovative technologies for the mitigation of these emerging contaminants.

Chapters 3 and **4** are intended to help understand the current state of environmental contamination by the two types of contaminants: pharmaceuticals and pesticides. In **Chapter 3**, antibiotics and antidepressants (including fluoxetine) were used as references for the search for pharmaceutical contamination. This monitorization was performed through the analysis of water and sediments samples collected in two rivers located at the North region of Portugal. In **Chapter 4**, glyphosate and glufosinate herbicides, along with the degradation product AMPA, were used as references for pesticide contamination and a review of the existent environmental contaminations (surface water, groundwater, and sediments) was performed. A legislation overview and an analysis of the contaminant's mobility were also performed.

Chapter 5 investigates the application of adsorption as treatment technology to water contaminated with the antidepressant fluoxetine. This study applied batch and column adsorption experiments onto biochars with different source feedstocks.

Chapter 6 assesses the application of the same treatment technologies – adsorption – but applied to water contaminated with herbicides glyphosate (alongside its degradation product, AMPA) and glufosinate. The adsorbent materials tested were biochars from different sources, soils and tailor-made Technosols. Batch adsorption experiments were performed, and the influence of some characteristics of the adsorbents were accomplished.

Chapter 7 summarizes and highlights this investigation's major conclusions and debates the repercussions of these outcomes, pointing out some recommendations for future research work.

CHAPTER 2 LITERATURE REVIEW

2.1 Environmental Pollution

One of the most critical challenges of our time is environmental pollution. The existence of humanity and other living organisms on planet Hearth is directly attached to the state of the environment. Environmental pollution is characterized as the disruption of natural environmental processes in the physical and biological components of the earth/atmosphere system. Occurs when by-products of human activities, due to their nature, characteristics, and/or concentration, overcome the environment's natural capacity to process and neutralize them, leading to structural or functional damage. This type of event has been present since the beginning of life but was potentialized by the industrial revolution in the 19th century, which led to a dramatic increase in scope and scale. Today, environmental contamination is a problem in developed and developing nations since World’s finite natural resources are widened by population growth, urbanization, and technological advancement (Cela-Dablanca *et al*., 2023; Muralikrishna & Manickam, 2017).

Increasing attention has been paid by environmental agencies and researchers to several emerging pollutants because of their potential impact on terrestrial ecosystems either directly or through their degradation products. Emerging pollutants are any synthetic or naturally occurring chemical or microorganism not systematically monitored or regulated in the environment, with suspected or known undesirable effects on the ecosystem and human health. These contaminants comprise various substances used in everyday life, namely pharmaceuticals, personal care products, pesticides, industrial and household products, metals, surfactants, industrial additives, and solvents (Cela-Dablanca *et al*., 2023; Terpenning & Öberg, 2017).

In many parts of the world, access to clean and safe drinking water is still a major challenge. According to the World Health Organization (WHO), in 2020 around 2 billion people lack access to safely managed drinking water services, and many more are exposed to contaminated water sources (WHO/UNICEF, 2021). Sub-Saharan Africa, Central and South Asia, and Eastern and South-Eastern Asia were the regions that, in 2020, presented a higher population that still without basic drinking water services (Figure 2.1). The population without basic drinking water services decreased by 193 million between 2015 and 2020, associated with the increased from 70% to 74% of the global safely managed drinking water coverage services (Figure 2.1).

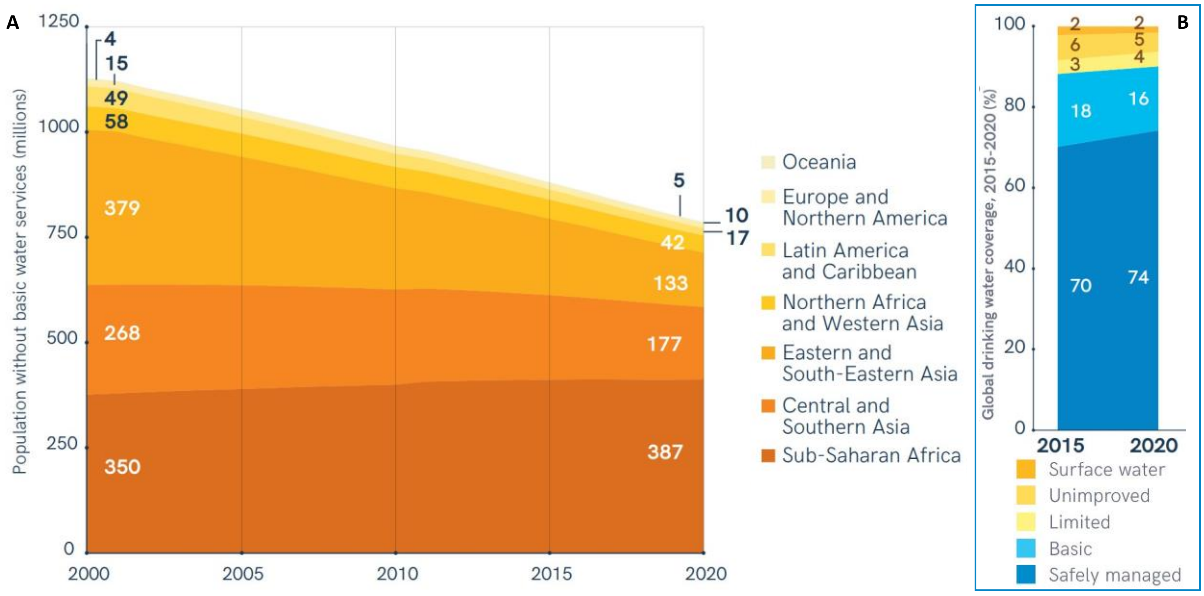


Figure 2.1 - Population without basic drinking water services, by sustainable development goal region, 2000-2020 (millions) and B) Global sanitation coverage, 2015-2020 (%) (Adapted with permission from (WHO/UNICEF, 2021). Copyright 2021, World Health Organization (WHO) and the United Nations Children's Fund (UNICEF)).

Additionally, in the same regions, the proportion of the population with access to at least basic sanitation services is also lower (Figure 2.2), with evident inequalities in coverage of these services among different countries and between urban and rural regions of the same country (WHO/UNICEF, 2021).

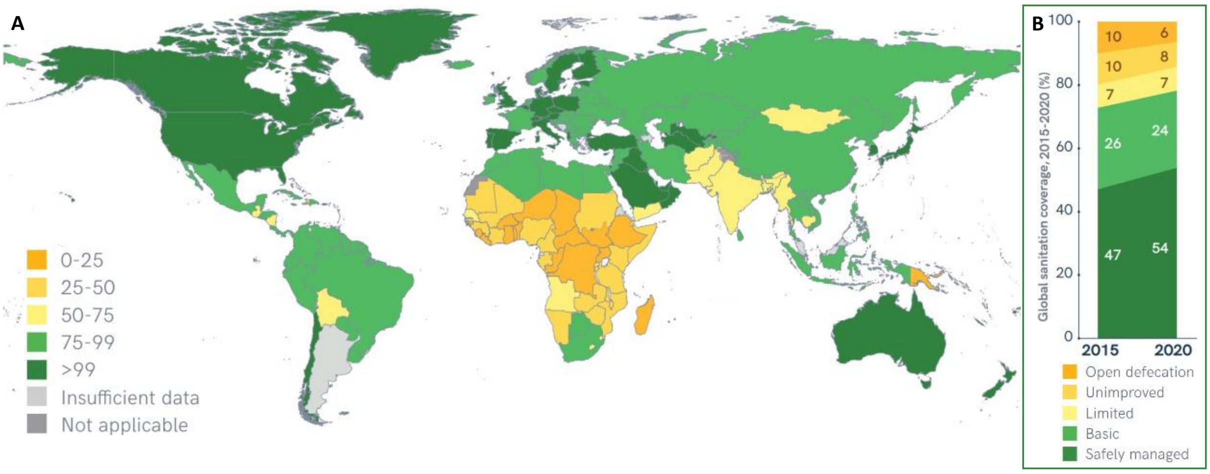


Figure 2.2 - A) Proportion of population using at least basic sanitation services, 2020 (%) and B) Global sanitation coverage, 2015-2020 (%) (Adapted with permission from (WHO/UNICEF, 2021). Copyright 2021, World Health Organization (WHO) and the United Nations Children's Fund (UNICEF)).

Therefore, water resource contamination with organic and inorganic recalcitrant pollutants has become a major global concern as they can cause serious health consequences for both humans and wildlife. These contaminants are usually released into the environment as a result of widespread or specific/punctual human activities, such as industrial processes, agricultural practices, transports, sewage discharge from domestic, hospital, or industrial sources, and animal rearing (J. Sharma *et al*., 2022).

Governments worldwide have implemented regulations and policies to address water pollution, such as the Clean Water Act in the United States and the Water Framework Directive in Europe. Many businesses have also implemented sustainability initiatives to reduce water use and prevent pollution.

However, despite these efforts, water pollution remains a significant problem in many regions. Climate change is also exacerbating water pollution, as rising temperatures and changing weather patterns can lead to increased runoff of pollutants into water sources.

Regardless of the progress over past decades, in ‘The European Environment - state and outlook 2020’, the European Environment Agency’s clearly demonstrated that Europe still faces environmental challenges of unprecedented scale and urgency (European Environment Agency, 2019). This complex and pressing issue requires immediate action to mitigate its adverse effects and protect future generations' environment, climate, and people’s health and well-being.

2.2 Pharmaceutical products

The significant population growth in the key metropolitan cities has led to remarkable alterations in consumption patterns, including pharmaceuticals. Pharmaceuticals are increasingly acknowledged as chemicals of emerging concern (CEC) with known negative impacts on aquatic species and ecosystems and potential effects on human health. Its consumption increase has made it imperative to safeguard the quality of urban surface and groundwater resources once apart from regulated organic, inorganic, and microbial contaminants. Pharmaceuticals have also been found to pose a threat to the quality of these essential resources (J. Sharma *et al*., 2022; Silori *et al*., 2022).

Pharmaceuticals could be classified by its therapeutic class, such as analgesics, anti-inflammatory, antibiotics, antidepressants, among others (Figure 2.3). Pharmaceutically active compounds could be composed of around 3000 different substances. Among this wide variety of components, some can severely impact humans and biota (Calvo-Flores *et al*., 2017; Puri *et al*., 2023; J. Sharma *et al*., 2022).

In the last years, numerous studies have described the presence of pharmaceutical compounds in the environment, becoming a growing concern worldwide. These compounds could be generated by their use by human and animal as well as by industry. Excretion of unmetabolized pharmaceutical drugs by the human/animal body after consumption, disposal or flushing down the toilets of unused products, and bathing, and washing off topically applied medications are three of the primary routes that promote the arrival of these contaminants to water bodies through WWTPs or direct discharge (J. L. Santos *et al.*, 2022; Silori *et al.*, 2022).

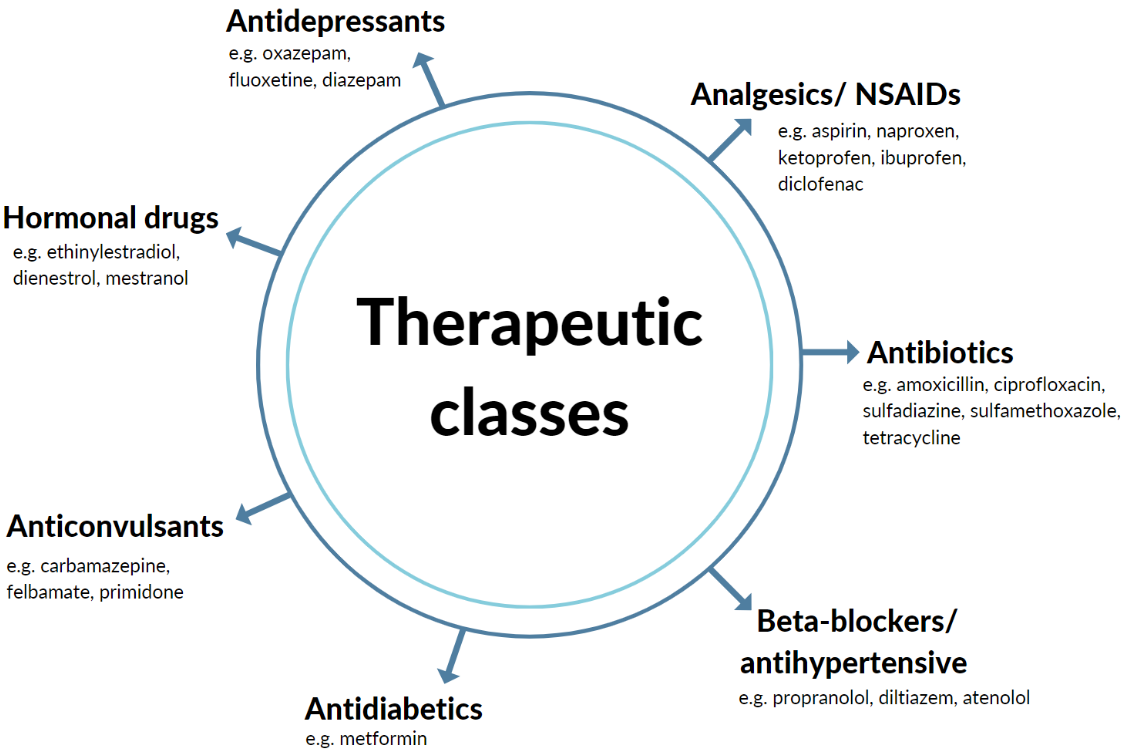


Figure 2.3 - Therapeutical classes of the most found pharmaceuticals in environmental matrixes (developed by the author).

Moreover, they continuously move into the environment through different pathways, namely their discharge from household, hospitals, or industry to wastewater treatment systems or directly to the environment. Additionally, the use of the sludges produced in WWTPs as organic amendments and nutrients source for agricultural purposes (highly frequent in European Union, with specific application rates throughout the Member States), and the irrigation with recycled water or wastewater treatment discharge, represent a probable pathway to these compounds to end up in soil or in the aquatic environment, increasing the risk of soil and water contamination (J. L. Santos *et al.*, 2022).

Thus, conventional WWTP represents a significant source of human pharmaceuticals in the environment. Since their treatment methods were not designed to remove these chemicals, and due to the pharmaceutical's complex structure and physicochemical properties, they are ineffective in entirely removing them (J. L. Santos *et al.*, 2022; J. Sharma *et al*., 2022; Silori *et al*., 2022). Nevertheless, the contamination sources and the entry points into the environmental compartments can vary greatly depending on the circumstances of each country. For example, in East African countries, improper pharmaceutical handling and disposal is the main challenge (Karungamye *et al*., 2022).

Regarding the removal of pharmaceuticals in WWTP, according to several studies, only in occasional cases was there a reduction in the concentration of these compounds in the influent compared to the effluent. This variance was highly dependent on the applied treatment levels and systems at the facility. The concentration reduction in water may not have been exclusively due to the removal of these compounds but rather to their concentration in the solid phase resulting from the various treatments (sludge). Additionally, the output concentration was higher for some pharmaceuticals than the input concentration. Concerning psychiatric drugs, no removal in the WWTP was observed (Lopez *et al*., 2022; Paula Paíga *et al*., 2016, 2019; Papageorgiou *et al*., 2016).

In Europe, the Water Framework Directive is the primary regulation for water protection. It applies on the quality of the inland, transitional, and coastal surface waters through the “daughter” Environmental Quality Standards Directive defined in the Directive 2000/60/EC (European Commission, 2000), and on the quality and quantity of groundwater, through the Groundwater Directive 2006/118/EC (European Commission, 2006). One of the several amending of Directive 2000/60/EC, the Directives 2008/105/EC of 16 December (European Commission, 2008) and 2013/39/EU of 12 August (European Commission, 2013) stipulated that the European Commission should establish a watch list of substances for which Union-wide monitoring data would be gathered to support future prioritization exercises in agreement with the Article 16 of the emended directive, complementing its articles 5 and 8. The continuous monitoring period for any individual substance included in the list must be at least 12 months and not exceed four years. Additionally, this list must be updated every 24 months after that, and any substance for which a risk-based assessment, as referred to in Article 16 (2) of Directive 2000/60/EC, can be concluded without additional monitoring data should be removed. Following the previously established, a watch list of substances for Union-wide monitoring in the field of water policy was created, starting with 10 substances or groups of substances (as recommended in the Directive 2013/39/EU), firstly defined in the Commission Implementing Decision (EU) 2015/495 of 20 March 2015 (Figure 2.4) (European Commission, 2015b). In its annex are included some indicative analytical method for each substance or group of substances and the maximum acceptable method detection limit. Substances included or added to the watch list must be carefully chosen from amongst those that exhibit signs of potentially significant risks to or via the aquatic environment at the European Union level but for which there is no sufficient data to make a conclusive determination. The watch list was updated in 2018 (European Commission, 2018), 2020 (European Commission, 2020b), and 2022 (European Commission, 2022a). Currently, this list includes 26 substances or groups of substances, and for most of these compounds, the SPE extraction method and LC, HPLC, or UPLC in tandem with MS/MS analysis method are suggested.

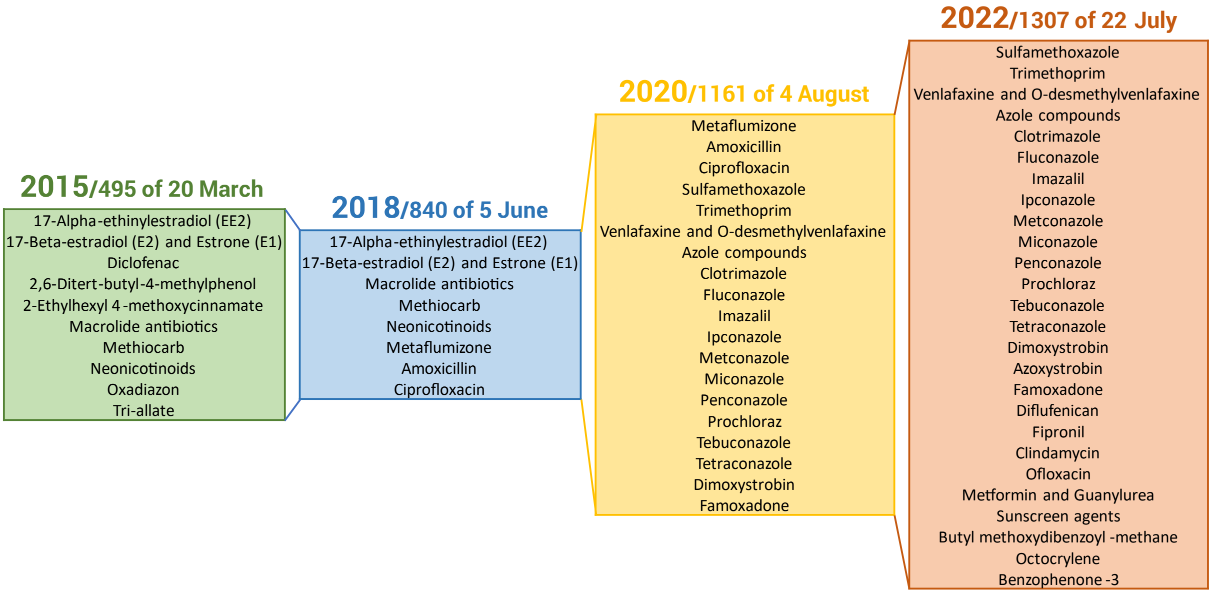


Figure 2.4 - Evolution of the watch list throughout the years (developed by the author).

Thus, increasing awareness of the environment's negative impacts, toxicity, fate, occurrences, and transfers of pharmaceutical products is essential to enhance our knowledge and regulate them. Hawash *et al*. (2023) executed a major review relative to the global occurrence of pharmaceuticals and personal care products residues in aquatic systems (drinking/tap water, surface water, groundwater, and WWTPs) in the period from 2012 to 2022. The highest concentrations of pharmaceutical products in surface waters were observed in Africa and South America, with a maximum reported concentration of 272,2 µg/L (amoxicillin - antibiotic) in Nigeria, 25.4 µg/L (aspirin - NSAID), and 23.5 µg/L (nalidixic - antibiotics), both in South Africa and 127.0 µg/L (caffeine - stimulant) and 21.0 (aspirin) in Brazil. In China, a caffeine maximum concentration of 9.8 µg/L was detected, followed by 2.8 µg/L of the antibiotic's erythromycin and oxytetracycline. In Europe, the maximum concentrations observed were 3.5 µg/L (caffeine), 3.0 µg/L (salicylic acid - NSAIDs/analgesics), and 2.05 µg/L (trimethoprim - antibiotic). From the class of antidepressant compounds, and already in a much lower concentration range, frequently detected venlafaxine was reported in a maximum concentration of 0.128 µg/L in Spain. Also fluoxetine was frequently detected, with maximum concentrations of 0.101 µg/L and 0.025 µg/L found in China and USA, respectively, and 0.017 µg/L in Spain (Hawash *et al*., 2023; Y. Xiang *et al*., 2021).

Concerning superficial waters in Portugal (Leiria, Lis river), the occurrence of 33 pharmaceuticals and metabolites between 2013 and 2014 was evaluated in river water, influents and effluents of two WWTPs located along the river (Paula Paíga *et al*., 2016). A detection frequency of 100% was obtained for ibuprofen, ketoprofen (both NSAIDs/analgesics), carbamazepine, and fluoxetine (both psychiatric drugs), and the metabolite salicylic acid (NSAIDs/analgesics), revealing the maximum level of 1.3 µg/L for ibuprofen and 0.53 µg/L for acetaminophen (NSAIDs/analgesics) (Paula Paíga *et al*., 2016).

Accordantly, Acuña *et al*. detected 50 of the 75 monitored pharmaceuticals in the Iberian Rivers (Ebro basin) and spotted a maximum concentration of 5.1 µg/L for Iopromide (β-blockers), 1.9 µg/L for gemfibrozil (lipid regulator), 1.75 µg/L for fluvastatin (statin), 1.15 µg/L for hydrochlorothiazide (diuretics) and 1.8 µg/L for valsartan (antihypertensive drugs) (Acuña *et al*., 2015). Fluoxetine, although not detected in high concentrations in surface water, usually has high detection frequencies (Paula Paíga *et al*., 2016; P. Zhang *et al*., 2017).

After achieving superficial waters, or once in the soil, these contaminants are persistent and mobile, allowing them to infiltrate groundwater through percolation (Mejías *et al*., 2021; J. Sharma *et al*., 2022; Silori *et al*., 2022).

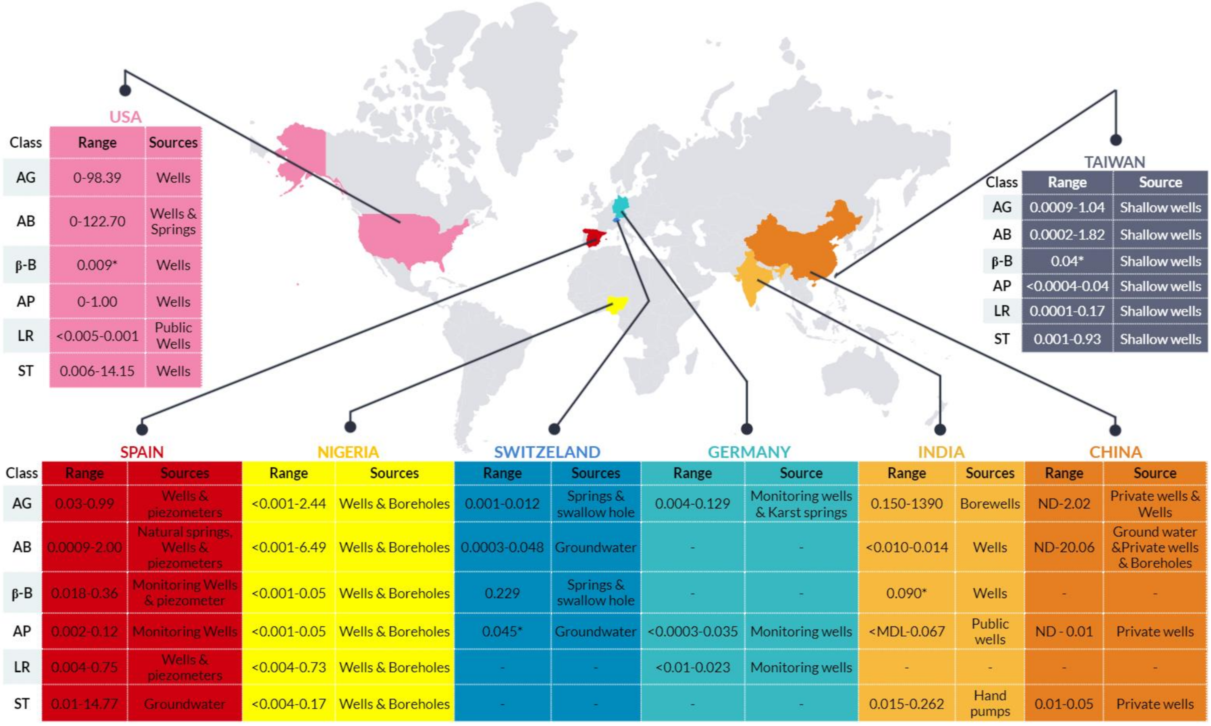
While groundwater is generally considered more resilient to contamination by emerging pollutants compared to surface water, traces of several contaminants, including pharmaceuticals, have been found in groundwater systems of several countries, namely China (L. Chen *et al*., 2018; Ma *et al*., 2022), Nigeria (Ebele *et al*., 2020; Olaitan *et al*., 2017), Brazil (Montagner *et al*., 2019), Bangladesh, Kenya (K'oreje *et al*., 2016), India (B. M. Sharma *et al*., 2019), Spain (Gasco Cavero *et al*., 2023), among many others. Removing them from matrices such as rocks, soil, sediments, and the unsaturated zone proves to be a challenging task.

In 2012, Lapworth *et al*. published a wide-ranging review highlighting the world's widespread contamination of groundwater resources by a large variety of emerging contaminants detected at potentially environmentally significant concentrations until 2011 (excluding agricultural pesticides and their degradation products). Regarding pharmaceuticals, the most frequently reported group of compounds in the analyzed studies presented average (maximum) values of 15.1 μg/L (120 μg/L) for paracetamol, 9.77 μg/L (110 μg/L) for caffeine and 5.31 μg/L (99,2 μg/L) for carbamazepine.

After the publication of the European Commission's Groundwater Directive 2006/118/EC (European Commission, 2006), aiming to 'prevent and control groundwater pollution' by several contaminants, in 2014, an amendment to its Annex II was published, highlighted that the lack of information made it impossible to create new groundwater quality standards for any pollutants (European Commission, 2014). It also emphasized the need to increase the availability of monitoring data on substances posing a risk or potential risk to groundwater bodies by determining background levels and establishing a "watch list for pollutants of groundwater". In 2019, a voluntary Groundwater Watch List (GWWL) was implemented, ranking as compounds of current concern nine pharmaceutical and two per-fluoroalkyl and polyfluoroalkyl substances (PFAS). Four additional PFAS were shortlisted for inclusion. The goal of the GWWL was to center attention on these priority compounds until detailed information is available to set regulatory levels. This list is active and constantly evolving. As new results are collected, others will be added to or replace listed ones possibly regulated.

Following the work of Lapworth *et al.*, and aiming to understand the evolution of groundwater contamination in Europe due to improvements of the Directive 2006/118/EC (European Commission, 2006), in 2021, Bunting *et al.*, reviewed the presence of emerging organic compounds, this time focusing in European groundwater, through the analysis of 39 published studies between 2012 and 2020. Once again, the most frequently reported category of compounds was 'Pharmaceuticals'. In this review, the most frequently detected compounds were the anti-epilepsy drug carbamazepine, the antibiotic sulfamethoxazole, the anti-inflammatories diclofenac, and ibuprofen (included in the 11 compounds of current concern of the GWWL), and the lipid regulator bezafibrate.

Recently, Silori *et al.*, (2022) also performed a systematic literature review concerning the occurrence of pharmaceuticals (among other CEC) in groundwater reported from of the second decade of 21st century in the world. Figure 2.5 highlights the contamination concentration range for six pharmaceutical classes in eight of the countries included in the reviewed research.



USA

Class	Range	Sources
AG	0-98.39	Wells
AB	0-122.70	Wells & Springs
β-B	0.009*	Wells
AP	0-1.00	Wells
LR	<0.005-0.001	Public Wells
ST	0.006-14.15	Wells

TAIWAN

Class	Range	Source
AG	0.0009-1.04	Shallow wells
AB	0.0002-1.82	Shallow wells
β-B	0.04*	Shallow wells
AP	<0.0004-0.04	Shallow wells
LR	0.0001-0.17	Shallow wells
ST	0.001-0.93	Shallow wells

	SPAIN		NIGERIA		SWITZELAND		GERMANY		INDIA		CHINA	
Class	Range	Sources	Range	Sources	Range	Sources	Range	Source	Range	Sources	Range	Source
AG	0.03-0.99	Wells & piezometers	<0.001-2.44	Wells & Boreholes	0.001-0.012	Springs & swallow hole	0.004-0.129	Monitoring wells & Karst springs	0.150-1390	Borewells	ND-2.02	Private wells & Wells
AB	0.0009-2.00	Natural springs, Wells & piezometers	<0.001-6.49	Wells & Boreholes	0.0003-0.048	Groundwater	-	-	<0.010-0.014	Wells	ND-20.06	Ground water &Private wells & Boreholes
β-B	0.018-0.36	Monitoring Wells & piezometer	<0.001-0.05	Wells & Boreholes	0.229	Springs & swallow hole	-	-	0.090*	Wells	-	-
AP	0.002-0.12	Monitoring Wells	<0.001-0.05	Wells & Boreholes	0.045*	Groundwater	<0.0003-0.035	Monitoring wells	<MDL-0.067	Public wells	ND - 0.01	Private wells
LR	0.004-0.75	Wells & piezometers	<0.004-0.73	Wells & Boreholes	-	-	<0.01-0.023	Monitoring wells	-	-	-	-
ST	0.01-14.77	Groundwater	<0.004-0.17	Wells & Boreholes	-	-	-	-	0.015-0.262	Hand pumps	0.01-0.05	Private wells

Figure 2.5 - Range of PPCPs' groundwater contamination (μg/L) of all the therapeutic classes - Analgesics/Antipyretics/NSAIDs (AG), antiepileptics (AP), β-blockers (β-B), antibiotics (AB), lipid regulators (LR) and stimulants (ST) - sample site. * Only the maximum concentration of the given therapeutic class (Adapted with permission from (Silori et al., 2022). Copyright 2022, Journal of Environmental Management).

The highest concentration was found in India, of 1 390 μg/L for diclofenac (NSAID), followed by ofloxacin (antibiotic) that presented a maximum concentration of 122.7 μg/L, by naproxen (NSAID) of 98.39 μg/L, and by sulfamethoxazole (antibiotic) of 32.00 μg/L, both in USA. Sulfamethoxazole was, also, the pharmaceutical compound with the maximum concentration reported in China (20.06 μg/L). In addition, Singapore presented a maximum concentration for caffeine (stimulants) of 16.25 μg/L (not included in the figure).

Monitorization studies in sediments contamination are less frequent. Xiang *et al.* (2021) reviewed the occurrence of pharmaceuticals in the aquatic environment in China, including sediments. The detection level in literature varies but several pharmaceuticals were found in concentrations higher than 100 µg/kg (103.0 - 384.59 µg/kg), including the antibiotics ofloxacin, enrofloxacin, oxytetracycline, tetracycline, trimethoprim, azithromycin, roxithromycin, and erythromycin. The highest detected concentration was found for azithromycin (1 179 µg/kg) and norfloxacin (1 140 µg/kg). Anti-inflammatory diclofenac (278.1 µg/kg) and Ibuprofen (227.1 µg/kg), antipyretic acetaminophen (320.7 µg/kg) and stimulant caffeine (482 µg/kg) were also detected (Y. Xiang *et al.*, 2021). Lower values have been reported in Kenya (maximum concentrations ranged 1.8 µg/kg – 47.4 µg/kg for trimethoprim, and ciprofloxacin, respectively) (Kairigo *et al.*, 2020), as well as in Brazil (maximum concentrations ranged 0.9 µg/kg – 15.5 µg/kg for diclofenac and naproxen, respectively) (de Oliveira Santos *et al*., 2022).

The consumption of psychiatric drugs (in which antidepressants are included) has seen a significant rise in recent years, probably due to the financial crisis in Europe, followed by the COVID-19 pandemic, which promoted adverse psychological effects and numerous psychiatric disorders and, consequently, increased their usage (Borova *et al*., 2014; Pazzagli *et al*., 2022).

Considering the previously reported high frequency of antibiotic detection and the increasing use of antidepressants, it is essential to continue to monitor the various environmental compartments for contamination by these products so that regulators and governments can understand how serious the current situation is and what measures will be most appropriate to address it.

Pharmaceutical manufacturers, regulatory agencies, and wastewater treatment plants managers are working to address the issue of pharmaceutical contamination in the environment. Strategies include improving the design of drugs to make them less persistent in the environment, increasing the effectiveness of wastewater treatment systems to remove pharmaceuticals, and promoting proper disposal of medications by patients (Kotwani *et al*., 2021). Individuals can also play and important role in reducing environment pharmaceutical contamination by properly disposing of unused medications through designated take-back programs or participating in at-home medication disposal methods recommended by the Environmental Protection Agency. Monitorizations is essential to measure the level of contamination and lead to studies of toxicity and new contamination treatments.

2.2.1 Fluoxetine antidepressant use

The consumption of antidepressants has been on the rise in recent decades, predominantly due to an increase in mental health issues such as depression and anxiety (Figure 2.6). The COVID-19 pandemic further exacerbated this trend, as it led to a heightened prevalence of psychological disorders. Consequently, there has been a significant rise in the use of antidepressants, including selective serotonin reuptake inhibitors (SSRIs). Antidepressant drugs, in 2020, accounted for 4% of pharmaceutical sales in Portugal, 2.7% in Spain, 2.2% in Austria, and 1.7% in Italy, suggesting a significant cost in some European countries (OECD.Stat, 2022). This growing consumption of antidepressants may pose a potential contamination risk to the environment. When individuals excrete these compounds and their metabolites, they can enter water bodies due to the insufficient removal rates in water treatment plants.

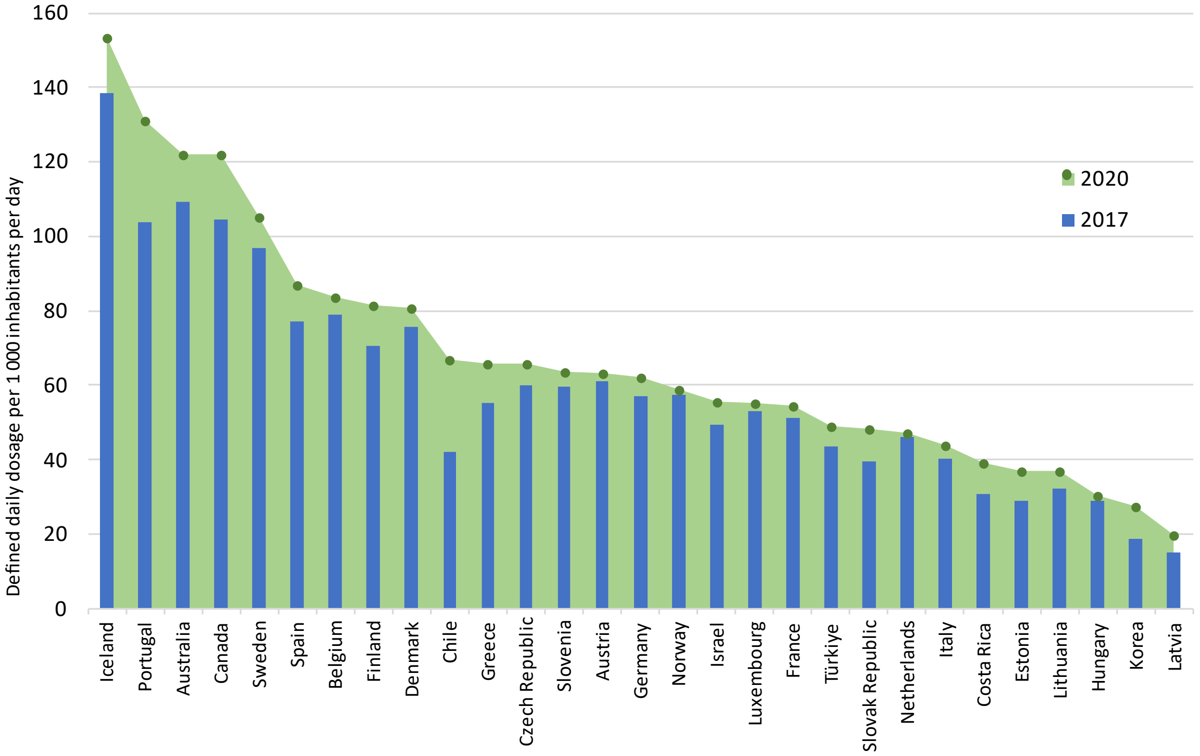


Figure 2.6 - Defined daily dosage per 1 000 inhabitants per day of antidepressant in 2017 and 2020 by the Organization for Economic Co-operation and Development (OECD) countries (Data source: (OECD.Stat, 2022) - developed by the author).

As a result, these substances are released into the environment at varying concentrations, which can have multiple and diverse effects on both terrestrial and aquatic species. Exposure to these substances can lead to consequences such as changes in genetic transcription, reproductive deficiencies, and impaired motility. Additionally, they can cause alterations in the behavior of organisms during migration and when defending against predators. Overall, the increased use of antidepressants is not only a reflection of the growing mental health challenges faced by society but also a potential environmental concern that needs to be addressed (Diaz-Camal *et al.*, 2022; Mole & Brooks, 2019).

Fluoxetine is a 2nd generation antidepressant categorized as a SSRI, acting on the central nervous system by blocking the serotonin transporter in the neuron membrane. Serotonin, is a prominent neuromodulator present in the nervous systems of both vertebrates and invertebrates, playing a significant role in various physiological processes encompassing behavior, growth, and reproduction (Correia *et al.*, 2023; National Center for Biotechnology

Information, 2023b). Is currently approved by the U.S. Food and Drugs Administration (FDA) indicated for both acute and maintenance treatment of major depressive disorder in patients aged eight years and older, including obsessive-compulsive disorder, panic disorder, and bulimia (Correia *et al*., 2023; Sohel *et al*., 2023). It is usually sold as Fluoxetine Hydrochloride under the trade name Prozac© (National Center for Biotechnology Information, 2023b). This antidepressant was discovered in 1974 by chemists at the pharmaceutical company Eli Lilly and authorized for commercialization by the FDA for the first time in 1987 (Correia *et al*., 2023). Fluoxetine is a well-established medication, the fourth most used SSRI antidepressants in the USA, with approximately 23 million total prescriptions in 2020 and ranking 25th on the list of the 200 most prescribed drugs (no accessible data found for Europe in recent years) (ClinCalc DrugStats Database, 2023).

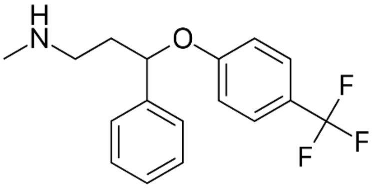
Fluoxetine has received substantial attention because of its frequent detection in surface waters and municipal effluents (Biel-Maeso *et al*., 2018; M. P. Gomes *et al*., 2022; Mejías *et al*., 2021; Paula Paíga *et al*., 2019). Given its ubiquity in the environment and these type of compounds mode of action in low doses, concerns have emerged regarding the potential impacts of fluoxetine, on aquatic organisms and their associated behavioral patterns, highlighting the importance of the applicable regulation (Bertram *et al*., 2018; Correia *et al*., 2023; de Farias *et al*., 2019). Further investigation is essential to: (i) clarify the extent to which fluoxetine exposure may alter the normal functioning of serotonin-mediated processes in aquatic species, between other alterations, consequently affecting their survival and overall ecosystem health and: (ii) to propose new treatment technologies.

2.2.2 Antidepressant Fluoxetine - chemical and physical properties

In addition to the amount consumed and excreted, same pharmaceutical properties could define their tendency to contaminate and accumulate in water over time. These properties include their solubility, persistence, and bioaccumulation potential. Pharmaceuticals are often designed to be soluble in water to ensure that they can be easily absorbed by the body and reach their target sites. This high solubility allows them to be transported by water and be readily absorbed by aquatic organisms. Many pharmaceuticals are categorized as environmentally persistent, since stability is often considered to be a beneficial property to their use by humans. Additionally, their persistence is also associated to their continuous flow into the environment (Patel *et al*., 2019). Concerning the bioaccumulation potential, described as the ability of pharmaceuticals to accumulate in the tissues of organisms over time, it occurs when organisms absorb the pharmaceuticals at a faster rate than they can eliminate them. As a result, the concentration of the pharmaceuticals in the organism's tissues and organs increases, potentially leading to harmful effects on the organism itself or predators that consume it (de Oliveira Santos *et al.*, 2022; Patel *et al.*, 2019).

The main fluoxetine physicochemical properties are resumed in Table 2.1.

Table 2.1 - Fluoxetine physicochemical properties (Data source: DrugBank and PubChem® 2022 database (National Center for Biotechnology Information, 2023d, 2023c))

Compound	**Glyphosate**
CAS	54910-89-3
IUPAC name	N-methyl-3-phenyl-3-[4-(trifluoromethyl)phenoxy]propan-1-amine
Chemical structure	
Formula	$C_{17}H_{18}F_3NO$
Molecular weight (g/mol)	309.33
Water solubility at 25 ◦C (mg/L^{-1})	1.7 (almost insoluble)[a]
$LogK_{ow}$	4.05
pK_a	9.8

[a] 14x10^3 mg/L as Fluoxetine Hydrochloride

The stability of pharmaceuticals can be influenced by the type of molecular fractions connected to the aromatic rings, such as nitro-, chloro-, and fluoro-functional groups, which typically increase the persistence of these compounds in the environment (Patel *et al.*, 2019). However, other factors like pH and temperature, as well as biotic factors such as microflora and fauna, present in the water body can negatively impact the stability of pharmaceutical compounds, leading to their degradation. Despite this degradation process, the continuous release of large quantities of pharmaceutical residues and their slower rate of auto-degradation can cause contamination levels to increase. This build-up of contamination can have harmful effects on human health, and aquatic life (Patel *et al.*, 2019; J. Sharma *et al.*, 2022). Fluoxetine half-life in natural waters range from 2 to 7 days according with several studies (Kosma *et al.*, 2020; Pan *et al.*, 2022), and can reach 183.2 days in ultrapure water (Yin *et al.*, 2017).

2.2.3 Antidepressant Fluoxetine - degradation and dissipation paths

When a pharmaceutical is consumed by a patient, it is first metabolized in the body, and it is either excreted as unchanged pharmaceutical residues or its metabolites (A. H. Khan *et al.*, 2022). Only 70-80% of the used fluoxetine is metabolized by the human body producing its metabolites norfluoxetine and fluoxetine glucuronide, while the remaining is passed unaltered to sewage systems (Munari *et al.*, 2014). Accordantly, pharmaceuticals as fluoxetine mainly enter the environment through the effluents of WWTPs or untreated sewage, following human consumption and excretion (Kosma *et al.*, 2020; Mole & Brooks, 2019). Additionally, in treatment facilities associated with hospitals and health treatment services, the effluent is potentially contaminated with higher concentrations of pharmaceuticals (Kosma *et al.*, 2020).

Figure 2.7 schematize the most significant sources of contamination by pharmaceuticals, particularly fluoxetine, namely household use, WWTP, landfill leachates, hospital waste or wastewater and pharmaceuticals manufacture industry.

Figure 2.7 - Sources and fate of fluoxetine in the environment (developed by the author).

Households refers to the location where this substances are used and discharged, including non-metabolized excreted fluoxetine and the non-used and flushed through the toilet (Hawash *et al*., 2023). The majority of the sewage produced in the urban centers are channeled to WWTP that discharge their effluent in surface water. Additionally, sewage sludge from WWTP is often applied in the field as well as recycled water is used of irrigation. Being contaminated with fluoxetine they could affect plants or animals when used as manure and led this pharmaceutical substance to infiltrate and percolate down, contaminating groundwater (A. H. Khan *et al*., 2022; J. L. Santos *et al*., 2022). Moreover, considering the urban centers, the waste produced and sent to landfill may be contaminated, potentiating the pollution of the landfill leachate that will be directed to a WWTP or directly discharged to surface waters. Hospitals, where a high pharmaceutical consumption occurs, produces contaminant-laden effluents and wastes with a mixture of chemicals such as pharmaceuticals. The same in pharmaceutical industries, that are also potential contamination sources (Hawash *et al*., 2023; Ishfaq Showket Mir *et al*., 2022; A. H. Khan *et al*., 2022; Kock *et al*., 2023; Veiga *et al*., 2023).

2.2.4 Analytical methodologies for Fluoxetine detection in environmental matrixes

The low environmental concentrations of pharmaceuticals associated with complex matrices require investment in analytical techniques to efficiently study these compounds. Currently, the basis of analytical methodologies to determine the presence of pharmaceutical compounds and their respective metabolites in environmental samples has been developed for surface water, effluents, sediments, and treatment plant sludges emphasizing extraction processes with greater adaptation to the properties of the analytes and operational robustness.

In pharmaceutical analysis, various analytical approaches have been used, such as gas chromatography with mass detector or a with high-resolution mass spectrometer in series (GC-MS) (Açikkol & Salkim, 2010) and liquid chromatography (LC) coupled with different detectors such as diode array detector (DAD) (Evagelista *et al*., 2020; Sarıkaya *et al*., 2021), ultraviolet (UV) (Ata *et al*., 2015), mass spectrometry (MS) (Mole & Brooks, 2019), and fluorescence (FLD) (Andreia Silva *et al*., 2022) detection are the most widely used techniques to determine antidepressant. Additionally, but less frequently, electrochemical methods are used in the detection of this compound (Ardelean *et al*., 2017).

For fluoxetine extraction, solid phase extraction (SPE) (Patel *et al*., 2019; Pérez-Fernández *et al*., 2017) is the most applied methodology. Other procedures for extracting antidepressants are also used as liquid–liquid extraction (LLE), and some miniaturized techniques as solid-phase microextraction (SPME), microextraction by packed sorbent (MEPS), and dispersive liquid–liquid microextraction (DLLME) (Soares *et al*., 2021). Furthermore, soil and sediments pharmaceutical extraction is mainly performed applying QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method (Cerqueira *et al*., 2014; Nannou *et al*., 2019).

2.3 Pesticides environmental contamination

Pesticides are a family of compounds with different physical and chemical properties, natural or synthetic, applied to either kill or prevent the growth of unwanted pests, namely insects, rodents, fungi, or weeds. Insecticides, herbicides, nematicides, fungicides, molluscicides, rodenticides, algicides, plant growth regulators, are some of the pesticide's groups based on target organism, one of the most used classifications (Figure 2.8). Categorization according to its main chemical class, mode of action or active ingredient including, for example, organophosphates, neonicotinoids and pyrethroids, it's also widely used. Within the general group of pesticides, subcategories could also be defined according to the common chemical characteristic or functional group (e.g., group: herbicides; chemical class: organophosphorus herbicides) (Pathak *et al*., 2022; Raj *et al*., 2023; Akanksha Sharma *et al*., 2020).

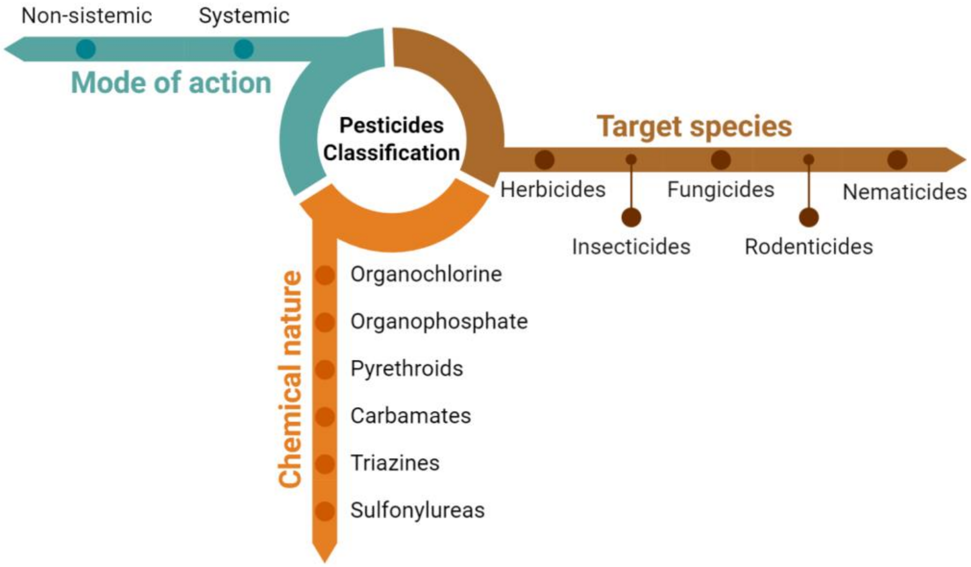


Figure 2.8 - Schematic representation of the three most employed classifications of pesticides based on target species, in its chemical nature and mode of action, and some examples (developed by the author).

Pesticides have become a crucial component of modern agriculture, applied to protect crops, enhance its quality, and increase yields (Rodríguez-Bolaña *et al*., 2023; Anket Sharma *et al*., 2019; Syafrudin *et al*., 2021). Thus, according to FAO data (Figure 2.9), in the last three decades, the use of pesticides has shown a considerable upsurge associated with growing production needs and the addition of new pests and diseases, representing an increase of more than 50% (FAO, 2022).

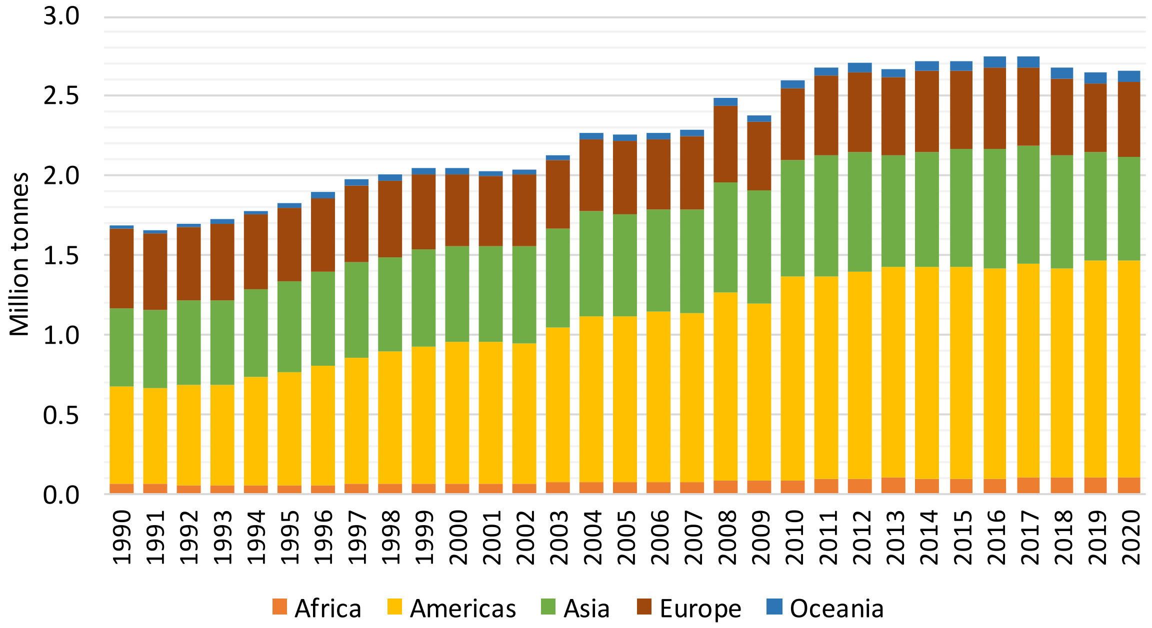


Figure 2.9 - Total pesticides agricultural use by region and year, from 1990 to 2020 (Data source (FAO, 2022) - developed by the author).

America was the continent where this increase was most pronounced, followed by Asia. Africa and Oceania also showed very significant growth, but less representative in total quantity in relation to the absolute values of pesticides used worldwide.

Referring to their class, herbicides were the pesticides with the most significant growth, having more than doubled the quantity used worldwide between 1990 and 2020 (Figure 2.10).

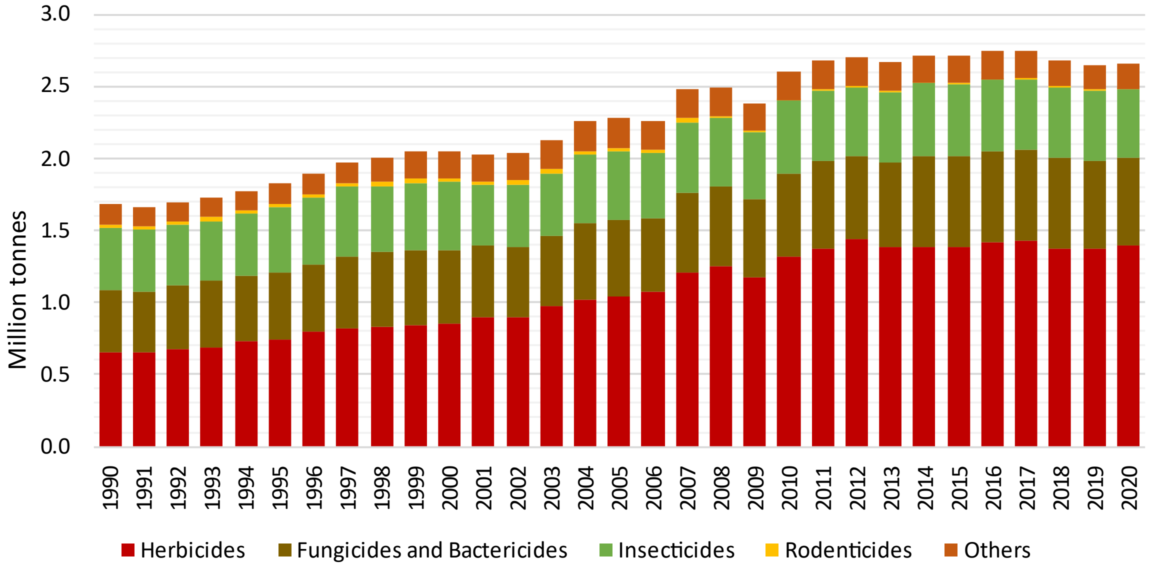


Figure 2.10 - Pesticides agricultural use by year and by category from 1990 to 2020 (Data source (FAO, 2022) - developed by the author).

Between 2010 and 2020, of the 29.6 million tons of pesticides used worldwide, 52% were herbicides, 23% were fungicides and bactericides, and 18% were insecticides. During the same decade, the top five pesticide-using countries in the world were the United States, Brazil, China, Argentina, and Canada. Spain was ranked 13th, and Portugal 38th (FAO, 2022).

Although the importance of pesticides in pest and disease management is widely recognized, their use has been associated with adverse effects on biodiversity and ecosystem functioning, including significant impacts on aquatic ecosystems (R. M. de Souza *et al*., 2020). Both currently used pesticides and those discontinued or banned for agricultural use can persist in the environment, contaminating surface waters and accumulating in organisms (R. M. de Souza *et al*., 2020; Pérez-Parada *et al*., 2018).

Even though its application method is mostly direct on the soil/plant, pesticides could be transported over significant distances through processes such as airborne, thru adsorption to dust particles, volatilization, and precipitation (Pazikowska-Sapota *et al*., 2020). Many factors impact the transport process and reach, including weather conditions, soil properties, human activities, application patterns, surface water runoff rates, aquifer thickness, and the physicochemical properties of pesticides (Andrade *et al*., 2021; Bento *et al*., 2018; Didoné *et al*., 2021).

Moreover, these substances can reach water bodies via several pathways as surface runoff and percolation through the soil, eventually contaminating groundwater. Consequently, reports of pesticide residues and their metabolites being found in groundwater, surface water, sediments, soil and food, with high detection frequency and high concentrations are becoming more and more frequent all around the world (R. M. de Souza *et al*., 2020; Kudsk & Mathiassen, 2020; Rodríguez-Bolaña *et al*., 2023; Schleiffer & Speiser, 2022). Because of their potential for contamination, ecological and health concerns have arisen, as pesticides are one of the most investigated contaminants in groundwater samples worldwide (Montagner *et al.*, 2019).

Throughout the world, in agricultural and forestry areas and surrounding water sources, an alarming density of pesticides has been discovered, as seen in the survey presented in Figure 2.11. Postigo *et al.*, (2021), searched for the presence of 102 pesticides in several surface and groundwater samples in Barcelona, Spain, and detected 28, with a maximum total pesticide concentration of 1.3 µg/L (winter) and 1.9 µg/L (summer) (Postigo *et al.*, 2021). Also in Europe, in Saxony-Anhalt, central Germany, 54 pesticides were monitored in surface water and soils (Tauchnitz *et al.*, 2020). In surface waters, this author's most frequently detected substances were herbicide glyphosate (also with the higher concentration found in waters, 58 µg/L), its degradation product AMPA, and herbicide bentazone. In soils, herbicide diflufenican and fungicides boscalid, tebuconazole, and epoxiconazole were the most frequently detected pesticides, but glyphosate and AMPA showed the highest concentrations, of 190 and 170 µg/kg, respectively (Tauchnitz *et al.*, 2020). This study observed that higher number of pesticides, frequency of detection and maximum concentrations were found in surface water samples in mostly urban surroundings and not in agricultural surroundings. Additionally, in most cases, pesticide detections were not consistent with farmers application data, suggesting that water quality may be also affected by urban sources. Moreover, pesticide adsorption onto the soil matrix was tested by the authors, and could be responsible for delayed inputs of the used compounds into surface waters (Tauchnitz *et al.*, 2020).

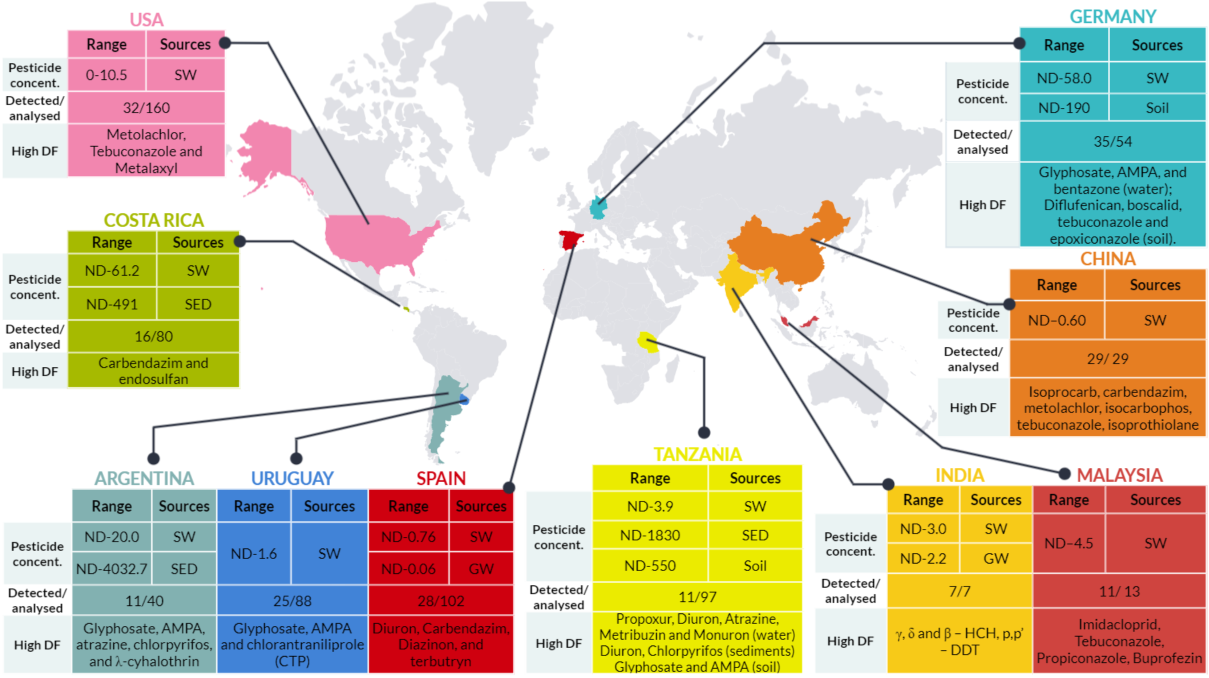


Figure 2.11 - Range of pesticides concentration (surface water (SW) and groundwater (GW): µg/L; sediments (SED) and soils: µg/kg) found in several studies (Data source: USA: Glinski et al., 2018; Spain: Postigo et al., 2021; Costa Rica: (Carazo-Rojas et al., 2018) Argentina: Mac Loughlin et al., 2022; Uruguay: Rodríguez-Bolaña et al., 2023; Tanzania: Materu et al., 2021;India: (Kurakalva & Aradhi, 2022);China: Xu et al., 2020; Germany: Tauchnitz et al., 2020; Malaysia: Elfikrie et al., 2020) DF: Detection Frequency; ND: under the detection limit (developed by the author).

Y. Chen *et al.* (2018) assessed 31 target pesticides in surface water from two important rivers in China used as drinking water source and found, with almost 100% detection frequency, 8 organochlorine pesticides, 16 organophosphate pesticides and 7 synthetic pyrethroids with maximum concentrations ranging from 0.02–0.09 µg/L, 0.01–0.3 µg/L, and from 0.02–0.1 µg/L, respectively. The maximum summed pesticide concentration was found to be 1.7 µg/L (Y. Chen *et al.*, 2018). Additionally, in a nearby river, Xu *et al.*, (2020) detected 29 pesticides, with a maximum concentration of 0.60 µg/L for the fungicide carbendazim and the total summed concentration of 1.04 µg/L in winter and 0.79 µg/L in summer (L. Xu *et al.*, 2020).

In Argentina, surface water and sediments from a small horticultural stream concerning the presence of 40 compounds were studied by Mac Loughlin *et al.*, (2022), that found herbicide glyphosate and its degradation product AMPA as the most frequently detected pesticides, with maximum concentrations in water of 20.0 µg/L and 4.9 µg/L, and in sediment of 1 146.5 µg/kg and 4 032.7 µg/kg. Pesticides were found in all matrices analyzed at every site sampled in 5 out of 6 sampling campaigns (Mac Loughlin *et al.*, 2022b). In Georgia, USA, the concentrations found in surface water were within the same order of magnitude, with a maximum value of 10.5 µg/L for the herbicide metolachlora (also the most frequently detected). The highest summed pesticide concentration was 39.67 µg/L, in summer (Glinski *et al.*, 2018).

In Uruguay, a monitoring survey was performed to investigate the presence of 88 pesticides in surface water (drinking water sources). 25 of the 88 analyzed pesticides were detected in surface water, with higher occurrences in spring and summer than in autumn and winter. Herbicide glyphosate, AMPA, and the insecticide chlorantraniliprole were the most frequently detected and presented values ranging 0.23-1.05 µg/L, 0.58-0.89 µg/L and 0.008-0.063 µg/L, respectively (Rodríguez-Bolaña *et al.*, 2023).

Carazo-Rojas *et al*. (2018) studied the Tempisque river basin, in Costa Rica, and reported the presence, with the highest concentrations detected in the water samples among other pesticides, of the insecticide dimethoate (0.4-61.2 µg/L), and the herbicides propanil (30.6 µg/L), diuron (0.1-22.8 µg/L) and terbutryn (0.05-4.8 µg/L). The fungicide carbendazim was the most frequently detected pesticide. In sediments, the most frequently detected pesticide was the insecticide endosulfan, and the highest levels were found to be of the insecticides triazophos (0.04-491 µg/kg), cypermethrin (0.8-71.5 µg/kg) and permethrin (47.8 µg/kg), followed by herbicide terbutryn (3.0-38.7 µg/kg) (Carazo-Rojas *et al.*, 2018). The authors also refer, as Tauchnitz *et al*. (2020) in Germany, that the agricultural practices near the studied water body, which involve high application rates and frequent use of some pesticides, do not appear to have a direct correlation with higher detection frequencies or concentrations found. This implies that other aspects, such as mobilization/transport, maybe more significant in determining the occurrence of pesticides in the region.

Also, in Tanzania, Materu *et al.*, (2021) found maximum levels of 3.9 µg/L (herbicide monuron) in waters, 1 830 µg/kg (insecticide chlorpyrifos) in sediments and 550 µg/kg (herbicide glyphosate) in soils and in Malaysia, Elfikrie *et al.*, (2020) has detected fungicide propiconazole as the pesticide with the higher concentration in the studied river water, with a value of 4.5 µg/L. In general, in the analyzed studies, and as expected, the levels of pesticides found in surface waters exhibit seasonal patterns, with greater concentrations detected during periods of intensive usage (such as spring and summer, during the preparations for cultivation), and lower levels during the winter and after the harvesting of crops.

Some of the detected compounds are banned compounds according to the country legislation (e.g. banned in Uruguayan: p,p'-DDT, p,p'-DDD, p,p'-DDE, atrazine, alpha-BHC and ethion; not approved for use in the European Union: acetochlor, bifenthrin, chlorpyrifos, diazinon, metalaxyl, permethrin, and simazine). This embodies a key challenge as these substances have been banned for their adverse effects on the ecosystem and human health (Rodríguez-Bolaña *et al*., 2023).

2.3.1 The use of glyphosate and glufosinate-based herbicides

Glyphosate or N-(phosphonomethyl) glycine, is a broad-spectrum herbicide widely used throughout the world. Comparable in structure to other organophosphate pesticides, this compound differs in terms of its toxicology, as it does not inhibit cholinesterase activity (IARC, 2017). It is used to control a wide variety of annual and perennial weeds in many crops, including corn, soybeans, cotton, and wheat. Agriculture, forestry, landscaping, and managing roadside vegetation also represent some of the glyphosate applications. When absorbed by the green parts of the plant and its root system (minority), it suppresses the function of the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS), which is an intermediary in the synthesis of aromatic amino acids via the shikimic acid pathway. These amino acids are vital to synthesizing proteins and producing secondary plant products including phenolic compounds, lignin, and various growth promoters and inhibitors. Besides photosynthesizing organisms, essentially plants and algae, and some microorganisms in the soil (bacteria and fungi), EPSPS is not expressed in mammals and other vertebrates, apparently keeping them safe from unintentional damage (Fogliatto *et al*., 2020; Padilla & Selim, 2020; Solomon, 2020).

Accidently discovered by Dr. Henri Martin in 1950 as a potential pharmaceutical, glyphosate's potential for use in agriculture was only recognized around 20 years later, when Dr. John Franz, the founder of Monsanto Company, revealed its capabilities as an herbicide (timeline presented in Figure 2.12). The patent for glyphosate was filled in 1972, and it was first introduced to the market in 1974 by Monsanto Company under the trade name Roundup®. Though, despite its efficiency as a nonselective, broad-spectrum herbicide, the global use of glyphosate has, firstly, increased slowly over time. Due to its initial limited applications, since it can only be applied to kill all vegetation in non-crop areas such as public or private parks, cemeteries, gardens, and along roads and railway tracks, and its use in agriculture was restricted to post-harvest or late-season applications, normally applied when other control measures have failed (Benbrook, 2016; Mesnage & Antoniou, 2017). In 1996, the Roundup Ready crop's introduction, a variety of crops genetically engineered to survive glyphosate-based herbicides application, led to a significant increase in the sales and usage of glyphosate, simplifying weed management processes (Benbrook, 2016; IARC, 2017; Mesnage & Antoniou, 2017).

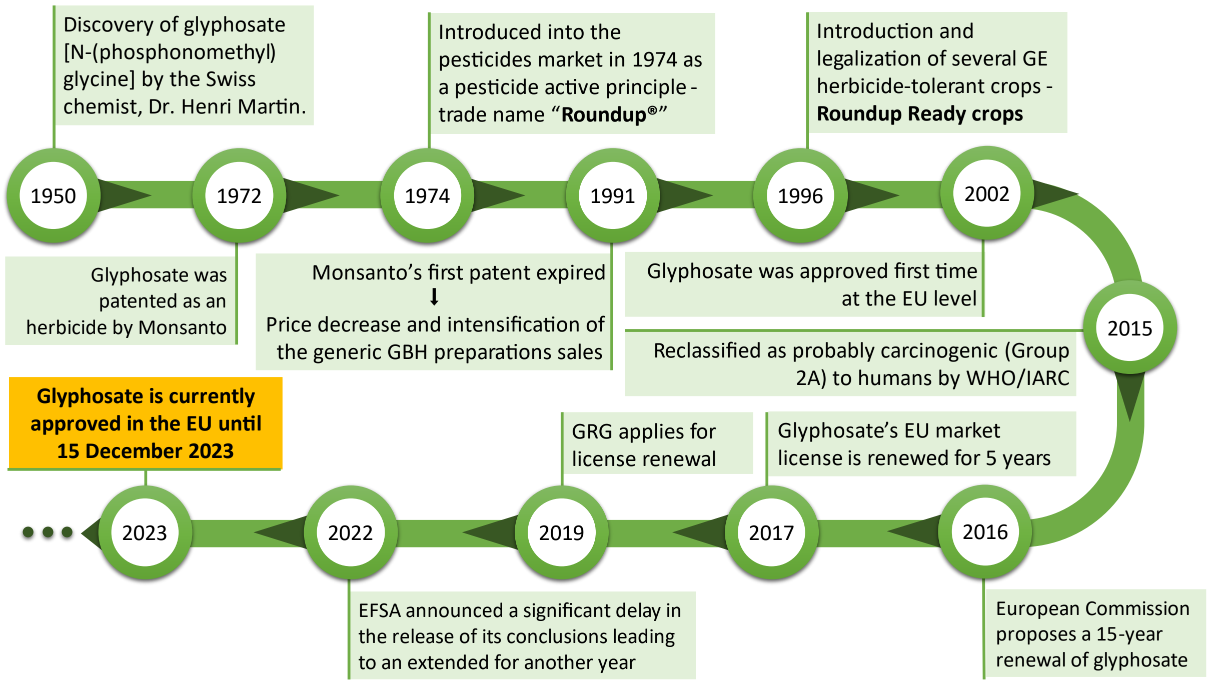


Figure 2.12 - Timeline displaying the highlights of glyphosate history; GE: genetically engineered; GBH: glyphosate-based herbicide; GRG: Glyphosate Renewal Group; WHO: World Health Organization (Data source: (EFSA, 2023; European Commission, 2023; Kudsk & Mathiassen, 2020) - developed by the author).

Subsequent to the introduction and spread of Roundup Ready crops use, the expiration of Monsanto's patent and the consequent development of new glyphosate formulations by other companies, led to an exponential growth in glyphosate agricultural application, and consequent increases of its residues presence in food (J. Xu *et al.*, 2019), feed (Zhao *et al.*, 2018), and environmental matrix as air (Ramirez-Haberkon, Aimar, *et al.*, 2021), soil (V. Silva *et al.*, 2018, 2019), and water (Suciu *et al.*, 2023).

Following the World Health Organization's reclassification of glyphosate as probably carcinogenic (Group 2A) to humans in 2015 by the IARC (EFSA, 2015; IARC, 2017), the amount of published articles related to several glyphosate approaches has been growing, and numerous review articles have been published on various glyphosate-related topics and its contentiousness (Gillezeau *et al.*, 2019; Muñoz *et al.*, 2021; Rivas-Garcia *et al.*, 2022; Solomon, 2020; J. Xu *et al.*, 2019).

In 2017, the Appeal Committee on Plant Protection Products legislation, involving representatives from EU member states, voted in favor of the EU Commission's proposal to re-approve the use of the herbicide glyphosate for a period of five years. However, due to intense discussions during the re-approval process, the responsibility for any further restrictions on glyphosate's use was delegated by the EU to individual Member States, contrary to the common harmonization strategy (European Commission, 2017; Huhn, 2018).

While several countries acknowledge the potential hazards of glyphosate, they currently lack safer alternatives and other weed management technologies that could provide an economically viable substitute for weed control (Alcántara-de la Cruz *et al*., 2021; Fogliatto *et al*., 2020). Known alternatives to glyphosate are currently limited, less effective, and more expensive. As a result, successful and profitable weed management in major agronomic crops without glyphosate represents a significant challenge and requires the acquisition of new knowledge and skills for a successful transition (Alcántara-de la Cruz *et al*., 2021; Beckie *et al*., 2020). These discrepancies have sparked widespread controversy and led to different regulations worldwide, ranging from complete bans to permissive policies (Rivas-Garcia *et al*., 2022).

The re-approval of glyphosate produced an intense debate regarding its probably carcinogenic effects. However, this IARC classification was opposed by other national agencies and organizations associated with the WHO, as well as the EU. This discrepancy caused a great deal of controversy surrounding the re-approval process, with the safety of glyphosate being a major point of disagreement (Huhn, 2018; Rivas-Garcia *et al*., 2022).

Aminomethylphosphonic acid (AMPA), a weak organic acid with a phosphonic acid group, is the primary degradation product of glyphosate. In addition, AMPA is also used in the production of amino-methylene-polyphosphonates, which are a type of phosphonates widely utilized in both household and industrial applications as detergents, flame retardants, anticorrosive, anti-scaling agents, and complexing agents (mainly in the textile industry), between other industrial applications. Nevertheless, the domestic contribution to urban loads of AMPA is negligible (Grandcoin *et al*., 2017).

Glufosinate (2-amino-4-(hydroxymethylphosphinyl)butanoic acid or D,L-phosphinothricin), also used as glufosinate-ammonium, is a non-selective herbicide with a broad weed control spectrum, also, an organophosphorus herbicide, used mostly for controlling weeds and unwanted plant growth. It is absorbed through the leaves and can cause leaf chlorosis and necrosis by inhibiting the enzyme glutamine synthetase (Takano & Dayan, 2020; C. Zhou *et al*., 2020). Introduced in the early 1990s, and found as a natural product, glufosinate was referred to as “a natural amino acid with unexpected herbicidal properties” (Hoerlein, 1994) and its use has a significant increase in the United States (US) over the past decade associated to the growing number of glyphosate-resistant weeds, with glufosinate serving as an alternative herbicide to glyphosate. Although glufosinate-resistant crops were available while glyphosate-resistant crops, they were less applied due to glufosinate’s lower efficacy and consistency in comparison to glyphosate. Nevertheless, the use of glufosinate is widespread in some regions such as North America, particularly in the Midwest and Southern US where glufosinate-resistant soybean and cotton are commonly grown. In South America, it is also widely used, especially in no-till cropping systems where glufosinate-resistant cotton is popular in northeast Brazil. Other crops such as rice, orchards, vineyards, and minor crops, as well as non-agricultural areas, also account for a significant portion of glufosinate use in the western United States and other parts of the world (Takano & Dayan, 2020). Concerning European countries, glufosinate is no longer applied because its market license expired in 2018 and its use was not re-approved by the European Commission due to concerns about its toxicology, being legally banned in Europe in 2020 (European Commission, 2020a, 2022a; C. Zhou *et al*., 2020). Additionally, its use and selling had already been prohibited in France since the end of 2017, due to its potential toxicity to human reproduction (C. Zhou *et al*., 2020).

Although glyphosate and glufosinate have been widely discussed in terms of their impact, the lack of publicly accessible data on their global use has resulted in increased uncertainty in the global estimates reported. Only a limited number of countries, including Portugal and Spain, make annual reports publicly available containing information about national herbicide and glyphosate/glufosinate use. Moreover, there is variability in the level of detail provided, with some reports only referring to total herbicides consumed or sold, without specifying the active ingredients. It has been observed that most of the increase in global glyphosate use can be associated with the adoption of genetically engineered herbicide-tolerant crops providing to be a solid basis to project total glyphosate use with greater confidence, in the countries where they are used. Benbrook, (2016) use this methodology to preview trends in glyphosate use in the U.S. from 1997 and 2014, being one of the most cited sources of information concerning the quantities used and, consequently, the potential for contamination. Concerning Europe, in 2019 European Network for the Durable Exploitation of crop protection strategies (ENDURE) network started a survey on the uses of glyphosate and the existing alternatives in 32 countries: the EU-28 countries plus Norway, Serbia, Switzerland, and Turkey (EU 28+4) (C. Antier *et al*., 2020). The main conclusions were that glyphosate sales were highest in France, Poland, Germany, Italy, and Spain (with Portugal in 10th place), that, on the other hand, considering the use of glyphosate per hectare of agricultural area, Denmark, Poland, Netherlands, Portugal, and France presented the highest values in 2017, and that glyphosate is essentially consumed by the agricultural sector (90% of total national glyphosate sales in the 13 countries where this information was available) (C. Antier *et al*., 2020).

Figure 2.13A shows the annual total values, concerning the years 2017 and 2019, for the agricultural use of glyphosate in some European countries (some of the countries with the highest expression in the use of glyphosate according to the ENDURE report (C. Antier *et al.*, 2020)) as well as the amount of all the other herbicides used in each country and in each year. Additionally, data on the use of glyphosate and other herbicides in the same years in Brazil and the USA, as well as in a total of 28 European countries plus Norway, Switzerland, and Turkey are shown in Figure 4B (information sources shown in the figure legend).

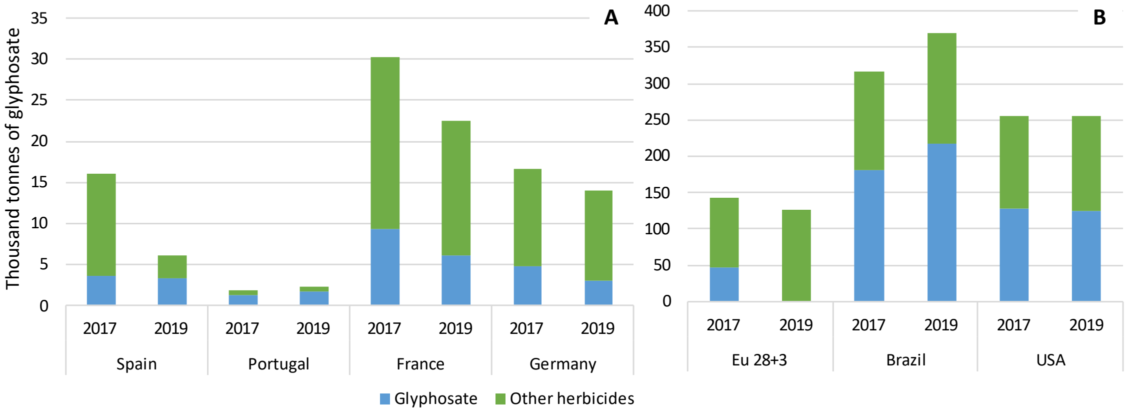


Figure 2.13 - Evolution of herbicides sales for agricultural use with a highlight on glyphosate from 2017 to 2019: A) in some EU countries (2017 data source: (C. Antier et al., 2020); 2019 data source: Spain: (Ministerio de Agricultura Alimentación y Medio Ambiente, 2021); Portugal: (DGAV, 2021); France: (Christine Veyrac, 2021); Germany: (Federal Office of Consumer Protection and Food Safety, 2021)) and B) sum of 28 EU plus Norway, Switzerland, and Turkey (2017 - data source: (C. Antier et al., 2020); 2019:(FAO, 2022)) compared with Brazil (IBAMA, 2022) and USA (IBAMA, 2022) (both 2017 and 2019) (EU 28+3 data about 2019 glyphosate use was not found) - developed by the author.

As shown in Figure 2.13A, in European countries there was a decline in the use of herbicides from 2017 to 2019, except for Portugal where a slight increase occurred (17%). Spain presented the most significant decrease, showing a reduction of about 62% in herbicide sales, assisted by a 10% reduction in glyphosate sales, followed by France, with a 26% reduction (35% in glyphosate sales), and finally Germany, with 17% overall reduction and 35% in glyphosate sales. In Figure 2.13B it can be seen that the global trend in the EU was a decrease of 11% in herbicide sales (data for glyphosate sales in 2019 for the EU28+3 were not available), in contrast with Brazil, which showed an increase in global sales of 17% and 21% in the case of glyphosate sales. The U.S. showed the same amounts of herbicides used in both years, with a 3% decrease in glyphosate sales.

For the use of glufosinate, access to information is even more difficult. With regard to the amount used, this active substance represented less than 0.05% of the total herbicides applied in Spain, France, and Germany. In Brazil, it represented 0.5% in 2017 and 0.3% in 2019, and for the U.S. 2.8% in 2017, the estimate for 2019 is not yet available for the latter.

Both glyphosate and glufosinate have been the subject of controversy and regulatory scrutiny in recent years due to concerns about their potential impact on human health and the environment. However, both herbicides are still widely used around the world, and their safety and efficacy continue to be evaluated by regulatory agencies and scientific researchers (Z. Li & Fantke, 2022; Novotny, 2022).

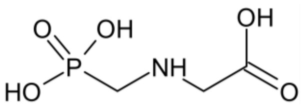
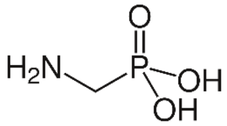
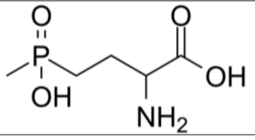
2.3.2 Chemical and physical properties of glyphosate and glufosinate

To ascertain the environmental fate and behavior of agrochemicals, it is imperative to consider their physicochemical properties. Key parameters in this evaluation include the organic carbon-soil partition coefficient (K_{OC}), octanol-water partition coefficient (K_{OW}), vapor pressure, solubility, and persistence, as represented by the time required for 50% of the parent compound to undergo transformation and dissipate from soil, water, or air (DT_{50}) (von Mérey *et al*., 2016).

Glyphosate and AMPA share similar physicochemical properties as its low vapor pressure, making its volatilization from soil insignificant, polarity and its moderate to high solubility in water (see Table 2.2) (EFSA, 2005, 2015). Glyphosate is a colorless, odorless, crystalline solid chemical with a three-polar functional group structure namely, amine, carboxylate and phosphonate, amphoteric and characterized by a linear arranged configuration (Ojelade *et al*., 2022; Spengler *et al*., 2021). Being a zwitterion, with four characteristic pK_a values, have an ionic form, a highly polarity and solubility due to the existence of this functional groups in its structure. Despite their water solubility, glyphosate and AMPA show a high affinity for soil particles, particularly in clay-rich soils. Numerous laboratory experiments have demonstrated a significant absorption capacity of the glyphosate molecule in soil, with absorption constants ranging from 8 to 377 dm^3/kg (López-Vázquez *et al*., 2023; Ojelade *et al*., 2022).

Glufosinate is a phosphinic acid belonging to the organophosphorus chemical family, unlike any other chemical class of herbicides. Glufosinate is a hydrophilic herbicide ($\log K_{ow}$: −4.0), also highly water soluble, with a low vapor pressure and with three different ionization constant (pK_a) values associated with the presence of the amine and hydroxyl groups in its structure (see Table 2.2).

Table 2.2 - Physical-chemical properties of glyphosate, AMPA and glufosinate (Data source FAO and PubChem® 2022 database (National Center for Biotechnology Information, 2023d, 2023c))

Compound	**Glyphosate**	**AMPA**	**Glufosinate**
CAS	1071-83-6	77521-29-0	51276-47-2
IUPAC name	N-(phosphonomethyl)glycine	(Aminomethyl)phosphonic acid	2-amino-4-[hydroxy(methyl)phosphoryl] butanoic acid
Chemical structure			
Formula	$C_3H_8NO_5P$	$C_7H_{10}N_2O_4$	$C_5H_{12}NO_4P$
Molecular weight (g/mol)	169.07	111.04	181.13
Water solubility at 25 ◦C (mg/L)	1.0×10^6	1.0×10^6	1370
Organic solvent solubility at 25 ◦C (mg/L)	Practically insoluble	Practically insoluble	$\approx 1\times10^{-6}$
$\mathrm{LogK_{ow}}$	-3.4	-2.17	-4.0
pKa	$pK_{a1}=0.8$, $pK_{a2}=2.3$, $pK_{a3}=5.6$, $pK_{a4}=11.0$	$pK_{a1}=1.8$, $pK_{a2}=5.4$, $pK_{a3}=10.0$	$pK_{a1}=2$, $pK_{a2}=2.9$, $pK_{a3}=9.8$
Koc	2600-4900	1.937	9.6-1229
Vapor pressure at 25 ◦C (atm)	1.29×10^{-10} (No volatility)	1.66×10^{-7}	1.16×10^{-12} (No volatility)

Usually is present as an ammonium salt (Figure 2.14) in the existing preparations, which, in aqueous solution, tends to dissociate.

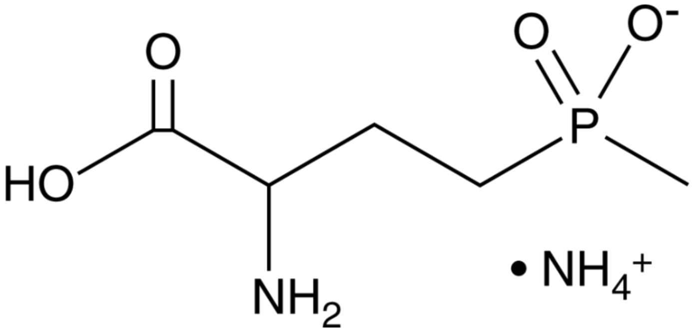


Figure 2.14 - Glufosinate (ammonium salt) molecular structure.

2.3.3 Glyphosate and Glufosinate - degradation and dissipation paths

Given the current understanding of glyphosate, glufosinate and AMPA persistence, mobility, leaching, and travel time it's possible to account for their presence in groundwater through various pathways, including point source contamination, favorable soil physicochemical properties, shallow groundwater, higher watersheds dimension, macropore flow, and the inflow of surface water or bank filtrate. Also, the existence of subsurface tile or storm drains, of sewers, and the occurrence of overland flow from developed and arid landscapes have been associated with sites with higher concentrations of these compounds (Medalie *et al*., 2020; Suciu *et al*., 2023).

The prolonged utilization of these herbicides over the past 45 years has raised apprehension regarding its potential impact on health and the environment. The process of manufacturing, transporting, and applying are believed to be the major weaknesses, being mostly associated to such concern (Meftaul *et al*., 2020).

As previously mentioned, the pervasiveness of glyphosate and AMPA across various substrates such as soil, surface/groundwater, and air has been extensively recorded. Moreover, it was even detected in human urine in several countries (Campbell *et al*., 2022; Nova *et al*., 2020; Suciu *et al*., 2023), indicating the extent of exposure that both humans and animals are subject to.

The exceedingly low vapor pressure of glyphosate and AMPA renders it resistance to significant volatilization, even in the event of processes as mineralization/degradation, immobilization, or leaching occurred following its application. In soils these two compounds are mostly degraded by microorganisms, which use these as nutrient sources. Glyphosate could be also subject, in minor extent and in specific environments, to photooxidation and abiotic degradation(Samson-Brais *et al*., 2022). Upon mineralization /degradation, the breakdown products include AMPA, the primary and major metabolite of glyphosate degradation, sarcosine, and glycine (Figure 2.15). The most frequent pathway occurs through the C-N bond oxidation, in which microorganisms degrade glyphosate using it as carbon source, producing AMPA and glyoxylate (an easily assimilable energy source). Subsequently, AMPA also could undergoes mineralization, producing methylamine or formaldehyde and phosphate (Castrejón-Godínez *et al*., 2021; Espinoza-Montero *et al*., 2020; Ojelade *et al*., 2022).

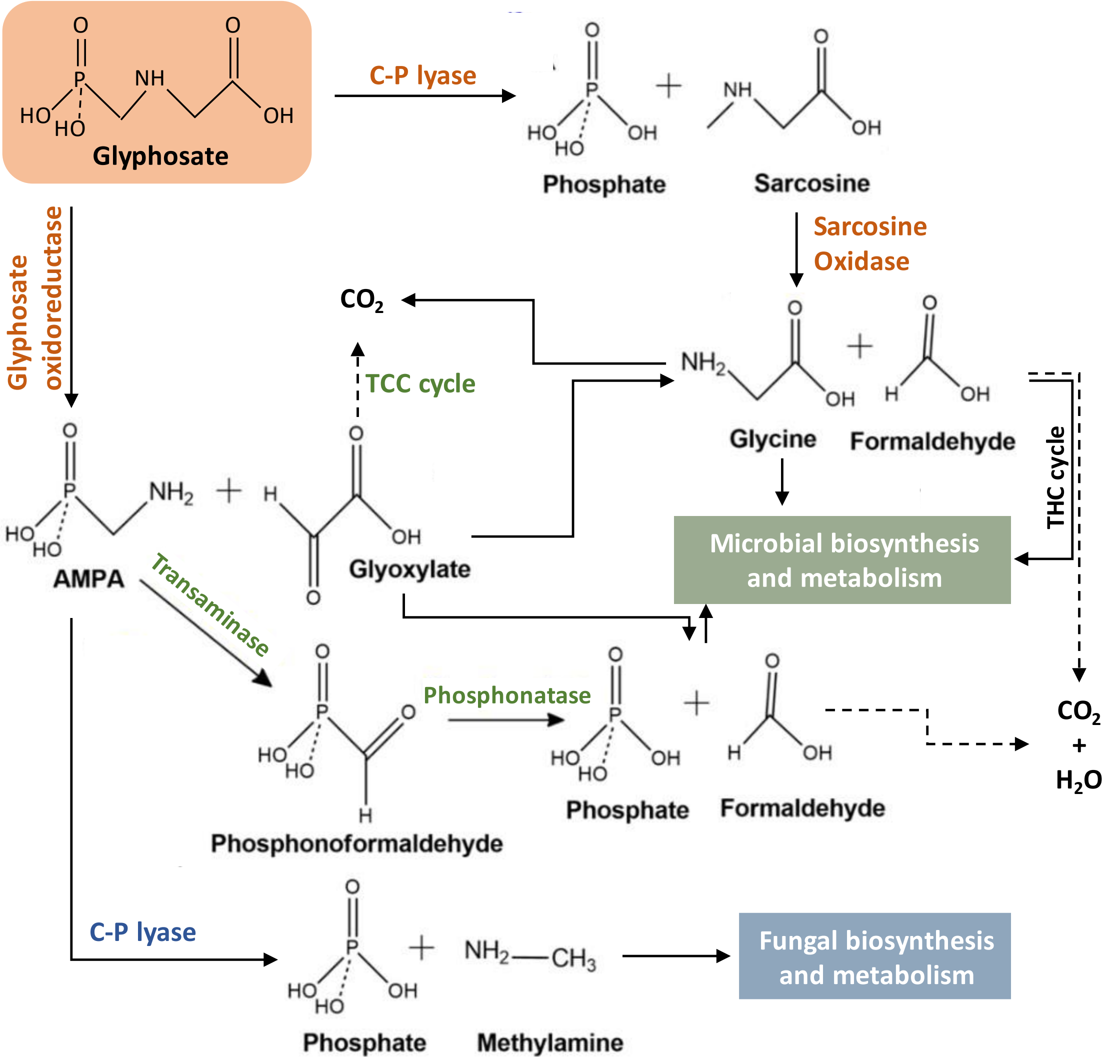


Figure 2.15 - Principal pathways of degradation of glyphosate through sarcosine and AMPA in the environment. TCC: tricarboxylic acid cycle; THC: tetrahydrofolate cycle; (adapted with permission from (Espinoza-Montero et al., 2020). Copyright 2020, Molecules).

AMPA is known to be 3 to 6 times more resistant to degradation than glyphosate, raising concerns about environmental safety (Sun *et al.*, 2019).

Otherwise, glufosinate is recognized for its ability to rapidly degrade in soil and leave no residual activity. This is attributed to its fast degradation by soil bacteria, which has been observed to be relatively fast when compared to other herbicides such as glyphosate (Suciu *et al.*, 2023; Takano & Dayan, 2020). According to same studies, and as shown in Figure 2.16, glufosinate initially undergoes a transformation process to produce the corresponding oxo acid, 2-oxo-4-(hydroxymethylphosphinyl)butanoic acid (PPO), which may involve a transamination reaction. The intermediate PPO is then converted to the main metabolite, 3-(hydroxymethyl-phosphinyl)propionic acid (MPP), which is considered to be stable in plants (Y. Li *et al.*, 2022; Vu *et al.*, 2021). Another possible transformation pathway for PPO is its reduction to 2-hydroxy-4-(hydroxymethylphosphinyl)butanoic acid (MHB). It is also possible that the metabolite 4-(hydroxymethylphosphinyl)butanoic acid (MPB) could be formed. Additionally, in same species metabolism the production of the non-phytotoxic N-acetyl derivative (N-acetyl-glufosinate; NAG) could occur, being, in transgenic plants, commonly considered as a stable metabolite (Jia *et al*., 2019; Müller *et al*., 2001).

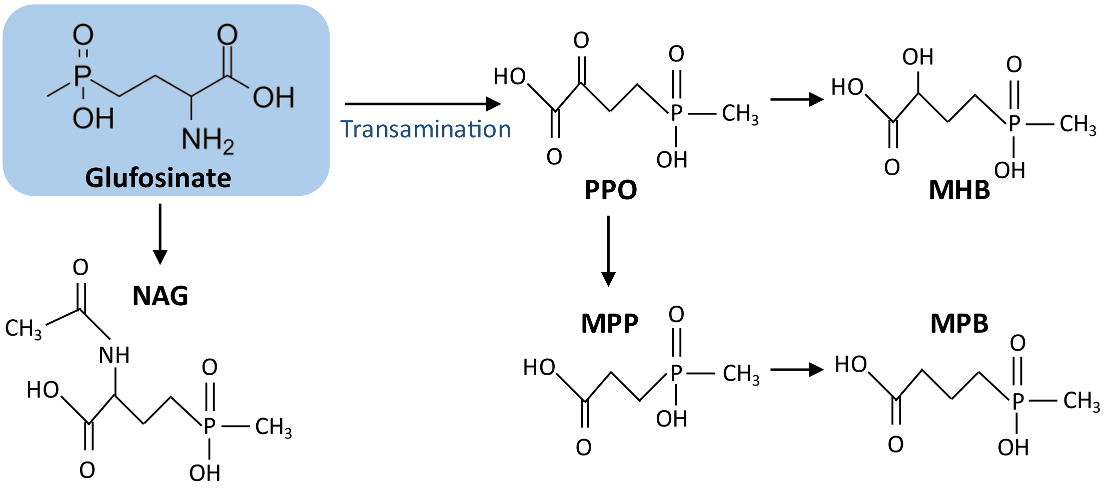


Figure 2.16 - Glufosinate main degradation pathways (developed by the author).

A reduced potential groundwater pollution risks was observed with the use of glufosinate. The process of glufosinate dissipation in the soil is primarily facilitated by oxidation, transamination, and ethanoylation reactions by soil microorganisms. The half-life of glufosinate in the field varies between 6 and 20 days, although it may be significantly extended in sterile soils (National Center for Biotechnology Information, 2023a; Suciu *et al*., 2023; Takano & Dayan, 2020). Moreover, other authors referred higher persistence, with a half-life of more than 300 days (Jia *et al*., 2019; National Center for Biotechnology Information, 2023a).

Once viewed as a safe chemical with low ecotoxicity, glyphosate has come under scrutiny in recent years for its potential toxicity and carcinogenicity. These concerns have sparked extensive debate and analysis from both the public and political spheres. Despite this, various studies and assessments by institutions have produced conflicting evidence, resulting in inconclusive and controversial findings (Meftaul *et al*., 2020). Glyphosate and its primary metabolite, AMPA, adsorption and subsequent release from soil is subject to the influence of various environmental factors, including soil type, constitution, temperature, and soil moisture. While glyphosate can attach to soil particles, its bonds can still be broken down into soil water in the presence of phosphates. Moreover, glyphosate has the ability to form compounds with metal ions, associated with the presence of its three functional groups (amine, carboxylate, and phosphonate) and its adsorption is positively influenced by the soil cation exchange capacity and soil clay content (la Cecilia & Maggi, 2020; A. D. Sharma & Lai, 2019). During the adsorption process, glyphosate is predominantly bonded to iron and aluminum oxides via the phosphonate group, that apparently have a greater capacity to adsorb glyphosate and phosphates than layer silicates, enlightening the significance of soil mineralogy in glyphosate sorption (Dotor-Robayo *et al*., 2022; A. D. Sharma & Lai, 2019). The risk of surface water contamination due to erosion is increased as glyphosate tends to adsorb to soil particles suspended in the runoff, thus being able to travel and spread over longer distances (Ojelade *et al*., 2022; Richards *et al*., 2018; Yang *et al*., 2015). Accordingly, soils that exhibit high levels of phosphate and pH, and low organic matter, Fe, and Al content are at a greater risk of experiencing losses of adsorbed glyphosate and AMPA because of its diminished ability to adsorb these substances, being more likely to leach them away (Ojelade *et al*., 2022). As already referred, both compounds are hydrophilic and practically insoluble in organic solvents. This characteristic indicates that the compounds will not have tendency to accumulate in living organisms since they cannot be dissolved and absorbed to it. Therefore, they are assumed to be non-bioaccumulative (Spengler *et al*., 2021).

The persistence of glyphosate in soil varies widely, with a half-life ranging from 1 to 215 days (Al-Rajab & Hakami, 2014; Muñoz *et al*., 2021; Zhelezova *et al*., 2017). On the other hand, AMPA remains more persistent in soil and water, with a half-life ranging from 23 to 958 days (Bento *et al*., 2016, 2017; Spengler *et al*., 2021; Yang *et al*., 2015).

Figure 2.17 provides an overview of the several possible sources of glyphosate, glufosinate and AMPA and the main pathways how they can enter the environment.

Groundwater contamination, besides being a complex process that involves multiple pathways and sources, is the result of the infiltration of pollutants from the land surface into the unsaturated zone and the subsequent transfer to the unconfined aquifer below. Shallow unconfined aquifers, including karstic, conduit, and fractured rock aquifers, are particularly susceptible to contamination, especially in areas where hazardous activities with uncontrolled contamination sources are present. Some characteristics of the route between the contamination and groundwater could play a crucial role in determining the travel time of contaminants between the source and the groundwater. A highly porous or permeable unsaturated zone, such as karst limestone, can lead to a relatively rapid transfer of contaminants from the surface to groundwater. On the other hand, the interaction of the contaminants with the unsaturated zone constituents can slow or even prevent contamination from reaching groundwater (Suciu *et al*., 2023).

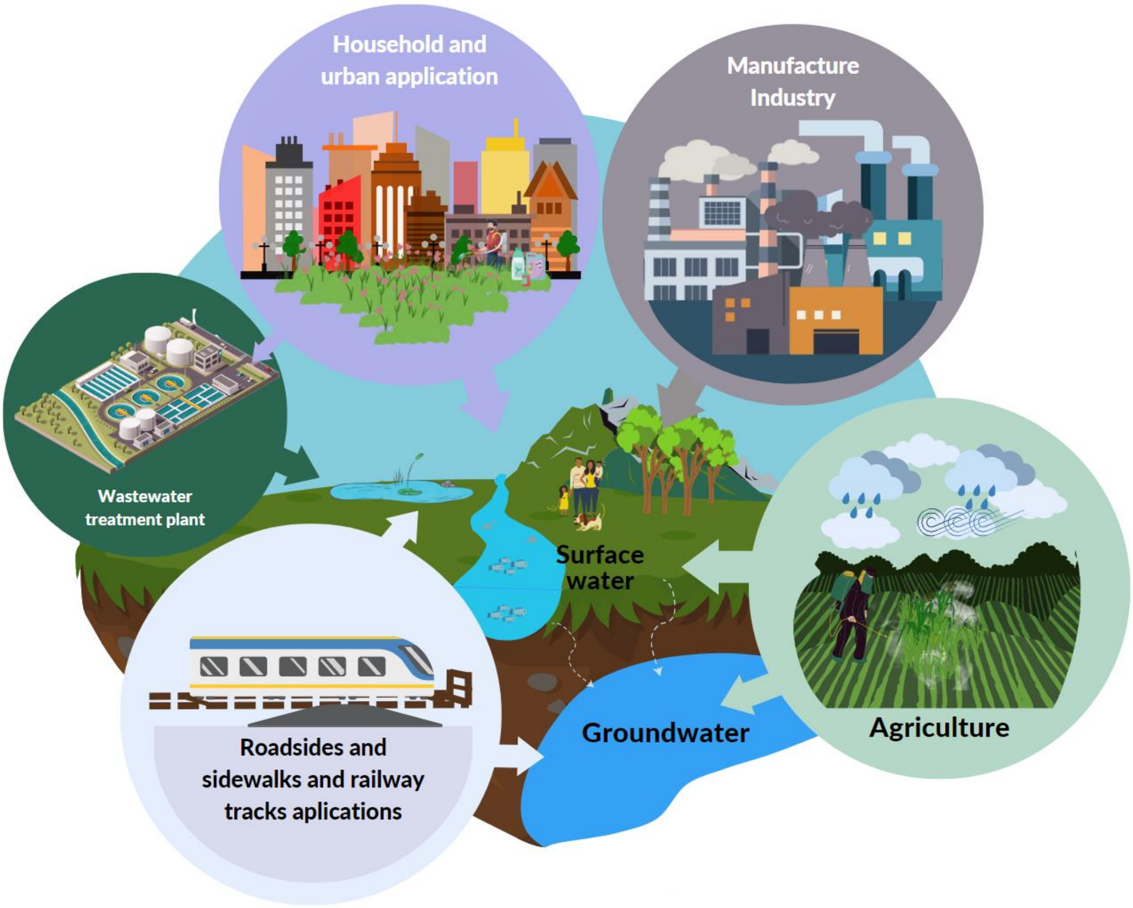


Figure 2.17 - Sources and fate of glyphosate, glufosinate and AMPA in the environment (developed by the author).

Other contamination routes that can affect both unconfined and confined aquifers, are the entrance of poor-quality groundwater in the aquifer through leakage, the leakage from incorrectly constructed, maintained, or decommissioned wells or its use to waste disposal (Didoné *et al*., 2021; Pradhan *et al*., 2023). Human-induced contamination can be broadly classified into point source and diffuse source. Point sources refer to localized contamination that is often centered on one or more identifiable locations. Alternatively, diffuse sources are broad-scale and can be caused by a widespread land-use practice, such as the use of agricultural pesticides, or a collection of small point sources, such as septic tanks in an unsewered area (Didoné *et al*., 2021; Pradhan *et al*., 2023; Natalia Verónica Van Opstal *et al*., 2022).

As summarized in Figure 2.17, the main sources of environment exposure to glyphosate, glufosinate and its metabolites are its application in home or urban/public garden weeds (urbans sources), their agricultural use, and their production industry. The agronomical practice, such as the crops and pesticide selection, soil cultivation and plant protection products application methods, and local environmental conditions are also of high importance. As an example, spray drift typically causes short or small-scale contamination. However, persistent pesticides as glyphosate and AMPA are present over a long time period and found in a wide variety of locations (Grandcoin *et al*., 2017; Schleiffer & Speiser, 2022).

The consumption of contaminated water or food, and the inhalation or dermal contact with sprayed compounds are some of the main paths to Human and animal exposure to their potential health impacts (Australian Government, 2013; Muñoz *et al*., 2021).

Therefore, understanding the multiple pathways and sources of groundwater contamination and the characteristics of the contaminants is essential for effective management and protection of groundwater resources. For the application of glyphosate, glufosinate and AMPA contamination reduction measures, both urban and agricultural sources should be considered. Improved monitoring and assessment of contamination sources and pathways is essential to identify areas at risk and inform the development of appropriate mitigation measures to safeguard groundwater quality (Tauchnitz *et al*., 2020). The different persistence levels of these compounds in soil and water highlight the need for developing effective methodologies for remediating environmental contamination caused by these compounds. Therefore, it is crucial to study and implement such methodologies for the sustainable use of these herbicides.

2.3.4 Analytical methodologies for Glyphosate, AMPA and Glufosinate detection in environmental matrixes

Despite being one of the most widely applied herbicides, glyphosate is also, along with AMPA and glufosinate, one of the most challenging to measure. Methods applied in their precise and reproducible detection and quantification are challenging, expensive and slow. The anionic nature of glyphosate poses a challenge for its detection using usual pesticide analysis methods. These methods often utilize reverse-phase chromatography, which is not effective in retaining highly polar compounds such as glyphosate and AMPA. As a result, alternative analytical techniques need to be employed to accurately detect and quantify glyphosate and AMPA in samples. These alternatives are usually more expensive and more time consuming (Ulrich & Ferguson, 2021). Therefore, legislative control measures are unsuccessful because these compounds usually cannot be detected by methods applied to simultaneously monitor different types of compounds and their metabolites in the same assay.

Chromatographic techniques such as liquid (LC) and gas chromatography (GC) are the most extensively used technique for determining the three compounds, with liquid chromatography-mass spectrometry (LC-MS) being currently the most used one (Rocío-Bautista *et al*., 2022). Glyphosate, AMPA and glufosinate are highly polar compounds, amphoteric, with a high-water solubility, and usually need to be derivatized before they can be analyzed using liquid chromatography coupled with fluorescence (LC-FLD), ultraviolet (LC-UV) and mass spectrometry (LC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS). HPLC combines speed, reproducibility, sensitivity, and high data capacity, but present high costs and complex working conditions. HPLC coupled with electrospray ionization (ESI), a technique used in mass spectrometry (MS) (ESI-MS/MS) allows for direct analysis of glyphosate and AMPA in ultra-trace concentrations with a simple sample preparation methodology (ESI in negative ion mode). ESI is used to generate either positive or negative glyphosate-FMOC derivative ions. Positive ESI is mostly used for FMOC derivatives offering nearly two times greater sensitivity than negative ESI (Kocadal *et al*., 2022; Raina-Fulton, 2014).

Ion chromatography (IC) coupled to tandem mass spectrometry (MS/MS) is also applied to glyphosate, AMPA and glufosinate determination, with which derivatization step can be omitted. IC is considered a direct, fast, and cheaper method for their quantification. ESI is the preferred introduction technique for IC-MS/MS, because of their polarity, providing a high sensitivity (Geerdink *et al*., 2020; Maroneze *et al*., 2014).

Some studies have been described to determine glyphosate, AMPA and glufosinate by GC-MS but this methodology present significant weaknesses compared to direct LC-MS or ion chromatography/mass spectrometry (IC-MS) (Kocadal *et al*., 2022; Tongo *et al*., 2022). GC is more suitable to be applied to determine volatile and semi-volatile substances, that is not the case of these compounds. In these case, derivatization step, either esterification or acylation, is required to improve their volatility, chromatographic retention, and sensitivity (Rocío-Bautista *et al*., 2022).

Commercially available enzyme-linked immunosorbent assay (ELISA) has been used to analyze glyphosate environmental concentration (Melendez-Pastor *et al*., 2021; Reynoso *et al*., 2020; Welch *et al*., 2019) Even though this method prevent the need for complex instrumentation and associated resources, as well as laboratory infrastructure required by the comprehensive instrumental methods, it is limited to the analysis of glyphosate, leaving out AMPA and glufosinate (Mahler *et al*., 2017; Tittlemier *et al*., 2017).

To remove the interferences, excessive derivatization reagent and/or pre-concentration the analytes to increase sensitivity, the commonly used method in the analysis of pesticides in water, including glyphosate, AMPA, and glufosinate is solid-phase extraction (SPE). SPE is a frequently used technique, applied to several sample matrix types, including aqueous samples, biological and clean-up of solid samples, although SPE cartridge are expensive and the method uses organic solvent during preparation and elution (Cheng *et al*., 2011; Pires *et al*., 2020). To water sample pre-concentration, lyophilization can also be applied (Pires *et al*., 2020, 2023).

After the use of these procedures, if it was necessary, two types of methodologies are commonly used: direct methods and those involving a derivatization step. Direct methods are advantageous due to their reduced sample preparation steps. However, the highly polarity of glyphosate, glufosinate, and AMPA make it impossible to directly separate these compounds through reverse-phase chromatography. Some analytical columns can provide better retention of analytes with this strongly anionic phosphonate structure. Recently, several chromatographic columns have been developed to measure these pesticides, seeking greater sensitivity, reproducibility and reducing the work associated with sample preparation. Among the indirect methods used, three types of derivatization steps are most commonly applied. The first is pre-column derivatization using FMOC-Cl in ACN reagent to diminish their polar character, facilitating chromatographic retention, and allowing analysis by liquid chromatography with mass spectrometry (Figure 2.18).

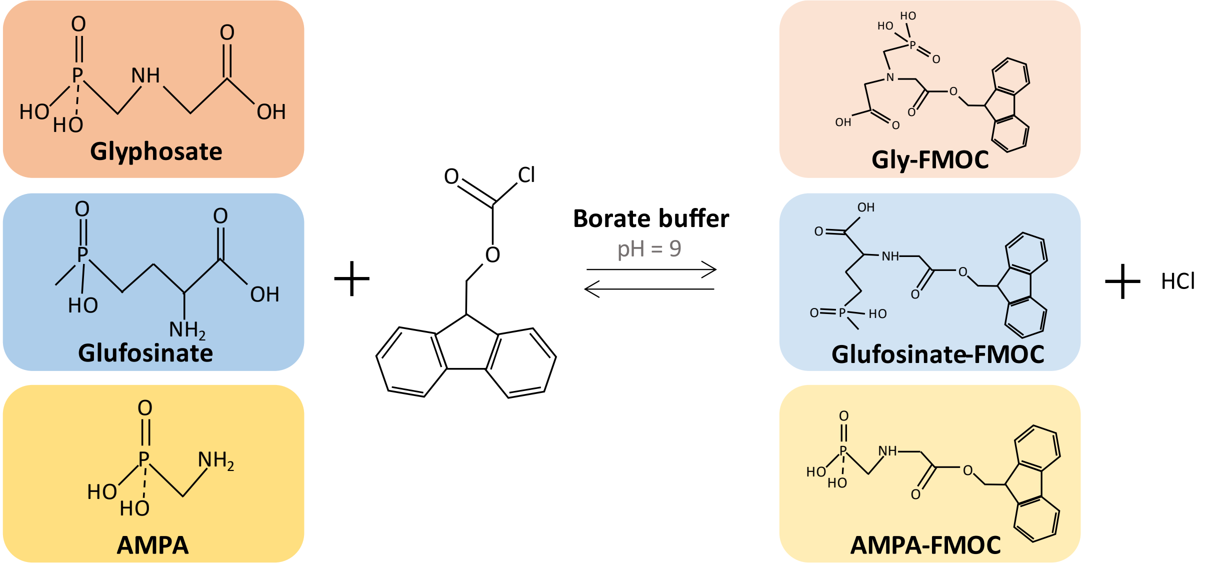


Figure 2.18 - Example of a pre-column derivatization of glyphosate, AMPA and glufosinate with FMOC (adapted with permission from (Campanale et al., 2022). Copyright 2022, Journal of Chromatography A).

The second is post-column derivatization, promoting the conversion of glyphosate into glycine and subsequent derivatization with o-phthalaldehyde, followed by a fluorescent detector. Derivatization with trifluoroacetic acid anhydride and heptafluorobutanol, is also applied to obtain volatile and stable molecules required for gas chromatography analysis (IARC, 2017; Marta Małysiak and Tomasz Kiljanek, 2022).

2.4 Innovative technologies for mitigation of new contaminants

Given the high frequency and persistence of the compounds under study in the environment and their potential impact on human and animal health, it has become essential to develop treatment processes to remediate environmental polluted matrixes. Soil and water remediation technologies are the methods used to clean up contaminated areas contained in these two environment compartments. These technologies can differ for distinct contaminants and types of contaminated matrix (soil or water).

Various techniques including physical, chemical, thermal, and biological methods could be utilized for the remediation of pharmaceutical and pesticide contaminations in water and/or soil (Narimani & Silva, 2020). Physical methods mainly focus on transferring the compounds from the aqueous phase to the solid phase. On the other hand, biological and chemical treatments involve chemical reactions with the compounds, leading to the formation of new metabolites or degradation products, with complete mineralization being a potential outcome (Narimani & Silva, 2020; Patel *et al*., 2019; Samal *et al*., 2022). Some of those technologies applied to remediate pharmaceuticals and pesticides contaminated soil, water, or both are presented in Figure 2.19.

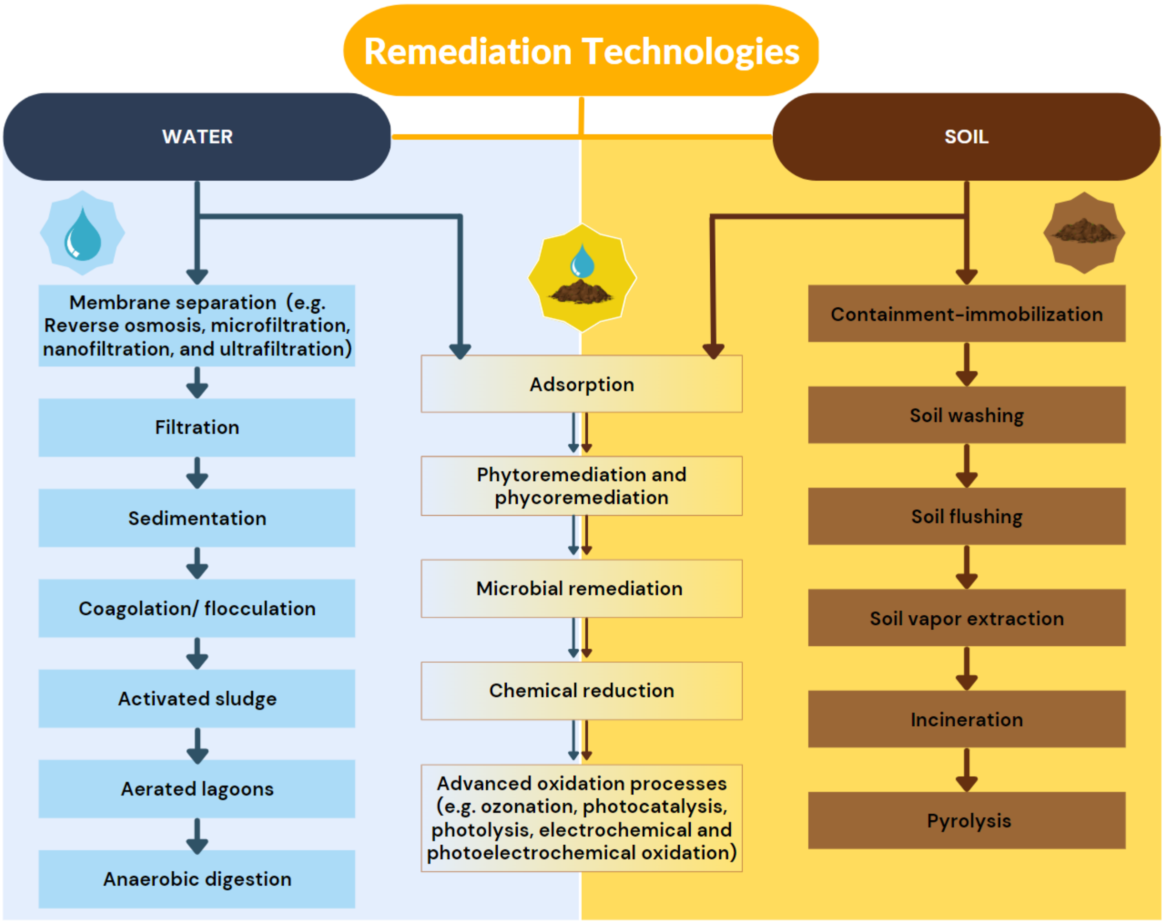


***Figure 2.19** - Resume of some remediation technologies applied to pharmaceuticals and pesticides contaminated soils, water, or both (developed by the author).*

Adsorption, electrodialysis, evaporation, dialysis, filtration, flocculation, reverse osmosis, sedimentation, and stream stripping are some of the available physical treatments, being adsorption and membrane separation the most used technologies for pharmaceutical and pesticides removal (Loganathan *et al*., 2023; Patel *et al*., 2019). Chemical methods include ion-exchange, neutralization, reduction, precipitation, calcination, and advanced oxidation processes (AOPs), this last one broadly used in tertiary treatments in WWTP (Loganathan *et al*., 2023; Patel *et al*., 2019). Thermal methods essentially include incineration and pyrolysis. Concerning biological methods, activated sludge, aerated lagoons, anaerobic digestion, trickling filters, and waste stabilization ponds are used (Patel *et al*., 2019). The activated sludge process, based on microbial degradation, is the primary applied biological process, largely used as a secondary treatment process in WWTPs (Loganathan *et al*., 2023). Many of the traditional methods have been employed to remove organic substances and suspended solids from wastewater. However, some proved to be inadequate for eliminating pharmaceuticals, particularly if they are hydrophilic, and pesticides. The need for an additional tertiary treatment process arises to effectively reduce the concentration of pharmaceuticals and pesticides in order to mitigate their potential entry and accumulation in surface water and groundwater resources (Pradhan *et al*., 2023).

Membranes are widely used as permeable or semi-permeable barrier that selectively allows certain substances to pass through while restricting others based on their properties such as size and charge and in a driving force. The driving forces required to promote the movement of substances across the membrane can include pressure difference, concentration gradient, and a potential field that initiates ions movement (Othman *et al*., 2022; Patel *et al*., 2019). Reverse osmosis, microfiltration, nanofiltration, and ultrafiltration are effective methods using membranes for removing antidepressant pharmaceuticals and synthetic organic contaminants such as organophosphate herbicides. Concerning reverse osmosis, the driving force is the pressure difference between the filtrate and feed sites of the separation membrane. On the other hand, the primary operational driving force of nano- and ultrafiltration is ion repulsion, since the membranes used are charged. Dalbosco *et al*. (2023) tested reverse osmosis and nanofiltration in fluoxetine removal from water. Nanofiltration presented a removal rate between 50 and 60%, and reverse osmosis demonstrated a rate of 98.8% (Dalbosco *et al*., 2023). The same two technologies were also tested in Non-steroidal anti-inflammatory drugs (NSAIDs) from groundwater demonstrating successful removal rates of over 85% (Patel *et al*., 2019). Although its efficiency, reverse osmosis can be expensive and requires regular maintenance. This physical treatment presents the advantage of does not lead to the development of contaminant byproducts (metabolites), as technologies such as AOPs or biological-based treatments, where these transformation products could also be of environmental concern (Rodriguez-Mozaz *et al*., 2015).

The employment of phytoremediation (i.e., the use of plants to absorb and detoxify chemical contaminants), phycoremediation (i.e., the use of algae to remove contaminants such as heavy metals, organic compounds, and nutrients, from contaminated water or soil), and microbial remediation technologies (i.e., the use of microorganisms such as bacteria, fungi, and cyanobacteria) are achieving prominence as a more cost-effective and environmentally sustainable alternative to traditional physical and chemical methods for removing heavy metals and organic contaminants, although it is a slower methodology (Bhat *et al*., 2020). Phycoremediation was tested using living and non-living microalgae to the removal of fluoxetine from aqueous solutions obtaining 100% of removal in six days (Andreia Silva *et al*., 2022).

Adsorption techniques have been a key methodology in water and wastewater treatment for a prolonged period, and their growing popularity corresponds, besides to their simple design, low cost, flexibility, easy to use, and insensitivity to toxic contaminants, with the ongoing emergence of novel micropollutants in aquatic environments as well as the discovery of sustainable and cost-effective adsorbents (Afzal Husain Khan *et al.*, 2022; Morone *et al.*, 2019; Samal *et al.*, 2022).

Several AOPs have been implemented to eliminate pesticides, including glyphosate, namely Fenton and Photo-Fenton processes, ozonation (O_3), photocatalysis, photolysis with hydrogen peroxide and UV light (H_2O_2-UV), electrochemical oxidation, and photoelectrochemical processes (Espinoza-Montero *et al.*, 2020; Feng *et al.*, 2020; Kudzin *et al.*, 2019). Ozonation is a promising AOP that applies ozone for the treatment of wastewater and soil. Ozone is a highly potent oxidant, possessing one of the highest oxidation potentials of any known substance. This versatile agent can be applied in either a gas or aqueous phase to facilitate a wide range of chemical reactions and is capable of oxidizing pesticides, and other contaminants. Furthermore, the *in-situ* generation of ozone is a notable advantage, as it can rapidly decay and be converted into oxygen via chemical decomposition, thereby minimizing the buildup of toxic byproducts and promoting aerobic biodegradation. (Martínez *et al.*, 2022). Treatment of concentrates contaminated with glyphosate and AMPA (obtained from a membrane system in a drinking water production plant) was tested applying three methodologies: ozonation, adsorption, and the combination of both. Complete degradation of both glyphosate and AMPA was observed for the highest applied ozone concentrations, mostly by direct ozonation. Adsorption onto activated carbon, on the other hand, was significantly low. These results were associated with glyphosate and AMPA high solubilities, the pH of the concentrate (8), and high natural organic matter concentrations. Adsorption followed by ozonation allowed the elimination of glyphosate and AMPA that cannot be removed by carbon adsorption. Additionally, other important advantages of this combination were lower operational costs due to reduced contact time (10 min versus 25 min) and equipment needs (Bozkaya-Schrotter *et al.*, 2008).

(Rezaei Kalantary *et al.*, 2022) tested the removal capacity of a conventional drinking water treatment plant (WTP) with primary sedimentation, coagulation, flocculation, clarifier, rapid filtration (with sand and granular activated carbon), followed by chlorine disinfection. This study concluded that most of the pesticide’s removal occurred in coagulation-flocculation and rapid sand filtration units (87%), outcomes associated with the hydrophobic nature, and in a filtration unit using granulated activated carbon. A good performance of the total pesticides removal from the water was achieved (50%), but the removed pesticides during the coagulation-flocculation process were accumulated into the sludge that, possibly, will be discharged into the environment without any treatment, ending up being released into the soil (Rezaei Kalantary *et al*., 2022).

In the environment, the main dissipation process of glyphosate from the soil is through biological breakdown, primarily driven by microbial activity, including actinomycetes, bacteria, fungi, and microcytes, in which bacteria play a dominant role. The microbial degrading capacity has been extensively studied and reviewed, and it is well established that bacteria can use it as a source of inorganic phosphorus, as well as nitrogen and carbon sources under certain conditions (Singh *et al*., 2020; Zabaloy *et al*., 2022; Zhan *et al*., 2018). Therefore, it is imperative to consider soil habitats as a crucial factor that regulates not only the biodegradation of glyphosate but also its adsorption and dissipation, thereby contributing to its overall presence in the environment (Zabaloy *et al*., 2022; Zhan *et al*., 2018).

Soil vapor extraction is a soil remediation technique that removes volatile contaminants, using a vacuum pump, but it can be costly and time-consuming (Baldissarelli *et al*., 2019). On the other hand, enhanced bioremediation is a treatment that implies adding nutrients to the soil to increase specific microorganisms' growth capable to degrade contaminants. This is a cost-effective and environmentally friendly technology, but time-consuming until the desired results are achieved (Pathak *et al*., 2022). Concerning electrokinetic remediation, in which an electric field is applied to the soil to promote the contaminants removal, is more effective for removing heavy metals and organic contaminants (as some pesticides), but it can be expensive and energy-intensive (Baldissarelli *et al*., 2019; F. L. Souza *et al*., 2016). For chemical oxidation treatments, the addition of an oxidizing agent is performed (to contaminated soil or water) resulting in the contaminant's oxidation. Effective for treating a wide range of contaminants, but it can be expensive and requires careful monitoring to avoid secondary contamination. Adsorption can also be applied to soil and water and is a process by which a solid material captures and holds molecules of a dissolved or suspended substance from a liquid or gas (Samal *et al*., 2022). This technology is widely used to remediate contaminated sites, as it can effectively remove a variety of pollutants.

The quest for novel methods to eliminate different pollutants in wastewater is an ongoing endeavor. However, it is equally important to establish that the treated matrices are environmentally safe, as any compound can pose a threat as a pollutant, depending on its concentration and the site where it occurs. Therefore, nonstop research and development of novel methods hold significant importance for the future elimination of a range of emerging contaminants (Diaz-Camal *et al*., 2022).

2.4.1 Adsorption

Adsorption is a process by which a solid material, called an adsorbent, captures, and holds onto molecules of a dissolved or suspended substance, called an adsorbate, from a liquid or gas. This is an interface process that involves physical interactions, such as electrostatic forces, and/or chemical bonds to attach species (adsorbates) from the gas or liquid phase to a solid material (adsorbent) (Sidoli *et al*., 2016). This process is widely used as a means to remediate contaminated sites or treat contaminated effluents, as it can effectively remove a variety of pollutants from water or soil (Espinoza-Montero *et al*., 2020; Morone *et al*., 2019).

Adsorption has several advantages for the remediation of the contaminated matrix. It can effectively remove a variety of pollutants, including heavy metals, organic compounds, as well as nutrients. It can, also, be used to treat groundwater, surface water, effluents, and soils. It is relatively simple to operate, with high removal rates of most pollutants and a cost-effective method compared to other remediation techniques (Espinoza-Montero *et al*., 2020; Sidoli *et al*., 2016).

Contaminants that can be removed by adsorption include pesticides, herbicides, and industrial chemicals (J. Chen *et al*., 2017; McGinley *et al*., 2022; Mojiri *et al*., 2020). Adsorption is also effective in removing lead, mercury, and arsenic (Guo *et al*., 2020). The effectiveness of adsorption depends on several factors, such as the type of adsorbent used, the concentration and type of contaminant, and the contact time between the adsorbent and the contaminated liquid or gas (Goldan *et al*., 2022).

In the case of water treatment, adsorption can be used as an individual technique or as part of a multi-step treatment process, such as in combination with biological or chemical treatment methods (Mukhopadhyay *et al*., 2022).

The most used adsorbents for the remediation of contaminated sites are activated carbon, biochar, zeolites, and clays. These materials have high surface areas and pore volumes, which allows them to adsorb many pollutants from the surrounding environment (Amalina *et al*., 2023; McGinley *et al*., 2022; Rissouli *et al*., 2017; Vasiljević *et al*., 2019). In addition, they can be easily modified to improve their adsorption capacity for specific pollutants (Tee *et al*., 2022).

The effectiveness of adsorption for remediation of contaminated sites depends on several factors, including the type and concentration of pollutants, the properties of the adsorbent, and the site conditions. In addition, the adsorption capacity of the adsorbent can be affected by factors such as temperature, pH, and the presence of competing ions (G. Oliveira *et al*., 2018).

Adsorption can be used in several ways for remediation of contaminated sites, including in-situ and ex-situ treatment. In-situ treatment involves treating the contaminated soil or water on-site, while ex-situ treatment involves removing the contaminated soil or water from the site for treatment. In-situ treatment is generally preferred, as it is more cost-effective and less disruptive to the surrounding environment. It could also be applied as a WWTP treatment, being included in the developed treatment process (Espinoza-Montero *et al*., 2020; Mukhopadhyay *et al*., 2022).

The extent of adsorption significantly influences the transfer and availability of contaminants as pesticides in soil and is one of the main mechanisms that control pesticide leaching. This process reduces the ability of pesticides to migrate and limits their potential to contaminate surface waters or groundwater, making it a crucial factor in preventing environmental pollution (Sidoli *et al*., 2016).

In summary, adsorption is a promising technique for remediation of contaminated sites. It is a simple and cost-effective method that can remove a wide range of pollutants from water and soil. However, careful consideration of site conditions and the selection of appropriate adsorbents are necessary to achieve successful results.

2.4.2 Prospective use of biochar to remediate contaminated sites

Biochar is a type of carbonaceous material produced thru the pyrolysis of organic materials, such as agricultural waste or forestry residues in an oxygen-limited environment. The thermal breakdown of lignin, cellulose, hemicellulose, fat, and starch contained in the feedstock occurs during pyrolysis and produces three distinct results: biochar (solid fraction), partly condensed volatile matter known as bio-oil (liquid fraction), and non-condensable gases (gaseous fraction) as CO_2, CO, CH_4, and H_2. These gases and bio-oil can be captured to generate energy and create worthwhile byproducts, such as food flavoring, biochemical compounds, adhesive, and wood preservatives, based on the feeds used (Goldan *et al*., 2022; Pokharel *et al*., 2020).

It has gained increasing attention as a potential tool for remediating contaminated soil or water due to its ability to adsorb and immobilize contaminants (Lehmann & Stephen, 2009; Z. Li & Fantke, 2022; McGinley *et al*., 2022).

The use of biochar for remediation technology, as adsorption, has several advantages. Firstly, biochar can be produced from a wide range of waste organic materials that are readily available, and acting as a recycling process, which makes it a cost-effective and sustainable solution (Rubio, 2018). Second, biochar has a high surface area, allowing it to adsorb several substances as heavy metals, organic compounds, and nutrients. Third, biochar is stable and can remain in the soil for hundreds of years, which makes it a long-term solution for contaminated sites. The last is that it is an organic carbon-rich material capable to improve soil conditions as: increases soil organic carbon content, porosity, water, and nutrient retention capacity, and develops microbial population and activity, inclusively stimulating the growth of beneficial microorganisms that combat plant diseases and acquire resistance to pests and diseases (K. Weber & Quicker, 2018). Therefore, biochar can be applied to contaminated soils through direct mixing with soil, incorporation into soil amendments, or application as a top layer. When biochar is mixed with soil, it can improve soil fertility, and water-holding capacity, promote carbon sequestration, and microbial activity, potentially enhancing plant growth (Ahmad *et al*., 2014; McGinley *et al*., 2022).

Several studies have shown that biochar can be effective in remediating contaminated soils and water and applicated in distinct approaches as directly in the contaminated site or used as adsorbents in water treatment facilities (Aghababaei *et al*., 2023; Bilias *et al*., 2021; Guo *et al*., 2020; McGinley *et al*., 2022; L. Xiang *et al*., 2022). According to existing literature, the addition of biochar to contaminated soils can effectively immobilize heavy metals and several persistent organic pollutants, reducing their bioavailability. Precipitation, electrostatic interaction, surface adsorption, and structural sequestration, are some of the immobilization mechanisms referred to as most predominant, leading to a facilitated decomposition. However, the extent of decontamination efficacy is dependent on several factors such as the biochar source, amendment rate, soil type, and pollutant species (Guo *et al*., 2020).

Xiang *et al*. (2022) reviewed the use of biochar, bacteria, and plants in the sustainable remediation of soils contaminated with organic pollutants. As shown in Figure 2.20 illustrate the potential mechanisms involved in this integrated approach, including plant uptake, bacterial degradation, and biochar adsorption, the integration of these three components can significantly enhance the removal efficiency of organic pollutants from soil. The use of such a comprehensive strategy provides a promising solution to the complex challenge of organic pollutant contamination in soil (L. Xiang *et al*., 2022).

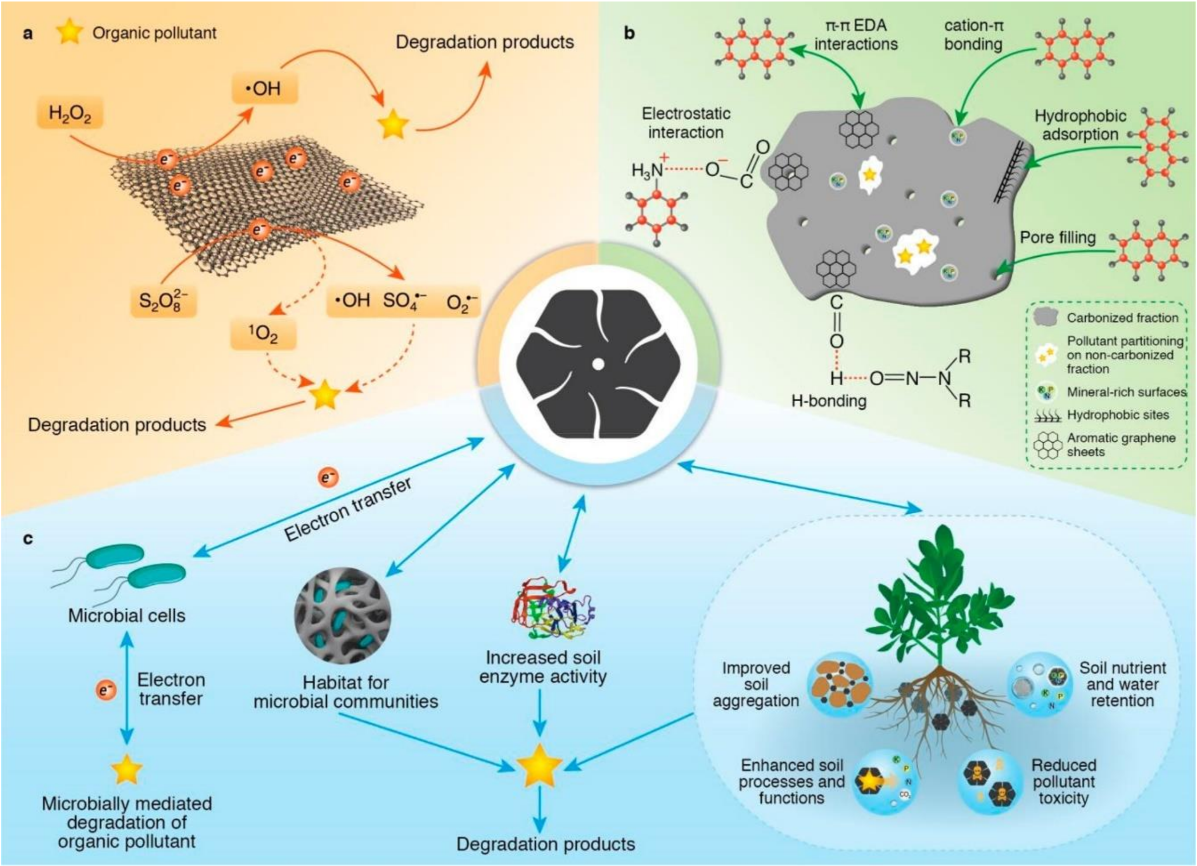


Figure 2.20 - Proposed mechanisms by which biochar mediates the remediation of organic pollutants in soil. (adapted with permission from: (L. Xiang et al., 2022). Copyright 2022, Environmental Science and Technology).

As highlighted in Figure 2.20, biochar facilitates organic pollutant oxidation/degradation via the production of reactive oxygen species, such as •OH, $SO_4^{\bullet -}$, and $O_2^{\bullet -}$, through free radical reactions with O_2, $S_2O_8^{2-}$, or H_2O_2 (Figure 2.20a). Organic pollutants can also be immobilized in soil via different biochar interactions, a process in which carbonized fraction of biochar intermediates adsorption (electrostatic attraction and nonpolar biochar–pollutant interactions), and uncarbonized faction intermediates partition (Figure 2.20b). Furthermore, biochar's porous surface can host soil microbial communities, restrain and release enzymes, and relocate electrons to microorganisms and pollutants, influencing organic pollutants metabolism of plant and microbial communities in soil (Figure 2.20c) (L. Xiang *et al.*, 2022).

However, the use of biochar for the remediation of contaminated sites has some limitations. First, the effectiveness of biochar depends on the type and concentration of contaminants in the contaminated matrix. Second, the optimal application rate and method of biochar application depend on the specific site conditions (when the application is in-site). Finally, the long-term effects of biochar application on soil properties and plant growth are not well understood and require further research (Bilias *et al.*, 2021).

In summary, the use of biochar for the remediation of contaminated sites shows promising potential. However, careful site assessment, selection of appropriate biochar feedstocks, and application methods are necessary to achieve successful results.

2.4.3 Prospective use of tailor-made Technosols to remediate contaminated sites

Technosols are a type of soils formed through anthropogenic activities, such as construction, urbanization, and land reclamation. These processes lead to the alteration of natural soil profiles and the introduction of various materials, such as construction debris and organic amendments, resulting in the formation of Technosols (Fabbri *et al*., 2021). Thus, Technosols are a reference soil group defined in the World reference base for soil resources (by the Food and Agriculture Organization (FAO) of the United Nations and International Union of Soil Sciences (IUSS)) as a combination of soils "*whose properties and pedogenesis are dominated by their technical origin. They contain a significant amount of artefacts (something in the soil recognizably made or strongly altered by humans or extracted from greater depths) or are sealed by technic hard material (hard material created by humans, having properties unlike natural rock) or contain a geomembrane.*" (IUSS Working Group WRB, 2015). Technosols could incorporate "*soils from wastes (landfills, sludge, cinders, mine spoils and ashes), pavements with their underlying unconsolidated materials, soils with geomembranes and constructed soils. Technosols are often referred to as Urban or Mine soils.*" (IUSS Working Group WRB, 2015).

Tailor-made Technosols (TMT), or engineered soils, are created by combining natural soil with man-made materials that determine soil processes and functionality to improve their properties for specific applications and can be an effective solution to remediate contaminated sites. Thus, TMT are constructed soils specifically designed to meet the requirements of a particular situation, composed of a mixture of organic and inorganic anthropogenic materials, derived from human activities, chosen according to their characteristics to fit specific needs (Napoletano *et al*., 2021). Natural soils are an active complex matrix, constantly evolving. TMT can replicate the functions of natural soils and offer a range of ecosystem services and soil functions, including creating favorable conditions for plant growth and production (e.g., food and biomass), remediating contaminated or degraded soil and water bodies, sequestering carbon, recharging groundwater, and promoting biodiversity (Macías & Arbestain, 2010; Ruiz *et al*., 2020). TMT can be designed to remediate a wide range of contaminants, including heavy metals (Camps Arbestain *et al*., 2008), organic compounds, and nutrients (Arán *et al*., 2018; E. S. Santos *et al*., 2019). They can be customized to meet the specific needs of the site, including its pH, electric conductivity, texture, and water-holding capacity (Arán *et al*., 2017, 2018; E. Santos *et al*., 2010; E. S. Santos *et al*., 2017).

One of the major advantages of TMT is that they are designed to be sustainable. They are made from locally sourced materials, which reduces the need for transportation and lowers carbon emissions (Fabbri *et al*., 2021). Choosing the appropriate components is essential when creating TMT, as the intended use of the soil must be considered. For example, if the Technosol is designed for a park within a city, it is important to ensure a high level of quality. On the other hand, when restoring a previously mined area, a lesser degree of soil performance might be acceptable. The selection of vegetation to be supported by the TMT is also dependent on the desired outcome and available resources. In situations where soil quality is lower and resources are limited, it is advisable to use establish plants that need minimal upkeep (Fabbri *et al*., 2021). To produce TMT, several residues could be used (Figure 2.21). Inorganic waste materials as construction and demolition waste (e.g. bricks and concrete waste), excavated soil, dredged sediment, residual sludge from stone processing and mining wastes and tailings. Concerning organic waste materials, compost from urban bio-wastes (food and garden – e.g. coffee grounds) and sewage sludge, anaerobic digestate from bio-waste, sewage sludge, agriculture and farms waste, urban green wastes, paper mill sludge and biochar represent some of the materials that can be applied (Fabbri *et al*., 2021).

Figure 2.21 - Examples of materials for TMT production (developed by the author).

Additionally, they can be designed to promote the growth of vegetation (E. S. Santos *et al.*, 2019), which can help to stabilize the soil and to reduce erosion or even intended for the reclamation or restoring abandoned sites or quarries or other brownfields (Barredo *et al.*, 2020; Grilli *et al.*, 2023; E. S. Santos *et al.*, 2017).

TMT has been used successfully to remediate contaminated sites around the world. For example, TMT were used to remediate a site contaminated with lead and arsenic. The Technosols were designed to have a high pH, which immobilized the contaminants and prevented them from leaching into the surrounding environment (Barredo *et al.*, 2020; Ferreiro, 2017; Grilli *et al.*, 2023; E. S. Santos *et al.*, 2017)..

Overall, TMT are a promising solution for remediating contaminated sites, restore the plant cover, improve ecosystem services, and decrease the environmental risk. They are sustainable, customizable, and have been proven effective in real-world applications. However, the success of Technosol remediation will depend on careful site assessment, design, and implementation.

2.4.4 Selection of the remediation technologies for glyphosate, AMPA, glufosinate, and fluoxetine contamination in soil and water

The best remediation technologies for glyphosate and pharmaceuticals contamination in soil and water depend on the specific type and extent of contamination, the location and environmental conditions of the site, and other factors.

The treatment site may also be different, leading to a different selection of treatment techniques. For example, in the case of fluoxetine, it enters the environment mostly through WWTP. Thus, the treatment applied throughout the time of its stay in these facilities may be the most appropriate to avoid contamination downstream. On the other hand, the approach for the treatment of herbicide contamination might be different since runoff from application sites is the most frequent pathway for contamination. In these cases, it may be beneficial to apply the treatment method at the point of herbicide application, avoiding the dispersion of this compound and the consequent contamination that is more difficult to control.

In summary, some remediation technologies have been used for the removal of glyphosate, AMPA, glufosinate, and fluoxetine as bioremediation, chemical oxidation, adsorption, soil washing, phytoremediation, and membrane filtration are some of the most effective remediation technologies for glyphosate and drug contamination in soil and water. The selection of the most appropriate technique depends on the specific factors of the contaminated area and the choice of the technique that is most effective and minimizes environmental and economic impacts.

Concluding, there are several soil and water remediation technologies available, each with its advantages and disadvantages. The choice of technology will depend on the type and extent of contamination, site conditions, and physicochemical properties of the contaminants, among other factors. It is essential to choose the most appropriate technology to achieve effective and cost-efficient remediation while minimizing the impact on the environment.

The appropriate treatment and elimination of antidepressants and these organophosphate herbicides and fluoxetine before their release into freshwater systems is crucial for preserving the ecosystem and mitigating the deleterious impacts of these persistent contaminants.

CHAPTER 3 ANTIBIOTICS AND ANTIDEPRESSANTS OCCURRENCE IN SURFACE WATERS AND SEDIMENTS COLLECTED IN THE NORTH OF PORTUGAL

This chapter conducts monitoring of river waters and sediments for both antibiotics and antidepressants. It focuses on the contamination of two water courses from the North of Portugal, Douro and Leça rivers. It aims to meet one of the specific objectives of the thesis, namely, to monitor sites contaminated with pharmaceuticals, namely fluoxetine, in the Iberian Peninsula.

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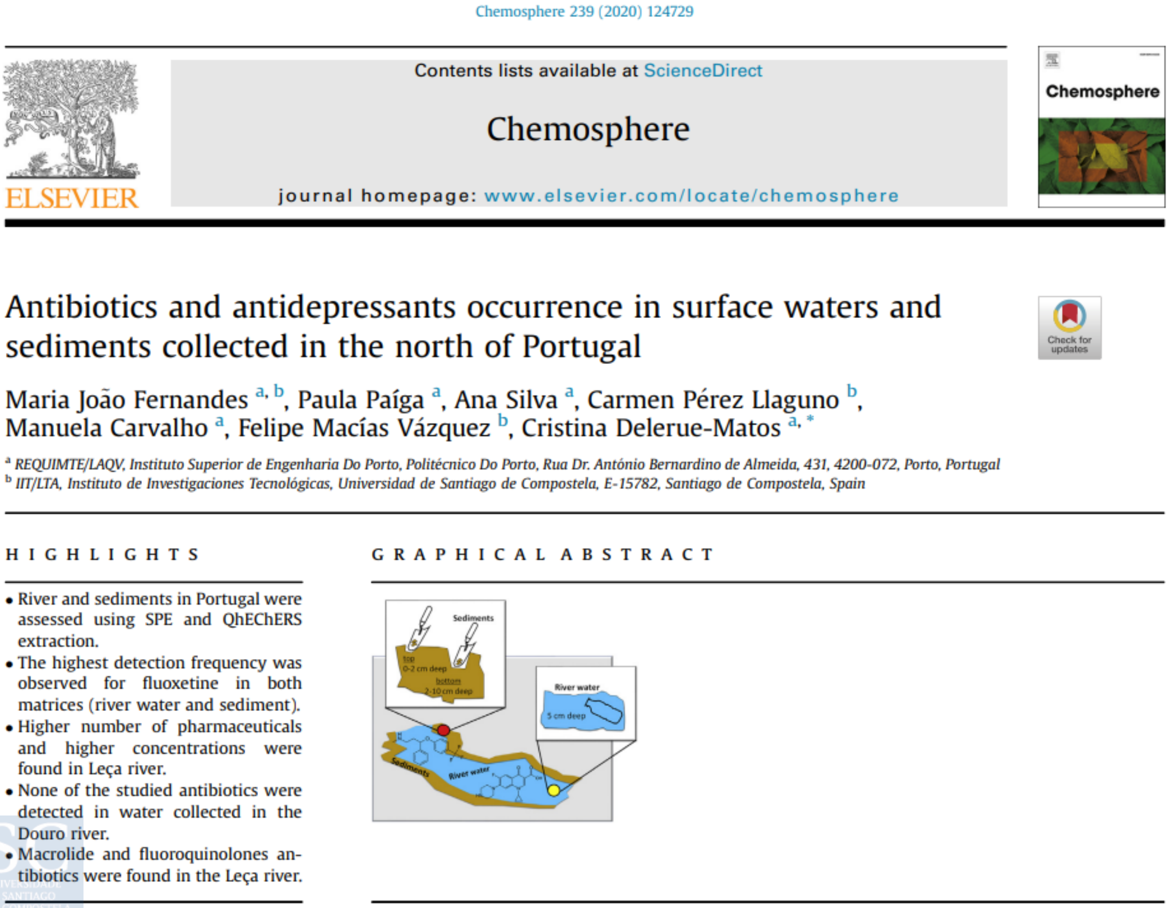

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Antibiotics and antidepressants occurrence in surface waters and sediments collected in the north of Portugal

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HIGHLIGHTS

- River and sediments in Portugal were assessed using SPE and QhEChERS extraction.
- The highest detection frequency was observed for fluoxetine in both matrices (river water and sediment).
- Higher number of pharmaceuticals and higher concentrations were found in Leça river.
- None of the studied antibiotics were detected in water collected in the Douro river.
- Macrolide and fluoroquinolones antibiotics were found in the Leça river.

GRAPHICAL ABSTRACT

Abstract

To our knowledge, this is the first study in Portugal for the analysis of both antibiotics and psychiatric drugs in river waters from Douro and Leça rivers and its sediments. Samples were extracted using solid phase extraction and QuEChERS procedures and the analysis was performed using liquid chromatography with tandem mass spectrometry.

Higher number of pharmaceuticals and higher concentrations were found in the Leça river for the two matrices under study. The highest detection frequency for the twenty-seven pharmaceuticals was observed for fluoxetine with 83.3% in both matrices. None of the studied antibiotics were detected in water collected in the Douro river however six antibiotics (azithromycin, ciprofloxacin, clarithromycin, moxifloxacin, ofloxacin, and trimethoprim) were found in the Leça river. Further, the analysis of sediments exhibits the occurrence of sulfamethoxypyridazine in the Douro river and azithromycin in the Leça river. The highest concentration was observed in Leça river for azithromycin in the river water (2,819 ng/L) and sediments (43.2 ng/g). Carbamazepine, citalopram, fluoxetine, sertraline, trazodone, and venlafaxine were the psychiatric drugs detected in river waters and sediments with more diazepam as water river contamination. Concentrations ranged from <method detection limit (MDL)) to 2.0 ng/L (river waters) and <MDL to 0.251 ng/g (sediments) in Douro river and between <MDL to 354 ng/L (river waters) and <MDL to 6.35 ng/g (sediments) in Leça river. To identify the possible sources of pollution more monitoring studies should be performed along the studied rivers.

Keywords: Pharmaceuticals, QuEChERS, Monitoring, Surface waters, Sediments, Solid Phase Extraction

3.1 Introduction

The presence of pharmaceuticals and its metabolites and degradation products in the environment requires continuous research and monitoring studies to assess their potential risks to the human and ecosystem's health (Paula Paíga *et al.*, 2019). These studies need to be performed for the assessment of pharmaceuticals in the different environmental compartments to evaluate their distribution, to identify contamination sources, and to contribute for establishing limit values to protect the environment and human health. The trend in sample preparation in trace analysis emphasized the optimization of extraction procedures for being simpler, faster, less expensive, and more environmentally friendly than traditional techniques. The analytical methodologies are better established and nowadays, the scientific community focuses more on monitoring studies.

The pharmaceuticals prevalence in the environment is currently a well-established and well-quantified problem and has become a matter of both scientific and public concern (Lolić *et al*., 2015; Paula Paíga *et al*., 2019) due to its environmental risk. Moreover, several studies have examined the bioaccumulation of pharmaceuticals and their toxicity on non-target organisms as fish, algae, crustaceans, mussels, snails, between other animals, presenting bioaccumulation factors from 1.4 to 32000 (Ebele *et al*., 2017).

There are several possible sources and routes for pharmaceuticals to reach the environment, but wastewater treatment plants (WWTP) have been identified as the main trail (Jelić *et al*., 2012) Sources of wastewater include domestic, but also hospital wastewaters, medicine manufactures, landfill leachates and direct disposal of unused drugs in the environment (Nikolaou *et al*., 2007; Ortiz de García *et al*., 2013). After the treatment performed in WWTP, the treated effluents are discharged into rivers, and the produced sludges are eliminated or reused in agricultural as a fertilizer product. As a consequence of the incomplete elimination of the pharmaceuticals and metabolites in the WWTP, these compounds reach all environmental compartments (Nikolaou *et al*., 2007). The incidence of pharmaceuticals in the aquatic environment is confirmed at wastewater, surface water, groundwater, and drinking water (Ortiz de García *et al*., 2013). However, since these compounds have the ability to partition to environmental solid phases (Minten *et al*., 2011), increasing attention has been paid, in recent years, for the contamination of pharmaceuticals in soils all over the world. Nonetheless, sediments are natural repositories of many chemical substances present in the water (Beretta *et al*., 2014) and sediments provides a wide variety of binding sites and act as major sinks for the deposition of pollutants (Ortega-Calvo *et al*., 2013; Sakari *et al*., 2014).

In recent years, antibiotic and psychiatrics pharmaceuticals consumption has attracted attention worldwide. As a result of the strategic plans for the reduction of antibiotic consumption in the European Union including Portugal (i.e. Program for Prevention and Control of Infections and Resistance to Antimicrobials), overall consumption of antibacterials has been declining in recent years, remaining at a still high level (21.6 daily doses defined per thousand inhabitants per day in 2016) for Portugal with similar value observed in Europe (21.9 daily doses defined per thousand inhabitants per day) (Rodrigues *et al*., 2018). Concerning to the psychiatric drugs and despite the implementation of the National Program for Mental Health that focus on the rationalization of its prescription and on the prevention of mental health problems, there has been an intensification of its consumption, with an increase of 15.2 M to 30.0 M consumed packages from 2013 to 2016 (Programa Nacional para a Saúde Mental, 2017).

Human survival depends on sustainable linkages with the environment. However, the "present" shows a different reality. The degradation of the environment is constant by the strong activities of the human being. Thus, stopping pollution is the most problematic subject of the planet. In the last decades, a new topic has attracted attention, the issue of pharmaceuticals and their potential environmental risk. Over the last years, the assessment of pharmaceuticals in surface waters has increased but fewer studies are being performed in soils and sediments. Thus, in the present study, the assessment of pharmaceuticals belonging to antibiotics and psychiatric drugs in surface water and sediments of two rivers (Douro and Leça) located in the North of Portugal was performed. Published studies performed by the scientific community in the Douro river showed that its pollution by pharmaceuticals is consistent and its occurrence is frequent, covering a wide area and displaying hot-spots (Lolić *et al*., 2015; Madureira *et al*., 2010). In the Leça river, data regarding the occurrence of pharmaceuticals in its basin is scarce, however, the existential pollution in the Leça river must not be neglect. Thus, solid phase extraction (SPE) for river waters collected along the Douro and Leça rivers and quick, easy, cheap, effective, rugged, and safe methodology (QuEChERS) used for in the sediments from the same rivers bank were the procedures used for the extraction of twenty-seven pharmaceuticals belonging to antibiotics and psychiatric drugs. The analysis was performed using liquid chromatography with tandem mass spectrometry (UHPLC−MS/MS) and the obtained results in river waters and sediments (top and bottom) were analyzed. The environment risk coefficient was performed as also the correlation between the parameters and the obtained concentration of the studied pharmaceuticals. To our knowledge, this is the first work in Portugal that simultaneously analyses river waters and sediments for the set of pharmaceuticals under study.

3.2 Materials and methods

3.2.1 Physical characteristics and points of pollution of the Douro and Leça rivers

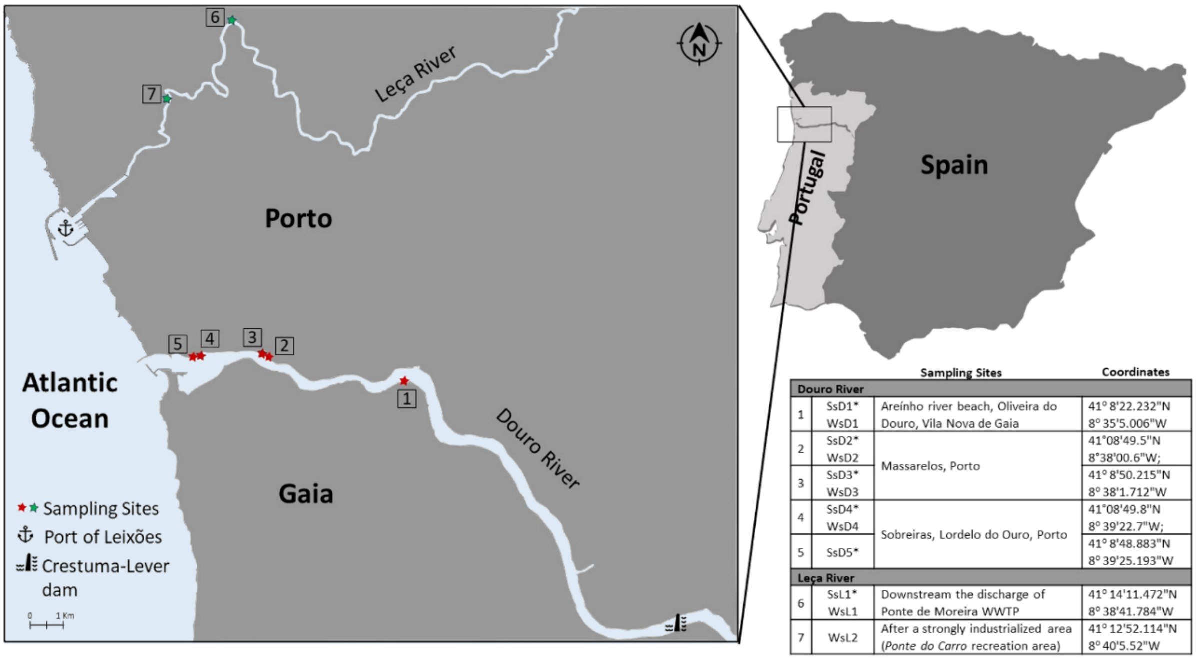
Draining to the Atlantic Ocean, Douro and Leça rivers are two of the rivers that cross the city of Porto in Portugal. Douro river, with its source in Urbion (Spain), covers an area of about 98 000 km^2 shared among Portugal and Spain, with a total length of 927 km and an average flow of 700 m^3/s. In the other hand, Leça river that rises in Monte Cordova, Santo Tirso (Portugal), covers an area of only 190 km^2, with a total length of 45 km and an average flow of 3.4 m^3/s. Its main information's are present in Table SM2 (Supplementary Material).

The Douro River receives effluents from several WWTPs. Two of them, located in the lower and medium stretch of the estuary, belonging to the metropolitan area of the Porto city are Sobreiras and Freixo WWTP, which together serve an equivalent population of about 370 000 inhabitants, achieving an average daily flow of about 90 000 m^3 (Cruzeiro *et al*., 2017; Madureira *et al*., 2010; Mendes *et al*., 2017).

The two most important WWTP that discharge effluents to Leça river are located in Maia (Parada and Ponte de Moreira WWTP). Those WWTP treat daily nearly 23,000 m^3 per day of urban wastewaters, from domestic and industrial effluents (A. I. Gomes *et al*., 2014). The Leça river receives untreated and treated effluents from numerous industries, of quite different typologies, namely: textile dyeing and printing, metallurgical, mechanical, and agro-food plants (A. I. Gomes *et al*., 2014).

3.2.2 River waters and sediments sampling

Samples (water river and sediments) were collected in November of 2017. The sampling points were numbered from Crestuma-Lever dam to the river mouth in Douro and from rural areas to the port of Leixões in Leça (Figure 3.1). Sampling sites 4 and 5 from the Douro River were located near the river mouth (approximately 1.5 km in the right riverbank), shortly after the discharge point of Sobreiras WWTP. In the same riverside, points 2 and 3, about 2 km upstream, were set in Massarelos. The first sampling point, about 4.5 km upstream, in the other riverbank (Vila Nova de Gaia), was located in the Areínho river beach. Concerning to Leça River sampling points, one was located in a recreational park, downstream the discharge of Ponte de Moreira WWTP (point 6), and point 7, in Ponte do Carro recreation area, also inserted in a revitalized zone, after a strongly industrialized area. The course of the Leça river is carried out between private agricultural fields and located in areas with reduced accessibility, limiting the access to the river. Thus, fewer sampling points were made in the Leça river.



		Sampling Sites	Coordinates
Douro River			
1	SsD1* WsD1	Areínho river beach, Oliveira do Douro, Vila Nova de Gaia	41° 8'22.232"N 8° 35'5.006"W
2	SsD2* WsD2	Massarelos, Porto	41°08'49.5"N 8°38'00.6"W;
3	SsD3* WsD3		41° 8'50.215"N 8° 38'1.712"W
4	SsD4* WsD4	Sobreiras, Lordelo do Ouro, Porto	41°08'49.8"N 8° 39'22.7"W;
5	SsD5*		41° 8'48.883"N 8° 39'25.193"W
Leça River			
6	SsL1* WsL1	Downstream the discharge of Ponte de Moreira WWTP	41° 14'11.472"N 8° 38'41.784"W
7	WsL2	After a strongly industrialized area (*Ponte do Carro* recreation area)	41° 12'52.114"N 8° 40'5.52"W

*Sediments were collected at two depths (top: 0-2 cm and bottom: 2-10 cm)

Figure 3.1 - Sampling locations of surface water and sediment samples in the Douro and Leça rivers.

River waters were collected five centimeters deep, near the margin of each river (approximately 50 cm), using a mat high-density polyethylene bottle pre-washed with ultrapure water. Sediments were collected in the same sampling points, at two depths (top: 0-2 cm and bottom: 2 to 10 cm), except at the collection point in the Ponte do Carro recreation area (point 7, Figure 3.1), since these sediments were not accessible due to the riverbed structure. A total of twelve samples (top and bottom) were collected. Subsequently, samples were kept at 4°C until arrival to the laboratory. Water samples were vacuum filtered through 0.45 µm nylon membrane filters (Fioroni Filters, Ingré, France).

All the samples were stored at -20°C until extraction (no more than one week).

3.2.3 River waters and sediments characterization

Water temperature (T), pH, conductivity (CE), redox potential (Eh), and dissolved oxygen (DO) were measured in situ, along the sampling campaign. Water quality parameters such as element analysis (F^-, Cl^-, Ca, Mg, Na, K, Fe, Al, Si), heavy metals (As, B, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn), and sulphate (SO_4^{2-}), ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-) ions were determined according to the procedure described in Ferreiro *et al*. (2017).

Parameters including pH (H_2O, KCl, and $CaCl_2$) (1:2.5 m:V), conductivity (CE), water content (WC), organic matter (OM), phosphate (PO_4^{3-}), and sulphate (SO_4^{2-}) (Mussa *et al*., 2009) were analyzed in sediment, and the same element analyzed in river waters and heavy metals analysis was performed (Ferreiro, 2017). Total Phosphorus (P) and extractable P (Olsen method) were measured, in addition to total carbon, nitrogen, and sulphur determination (analyzed by combustion with a LECO analyzer). A particle size distribution characterization was performed using a laser diffractometer (Mastersizer 2000, Malvern, UK) coupled with a dispersion unit - Hydro G, (Malvern, UK), capable to analyze particle size between 0.02 to 2000 µm. The refractive index for the dispersed phase was 1.65 and the absorbance was 0.1. The used continuous phase was water, with a refractive index of 1.330. The sample amount placed within the measurement system, with a velocity of the stirrer of 600 r.p.m. and pump speed set at 1250 r.p.m., was such that the value of obscure fell within the range of 10-20%.

3.2.4 Reagents and chemicals

For the extraction, acetonitrile (assay 99.99%) and methanol (assay 100%) were purchased from VWR Chemicals (Fontenay-sous-Bois, France), hydrochloric acid (HCl) 37% were supplied by Carlo Erba (Rodano, Italy), ammonium hydroxide solution (NH3aq, 28.0–30.0%) was obtained from Sigma-Aldrich (Steinheim, Germany), and ethylenediaminetetraacetic acid disodium salt 2-hydrate (Na_2EDTA) (assay >99.0%) was obtained from Panreac (Barcelona, Spain). Acetic acid glacial (assay 100%) was purchased from VWR Chemicals (Fontenay-sous-Bois, France).

For the analysis in UHPLC-MS/MS, methanol and acetonitrile, both LC-MS grade, were supplied by Scharlau (Barcelona, Spain), propanol LC-MS grade was obtained from Sigma-Aldrich (Steinheim, Germany), and formic acid (PA-ACS) was supplied by Carlo Erba (Rodano, Italy). A Simplicity 185 system (Millipore, Molsheim, France) was used for producing ultra-pure water (resistivity of 18.2 MΩ.cm).

All chromatographic solvents were filtered through a 0.22 µm nylon membrane filter (Supelco, Bellefonte, PA, USA) using a vacuum pump (Dinko D-95, Barcelona, Spain) and degassed for 15 min in an ultrasonic bath (Sonorex Digital 10P, Bandelin DK 255P, Germany). All samples were filtered through a PTFE syringe filter (0.20 µm) prior to the injection in the UHPLC- MS/MS system.

All antibiotics and psychiatric drugs and isotopically-labelled internal standards were of high purity grade (≥98%). Lomefloxacin, moxifloxacin, fluoxetine, norfluoxetine, paroxetine, sertraline, trazodone, venlafaxine, ciprofloxacin-d8, and fluoxetine-d5 were obtained in the form of the hydrochloride salt. The chemical abstract service (CAS), molecular weight, formula, structure, supplier company, and the solution used for prepared each stock solution are listed in Table SM1 (Supplementary Material).

Individual stock standard at a concentration of 1 g/L was prepared on a weight basis in solvent (See Table SM1, Supplementary material) and stored at -20ºC and an intermediate solution (mixture of all compounds), with a fixed concentration of 20 mg/L, was prepared by adding an appropriate amount of each stock solution. Working standard solutions were prepared from the intermediate solution in acetonitrile:ultra-pure water (30:70, v/v) before each analytical run and for the fortification tests.

3.2.5 SPE cartridges and QuEChERS tube

SPE cartridges Strata-X (200 mg, 3 mL) from Phenomenex (California, USA) and original QuEChERS extract tubes (1 g NaCl and 4 g MgSO4) obtained from Agilent Technologies (Lake Forest, CA, USA) were used for the extraction of waters and sediments, respectively. After QuEChERS extraction, a dispersive SPE (150 mg C18 and 900 mg MgSO4) was used for clean-up step (Agilent Technologies (Lake Forest, CA, USA)).

3.2.6 River waters and sediments extraction procedures

SPE and QuEChERS extraction methodologies used were adapted from the work of P. Paíga *et al.* (2017) for river waters and Santos *et al.* (2016) for sediments, respectively. The steps used in the two extraction methods were illustrated in Figure SM1 (Supplementary material). At the end of each extraction, the extracts were evaporated under a gentle stream of nitrogen to dryness and the residues were reconstituted with 500 µL of acetonitrile:ultra-pure water (3:7, v/v). Finally, 5 µL of a mixture of isotopically-labelled internal standards solutions was added.

3.2.7 UHPLC-MS/MS analysis

The chromatographic and mass spectrometry (MS) conditions used for the antibiotics and psychiatric drugs under study are described in the article published by the authors (P. Paíga *et al.*, 2017). A representative chromatogram of a 500 µg/L standard mixture of the selected pharmaceuticals is present in Figure SM2 (Supplementary material). Retention time and ion ratio for all compounds are listed in Table SM4 (Supplementary Material). The concentration of isotopically-labelled internal standards in the standards and in the extracts of river waters and in sediments are shown in Table SM3 (Supplementary Material).

3.2.8 Validation

The quality and consistency of the analytical results was check in method validation for the twenty-seven pharmaceuticals under study. SPE and QuEChERS were the methodologies used for the extraction of the compounds in river waters and in sediments and UHPLC-MS/MS was used for the analysis. Linearity, precision, matrix effect (ME), method detection limit (MDL), method quantification limit (MQL), and recovery were the parameters analyzed for both matrices.

3.2.9 Statistical analysis

Descriptive statistics was used to summarize the results of pharmaceutical and physicochemical contamination in water and sediments samples. Pairwise correlation coefficients between the variables in the river water and sediments were done (Pearson correlation coefficient). Principal Component Analysis (PCA) was performed using XLSTAT Version 2019.3.1 to explore possible relationships between the levels of pharmaceuticals in water and sediment (both layers) with the water and sediments properties. Statistical significance was defined at $p < 0.05$. Of the twenty-seven pharmaceuticals, only the detected were considered in this analysis. When applicable, values were assumed to be equal to half of the limit of detection/quantification.

3.2.10 Risk assessment

The protection of the aquatic ecosystem from pharmaceuticals pollution is utmost important and its impact on the environment should be evaluated. Risk assessment was determined following the work published by Paíga *et al*. (2019).

3.3 Results and discussion

3.3.1 Parameters

The physical and chemical parameters were analyzed in river waters and in sediments from Douro and Leça rivers (Table SM5 and SM6, Supplementary Material). According to the particle size distribution results, all the sediments presented a sandy texture. The analysis for E.C., DO, chloride, nitrate and sulphate show the same profile in the samples WsD3, WsL1, and WsL2, standing out as the points with the lowest values for these parameters.

Figure 3.2 presents the levels of elements content in the sediments and river waters. The concentration levels and the pattern of distribution of elements in both matrices and different sampling points were different. The element quantity levels found in sediments were typically higher than in the corresponding river waters. The bottom sediment sample SsD3 present a higher concentration of almost all the analyzed elements. The main highlights to the river water were the sodium (64.85-67.65 mg/L in Leça and 69.62-4,863 mg/L in Douro), chloride (76-79 mg/L in Leça and 63-11 552 mg/L in Douro) and sulphate (38-71 mg/L in Leça and 51-1,548 mg/L in Douro) which, together with the electrical conductivity, show an increase on the Douro River as it approaches the sea. This salinity increment in the river course near to ocean is coincident with other studies (Liu *et al.*, 2019). This characteristic shows the slightest influence that the sea presents on the Leça river, since its mouth is located at Port of Leixões basin.

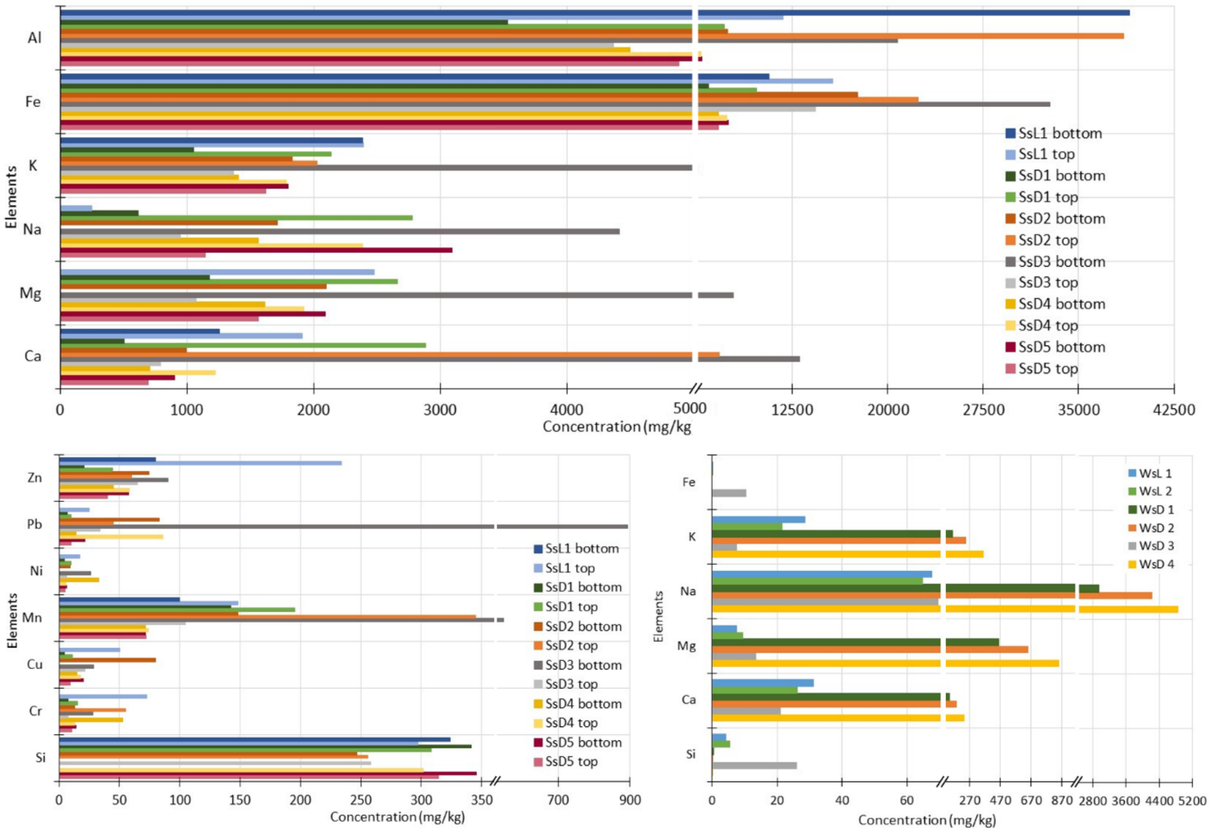


Figure 3.2 - Element concentration in river water and sediment samples (Si in g/Kg).

3.3.2 Method performance for pharmaceutical monitoring

Linearity, MDLs, MQLs, repeatability, reproducibility, ME, and recoveries were analyzed. The obtained results are presented in the following subsections. Detailed information's are mentioned in the section 1 (Supplementary material).

Calibration curve, method limits of detection (MDL) and quantification (MQL), and repeatability.

Good linearity was obtained for the selected pharmaceuticals in all calibrations' curves with a correlation coefficient (R) higher than 0.9944. The results of MDL and MQL obtained in both matrices are presented in Table SM7 (Supplementary Material). In general, lowest MDLs and MQLs limits were obtained for psychiatric drugs when compared with the limits found in antibiotics. The range of the MDLs found for river waters was between 0.0750 (clarithromycin) to 65.2 ng/L (sulfadimethoxine) for antibiotics and from 0.500 (citalopram) to 8.25 ng/L (norfluoxetine) for psychiatric drugs. Belonging to the same therapeutic class, sulfadimethoxine and sulfamethoxypyridazine were the two antibiotics with the highest limits, followed by the macrolide's antibiotics ciprofloxacin, lomefloxacin, moxifloxacin, and norfloxacin. For psychiatric drugs, the highest level was found for norfluoxetine. Regarding the watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC (European Commission, 2018), the maximum acceptable MDL (ng/L) for macrolide antibiotics (erythromycin, clarithromycin, and azithromycin) was 19 ng/L and for ciprofloxacin was 89 ng/L. The MDLs obtained in river waters were lower than the limits set in Directive 2008/105/EC.

In sediments, MDLs ranged from 0.00200 (clarithromycin and azithromycin) to 5.43 ng/g (lomefloxacin) for antibiotics and 0.00214 (fluoxetine) to 0.369 ng/g (paroxetine) for psychiatric drugs.

Standards were repeated sequential (n=6), and RSD values ranged from 0.0688% (sulfamethoxazole) to 7.91% (sulfapyridine) for the lowest standard concentration and from 0.850 (carbamazepine) to 3.96% (azithromycin) for the highest concentration. After, standards were repeat along the batch and RSD values varies from 3.12 (carbamazepine) to 29.6% (azithromycin) in the lowest concentration and from 1.91 (diazepam) to 11.5% (sulfadimethoxine) for the highest concentration of the standard. In the lowest concentration level, pharmaceuticals with the lowest sensitivity are more susceptive to have higher deviation.

3.3.2.1 Matrix effect

The results of ME found in river waters and sediments are shown in Figure 3.3. In river waters, all psychiatric drugs had an ion suppression signal, being the highest ME suppression verified for norfluoxetine and the lowest ion suppression signal observed for trazodone. The ion enhancement signal was only observed for 4 antibiotics, namely: prulifloxacin, sulfamethoxypyridazine, azithromycin, and sulfamethazine. The highest ion enhancement was observed for prulifloxacin and the highest ion suppression was found for erythromycin.

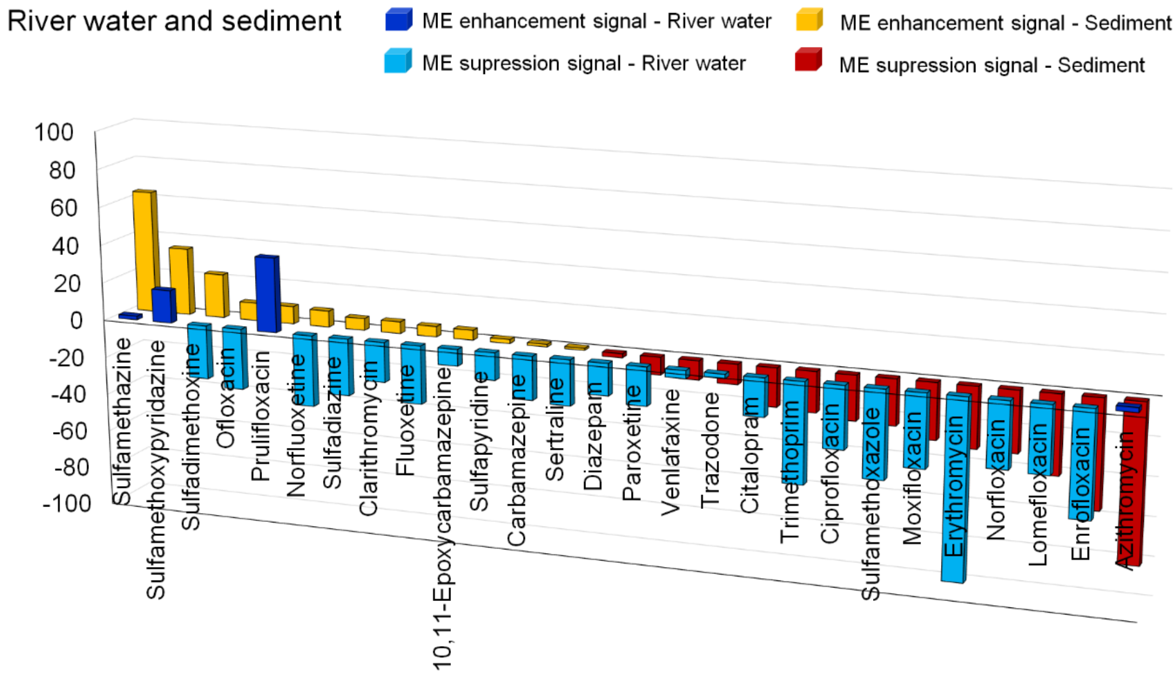


Figure 3.3 - Matrix effect for the studied pharmaceuticals in river water and sediment samples.

For sediments, more compounds had an ion enhancement signal. The highest ion enhancement signal was observed for sulfamethazine and the highest ion suppression signal was registered for azithromycin. Equal number of psychiatric drugs are distributed for ion enhancement and ion suppression signals. In the case of antibiotics, 47.0% of pharmaceuticals had ion enhancement signal and 53.0% of pharmaceuticals had ion suppression signal. All sulfonamide antibiotics showed an ion enhancement signal except for sulfamethoxazole and trimethoprim. For macrolides, only clarithromycin had ion enhancement signal. It was observed that for almost all fluoroquinolones antibiotics an ion suppression signal was observed with the exception for ofloxacin and prulifloxacin.

When both matrices were compared, it was observed that more pharmaceuticals had ME enhancement signal in sediments. Prulifloxacin, sulfamethoxypyridazine, and sulfamethazine had ion enhancement signal in both matrices. Azithromycin had a slightly pronounced ion enhancement signal (< 5%) in river waters and had a strong ion suppression signal (81.6%) in sediments. Sulfamethazine had in both matrices an ion enhancement signal with a less pronounced effect found for river waters (1.90%) and a more pronounced effect observed in sediments (63.8%). Sulfadimethoxine, ofloxacin, norfluoxetine, sulfadiazine, clarithromycin, fluoxetine, 10,11-epoxicarbamazepine, sulfapyridine, carbamazepine, and sertraline have an ion enhancement signal observed in sediments and ion suppression signal in river waters. Trimethoprim and erythromycin had ion suppression signal and prulifloxacin had ion enhancement signal for both matrices but more highlighted in river waters. Similar effect was achieved for citalopram, norfloxacin, lomefloxacin, and enrofloxacin in river waters and sediments, respectively.

Important considerations were published in the theme of the matrix effect by Pavlović *et al.* (2012) (Pavlovic *et al.*, 2012). Almost all pharmaceuticals under their study had signal suppression in sediments (sulfaguanidine, sulfamethoxazole, febantel, enrofloxacin, ciprofloxacin, norfloxacin, roxithromycin, procaine). The remain pharmaceuticals had an ion enhancement signal (sulfamethazine, sulfadiazine, praziquantel, and trimethoprim). It is important to emphasize that for sulfamethazine, sulfamethoxazole, praziquantel, and procaine were not significantly affected by the matrix components, since the signal change was less than 20% in the whole investigated concentration range. The authors stated that there is no general pattern because the influence of the matrix interference was different for each pharmaceutical and it is not possible to test the matrix effect only once and considered constant because the influence of the matrix is very variable. Moreover, Chambers *et al.* (2007) mentioned that matrix effect can be highly variable and can be difficult to control and predict (Chambers *et al.*, 2007). In the present study differences in the matrix effect were observed for different therapeutic classes as also in the same therapeutic classes.

3.3.2.2 Recovery tests

Recovery tests were performed at three fortification levels in river waters and in sediments. SPE and QuEChERS methodologies used were optimized previous (P. Paíga *et al.*, 2017; L. H. M. L. M. Santos *et al.*, 2016). These extractions methodologies were adapted for this study. The recoveries found for the two types of samples and for our pharmaceuticals are shown in Figure 3.4 and in Tables SM8 and SM9 presented in Supplementary Material. The concentrations found in the river water and in the sediments were corrected with the recoveries found for the two types of samples using SPE or QuEChERS methodologies. In general, recoveries are higher in the river waters than in the sediment's matrix, except for clarithromycin and diazepam, where a slight increase in recovery was observed when sediments was used. Similar recoveries in river waters and sediments were achieved for azithromycin, erythromycin, trimethoprim, carbamazepine, and 10,11-epoxicarbamazepine, respectively.

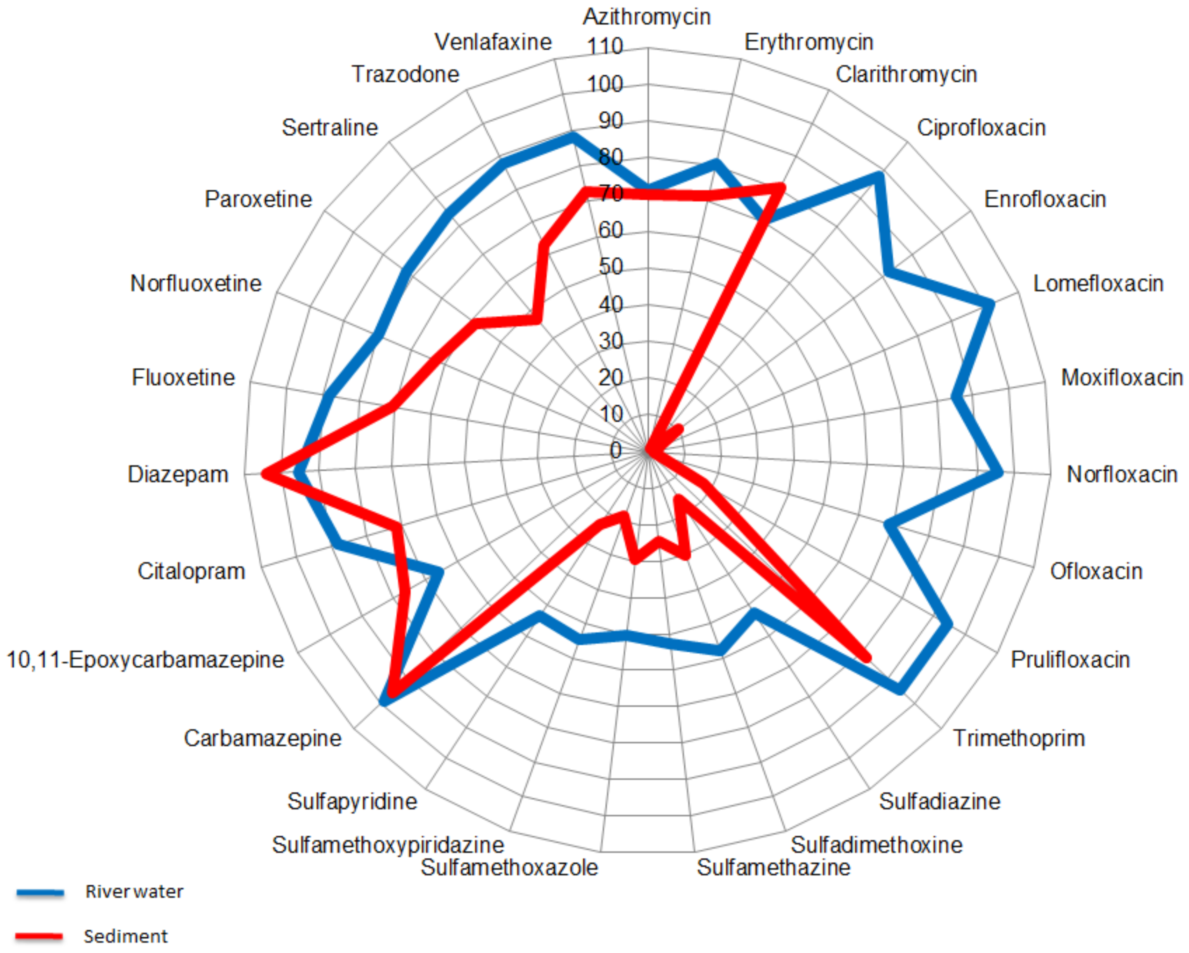


Figure 3.4 - Average recoveries (%) for antibiotics and psychiatric drugs in river water and sediment samples.

Comparing both extraction methods, a slight difference in average recoveries was observed for psychiatric drugs (85.9% (river waters) and 72.3% (sediments)) but in the case of antibiotics the difference is quite evident (74.4% (river waters) and 28.5% (sediments)) (Figure 3.4).

Either for river waters either for sediments the extraction methods, SPE and QuEChERS, were suitable for the extraction of psychiatric drugs under study and recoveries ranged from 65.9% (10,11-epoxycarbamazepine) to 98.9% (carbamazepine) in river waters and between 47.2% (sertraline) to 104% (diazepam) in sediments. In the case of antibiotics, the results vary according to the family (Figure 3.4). Thus, the conditions used in each extraction method and the pK_a of each pharmaceutical were crossed with recoveries results (Table SM1, Supplementary Material). The conclusions obtained are discussed in the following paragraphs.

In river water, decreasing the pH of the samples to pH 2 increases the interaction of the pharmaceuticals with the reversed-phase sorbent of the Strata-X cartridge and good recoveries were achieved for almost pharmaceuticals. Recoveries higher than 65% was found for psychiatric drug and fluoroquinolones and macrolides antibiotics. But lower recoveries were found for sulfonamide group. At pH 2 sulfonamide antibiotics are both uncharged form and positively charged and the interaction with Strata-X columns allows only recoveries around 50%.

The good recoveries achieved in sediments for psychiatric drugs and for macrolides antibiotics were due to the basic acetonitrile solvent used as extraction solvent that ensures that pharmaceuticals are in their uncharged form allowing them to have more affinity for the extraction solvent. Thus, higher recovery was found for trimethoprim with 84.4% and macrolide's erythromycin, clarithromycin, and azithromycin with recoveries higher than 70%. However, the same was not observed for sulfonamide and fluoroquinolone antibiotics. Recoveries lower than 20% for all fluoroquinolones and lower than 30% for almost all sulfonamide antibiotics were observed. The exception in sulfonamide antibiotics was observed in trimethoprim (Figure 3.4). As also stated in the study of Pavlović *et al*. (2012) the reason for lower recoveries for fluoroquinolones is possibly due to the strong interaction among the fluoroquinolones and the sediment, which makes these antibiotics difficult to extract. In our study it was observed the strong sediment interaction between fluoroquinolone and sulfonamide antibiotics (Pavlovic *et al*., 2012). Analyzing the microspecies distribution vs pH (data not shown) in basic pH, these sulfonamide and fluoroquinolone antibiotics are negatively charged with exception for lomefloxacin and moxifloxacin which are positively charged. For all fluoroquinolones, recoveries were similar, and lower recovery was found whatever was the charge of the molecule. Therefore, and according to the results obtained, QuEChERS extraction reveals not to be a suitable extraction method for sulfonamide (with exception of trimethoprim) and fluoroquinolones antibiotics due to the low affinity of the charged molecules with the extraction solvent and with the QuEChERS content.

3.3.3 River waters and sediments monitoring

Pollution penetrates in all courses of the rivers, in small or large quantities and the sources are from either rural or urban areas. Thus, collecting both river waters and sediments in different areas from Douro and Leça rivers is of utmost important to assess the pollution from pharmaceuticals (antibiotics and psychiatric drugs).

3.3.3.1 River waters

The river waters were collected in two rivers, located in the North of Portugal, which suffer different pressures from human activities (Table SM2, Supplementary Material). Thus, a total of six river waters collected in Douro and Leça rivers was sampled. The concentrations of the detected pharmaceuticals are present in Table 3.1.

Table 3.1 - Concentration of detected antibiotics and psychiatric drugs expressed in ng/L for river water samples and relative standard deviation (%RSD)

Pharmaceuticals	Douro River				Leça River		Detention frequency %
	WsD1	WsD2	WsD3	WsD4	WsL1	WsL2	
	Conc (%RSD) ng/L	Conc (%RSD) ng/L	Conc (%RSD) ng/L	Conc (%RSD) ng/L	Conc (%RSD) ng/L	Conc (%RSD) ng/L	
Antibiotics							
Azithromycin	n.d.	n.d.	n.d.	n.d.	**2,819** (4.8)	**221** (2.4)	33.3
Ciprofloxacin	n.d.	n.d.	n.d.	n.d.	**339** (4.3)	n.d.	16.7
Clarithromycin	n.d.	n.d.	n.d.	n.d.	**269** (19)	**76.6** (8.3)	33.3
Moxifloxacin	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	16.7
Ofloxacin	n.d.	n.d.	n.d.	n.d.	**120** (14)	n.d.	16.7
Trimethoprim	n.d.	n.d.	n.d.	n.d.	**110** (4.3)	n.d.	16.7
Psychiatric drugs							
Carbamazepine	<MDL	<MDL	n.d.	n.d.	**354** (0.41)	**206** (18)	66.7
Citalopram	n.d.	n.d.	n.d.	n.d.	**67.9** (3.3)	<MDL	33.3
Diazepam	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	16.7
Fluoxetine	**1.97** (5.3)	**1.94** (13)	n.d.	**1.87** (17)	**28.9** (11)	**6.69** (6.1)	83.3
Sertraline	n.d.	n.d.	n.d.	n.d.	**5.4** (3.8)	n.d.	16.7
Trazodone	n.d.	n.d.	n.d.	n.d.	<MDL	<MDL	33.3
Venlafaxine	n.d.	n.d.	n.d.	n.d.	**641** (0.75)	**235** (0.42)	33.3

Pharmaceuticals organized by alphabetic order and by its therapeutic group.
Detention frequency was calculated taking into account for all samples
Conc-Concentration; **n.d.**- Not detected; **MDL**-Method detection limit; **MQL**-Method Quantification Limit; **RSD**-Relative Standard Deviation

Comparing the samples collected in both rivers, Leça stands out due to the higher number of the pharmaceuticals and the highest concentrations found for the studied compounds. The highest detection frequency was observed for fluoxetine with 83.3% followed by carbamazepine with 66.7%.

In Douro, only carbamazepine and fluoxetine were detected, carbamazepine with values lower than MDL in two samples and fluoxetine with a similar concentration (between 1.87 to 1.94 ng/L) in three of the four collected samples. In Leça, thirteen pharmaceuticals (azithromycin, ciprofloxacin, clarithromycin, moxifloxacin, ofloxacin, trimethoprim, carbamazepine, citalopram, diazepam, fluoxetine, sertraline, trazodone, and venlafaxine) were detected. Concentration ranged from <MDL (trazodone) to 2,819 ng/L (azithromycin) in WsL1 and between <MDL (citalopram and trazodone) to 235 ng/L (venlafaxine) in WsL2. The highest concentration was achieved for azithromycin in µg/L levels in sample WsL1 for antibiotics and carbamazepine and venlafaxine for psychiatric drugs in ng/L levels. For all pharmaceuticals higher levels were achieved in sample WsL1 when compared with sample WsL2. This can be explained by the location of the sampling point. Sample WsL1 was collected near the WWTP effluent discharge. The greatest difference between samples WsL1 and WsL2 was observed for azithromycin since the concentration found in sample WsL1 is approximately 12 times higher than the concentration found in sample WsL2.

Referring to the Douro water sampling points and to the detected compounds, a slight reduction of concentrations along the river can be observed, except for point WsD3, in which no compound was detected. The presence of a water discharge point (of unknown origin) between the point WsD2 and WsD3 may have promoted the dilution of the pollutants at this point.

The potential environmental risk posed by the detected pharmaceuticals in the Douro and Leça rivers was assessed in three different trophic levels (fish, Daphnia magna, and algae). Azithromycin, ciprofloxacin, clarithromycin, ofloxacin, trimethoprim, carbamazepine, citalopram, fluoxetine, sertraline, trazodone, and venlafaxine were the pharmaceuticals with measured concentrations in Leça river and carbamazepine and fluoxetine in Douro River. The risk quotient was calculated using the highest concentration detected in both rivers (Table 1). The results are presented in Figure SM3 (Supplementary Material). Carbamazepine exceeds the threshold value of one, showing a potential risk to algae and venlafaxine is too close to reach the environment potential risk also to algae, in Leça river.

3.3.3.2 Sediments

Many pollutants, originally introduced into water, have affinity for sediments particles due to their hydrophobic/lipophilic properties (Perelo, 2010; Reid *et al*., 2000). Therefore, our study was extended to the extraction and analysis of pharmaceuticals in sediments and six sampling points were selected along Douro and Leça for collect sediments samples. Then, two samples were collected at each sampling point. One sample was collected at the top (0-2 cm depth) and the second sample was collected at the bottom (2-10 cm) zone (see section 2.6). Concentrations were compared not only between the different sampling points but also between different depths of the same sampling point (top, bottom) (Table 3.2).

Table 3.2 - Concentration of detected antibiotics and psychiatric drugs expressed ng/g for sediment samples and relative standard deviation (%RSD).

Pharmaceutical	SsD1 top	SsD1 bottom	SsD2 top	SsD2 bottom	SsD3 top	SsD3 bottom	SsD4 top	SsD4 bottom	SsD5 top	SsD5 bottom	SsL1 top	SsL1 top	Detection Frequency (%)
	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	Conc (% RSD) ng/g	
Antibiotics													
Azithromycin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**43.2** (7.24)	n.d.	*8.33*
Sulfamethoxypyridazine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**<MDL**	n.d.	n.d.	n.d.	n.d.	n.d.	*8.33*
Phychiatric drugs													
Carbamazepine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**<MDL**	**<MDL**	*16.7*
Citalopram	n.d.	n.d.	**<MDL**	n.d.	n.d.	n.d.	**<MDL**	n.d.	**<MDL**	**<MDL**	**4.42** (10)	**0.291** (15)	*50.0*
Fluoxetine	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**<MDL**	n.d.	**<MDL**	n.d.	**<MDL**	**<MDL**	**2.53** (5.0)	**1.58** (3.8)	*83.3*
Sertraline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**6.35** (6.5)	**1.56** (0.50)	*16.7*
Trazodone	**<MDL**	**<MDL**	**<MDL**	**<MDL**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**<MDL**	**<MDL**	*50.0*
Venlafaxine	n.d.	**0.251** (1.6)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**5.56** (6.2)	**3.45** (14)	*25.0*

Pharmaceuticals organized by alphabetic order and by its therapeutic group.
Detention frequency was calculated taking into account for all samples.
Conc-Concentration; **n.d.**- Not detected; **MDL**-Method detection limit; **RSD**- Relative Standard Deviation

Two antibiotics (azithromycin and sulfamethoxypyridazine) and six psychiatric drugs (carbamazepine, citalopram, fluoxetine, sertraline, trazodone, and venlafaxine) were detected in the sediments. Concentrations were below the MDL with exception of venlafaxine (0.251 ng/g) for sediments collected in Douro and from <MDL (carbamazepine and trazodone) to 43.2 ng/g (azithromycin) in Leça sediments. Fluoxetine had the highest detection frequency. Only one antibiotic was detected either in the Douro sediments (sulfamethoxypyridazine, <MDL, SsD4 top) either in the Leça sediments (azithromycin, 43.2 ng/g, SsL1 top).

When top and bottom zones were compared, it must be taken into account that soils with sandy texture do not have sufficient organic matter that slows the migration of pharmaceuticals, increasing the risk of its infiltration through the soil (Fehsenfeld, 2015). In the present study, sulfamethoxypyridazine, citalopram, fluoxetine, and trazodone detected in Douro sediments had insignificant differences between the top and the bottom zones due to the lower levels (<MDL) found. In the other hand, venlafaxine in sample SsD1 was not detected at the top and detected at the bottom zone, showing its migration through the SsD1 sediment sample. In Leça, results revealed lower concentrations in the bottom when compared with the top zone for azithromycin, citalopram, fluoxetine, sertraline, and venlafaxine. The detection of these pharmaceuticals in bottom zone also demonstrates the migration of the pharmaceuticals through sediment. For the authors, the higher concentration at the top zone, could be an evidence of recent contamination. For carbamazepine and trazodone, similar concentration in the two zones with values below the MDL was observed.

3.3.4 Statistical analysis

Of the twenty-seven pharmaceuticals, only the detected were considered in PCA. In the general analysis, performed with all the water and sediment samples of both studied rivers, PCA expresses 42.46% of total variance, highlighting the opposition among the water samples WsL1 and WsL2, both from Leça River, with WsD4, from Douro River. SsD3 and SsD2 bottom and SsL1 and SsD1 top, are characterizes by the higher element concentration (except for B and Na). WsL1 and WsL2 were the most contaminated water samples and most associated with NO_2, NH_4^+, Cl^- and Eh (Figure 3.5.A).

According to the Pearson matrix (data not shown), no significant correlations among levels of pharmaceuticals in water and sediments samples and its characterization were found except for the NH_4^+ and the pharmaceuticals moxifloxacin and diazepam.

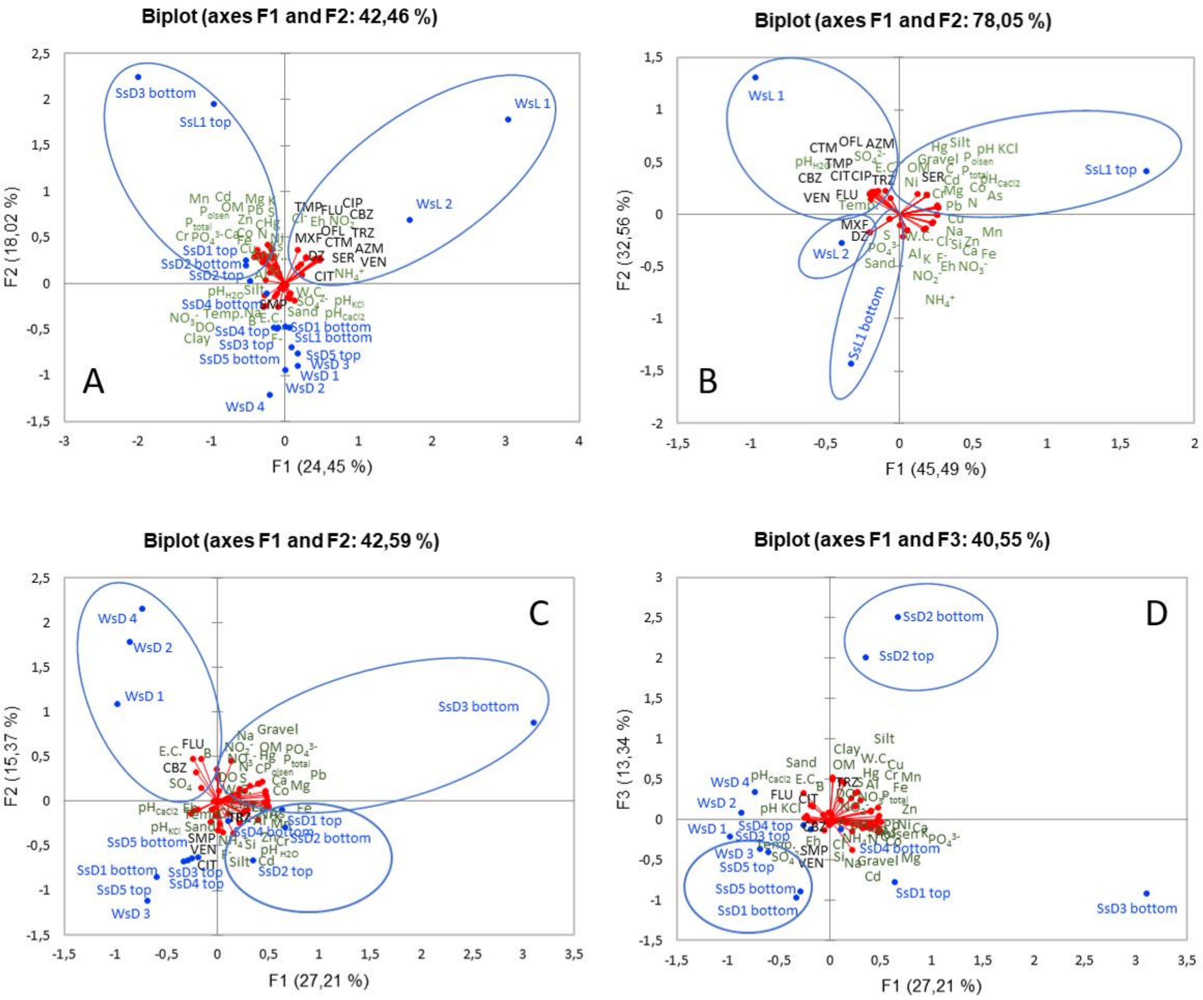


Figure 3.5 - PCA analysis of pharmaceutical levels and characteristics of the water and sediments samples from Douro and Leça River (A); From Leça River (B) and from Douro River (C and D) (AZM - Azithromycin; SMP - Sulfamethoxypyridazine; CIP - Ciprofloxacin; CTM - Clarithromycin; MXF - Moxifloxacin; OFL - Ofloxacin; TMP - Trimethoprim; CBZ - Carbamazepine; CIT- Citalopram; DZ - Diazepam; FLU - Fluoxetine; SER - Sertraline; TRZ - Trazodone; VEN - Venlafaxine; Temp - Temperature).

Between the sediments and water samples characteristics, some of the significant correlations found were the OM with the Silt and Clay percentage, Pb and Ca with the PO_4^{3-} concentration and P_{total} with C and N percentage, Cd and P_{olsen} concentration.

In the Leça River samples, the first two principal components explained 45.49% and 32.56% of the total variance, respectively. Significant differences can be observed in the distribution of pharmaceutical substances in both water and sediments. High levels of pharmaceutical were found in the sample WsL1, as well as higher values of EC, pH H_2O, SO_4^{2-} and temperature. It is, also, accentuated the opposition among the sediment samples SsL1 bottom and top. PO_4^{3-}, Sand and S were more associated with the bottom layer and the trace elements Hg, Mg, As, Cd, Co, Cr, Ni, and Pb with the top layer, as well as sertraline (SER) higher concentration. pH (KCl and $CaCl_2$), P_{olsen} and P_{total}, OM and the percentage of Silt and Gravel were, also, more associated with the top layer sample (Figure 3.5.B). In addition, the significant correlations among pharmaceuticals concentration in water and sediments, and its characterization were found among the trazodone (TRZ) concentration, the E.C., and the concentration of Si, Ca, K, Fe and Mn. Also, SO_4^{2-} presents a significant correlation with the concentration of clarithromycin (CTM), carbamazepine (CBZ) and venlafaxine (VEN). A strong correlation also can be observed between concentration of carbamazepine (CBZ) and E.C.

In Douro River, the first two principal components explained 27,21% and 15.37% of the total variance, respectively. The samples WsD1, WsD2 and WsD4 were strongly associated with higher carbamazepine (CBZ) and fluoxetine (FLU) concentrations, and the samples SsD2 top and bottom between each other and with the SsD4 bottom and SsD1 top. The samples SsD3 bottom showed opposition relatively to the samples SsD1 bottom, SsD3 and SsD4 top and SsD5 top and bottom, presenting higher concentration of, PO_4^{3-}, P_{total}, P_{olsen}, NO_3^-, NO_2^-, Hg, Ca, Mg, Na, Co, Pb and percentage of Water content, OM, C, N, S and Gravel (Figure 5.C).

Including the third components explaining, in accumulated, 55,93% of the total variance, some of the associations were emphasized, as the strong relation between SsD2 bottom and top and between WsD2 and WsD4 (Figure 5.D). Also, the opposition between the samples WsD3, SsD5 top and bottom and SsD1 bottom and SsD2 bottom, and top is highlighted. In addition, no significant correlations among pharmaceuticals concentration in the Douro samples and its characteristics were found except between fluoxetine (FLU) and Si concentration and with EC.

3.3.5 Concentration found in literature

Research was carried out in the literature considering the matrix, the pharmaceuticals included in our study, and the works published in the last decade. The measured concentration obtained in these studies is listed in Table SM10 (Supplementary Material) for river waters (ng/L) and sediments (ng/g).

Several monitoring studies were found for river waters however few studies were published with results from the monitoring of pharmaceuticals in sediments and even less in sediments and river waters from the same site. Moreover, using the keywords "pharmaceuticals", "sediments", and "Portugal", thirty works were achieved, although these studies were focus on issues such as biodegradation, remediation, and bioremediation. At our knowledge and for our set of pharmaceuticals, no works were founded in monitoring studies in Portugal for sediments. The pharmaceuticals detected and its concentrations worldwide are showed in Table SM10 (Supplementary Material) and discussed in the following paragraphs.

The highest concentrations found for antibiotics in the literature stand out for sulfonamide antibiotics trimethoprim (13 600 ng/L) in Laizhou Bayin in China (R. Zhang *et al*., 2012) and for sulfamethazine (1 090 ng/L) and sulfamethoxazole (5 320 ng/L) in Msunduzi River in South Africa (Matongo *et al*., 2015) in river water and for fluoroquinolone ciprofloxacin (1 290 ng/g) in Hai River (L. J. Zhou *et al*., 2011) in sediments. The µg/L and µg/g levels found in these studies could be either an indication that point source pollution occurred in the studied area at the time of sampling as also a result of constant and aggressive pollution. For the remain studies, the concentration of antibiotics ranged from <MDL to ng/L or ng/g levels. Prulifloxacin and moxifloxacin were not detected in any work.

In Pearl, Ba, and Huangpu rivers in China and Msunduzi river in South Africa, pharmaceuticals were assessed in both matrices (S. Li *et al*., 2018; Liang *et al*., 2013; Matongo *et al*., 2015) but more antibiotics were detected in Pearl river (S. Li *et al*., 2018; Liang *et al*., 2013). These studies were compared between themselves for each pharmaceutical and generally, when a concentration is higher in the river water is also higher in its sediments or vice versa. However, this pattern was not always verified. The unexpected profile can result in a point-source pollution that occurs in the area as also must be consider the migration of the pollutants through soils. Our results, in river water were in accordance with the results found in Pearl River but with lower concentration for trimethoprim (WsL1 sample). The two antibiotics found in our study for sediments collected in Douro and Leça rivers were not a target of studies in the literature.

In Portugal, pharmaceuticals were analyzed in thirteen rivers (Antuã, Arade, Ave, Cértima, Guadiana, Leça, Lis, Mondego, Tagus, Tâmega, Trancão, Tua, and Xarrama rivers) but no studies were performed in sediments. Concentrations of antibiotics found in Leça River were higher than the concentrations found in the other studies conducted in Portugal.

For psychiatric drugs, all studies were carried out in river waters except for the study performed in South Africa in which both matrices were assessed. Matongo *et al*. in 2015 found for carbamazepine concentration between 130 to 3 240 ng/L in Msunduzi River and between <0.535 to 6.07 ng/g in sediments (Matongo *et al*., 2015). The highest concentration of psychiatric drugs (carbamazepine) was found in the study of Matongo *et al*. The levels found in our study were in accordance with the remain results in Portugal, however for sample WsL1 (Leça river) venlafaxine have higher concentration.

3.4 Conclusions

In multiresidue method, good results for all compounds are not always found in one single extraction, namely: sulfonamides and fluoroquinolones. The differences of the physicochemical properties of these compounds and the extraction conditions used often do not allow higher recoveries for all target analytes. Optimizing single extraction for each compound is not acceptable since the costs, extraction time, solvents, and the produced wastes would be increased, and the principles of Green Chemistry are set aside. In our study, the adopted extraction procedures, SPE and QuEChERS methodologies, yielded good recoveries for most of the study pharmaceuticals.

River waters and sediments (top and bottom) were collected along Douro and Leça rivers. All samples were characterized, and pharmaceuticals were analyzed in both matrices. Higher concentration was found in samples (river water and sediments) collected in Leça when compared with samples collected in Douro. In river water, only two psychiatric drugs were found (carbamazepine and fluoxetine). In the other hand, thirteen (six antibiotics and sevens psychiatric drugs) of the twenty-seven pharmaceuticals were detected in Leça river waters. It must be highlighted the highest concentration found for azithromycin in µg/L level. Sampling point WsL1 is located near to the WWTP effluent discharge, this can justify the values found. Carbamazepine and venlafaxine showed a potential risk to algae in Leça river.

In the case of sediments, sulfamethoxypyridazine was found in Douro sediment and azithromycin in Leça sediment. Psychiatric drugs were found in the collected samples: four in Douro sediment) and six in Leça sediments. The concentration found in the top and at the bottom in each sample were compared: in Douro sediment venlafaxine had a higher concentration in the bottom zone which could be correlated with the migration of the pharmaceutical through the soil. In Leça sediments higher concentration was found in top zone, which could be attributed to recent pollution in the studied area.

Comparing the works reported in literature there is no pattern of the concentration found in both matrices due to the point-source pollutions in the river water and migration of the pollutants in the sediments. From the results obtained in our study, more monitoring studies need to be performed in all courses of the rivers. Source of pollution need to be identified; thus samples need to be collected in the rural area, in the industrialized area, and near to the harbor.

As few studies were found in literature in sediments as also embracing together river waters and sediments, the contribution of this article is important for further monitoring studies. Pharmaceutical pollution not only reaches the watercourses, because also sediments, soil, and groundwater are affected.

CRediT authorship contribution statement

Maria Joao Fernandes: ~ Writing - original draft, Investigation, Data curation. Paula Paíga: Writing - original draft, Investigation, Validation, Data curation. Ana Silva: Writing - original draft, Resources. Carmen Perez Llaguno: Investigation, Validation. Manuela Carvalho: Formal analysis, Resources, Writing - review & editing. Felipe Macías Vazquez: Conceptualization, Formal analysis, Resources, Writing - review & editing, Supervision. Cristina Delerue-Matos: Conceptualization, Formal analysis, Resources, Writing - review & editing, Project administration, Supervision.

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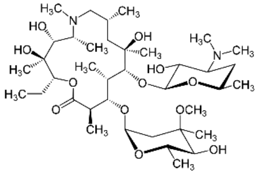
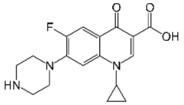
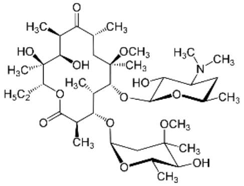
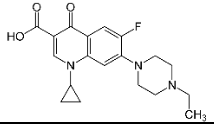
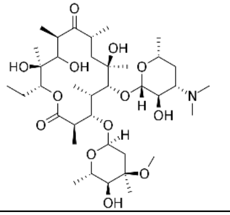
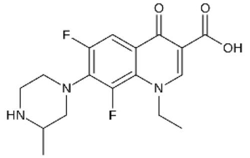
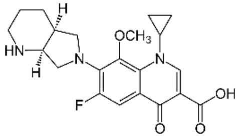
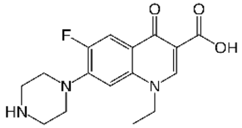
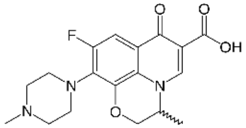
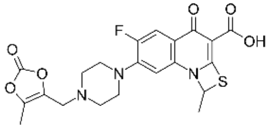
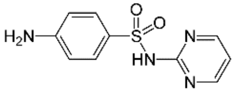
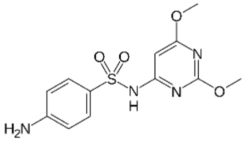
Appendix A. Supplementary data

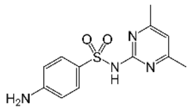
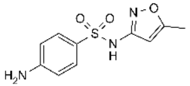
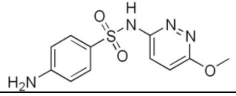
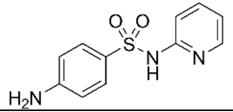
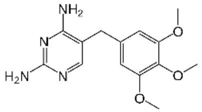
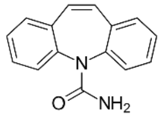
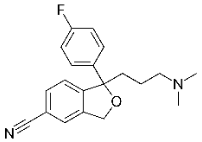
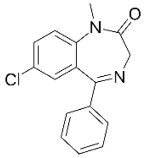
Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.124729.

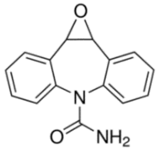
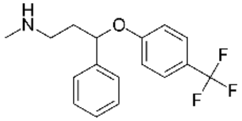
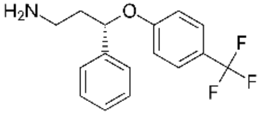
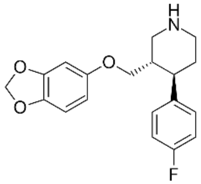
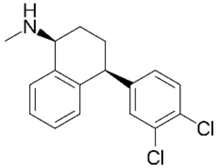
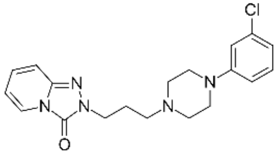
Appendix A. Supplementary data

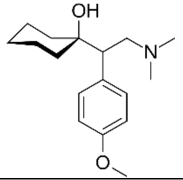
Table SM1. Pharmaceuticals, metabolites, isotopically-labelled internal standards, Chemical Abstracts Service (CAS), molecular weight, formula, structure, solvent used, and supplier company.

Pharmaceuticals and Isotopically-Labelled Internal Standards		**CAS**$^{*,¥}$	**Molecular Weight**$^{¥}$ **(g/mol)**	**Formula and Structure**$^{¥}$	**pk$_a$**	**Solvent used for the preparation of the stock solution**	**Supplier Company**
Antibiotics	**Azithromycin**	83905-01-5	748.996	$C_{38}H_{72}N_2O_{12}$ 	Strongest acidic pKa: 12.43 Strongest basic pKa: 9.57	Methanol	Sigma-Aldrich (Madrid, Spain)
	Ciprofloxacin	85721-33-1	331.347	$C_{17}H_{18}FN_3O_3$ 	5.76; 8.68	Milli-Q Water-10% acetic acid in Milli-Q water (1:1,v/v)	Sigma-Aldrich (Madrid, Spain)
	Clarithromycin	81103-11-9	747.964	$C_{38}H_{69}NO_{13}$ 	Strongest acidic pKa: 12.46 Strongest basic pKa: 8.38	Methanol	Sigma-Aldrich (Madrid, Spain)
	Enrofloxacin	93106-60-6	359.401	$C_{19}H_{22}FN_3O_3$ 	5.69: 6.68	Milli-Q Water-10% acetic acid in Milli-Q water (1:1, v/v)	Sigma-Aldrich (Madrid, Spain)
	Erythromycin	643-22-1	733.937	$C_{37}H_{67}NO_{13}$ 	Strongest acidic pKa: 12.45 Strongest basic pKa: 8.38	Methanol	Sigma-Aldrich (Madrid, Spain)

Lomefloxacin	98079-51-7	351.354	$C_{17}H_{19}F_2N_3O_3$ 	Strongest acidic pKa: 5.45 Strongest basic pKa: 8.7	Milli-Q Water-10% acetic acid in Milli-Q water (1:1,v/v)	
Moxifloxacin	151096-09-2	401.438	$C_{21}H_{24}FN_3O_4$ 	Strongest acidic pKa: 5.49 Strongest basic pKa: 9.42	Milli-Q Water-10% acetic acid in Milli-Q water (1:1,v/v)	
Norfloxacin	70458-96-7	319.33	$C_{16}H_{18}FN_3O_3$ 	Strongest acidic pKa: 5.58 Strongest basic pKa: 8.68	Milli-Q Water-10% acetic acid in Milli-Q water (1:1,v/v)	Sigma-Aldrich (Madrid, Spain)
Ofloxacin	82419-36-1	361.373	$C_{18}H_{20}FN_3O_4$ 	5.45; 6.20	Milli-Q Water-10% acetic acid in Milli-Q water (1:1,v/v)	Sigma-Aldrich (Madrid, Spain)
Prulifloxacin	123447-62-1	461.464	$C_{21}H_{20}FN_3O_6S$ 	Strongest acidic pKa: 5.93 Strongest basic pKa: 5.27	Milli-Q Water-10% acetic acid in Milli-Q water (1:1,v/v)	Toronto Research Chemicals Inc. (Ontario, Canada)
Sulfadiazine	68-35-9	250.276	$C_{10}H_{10}N_4O_2S$ 	2.01; 6.99	Methanol	Sigma-Aldrich (Madrid, Spain)
Sulfadimethoxine	122-11-2	310.328	$C_{12}H_{14}N_4O_4S$ 	1.95; 6.91	Methanol	Sigma-Aldrich (Madrid, Spain)

	Sulfamethazine	57-68-1	278.33	$C_{12}H_{14}N_4O_2S$ 	2.94; 6.99	Methanol	Sigma-Aldrich (Madrid, Spain)
	Sulfamethoxazole	723-46-6	253.276	$C_{10}H_{11}N_3O_3S$ 	Strongest acidic pKa: 6.16 Strongest basic pKa: 1.97	Methanol	Sigma-Aldrich (Madrid, Spain)
	Sulfamethoxypyridazine	80-35-3	280.302	$C_{11}H_{12}N_4O_3S$ 	2.02; 6.84	Methanol	Sigma-Aldrich (Madrid, Spain)
	Sulfapyridine	144-83-2	249.288	$C_{11}H_{11}N_3O_2S$ 	1.96; 2.63; 6.24	Methanol	Sigma-Aldrich (Madrid, Spain)
	Trimethoprim	738-70-5	290.323	$C_{14}H_{18}N_4O_3$ 	7.16	Methanol	Sigma-Aldrich (Madrid, Spain)
Pshyhiatric drugs	**Carbamazepine**	298-46-4	236.274	$C_{15}H_{12}N_2O$ 	15.96	Methanol	Sigma-Aldrich (Madrid, Spain)
	Citalopram	59729-33-8	324.399	$C_{20}H_{21}FN_2O$ 	9.78	Methanol	Sigma-Aldrich (Madrid, Spain)
	Diazepam	439-14-5	284.743	$C_{16}H_{13}ClN_2O$ 	2.92	Methanol	Lipomed AG (Arlesheim, Switzerland)

10,11-Epoxycarbamazepine	36507-30-9	252.273	$C_{15}H_{12}N_2O_2$ 	3.65; 5.13	Methanol	Sigma-Aldrich (Madrid, Spain)
Fluoxetine	54910-89-3	309.332	$C_{17}H_{18}F_3NO$ 	9.80	Methanol	Sigma-Aldrich (Madrid, Spain)
Norfluoxetine (Desmethylfluoxetine)	83891-03-6	295.305	$C_{16}H_{16}F_3NO$ 	Information not available in chemicalize	Methanol	Sigma-Aldrich (Madrid, Spain)
Paroxetine	110429-35-1	329.371	$C_{19}H_{20}FNO_3$ 	9.77	Methanol	Sigma-Aldrich (Madrid, Spain)
Sertraline	79617-96-2	306.23	$C_{17}H_{17}Cl_2N$ 	9.85	Methanol	Sigma-Aldrich (Madrid, Spain)
Trazodone	19794-93-5	371.869	$C_{19}H_{22}ClN_5O$ 	7.09	Methanol	Sigma-Aldrich (Madrid, Spain)

	Venlafaxine	93413-69-5	277.408	$C_{17}H_{27}NO_2$ 	8.91	Methanol	Sigma-Aldrich (Madrid, Spain)
Isotopically-labelled internal standards	Azithromycin-d3	163921-65-1	752.014	$C_{38}H_{69}D_3N_2O_{12}$		Methanol	Toronto Research Chemicals Inc. (Ontario, Canada)
	Carbamazepine-d10	132183-78-9	246.33	$C_{15}H_2D_{10}N_2O$		Purchased as methanolic solution	Cerilliant Certified Reference Materials (Texas, USA)
	Ciprofloxacin-d8 hydrochloride	1216659-54-9	375.85	$C_{17}H_{11}D_8ClFN_3O_3$		Milli-Q Water-10% acetic acid in Milli-Q water (1:1,v/v)	Toronto Research Chemicals Inc. (Ontario, Canada)
	Diazepam-d5	65854-76-4	289.77	$C_{16}H_8D_5ClN_2O$		Purchased as methanolic solution	Lipomed AG (Arlesheim, Switzerland)
	Fluoxetine-d5 hydrochloride	1173020-43-3	350.821	$C_{17}H_{14}D_5ClF_3NO$		Methanol	Sigma-Aldrich (Madrid, Spain)
	Sulfamethoxazole-d4	1020719-86-1	257.3	$C_{10}H_7D_4N_3O_3S$		Methanol	Toronto Research Chemicals Inc. (Ontario, Canada)
	Venlafaxine-d6	1062606-12-5	319.90	$C_{17}H_{22}ClD_6NO_2$		Purchased as methanolic solution	Cerilliant Certified Reference Materials (Texas, USA)

Pharmaceuticals organized by alphabetic order and by its therapeutic group.

*CAS is a unique numerical identifier assigned by the Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature.

¥CAS, molecular weight, and formula for all the compounds were obtained in the web site of PubChem (PubChem is an open chemistry database at the National Institutes of Health (NIH) (PubChem. Available at: https://pubchem.ncbi.nlm.nih.gov/), Accessed date December of 2018).
Pka: Information was obtained in the web page of Chemicalize (Chemicalize, *Instant Cheminformatics Solutions*. Available at: http://chemicalize.com, Accessed data: March 2018).

Table SM2. Information's on the Douro and Leça rivers.

Characteristics	**River**	
	Douro	**Leça**
Image		
Source	• Urbion (Spain)	• Monte Córdova, Santo Tirso
Area	• Cover an area of about 98,000 km^2	• Covers an area of about 190 km^2
Total length	• 927 km	• 45 km
Average flow	• 700 m^{3}s^{-1}	• 3.4 m^{3}s^{-1}
Basin	• Longest rivers of the Iberian Peninsula (Ribeiro *et al*., 2018). • Basin shared among Portugal and Spain (Ribeiro *et al*., 2018). • Basin mainly characterized by agro-forest areas, being its mouth, in both margins, heavily populated and impacted by anthropogenic activities (Ribeiro *et al*., 2018). • Upstream, its estuary is controlled by the Crestuma-Lever dam, approximately 21.6 km from the river mouth and presents an average depth of 8 m with semidiurnal tides ranging from 2 to 4 m (Cruzeiro *et al*., 2017; Madureira *et al*., 2010) • It is responsible for delivering about 87% of the fluvial sediments discharged into the NW Iberian coast (Mendes *et al*., 2017).	• Cross several municipalities until its mouth, located at Leixões 87arbour basin, an international 87arbour with dock services for commercial, cruise, and fishing vessels and an oil termina l (Barbosa *et al*., 2018; Gomes *et al*., 2014; Rocha *et al*., 2012) • Downstream, it is characterized by an high industrial and urban densities, contrasting with the barely populated, agricultural and forested areas at its upstream stretch (Barbosa *et al*., 2018; Gomes *et al*., 2014; Rocha *et al*., 2012).
Source of pollution	• Douro River receives effluents from several WWTPs (Cruzeiro *et al*., 2017; Madureira *et al*., 2010).	• Leça river receives effluents from numerous industries, of quite different typologies, namely textile dyeing and printing, metallurgical, mechanical, and agro-food plants. Some of them discharging untreated effluents into the river (Gomes *et al*., 2014). • Collects also the treated effluents of several WWTP (Gomes *et al*., 2014).

Table SM3. Ionization mode, precursor and product ions, and MS conditions for quantification product and identification product of antibiotics and psychiatric drugs and it´s correspond isotopically-labelled internal standards (ILIS) in the positive ionization mode.

Antibiotics, psychiatric drugs and Isotopically-Labelled Internal Standards	**Precursor (m/z)**	**Quantification product**				**Identification Product**				**Dwell Time (msec)**	**Concentration* (ILIS) (µg/L)**
		m/z	*Q1 Pre Bias (V)*	*CE*	*Q3 Pre Bias (V)*	*m/z*	*Q1 Pre Bias (V)*	*CE*	*Q3 Pre Bias (V)*		
Antibiotics											
Azithromycin	749.30	83.20	-20.0	-55.0	-16.0	116.10	-20.0	-51.0	-23.0	10.0	-
Ciprofloxacin	331.90	314.10	-10.0	-23.0	-21.0	231.00	-10.0	-41.0	-24.0	10.0	-
Clarithromycin	748.20	158.10	-28.0	-33.0	-21.0	83.15	-20.0	-53.0	-16.0	10.0	-
Enrofloxacin	359.90	342.15	-11.0	-23.0	-23.0	316.15	-11.0	-20.0	-22.0	10.0	-
Erythromycin	734.50	158.00	-20.0	-35.0	-16.0	83.15	-20.0	-54.0	-16.0	10.0	-
Lomefloxacin	352.00	334.10	-11.0	-22.0	-24.0	265.10	-11.0	-26.0	-18.0	10.0	-
Moxifloxacin	401.95	384.10	-12.0	-24.0	-28.0	96.15	-10.0	-48.0	-19.0	10.0	-
Norfloxacin	320.00	302.05	-10.0	-23.0	-21.0	231.00	-10.0	-42.0	-26.0	10.0	-
Ofloxacin	362.00	318.15	-14.0	-20.0	-22.0	261.05	-11.0	-30.0	-18.0	10.0	-
Prulifloxacin	461.90	443.95	-10.0	-23.0	-22.0	360.10	-10.0	-32.0	-25.0	10.0	-
Sulfadiazine	250.90	156.00	-13.0	-18.0	-16.0	92.10	-10.0	-31.0	-17.0	10.0	-
Sulfadimethoxine	310.80	155.95	-12.0	-22.0	-16.0	92.10	-10.0	-35.0	-17.0	10.0	-
Sulfamethazine	278.80	186.05	-13.0	-20.0	-19.0	92.10	-11.0	-33.0	-18.0	10.0	-
Sulfamethoxazole	254.00	156.00	-10.0	-17.0	-16.0	92.10	-10.0	-30.0	-17.0	10.0	-
Sulfamethoxypyridazine	280.80	156.00	-10.0	-19.0	-16.0	92.10	-11.0	-32.0	-17.0	10.0	-
Sulfapyridine	249.80	92.05	-10.0	-30.0	-17.0	156.00	-10.0	-18.0	-16.0	10.0	-
Trimethoprim	290.80	230.10	-14.0	-26.0	-16.0	123.10	-14.0	-27.0	-24.0	10.0	-
Psychiatric drugs											
Carbamazepine	236.95	194.10	-12.0	-20.0	-13.0	192.05	-12.0	-25.0	-13.0	10.0	-
Citalopram	324.95	109.10	-20.0	-30.0	-20.0	262.10	-10.0	-21.0	-18.0	10.0	-

Diazepam	284.95	154.10	-11.0	-29.0	-16.0	193.10	-11.0	-35.0	-21.0	10.0	-
10,11-Epoxycarbamazepine	253.00	180.05	-10.0	-27.0	-19.0	236.10	-10.0	-13.0	-16.0	10.0	-
Fluoxetine	310.05	44.00	-20.0	-15.0	-20.0	148.15	-20.0	-15.0	-20.0	10.0	-
Norfluoxetine (Desmethylfluoxetine)	296.00	134.10	-11.0	-9.0	-13.0	30.20	-11.0	-14.0	-30.0	10.0	-
Paroxetine	330.00	44.05	-10.0	-28.0	-17.0	70.15	-12.0	-34.0	-20.0	10.0	-
Sertraline	305.95	274.90	-14.0	-15.0	-19.0	158.90	-12.0	-28.0	-21.0	10.0	-
Trazodone	371.95	176.00	-20.00	-25.0	-20.0	147.95	-19.0	-40.0	-20.0	10.0	-
Venlafaxine	278.00	58.00	-20.0	-20.0	-20.0	260.10	-15.0	-14.0	-19.0	10.0	-
Isotopically-labelled internal standards											
Azithromycin-d3	752.30	83.15	-20.0	-55.0	-16.0	¥	¥	¥	¥	10.0	1000
Carbamazepine-d10	246.95	204.10	-10.0	-22.0	-23.0	¥	¥	¥	¥	10.0	100
Ciprofloxacin-d8	339.90	322.05	-11.0	-22.0	-23.0	¥	¥	¥	¥	10.0	1000
Diazepam-d5	289.90	154.05	-14.0	-31.0	-16.0	¥	¥	¥	¥	10.0	200
Fluoxetine-d5	315.05	44.05	-20.0	-15.0	-20.0	¥	¥	¥	¥	10.0	50
Sulfamethoxazole-d4	258.00	96.10	-10.0	-33.0	-18.0	¥	¥	¥	¥	10.0	500
Venlafaxine-d6	283.80	64.05	-20.0	-25.0	-20.0	¥	¥	¥	¥	10.0	88.6

Pharmaceuticals organized by alphabetic order and by its therapeutic group.

¥For the Isotopically-Labelled Internal Standards only one transition is needed.

*Final concentration of the Isotopically-Labelled Internal Standards (ILIS) in the stock solutions and in the water and sediment samples (µg/L).

***Table SM4**. Retention time and ion ratio for antibiotic, psychiatric drugs, and isotopically-labelled internal standards.*

Pharmaceuticals	**tr (min)**			**Ion Ratio (%)**				
	tr average (min)	RSD (%)	n	-20%	Ion Ratio Average (%)	+20%	RSD (%)	n
Antibiotics								
Azithromycin	2.317	0.234	30	1.36	1.71	2.05	4.37	18
Ciprofloxacin	2.265	0.321	30	0.942	1.18	1.41	3.30	13
Clarithromycin	2.751	0.140	30	0.968	1.21	1.45	1.87	20
Enrofloxacin	2.302	0.313	30	4.50	5.62	6.75	3.74	17
Erythromycin	2.606	0.100	30	3.29	4.11	4.93	2.37	16
Lomefloxacin	2.279	0.236	30	0.814	1.02	1.22	4.90	17
Moxifloxacin	2.403	0.356	30	0.897	1.12	1.35	3.44	27
Norfloxacin	2.250	0.219	30	0.964	1.21	1.45	3.80	26
Ofloxacin	2.249	0.326	30	1.22	1.52	1.83	2.92	25
Prulifloxacin	2.701	0.165	30	0.993	1.24	1.49	4.05	27
Sulfadiazine	2.435	0.307	30	1.13	1.42	1.70	2.55	28
Sulfadimethoxine	2.989	0.0946	30	1.60	2.00	2.40	1.92	27
Sulfamethazine	2.629	0.214	30	1.00	1.25	1.50	2.90	22
Sulfamethoxazole	2.856	0.114	30	0.955	1.19	1.43	2.47	28
Sulfamethoxypyridazine	2.634	0.110	30	1.53	1.92	2.30	3.10	23
Sulfapyridine	2.482	0.164	30	0.777	0.97	1.16	2.54	23
Trimethoprim	2.217	0.199	30	2.18	2.72	3.27	3.85	18
Psychiatric drugs								
Carbamazepine	3.095	0.0843	30	3.81	4.76	5.72	2.86	28
Citalopram	2.631	0.118	30	27.9	34.8	41.8	4.94	21
Diazepam	3.529	0.110	30	1.01	1.26	1.51	2.51	25
10,11-Epoxycarbamazepine	2.869	0.108	30	1.12	1.40	1.68	2.99	26
Fluoxetine	2.789	0.0991	30	2.22	2.78	3.33	2.85	25
Norfluoxetine	2.763	0.389	30	2.60	3.25	3.90	2.03	24
Paroxetine	2.694	0.0770	30	0.833	1.04	1.25	3.60	28
Sertraline	2.811	0.160	30	1.16	1.45	1.74	2.35	24
Trazodone	2.501	0.0702	30	0.923	1.15	1.39	4.07	25
Venlafaxine	2.462	0.116	30	0.888	1.11	1.33	2.36	27
Isotopically-labelled internal standards								
Azithromycin-d3	2.315	0.152	30					
Carbamazepine-d10	3.080	0.101	30					
Ciprofloxacin-d8	2.262	0.132	30					
Diazepam-d5	3.515	0.0500	30					
Fluoxetine-d5	2.785	0.0974	30					
Sulfamethoxazole-d4	2.851	0.0664	30					
Venlafaxine-d6	2.462	0.0878	30					

Pharmaceuticals organized by alphabetic order and by its therapeutic group.

Table SM5. Analyzed parameters in sediment samples from Douro and Leça rivers.

Parameters	**SsD1 top**	**SsD1 bottom**	**SsD2 top**	**SsD2 bottom**	**SsD3 top**	**SsD3 bottom**	**SsD4 top**	**SsD4 bottom**	**SsD5 top**	**SsD5 bottom**	**SsL1 top**	**SsL1 bottom**
pH H_2O	8.10	7.55	8.06	7.15	8.31	7.21	7.85	7.58	7.62	7.56	6.74	6.36
pH KCl	7.90	7.15	8.07	7.00	8.55	6.87	7.89	7.55	7.91	7.18	6.42	5.91
pH $CaCl_2$	7.32	6.97	7.45	6.96	n.a.	6.79	7.31	n.a.	7.08	6.97	6.07	6.06
C.E. (mS cm^{-1})	3.01	1.49	5.72	7.29	n.a.	4.21	5.70	n.a.	2.57	1.50	0.44	0.36
Water Content (%)	9.4	14.9	33.7	39.0	n.a.	18.8	21.2	n.a.	7.0	4.4	74.4	22.25
OM (%)	2.03	1.02	3.12	5.65	n.a.	2.21	1.30	n.a.	1.45	0.29	1.88	1.00
SO_4^{2-} (g L^{-1})	n.d.	0.22	n.d.	1.89	n.a.	n.d.	n.d.	n.a.	0.29	0.23	n.d.	0.28
PO_4^{3-} (mg L^{-1})	n.d.	0.06	0.18	n.d.	n.a.	1.22	n.d.	n.a.	n.d.	0.01	n.d.	0.01
P_{total} (mg/Kg)	395.50	218.19	n.a.	432.72	251.37	614.24	371.38	345.31	185.54	156.30	1,115.25	n.d.
P_{olsen} (mg/Kg)	30.63	4.55	n.a.	13.32	6.96	40.18	16.79	15.92	5.31	3.40	54.71	n.d.
C (%)	0.99	0.26	n.a.	0.57	0.28	2.10	0.44	0.59	0.28	0.21	2.30	n.d.
N (%)	0.17	0.03	n.a.	0.04	0.03	0.14	0.04	0.08	0.02	0.03	0.27	n.d.
S (%)	0.051	0.004	0.320	0.053	0.020	0.168	0.055	0.060	0.014	0.01	0.137	0.195
Gravel (%)	65.37	48.71	9.61	7.21	n.a.	62.74	22.96	n.a.	12.05	34.62	30.20	4.40
Sand (%)	32.61	51.03	81.92	80.51	n.a.	36.93	76.02	n.a.	87.95	65.38	69.32	95.60
Silt (%)	1.97	0.26	8.06	11.30	n.a.	0.33	1.02	n.a.	0.00[b]	0.00[b]	0.48	0.00[b]
Clay (%)	0.05	0.00[a]	0.41	0.98	n.a.	0.00[a]	0.00[a]	n.a.	0.00[a]	0.00[a]	0.00[a]	0.00[a]
Texture	Sandy	Sandy	Sandy	Sandy	n.a.	Sandy	Sandy	-	Sandy	Sandy	Sandy	Sandy

n.a. – not analysed

[a] – the result of the sum of all the granulometric fractions under 0.002 mm was 0.00.

[b] – the result of the sum of all the granulometric fractions between 0.002-0.02 mm was 0.00.

Table SM6. Analysed parameters in water samples from Douro and Leça rivers.

Parameters	WsD 1	WsD 2	WsD 3	WsD 4	WsL 1	WsL 2
Temperature (ºC)	19.8	18.5	19.4	19.0	18.9	14.6
pH	7.24	6.09	7.38	7.20	7.15	7.05
E.C. (μS/cm)	11,490	15,770	578	20,600	932	818
Eh (mV)	456	403	383	360	438	483
DO (mg/L)	11.0	11.6	n.a.	11.8	n.a.	n.a.
F^- (mg/L)	0.39	0.54	1.01	0.67	0.09	0.10
Cl^- (mg/L)	5,658	8,713	63	11,552	76	79
SO_4^{2-} (mg/L)	705	1,040	51	1,548	71	38
NH_4^+ (mg/L)	< 0.03	< 0.03	1.16	0.22	6.70	22.21
NO_3^- (mg/L)	10	12	1	38	n.a.	3
NO_2^- (mg/L)	0.10	0.64	0.13	1.65	2.62	3.07

n.a. – not analysed

Section 1. Method validation

Calibration curve

Linearity was studied using standards prepared in the solvent, in river waters, and in sediments extracts. Thus, for all pharmaceuticals, ten concentration levels for calibration curve in solvent between 5.0 and 1,000 µg/L and six concentration levels for a matrix-matched calibration curve between 5.0 and 500 µg/L were used. Calibration curves were made in both MRM transitions. Three replications (with an injection volume of 5 µL) were made for each standard solution to check the repeatability at each concentration level.

Method Limits of detection (MDL) and quantification (MQL)

MDL and MQL were determined as the minimum amount detectable of the analyte with a signal-to-noise ratio of 3 and 10, respectively. The limits were determined in river waters and in sediments but only if the pharmaceutical was detected in these samples, otherwise limits were determined in the matrix-matched calibration curve.

Repeatability

Repeatability analysis expressed as the relative standard deviation (RSD (%)). Three concentration of standards (100, 250, 500 µg/L) were repeated six-time sequential and repeated along the batch (n=6).

Matrix effect

The influence of the ME was evaluated comparing one standard prepared in solvent and one standard prepared in the matrix (Jelić *et al*., 2012). For each compound recovery was calculated by comparing its area in the samples spiked prior to SPE extraction (pre-spiked sample) with the area in the samples spiked after SPE extraction (post-spiked sample) (Paíga and Delerue-Matos, 2016). Thus, for river waters and sediments, a blank and fortified sample were carried out for the pre- and post-spiked samples. A positive value of ME is an indicative of ion enhancement signal and a negative value represents an ion suppression signal (Jelić *et al*., 2012).

References

Jelić, A., Gros, M., Petrovic, M., Ginebreda, A., Barceló, D., 2012. Occurrence and Elimination of Pharmaceuticals During Conventional Wastewater Treatment. Emerg. Prior. Pollut. Rivers. Handb. Environ. Chem. 19, 1–24. https://doi.org/10.1007/978-3-642-25722-3

Paíga, P., Delerue-Matos, C., 2016. A throughput method using the quick easy cheap effective rugged safe method for the quantification of ibuprofen and its main metabolites in soils. J. Sep. Sci. 39, 3436–3444. https://doi.org/10.1002/jssc.201600412

Table SM7. Method detection and method quantification limits (MDL, MQL) in river water (ng/L) and sediment samples (ng/g).

	Pharmaceuticals	***River water***		***Decision 2018/840 of 5 June 2018****	***Sediment****	
		MDL (ng/L)	MQL (ng/L)	MDL (ng/L)	MDL (ng/g)	MQL (ng/g)
	Antibiotics			n.a.		
*	Azithromycin	3.98	13.3	**19**	0.00200	0.00667
*	Ciprofloxacin	41.1	137	**89**	1.04	3.46
*	Clarithromycin	0.0750	0.225	**19**	0.00200	0.00667
	Enrofloxacin	1.55	5.18	n.a.	1.31	4.38
*	Erythromycin	9.20	30.7	**19**	0.00400	0.0150
	Lomefloxacin	37.8	126	n.a.	5.43	18.1
	Moxifloxacin	39.6	132	n.a.	1.16	3.85
	Norfloxacin	23.5	78.3	n.a.	3.39	11.3
	Ofloxacin	0.450	1.53	n.a.	0.0170	0.0560
	Prulifloxacin	12.1	40.4	n.a.	0.294	0.979
	Sulfadiazine	7.50	25.0	n.a.	0.0430	0.144
	Sulfadimethoxine	65.2	217	n.a.	0.0300	0.0990
	Sulfamethazine	2.35	7.80	n.a.	0.114	0.379
	Sulfamethoxazole	0.150	0.475	n.a.	0.225	0.752
	Sulfamethoxypyridazine	55.5	185	n.a.	0.0490	0.163
	Sulfapyridine	9.33	31.1	n.a.	0.0660	0.219
	Trimethoprim	9.45	31.5	n.a.	0.0810	0.272
	Psychiatricdrugs					
	Carbamazepine	1.05	3.48	n.a.	0.00643	0.0257
	Citalopram	0.500	1.63	n.a.	0.00429	0.0143
	Diazepam	3.70	12.35	n.a.	0.00400	0.0133
	10,11-Epoxycarbamazepine	2.28	7.60	n.a.	0.00900	0.0300
	Fluoxetine	0.225	0.750	n.a.	0.00214	0.00710
	Norfluoxetine	8.25	27.5	n.a.	0.189	0.630
	Paroxetine	0.0500	0.150	n.a.	0.369	1.23
	Sertraline	0.125	0.425	n.a.	0.00214	0.00710
	Trazodone	0.850	2.85	n.a.	0.00900	0.0300
	Venlafaxine	0.575	1.93	n.a.	0.0364	0.120

Pharmaceuticals organized by alphabetic order and by its therapeutic group.

*****Pharmaceuticals with maximum acceptable method detection limit (ng/l) in the Commission Implementing Decision (EU) 2018/840 of 5 June 2018 (Official Journal of the European Union, L 141/9. COMMISSION IMPLEMENTING DECISION (EU) 2018/840 of 5 June 2018 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council and repealing Commission Implementing Decision (EU) 2015/495. Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018D0840&from=EN, Accessed data: November 2018)

n.a. - No Limit was applicable in the water samples

** - No Limit was applicable in the sediments samples

Table SM8. Recoveries (%) at three levels of fortification for river sample matrix.

Pharmaceuticals	***Level I***		***Level II***		***Level III***		Average recovery*
	Recovery (%)	**RSD (%)**	**Recovery (%)**	**RSD (%)**	**Recovery (%)**	**RSD (%)**	
Antibiotics							
Azithromycin	66.5	3.7	73.7	6.1	**Note**	**Note**	70.1
Ciprofloxacin	102	5.1	95.6	6.7	96.5	2.7	98.0
Clarithromycin	74.0	2.0	67.0	4.1	70.5	1.1	70.5
Enrofloxacin	83.6	2.3	78.9	2.3	83.8	3.7	82.1
Erythromycin	82.3	4.6	78.7	4.1	80.8	6.7	80.6
Lomefloxacin	107.9	4.1	102	5.4	94.6	3.4	101.5
Moxifloxacin	87.4	1.2	88.8	4.7	79.6	1.4	85.3
Norfloxacin	92.4	4.3	96.2	4.6	98.8	5.3	95.8
Ofloxacin	71.1	2.7	70.3	3.7	64.6	2.5	68.7
Prulifloxacin	86.8	2.1	94.3	0.57	102	1.8	94.3
Sulfadiazine	52.1	3.4	49.1	5.7	56.5	3.1	52.6
Sulfadimethoxine	56.6	5.8	61.5	3.8	55.2	4.1	57.8
Sulfamethazine	51.2	3.9	52.4	6.6	54.7	2.3	52.8
Sulfamethoxazole	47.8	1.8	50.5	3.2	53.4	5.3	50.6
Sulfamethoxypiridazine	58.1	4.1	53.7	2.0	51.4	3.4	54.4
Sulfapyridine	55.5	2.1	52.6	4.1	52.9	2.7	53.7
Trimethoprim	91.3	2.1	95.6	3.8	97.5	3.5	94.8
Psychiatric drugs							
Carbamazepine	103	3.1	95.1	2.9	98.6	1.8	98.9
Citalopram	89.5	9.3	89.5	2.7	85.5	2.8	88.2
Diazepam	97.0	3.9	94.4	1.1	94.8	6.6	95.4
10,11-Epoxycarbamazepine	63.7	2.6	64.9	4.4	69.1	0.59	65.9
Fluoxetine	90.5	2.5	88.3	1.6	85.1	1.6	88.0
Norfluoxetine	80.6	4.3	77.8	3.8	81.4	2.5	79.9
Paroxetine	83.5	4.8	84.2	1.2	85.8	5.4	84.5
Sertraline	85.7	1.6	91.3	1.5	86.1	1.9	87.7
Trazodone	89.1	1.7	93.2	3.7	81.7	2.5	88.0
Venlafaxine	91.1	5.4	98.2	3.6	93.4	5.4	94.2

Pharmaceuticals organized by alphabetic order and by its therapeutic group.

***** Average recovery embracing the three fortified levels.

Note: in spiking level III azithromycin was not detect. Some problem must have occurred during the extraction and this level was discharged.

Table SM9. Recoveries (%) at three levels of fortification for sediment sample matrix.

Pharmaceuticals	***Level I***		***Level II***		***Level III***		Average recovery*
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Antibiotics							
Azithromycin	66.9	2.8	74.4	4.5	87.8	2.4	76.4
Ciprofloxacin	2.15	49	0.89	41	0.340	33	1.13
Clarithromycin	76.9	2.0	80.9	5.6	83.7	7.6	80.5
Enrofloxacin	10.2	6.3	13.1	34	7.39	49	10.2
Erythromycin	86.4	0.66	63.5	7.4	64.3	12	71.4
Lomefloxacin	3.16	35	5.8	58	2.52	60	3.82
Moxifloxacin	3.11	65	3.3	40	1.92	96	2.76
Norfloxacin	2.86	53	0.75	48	0.512	16	1.37
Ofloxacin	2.29	37	1.9	61	1.20	65	1.80
Prulifloxacin	16.0	20	18.8	3.5	18.2	12	17.7
Sulfadiazine	13.3	18	17.2	29	15.9	1.0	15.4
Sulfadimethoxine	29.1	17	31.5	25	30.1	19	30.2
Sulfamethazine	18.7	8.8	26.2	4.1	29.5	4.3	24.8
Sulfamethoxazole	28.1	21	29.5	22	31.2	19	29.6
Sulfamethoxypiridazine	13.9	22	21.4	28	21.2	4.7	18.8
Sulfapyridine	18.0	11	27.8	31	24.9	12	23.6
Trimethoprim	74.8	7.0	92.8	7.7	78.2	6.2	81.9
Psychiatric drugs							
Carbamazepine	91.4	6.1	103	3.6	91.9	5.1	95.6
Citalopram	71.0	7.4	74.3	4.6	68.6	3.0	71.3
Diazepam	100	6.1	108	5.0	106	5.0	104.3
10,11-Epoxycarbamazepine	73.9	2.9	81.9	6.8	73.2	2.6	76.3
Fluoxetine	68.7	2.6	75.7	1.2	67.2	6.7	70.5
Norfluoxetine	63.6	10	67.9	8.2	57.8	4.8	63.1
Paroxetine	56.8	3.3	64.2	1.9	54.8	2.9	58.6
Sertraline	46.6	11	50.7	3.8	44.2	6.0	47.2
Trazodone	59.9	10	66.6	6.4	62.7	6.0	63.1
Venlafaxine	70.4	6.0	75.9	3.6	72.4	5.0	72.9

Pharmaceuticals organized by alphabetic order and by its therapeutic group.

* Average recovery embracing the three fortified levels.

Table SM10. Measured concentrations (ng/L) for the target analytes river water and sediment from the research conducted by the scientific community in the last years.

Pharmaceuticals	**Continent**	**River (Country)**	**Water Concentration (ng/L)**	**Sediment Concentration (ng/g)**	**Reference**
Antibiotics					
Ciprofloxacin	Asia	China (Xiangjiang River)	n.d.		(Lin *et al*., 2018)
	Asia	Pearl River Estuary (Zhuhai City, China)	24.6-365	0.09-104	(Li *et al*., 2018)
	Asia	Ba River (Lantian County, Shannxi Province)	2.66-28.6	2.40-62.5	(Jia *et al*., 2018)
	Asia	Yellow River (China)		n.d.-32.8	(Zhou *et al*., 2011)
	Asia	Hai River (China)		2.05 - 1,290	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d.-28.7	(Zhou *et al*., 2011)
	Asia	Huangpu River (Shangai, China)	n.d. - <LOQ (9.33)		(Jiang *et al*., 2011)
	Asia	Huangpu River (Shanghai, China)	n.d.-34.2		(Chen and Zhou, 2014)
	Asia	Laizhou Bay-river discharge points (China)	n.d. - 346		(Zhang *et al*., 2012)
	Asia	Chao Phraya River (Thailand)	48 (max.)		(Tewari *et al*., 2013)
	Europe	Seine River (Paris, France)	n.d.		(Tamtam *et al*., 2008)
	Europe	Tâmega River (Chaves, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Tua River (Mirandela, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Mondego River (Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Trancão River (Lisbon, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Tagus River (Lisbon, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Xarrama River (Évora, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Guadiana River (Vila Real de Santo António, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Lis River (Leiria, Portugal)	n.d.-88.7		(Paíga *et al*., 2016)
Enrofloxacin	Asia	China (Xiangjiang River)	n.d.		(Lin *et al*., 2018)
	Asia	Huangpu River (Shangai, China)	n.d. - <LOQ (11.34)		(Jiang *et al*., 2011)
	Asia	Laizhou Bay-river discharge points (China)	n.d.-24.6		(Zhang *et al*., 2012)
	Asia	Pearl River (China)	n.d.	1.43*	(Liang *et al*., 2013)
	Asia	Huangpu River (Shanghai, China)	n.d.-14.6	n.d.-8.9	(Chen and Zhou, 2014)
	Europe	Seine River (Paris, France)	n.d.		(Tamtam *et al*., 2008)
	Europe	Ave River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.-44.99		(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	n.d.-343.28		(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.-45.53		(Barbosa *et al*., 2018)
Ofloxacin	Asia	China (Xiangjiang River)	n.d.-23		(Lin *et al*., 2018)
	Asia	Pearl River Estuary (Zhuhai City, China)	0.80–195	n.d.-157	(Li *et al*., 2018)
	Asia	Qiantang River basin (China)	40 62		(Chen *et al*., 2012)
	Asia	Yellow River (China)		n.d.-124	(Zhou *et al*., 2011)
	Asia	Hai River (China)		1.96-653	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d.-50.5	(Zhou *et al*., 2011)
	Asia	Laizhou Bay-river discharge points (China)	n.d.-45.4		(Zhang *et al*., 2012)
	Asia	Pearl River (China)	15.8*	13.7*	(Liang *et al*., 2013)
	Asia	Huangpu River (Shangai, China)	<LOQ (8.34)		(Jiang *et al*., 2011)
	Asia	Huangpu River (Shanghai, China)	n.d.-28.5	n.d.-12.4	(Chen and Zhou, 2014)
	Europe	Seine River (Paris, France)	n.d.-30		(Tamtam *et al*., 2008)
	Europe	Ave River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.		(Barbosa *et al*., 2018)

Norfloxacin	Asia	China (Xiangjiang River)	n.d.		(Lin *et al*., 2018)
	Asia	Pearl River Estuary (Zhuhai City, China)	32.8-381	3.38-444	(Li *et al*., 2018)
	Asia	Ba River (Lantian County, Shannxi Province)	5.33-122	6.04-680	(Jia *et al*., 2018)
	Asia	Qiantang River basin (China)	n.d.-500		(Chen *et al*., 2012)
	Asia	Yellow River (China)		n.d.-142	(Zhou *et al*., 2011)
	Asia	Hai River (China)		n.d.-5770	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d.-177	(Zhou *et al*., 2011)
	Asia	Laizhou Bay-river discharge points (China)	n.d. - 572		(Zhang *et al*., 2012)
	Asia	Pearl River (China)	136*	20.5*	(Liang *et al*., 2013)
	Asia	Huangpu River (Shangai, China)	n.d.		(Jiang *et al*., 2011)
	Asia	Huangpu River (Shanghai, China)	n.d.-0.2		(Chen and Zhou, 2014)
	Europe	Seine River (Paris, France)	n.d.-46		(Tamtam *et al*., 2008)
Moxifloxacin					
Lomefloxacin	Asia	Yellow River (China)		n.d.	(Zhou *et al*., 2011)
	Asia	Hai River (China)		1.67	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d.	(Zhou *et al*., 2011)
	Europe	Seine River (Paris, France)	n.d.		(Tamtam *et al*., 2008)
Prulifloxacin					
Trimethoprim	Asia	China (Xiangjiang River)	n.d.-93		(Lin *et al*., 2018)
	Asia	Pearl River Estuary (Zhuhai City, China)	n.d.-492	n.d.-210	(Li *et al*., 2018)
	Asia	Ba River (Lantian County, Shannxi Province, China)	11.3-106	0.79-31.4	(Jia *et al*., 2018)
	Asia	Qiantang River basin (China)	n.d.		(Chen *et al*., 2012)
	Asia	Yellow River (China)		n.d.-2.86	(Zhou *et al*., 2011)
	Asia	Hai River (China)		n.d.-5.63	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d.-9.84	(Zhou *et al*., 2011)
	Asia	Brahmaputra River (Bangladesh)	< 0.08-17.20		(Hossain *et al*., 2018)
	Asia	Chao Phraya River (Thailand)	3*		(Tewari *et al*., 2013)
	Asia	Laizhou Bay-river discharge points (China)	n.d.-13,600		(Zhang *et al*., 2012)
	Africa	Msunduzi River, KwaZulu-Natal, South Africa	n.d.-290	<MDL (0.246)-87.55	(Matongo *et al*., 2015)
	America	Hudson River (New York)	n.d.-350		(Cantwell *et al*., 2018)
	Europe	Danube River (Serbia, Belgrade)	n.d.-25		(Grujić *et al*., 2009)
	Europe	Sava River (Serbia, Belgrade)	n.d.		(Grujić *et al*., 2009)
	Europe	Tamis River (Serbia)	24		(Grujić *et al*., 2009)
	Europe	Seine River (Paris, France)	12-27		(Tamtam *et al*., 2008)
	Europe	River Foss (United Kingdom)	n.d.-76		(Burns *et al*., 2018)
	Europe	River Ouse (United Kingdom)	n.d.-22.9		(Burns *et al*., 2018)
	Europe	Lis River (Leiria, Portugal)	n.d.		(Paíga *et al*., 2016)
	Europe	Ave River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.-15.63		(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	n.d.-64.14		(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.-12.68		(Barbosa *et al*., 2018)
Sulfamethoxypyridazine	Asia	Luan River (North China)	0.16-3.1		(Li *et al*., 2014)
	Europe	Ebro River (Northeast Spain)	0.6-18.1		(García-Galán *et al*., 2011)
Sulfapyridine	Asia	Pearl River Estuary (Zhuhai City, China)	n.d.-58.3	n.d.-126	(Li *et al*., 2018)
	Asia	Yellow River (China)		n.d.	(Zhou *et al*., 2011)
	Asia	Hai River (China)		n.d.	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d.	(Zhou *et al*., 2011)
	Asia	Huangpu River (Shanghai, China)	2.54-16.6		(Jiang *et al*., 2011)
	Asia	Huangpu River (Shanghai, China)	n.d.-103.1	n.d.-6.6	(Chen and Zhou, 2014)

	Asia	Luan River (North China)	<0.1-3.4		(Li *et al*., 2014)
	Europe	Ebro River (Northeast Spain)	0.1-42.5		(García-Galán *et al*., 2011)
	Europe	Lis River (Leiria, Portugal)	n.d.		(Paíga *et al*., 2016)
Sulfamethazine	Asia	Xiangjiang River (China)	n.d.-60		(Lin *et al*., 2018)
	Asia	Pearl River Estuary (Zhuhai City, China)	n.d.-226	n.d.-72.3	(Li *et al*., 2018)
	Asia	Ba River (Lantian County, Shannxi Province)	8.64-464	7.80-690	(Jia *et al*., 2018)
	Asia	Yellow River (China)		n.d.	(Zhou *et al*., 2011)
	Asia	Hai River (China)		n.d.-5.69	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d.	(Zhou *et al*., 2011)
	Asia	Brahmaputra River (Bangladesh)	< 0.01-11.35		(Hossain *et al*., 2018)
	Asia	Luan River (North China)	0.21-3.7		(Li *et al*., 2014)
	Asia	Huangpu River (Shangai, China)	5.45-313.44		(Jiang *et al*., 2011)
	Asia	Huangpu River (Shanghai, China)	19.9-389.4	0.2-2.7	(Chen and Zhou, 2014)
	Asia	Laizhou Bay-river discharge points (China)	<LOQ - 108		(Zhang *et al*., 2012)
	Africa	Msunduzi River, KwaZulu-Natal, South Africa	n.d.-1,090	n.d.	(Matongo *et al*., 2015)
	Asia	Pearl River (China)	218*	3.24*	(Liang *et al*., 2013)
	Asia	Chao Phraya River (Thailand)	5*		(Tewari *et al*., 2013)
	Europe	Ebro River (Northeast Spain)	2.5-65.2		(García-Galán *et al*., 2011)
	Europe	Seine River (Paris, France)	n.d.		(Tamtam *et al*., 2008)
	Europe	Lis River (Leiria, Portugal)	n.d.-123		(Paíga *et al*., 2016)
	Europe	Mess River (Luxembourg)	19 (max)		(Meyer *et al*., 2011)
Sulfadimethoxine	Asia	Brahmaputra River (Bangladesh)	n.d.		(Hossain *et al*., 2018)
	Asia	Luan River (North China)	0.95-3.56		(Li *et al*., 2014)
	Europe	Ebro River (Northeast Spain)	1-23.1		(García-Galán *et al*., 2011)
	Europe	Mess River (Luxembourg)	n.d.		(Meyer *et al*., 2011)
Sulfadiazine	Asia	China (Xiangjiang River)	n.d.-68		(Lin *et al*., 2018)
	Asia	Pearl River Estuary (Zhuhai City, China)	n.d.-50.7	n.d.-198	(Li *et al*., 2018)
	Asia	Ba River (Lantian County, Shannxi Province)	1.69-36.8	0.59-7.10	(Jia *et al*., 2018)
	Asia	China, Hanjiang River (through Hubei and Shaanxi)	1.9-6.3	0.35-0.54	(Hu *et al*., 2018)
	Asia	Yellow River (China)		n.d.-22.0	(Zhou *et al*., 2011)
	Asia	Hai River (China)		n.d.-1.71	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d.-11	(Zhou *et al*., 2011)
	Asia	Huangpu River (Shangai, China)	2.66-22.33		(Jiang *et al*., 2011)
	Asia	Huangpu River (Shanghai, China)	4.9-112.5	0.07-0.71	(Chen and Zhou, 2014)
	Asia	Pearl River (China)	18.0*	n.d.*	(Liang *et al*., 2013)
	Asia	Laizhou Bay-river discharge points (China)	n.d.-18.7		(Zhang *et al*., 2012)
	Asia	Brahmaputra River (Bangladesh)	< 0.01-0.58		(Hossain *et al*., 2018)
	Asia	Luan River (North China)	0.35-10.86		(Li *et al*., 2014)
	Europe	Ebro River (Northeast Spain)	0.7-6.4		(García-Galán *et al*., 2011)
	Europe	Lis River (Leiria, Portugal)	n.d.		(Paíga *et al*., 2016)
Sulfamethoxazole	Asia	Pearl River Estuary (Zhuhai City, China)	n.d.-195	0.37–219	(Li *et al*., 2018)
	Asia	Yellow River (China)		n.d.	(Zhou *et al*., 2011)
	Asia	Hai River (China)		n.d.	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d. - <LOQ	(Zhou *et al*., 2011)
	Asia	Huangpu River (Shangai, China)	6.78-28.34		(Jiang *et al*., 2011)
	Asia	Huangpu River (Shanghai, China)	2.2-764.9	0.05-0.6	(Chen and Zhou, 2014)
	Asia	Laizhou Bay-river discharge points (China)	0.36 - 527		(Zhang *et al*., 2012)
	Asia	Pearl River (China)	37.6*	n.d.	(Liang *et al*., 2013)
	Asia	Chao Phraya River (Thailand)	2*		(Tewari *et al*., 2013)

	Asia	Brahmaputra River (Bangladesh)	<0.03-7.24		(Hossain *et al*., 2018)
	Asia	Luan River (North China)	<0.11-7.23		(Li *et al*., 2014)
	Africa	Msunduzi River, KwaZulu-Natal, South Africa	n.d.-5,320	<MDL	(Matongo *et al*., 2015)
	America	Hudson River (New York)	n.d.-616.6		(Cantwell *et al*., 2018)
	Europe	Ebro River (Northeast Spain)	0.2-35.6		(García-Galán *et al*., 2011)
	Europe	River Foss (United Kingdom)	n.d.-33		(Burns *et al*., 2018)
	Europe	Seine River (Paris, France)	140-37		(Tamtam *et al*., 2008)
	Europe	River Ouse (United Kingdom)	n.d.		(Burns *et al*., 2018)
	Europe	Lis River (Leiria, Portugal)	n.d. - 43		(Paíga *et al*., 2016)
	Europe	Mess River (Luxembourg)	118 (max)		(Meyer *et al*., 2011)
Clarithromycin	Asia	China (Xiangjiang River)	n.d.-100		(Lin *et al*., 2018)
	Asia	Pearl River Estuary (Zhuhai City, China)	n.d.-287	n.d.-25.8	(Li *et al*., 2018)
	Asia	Laizhou Bay-River discharge points (China)	n.d.-32.90		(Zhang *et al*., 2012)
	Asia	Mankyung River (South Korea)	n.d. - 443		(Kim *et al*., 2009)
	Europe	Tâmega River (Chaves, Portugal)	n.d.-24.8		(Pereira *et al*., 2017)
	Europe	Tua River (Mirandela, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Mondego River (Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Trancão River (Lisbon, Portugal)	n.d.-39.10		(Pereira *et al*., 2017)
	Europe	Tagus River (Lisbon, Portugal)	n.d.-35.77		(Pereira *et al*., 2017)
	Europe	Xarrama River (Évora, Portugal)	n.d.-36.87		(Pereira *et al*., 2017)
	Europe	Guadiana River (Vila Real de Santo António, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Ave River (North of Portugal)	n.d.-43.90		(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.-32.98		(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	n.d.-7.71		(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.-3.87		(Barbosa *et al*., 2018)
	Europe	Lis River (Leiria, Portugal)	n.d.-26.8		(Paíga *et al*., 2016)
Azithromycin	Asia	China (Xiangjiang River)	n.d.-99		(Lin *et al*., 2018)
	Asia	Laizhou Bay-river discharge points (China)	n.d.-88.0		(Zhang *et al*., 2012)
	Europe	Danube River (Serbia, Belgrade)	n.d.-55		(Grujić *et al*., 2009)
	Europe	Sava River (Serbia, Belgrade)	n.d.		(Grujić *et al*., 2009)
	Europe	Tamis River (Serbia)	36		(Grujić *et al*., 2009)
	Europe	Tâmega River (Chaves, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Tua River (Mirandela, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Mondego River (Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Trancão River (Lisbon, Portugal)	n.d.-35.66		(Pereira *et al*., 2017)
	Europe	Tagus River (Lisbon, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Xarrama River (Évora, Portugal)	n.d.-32.15		(Pereira *et al*., 2017)
	Europe	Guadiana River (Vila Real de Santo António, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Ave River (North of Portugal)	n.d.-31.74		(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.-49.57		(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	0.91-14.08		(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.-26.08		(Barbosa *et al*., 2018)
Erythromycin	Asia	China (Xiangjiang River)	n.d.-43		(Lin *et al*., 2018)
	Asia	Pearl River Estuary (Zhuhai City, China)	n.d.-70.2	n.d.-62.4	(Li *et al*., 2018)
	Asia	Ba River (Lantian County, Shannxi Province)	16.3-300	3.95-201	(Jia *et al*., 2018)
	Asia	Qiantang River basin (China)	21-42		(Chen *et al*., 2012)
	Asia	Yellow River (China)		n.d.-49.8	(Zhou *et al*., 2011)
	Asia	Hai River (China)		n.d.-67.2	(Zhou *et al*., 2011)
	Asia	Liao River (China)		n.d.-40.3	(Zhou *et al*., 2011)

	Asia	Huangpu River (Shanghai, China)	0.4-6.9	1.5-24.6	(Chen and Zhou, 2014)
	Asia	Mankyung River (South Korea)	n.d.-137		(Kim *et al*., 2009)
	Asia	Pearl River (China)	121*	14.0*	(Liang *et al*., 2013)
	Asia	Brahmaputra River (Bangladesh)	< 0.04-6.46		(Hossain *et al*., 2018)
	Asia	Laizhou Bay-river discharge points (China)	0.38-282		(Zhang *et al*., 2012)
	Asia	Luan River (China)	1.04-3.15		(Li *et al*., 2014)
	Africa	Msunduzi River, KwaZulu-Natal, South Africa	n.d.-240	<MDL	(Matongo *et al*., 2015)
	Europe	River Foss (United Kingdom)	n.d.-263		(Burns *et al*., 2018)
	Europe	River Ouse (United Kingdom)	n.d.-33.9		(Burns *et al*., 2018)
	Europe	Tâmega River (Chaves, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Tua River (Mirandela, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Mondego River (Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Trancão River (Lisbon, Portugal)	n.d.-38.80		(Pereira *et al*., 2017)
	Europe	Tagus River (Lisbon, Portugal)	n.d.-34.85		(Pereira *et al*., 2017)
	Europe	Xarrama River (Évora, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Guadiana River (Vila Real de Santo António, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Ave River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.		(Barbosa *et al*., 2018)
Psychiatric drugs					
Norfluoxetine	Europe	Lis River (Leiria, Portugal)	n.d.		(Paíga *et al*., 2016)
	Europe	Tâmega River (Chaves, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Tua River (Mirandela, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Mondego River (Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Trancão River (Lisbon, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Tagus River (Lisbon, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Xarrama River (Évora, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Guadiana River (Vila Real de Santo António, Portugal)	n.d.		(Pereira *et al*., 2017)
	Europe	Ave River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	n.d.		(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.		(Barbosa *et al*., 2018)
Carbamazepine	Asia	Huangpu River (China)	5.0-75.5		(Wu *et al*., 2015)
	Asia	Mankyung River (South Korea)	n.d.-595		(Kim *et al*., 2009)
	Asia	Liuxi River	n.d.-17.9		(Zhao *et al*., 2010)
	Asia	Zhujiang River	4.5-25.5		(Zhao *et al*., 2010)
	Asia	Shijing River	22-43.1		(Zhao *et al*., 2010)
	Asia	Brahmaputra River (Bangladesh)	<0.01-8.80		(Hossain *et al*., 2018)
	Africa	Msunduzi River, KwaZulu-Natal, South Africa	130-3,240	<0.535-6.07	(Matongo *et al*., 2015)
	America	Hudson River (New York)	0.9-542.6		(Cantwell *et al*., 2018)
	Europe	Henares-Jarama-Tajo basin (Madrid, Spain)	n.d-104		(Fernández *et al*., 2010)
	Europe	Lahn (Oberbiel), Kinzig (Hanau), Fulda (Wahnhausen), Werra (Heldra), Main (Bischofsheim), Rhine (Mainz), Nidda (Nied) rivers (Germany)	250		(Ternes, 1998)
	Europe	Danube River (Serbia, Belgrade)	n.d.-130		(Grujić *et al*., 2009)
	Europe	Sava River (Serbia, Belgrade)	29-50		(Grujić *et al*., 2009)
	Europe	Tamis River (Serbia)	30		(Grujić *et al*., 2009)
	Europe	River Foss (United Kingdom)	n.d.-195		(Burns *et al*., 2018)

	Europe	River Ouse (United Kingdom)	1-54.4	(Burns *et al*., 2018)
	Europe	Tâmega River (Chaves, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Tua River (Mirandela, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Mondego River (Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Trancão River (Lisbon, Portugal)	n.d.-<10.90	(Pereira *et al*., 2017)
	Europe	Tagus River (Lisbon, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Xarrama River (Évora, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Guadiana River (Vila Real de Santo António, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Ave River (North of Portugal)	n.d.-24.50	(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.-98.59	(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	3.43-81.13	(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	3.96-177.01	(Barbosa *et al*., 2018)
	Europe	Arade River (Algarve, Portugal)	13-31	(Gonzalez-Rey *et al*., 2015)
	Europe	Lis River (Leiria, Portugal)	24.9-214	(Paíga *et al*., 2016)
Fluoxetine	Asia	Huangpu River (China)	0.1-1.3	(Wu *et al*., 2015)
	Europe	Henares-Jarama-Tajo basin (Madrid, Spain)	NQ-66.1	(Fernández *et al*., 2010)
	Europe	Vistula and Utrata rivers (Varsóvia, Polonia)	n.d.-5.5	(Giebułtowicz and Nałecz-Jawecki, 2014)
	Europe	Tâmega River (Chaves, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Tua River (Mirandela, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Mondego River (Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Trancão River (Lisbon, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Tagus River (Lisbon, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Xarrama River (Évora, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Guadiana River (Vila Real de Santo António, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Ave River (North of Portugal)	n.d.-27.45	(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.-12.20	(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	n.d.-9.74	(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.-12.34	(Barbosa *et al*., 2018)
	Europe	Arade River (Algarve, Portugal)	1-2	(Gonzalez-Rey *et al*., 2015)
	Europe	Lis River (Leiria, Portugal)	2.01-19.5	(Paíga *et al*., 2016)
Sertraline	Europe	Vistula and Utrata rivers (Varsóvia, Poland)	n.d.->MQL (3.1- 6.1)	(Giebułtowicz and Nałecz-Jawecki, 2014)
	Europe	River Foss (United Kingdom)	n.d.-21.2	(Burns *et al*., 2018)
	Europe	River Ouse (United Kingdom)	n.d.-7.2	(Burns *et al*., 2018)
	Europe	Tâmega River (Chaves, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Tua River (Mirandela, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Mondego River (Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Trancão River (Lisbon, Portugal)	n.d.-23.30	(Pereira *et al*., 2017)
	Europe	Tagus River (Lisbon, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Xarrama River (Évora, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Guadiana River (Vila Real de Santo António, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Lis River (Leiria, Portugal)	n.d.-< MDL	(Paíga *et al*., 2016)
Citalopram	Europe	Vistula and Utrata rivers (Varsóvia, Poland)	n.d.-17	(Giebułtowicz and Nałecz-Jawecki, 2014)
	Europe	River Foss (United Kingdom)	n.d.-71.4	(Burns *et al*., 2018)
	Europe	River Ouse (United Kingdom)	n.d.-22.9	(Burns *et al*., 2018)
	Europe	Tâmega River (Chaves, Portugal)	n.d.-52.97	(Pereira *et al*., 2017)
	Europe	Tua River (Mirandela, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Mondego River (Portugal)	n.d.-46.82	(Pereira *et al*., 2017)
	Europe	Trancão River (Lisbon, Portugal)	n.d.-43.71	(Pereira *et al*., 2017)
	Europe	Tagus River (Lisbon, Portugal)	n.d.-28.80	(Pereira *et al*., 2017)

	Europe	Xarrama River (Évora, Portugal)	n.d.-51.82	(Pereira *et al*., 2017)
	Europe	Guadiana River (Vila Real de Santo António, Portugal)	n.d.	(Pereira *et al*., 2017)
	Europe	Ave River (North of Portugal)	n.d.	(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.	(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	n.d.-30.20	(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.	(Barbosa *et al*., 2018)
	Europe	Lis River (Leiria, Portugal)	n.d.-28.9	(Paíga *et al*., 2016)
Venlafaxine	Europe	Vistula and Utrata rivers (Varsóvia, Poland)	0.8-250	(Giebułtowicz and Nałecz-Jawecki, 2014)
	Europe	River Foss (United Kingdom)	n.d.-102	(Burns *et al*., 2018)
	Europe	River Ouse (United Kingdom)	n.d.-8.5	(Burns *et al*., 2018)
	Europe	Ave River (North of Portugal)	n.d.-20.77	(Barbosa *et al*., 2018)
	Europe	Leça River (North of Portugal)	n.d.-149.19	(Barbosa *et al*., 2018)
	Europe	Antuã River (North of Portugal)	n.d.-199.07	(Barbosa *et al*., 2018)
	Europe	Cértima River (North-Central Portugal)	n.d.-170.24	(Barbosa *et al*., 2018)
	Europe	Lis River (Leiria, Portugal)	n.d.-159	(Paíga *et al*., 2016)
Paroxetine	Europe	Vistula and Utrata rivers (Varsóvia, Poland)	< MDL	(Giebułtowicz and Nałecz-Jawecki, 2014)
	Europe	Lis River (Leiria, Portugal)	n.d.-25.6	(Paíga *et al*., 2016)
Trazodone	Europe	Vistula and Utrata rivers (Varsóvia, Poland)	n.d.-0.9	(Giebułtowicz and Nałecz-Jawecki, 2014)
	Europe	Lis River (Leiria, Portugal)	n.d.-27.6	(Paíga *et al*., 2016)
Diazepam	Asia	Huangpu River (China)	4.6-75.5	(Wu *et al*., 2015)
	South América	Guandu River (Rio de Janeiro, Brazil)	52.75-241.25	(Aldo Pacheco Ferreira, 2014)
	Europe	River Foss (United Kingdom)	n.d.-2.3	(Burns *et al*., 2018)
	Europe	River Ouse (United Kingdom)	n.d.	(Burns *et al*., 2018)
	Europe	Arade River (Algarve, Portugal)	0-2	(Gonzalez-Rey *et al*., 2015)
	Europe	Lis River (Leiria, Portugal)	n.d.	(Paíga *et al*., 2016)
10,11-Epoxycarbamazepine	Europe	Lis River (Leiria, Portugal)	n.d.-44.4	(Paíga *et al*., 2016)

Concentration values are presented with the decimals number that each author published

*Higher concentration

Appendix table SM10 - References

Aldo Pacheco Ferreira, 2014. Environmental investigation of psychiatric pharmaceuticals: Guandu River, Rio de Janeiro state, Southeast Brazil. J. Chem. Heal. Risks 4, 25 – 32.

Barbosa, M.O., Ribeiro, A.R., Ratola, N., Hain, E., Homem, V., Pereira, M.F.R., Blaney, L., Silva, A.M.T., 2018. Spatial and seasonal occurrence of micropollutants in four Portuguese rivers and a case study for fluorescence excitation-emission matrices. Sci. Total Environ. 644, 1128–1140. https://doi.org/10.1016/j.scitotenv.2018.06.355

Burns, E.E., Carter, L.J., Kolpin, D.W., Thomas-Oates, J., Boxall, A.B.A., 2018. Temporal and spatial variation in pharmaceutical concentrations in an urban river system. Water Res. 137, 72–85. https://doi.org/10.1016/j.watres.2018.02.066

Cantwell, M.G., Katz, D.R., Sullivan, J.C., Shapley, D., Lipscomb, J., Epstein, J., Juhl, A.R., Knudson, C., O'Mullan, G.D., 2018. Spatial patterns of pharmaceuticals and wastewater tracers in the Hudson River Estuary. Water Res. 137, 335–343. https://doi.org/10.1016/j.watres.2017.12.044

Chen, H., Li, X., Zhu, S., 2012. Occurrence and distribution of selected pharmaceuticals and personal care products in aquatic environments: A comparative study of regions in China with different urbanization levels. Environ. Sci. Pollut. Res. 19, 2381–2389. https://doi.org/10.1007/s11356-012-0750-2

Chen, K., Zhou, J.L., 2014. Occurrence and behavior of antibiotics in water and sediments from the Huangpu River, Shanghai, China. Chemosphere 95, 604–612. https://doi.org/10.1016/j.chemosphere.2013.09.119

Cruzeiro, C., Amaral, S., Rocha, E., Rocha, M.J., 2017. Determination of 54 pesticides in waters of the Iberian Douro River estuary and risk assessment of environmentally relevant mixtures using theoretical approaches and Artemia salina and Daphnia magna bioassays. Ecotoxicol. Environ. Saf. 145, 126–134. https://doi.org/10.1016/j.ecoenv.2017.07.010

Fernández, C., González-Doncel, M., Pro, J., Carbonell, G., Tarazona, J. V., 2010. Occurrence of pharmaceutically active compounds in surface waters of the henares-jarama-tajo river system (madrid, spain) and a potential risk characterization. Sci. Total Environ. 408, 543–551. https://doi.org/10.1016/j.scitotenv.2009.10.009

García-Galán, M.J., Díaz-Cruz, M.S., Barceló, D., 2011. Occurrence of sulfonamide residues along the Ebro river basin. Removal in wastewater treatment plants and environmental impact assessment. Environ. Int. 37, 462–473. https://doi.org/10.1016/j.envint.2010.11.011

Giebułtowicz, J., Nałecz-Jawecki, G., 2014. Occurrence of antidepressant residues in the sewage-impacted Vistula and Utrata rivers and in tap water in Warsaw (Poland). Ecotoxicol. Environ. Saf. 104, 103–109. https://doi.org/10.1016/j.ecoenv.2014.02.020

Gomes, A.I., Pires, J.C.M., Figueiredo, S.A., Boaventura, R.A.R., 2014. Optimization of River Water Quality Surveys by Multivariate Analysis of Physicochemical, Bacteriological and Ecotoxicological Data. Water Resour. Manag. 28, 1345–1361. https://doi.org/10.1007/s11269-014-0547-9

Gonzalez-Rey, M., Tapie, N., Le Menach, K., Dévier, M.H., Budzinski, H., Bebianno, M.J., 2015. Occurrence of pharmaceutical compounds and pesticides in aquatic systems. Mar. Pollut. Bull. 96, 384–400. https://doi.org/10.1016/j.marpolbul.2015.04.029

Grujić, S., Vasiljević, T., Laušević, M., 2009. Determination of multiple pharmaceutical classes in surface and ground waters by liquid chromatography-ion trap-tandem mass spectrometry. J. Chromatogr. A 1216, 4989–5000. https://doi.org/10.1016/j.chroma.2009.04.059

Hossain, A., Nakamichi, S., Habibullah-Al-Mamun, M., Tani, K., Masunaga, S., Matsuda, H., 2018. Occurrence and ecological risk of pharmaceuticals in river surface water of Bangladesh. Environ. Res. 165, 258–266. https://doi.org/10.1016/j.envres.2018.04.030

Hu, Y., Yan, X., Shen, Y., Di, M., Wang, J., 2018. Antibiotics in surface water and sediments from Hanjiang River, Central China: Occurrence, behavior and risk assessment. Ecotoxicol. Environ. Saf. 157, 150–158. https://doi.org/10.1016/j.ecoenv.2018.03.083

Jia, J., Guan, Y., Cheng, M., Chen, H., He, J., Wang, S., Wang, Z., 2018. Occurrence and distribution of antibiotics and antibiotic resistance genes in Ba River, China. Sci. Total Environ. 642, 1136–1144. https://doi.org/10.1016/j.scitotenv.2018.06.149

Jiang, L., Hu, X., Yin, D., Zhang, H., Yu, Z., 2011. Occurrence, distribution and seasonal variation of antibiotics in the Huangpu River, Shanghai, China. J. Comb. Math. Comb. Comput. 82, 822–828. https://doi.org/https://doi.org/10.1016/j.chemosphere.2010.11.028

Kim, J.-W., Jang, H.-S., Kim, J.-G., Ishibashi, H., Hirano, M., Nasu, K., Ichikawa, N., Takao, Y., Shinohara, R., Arizono, K., 2009. Occurrence of Pharmaceutical and Personal Care Products (PPCPs) in Surface Water from Mankyung River, South Korea. J. Heal. Sci. 55, 249–258. https://doi.org/10.1248/jhs.55.249

Li, N., Zhang, X., Wu, W., Zhao, X., 2014. Occurrence, seasonal variation and risk assessment of antibiotics in the reservoirs in North China. Chemosphere 111, 327–335. https://doi.org/10.1016/j.chemosphere.2014.03.129

Li, S., Shi, W., Li, H., Xu, N., Zhang, R., Chen, X., Sun, W., Wen, D., He, S., Pan, J., He, Z., Fan, Y., 2018. Antibiotics in water and sediments of rivers and coastal area of Zhuhai City, Pearl River estuary, south China. Sci. Total Environ. 636, 1009–1019. https://doi.org/10.1016/j.scitotenv.2018.04.358

Liang, X., Chen, B., Nie, X., Shi, Z., Huang, X., Li, X., 2013. The distribution and partitioning of common antibiotics in water and sediment of the Pearl River Estuary, South China. Chemosphere 92, 1410–1416. https://doi.org/10.1016/j.chemosphere.2013.03.044

Lin, H., Chen, L., Li, H., Luo, Z., Lu, J., Yang, Z., 2018. Pharmaceutically active compounds in the Xiangjiang River, China: Distribution pattern, source apportionment, and risk assessment. Sci. Total Environ. 636, 975–984. https://doi.org/10.1016/j.scitotenv.2018.04.267

Madureira, T.V., Barreiro, J.C., Rocha, M.J., Rocha, E., Cass, Q.B., Tiritan, M.E., 2010. Spatiotemporal distribution of pharmaceuticals in the Douro River estuary (Portugal). Sci. Total Environ. 408, 5513–5520. https://doi.org/10.1016/j.scitotenv.2010.07.069

Matongo, S., Birungi, G., Moodley, B., Ndungu, P., 2015. Pharmaceutical residues in water and sediment of Msunduzi River, KwaZulu-Natal, South Africa. Chemosphere 134, 133–140. https://doi.org/10.1007/s11356-015-4217-0

Mendes, R., Saldías, G.S., deCastro, M., Gómez-Gesteira, M., Vaz, N., Dias, J.M., 2017. Seasonal and interannual variability of the Douro turbid river plume, northwestern Iberian Peninsula. Remote Sens. Environ. 194, 401–411. https://doi.org/10.1016/j.rse.2017.04.001

Meyer, B., Pailler, J.Y., Guignard, C., Hoffmann, L., Krein, A., 2011. Concentrations of dissolved herbicides and pharmaceuticals in a small river in Luxembourg. Environ. Monit. Assess. 180, 127–146. https://doi.org/10.1007/s10661-010-1777-9

Paíga, P., Santos, L.H.M.L.M., Delerue-Matos, C., 2017. Development of a multi-residue method for the determination of human and veterinary pharmaceuticals and some of their metabolites in aqueous environmental matrices by SPE-UHPLC–MS/MS. J. Pharm. Biomed. Anal. 135, 75–86. https://doi.org/10.1016/j.jpba.2016.12.013

Paíga, P., Santos, L.H.M.L.M., Ramos, S., Jorge, S., Silva, J.G., Delerue-Matos, C., 2016. Presence of pharmaceuticals in the Lis river (Portugal): Sources, fate and seasonal variation. Sci. Total Environ. 573, 164–177. https://doi.org/10.1016/j.scitotenv.2016.08.089

Pereira, A.M.P.T., Silva, L.J.G., Laranjeiro, C.S.M., Meisel, L.M., Lino, C.M., Pena, A., 2017. Human pharmaceuticals in Portuguese rivers: The impact of water scarcity in the environmental risk. Sci. Total Environ. 609, 1182–1191. https://doi.org/10.1016/j.scitotenv.2017.07.200

Ribeiro, C., Couto, C., Ribeiro, A.R., Maia, A.S., Santos, M., Tiritan, M.E., Pinto, E., Almeida, A.A., 2018. Distribution and environmental assessment of trace elements contamination of water, sediments and flora from Douro River estuary, Portugal. Sci. Total Environ. 639, 1381–1393. https://doi.org/10.1016/j.scitotenv.2018.05.234

Rocha, M.J., Ribeiro, M., Ribeiro, C., Couto, C., Cruzeiro, C., Rocha, E., 2012. Endocrine disruptors in the Leça River and nearby Porto Coast (NW Portugal): Presence of estrogenic compounds and hypoxic conditions. Toxicol. Environ. Chem. 94, 262–274. https://doi.org/10.1080/02772248.2011.644291

Santos, L.H.M.L.M., Ramalhosa, M.J., Ferreira, M., Delerue-Matos, C., 2016. Development of a modified acetonitrile-based extraction procedure followed by ultra-high performance liquid chromatography-tandem mass spectrometry for the analysis of psychiatric drugs in sediments. J. Chromatogr. A 1437, 37–48. https://doi.org/10.1016/j.chroma.2016.01.079

Tamtam, F., Mercier, F., Le Bot, B., Eurin, J., Tuc Dinh, Q., Clément, M., Chevreuil, M., 2008. Occurrence and fate of antibiotics in the Seine River in various hydrological conditions. Sci. Total Environ. 393, 84–95. https://doi.org/10.1016/j.scitotenv.2007.12.009

Ternes, T.A., 1998. Occurrence of drugs in German sewage treatment plants and rivers. Water Res. 32, 3245–3260. https://doi.org/10.1016/S0043-1354(98)00099-2

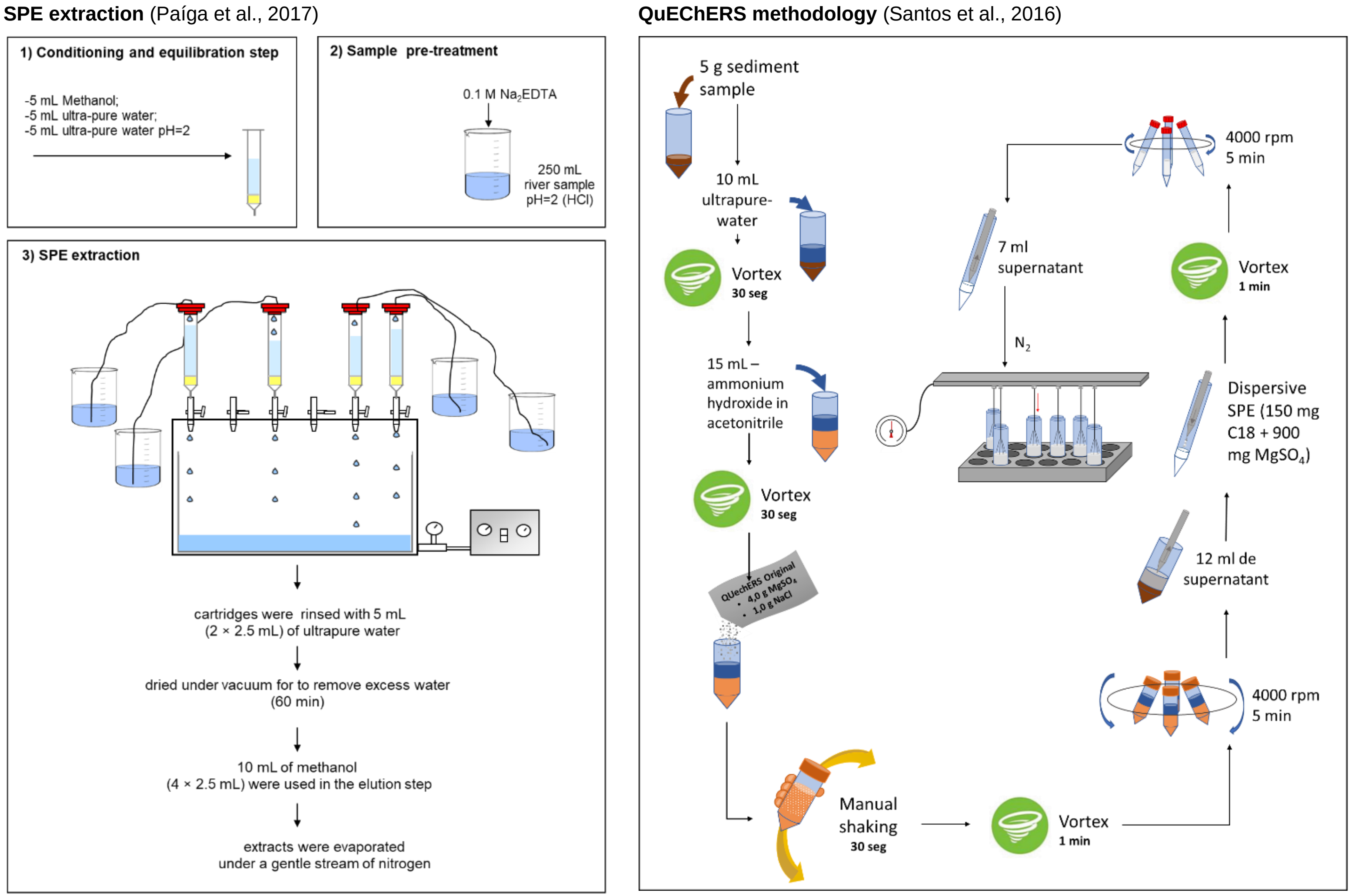
Tewari, S., Jindal, R., Kho, Y.L., Eo, S., Choi, K., 2013. Major pharmaceutical residues in wastewater treatment plants and receiving waters in Bangkok, Thailand, and associated ecological risks. Chemosphere 91, 697–704. https://doi.org/10.1016/j.chemosphere.2012.12.042

Wu, M., Xiang, J., Que, C., Chen, F., Xu, G., 2015. Occurrence and fate of psychiatric pharmaceuticals in the urban water system of Shanghai, China. Chemosphere 138, 486–493. https://doi.org/10.1016/j.chemosphere.2015.07.002

Zhang, R., Zhang, G., Zheng, Q., Tang, J., Chen, Y., Xu, W., Zou, Y., Chen, X., 2012. Occurrence and risks of antibiotics in the Laizhou Bay, China: Impacts of river discharge. Ecotoxicol. Environ. Saf. 80, 208–215. https://doi.org/10.1016/j.ecoenv.2012.03.002

Zhao, J.L., Ying, G.G., Liu, Y.S., Chen, F., Yang, J.F., Wang, L., Yang, X.B., Stauber, J.L., Warne, M.S.J., 2010. Occurrence and a screening-level risk assessment of human pharmaceuticals in the pearl river system, South China. Environ. Toxicol. Chem. 29, 1377–1384. https://doi.org/10.1002/etc.161

Zhou, L.J., Ying, G.G., Zhao, J.L., Yang, J.F., Wang, L., Yang, B., Liu, S., 2011. Trends in the occurrence of human and veterinary antibiotics in the sediments of the Yellow River, Hai River and Liao River in northern China. Environ. Pollut. 159, 1877–1885. https://doi.org/10.1016/j.envpol.2011.03.034

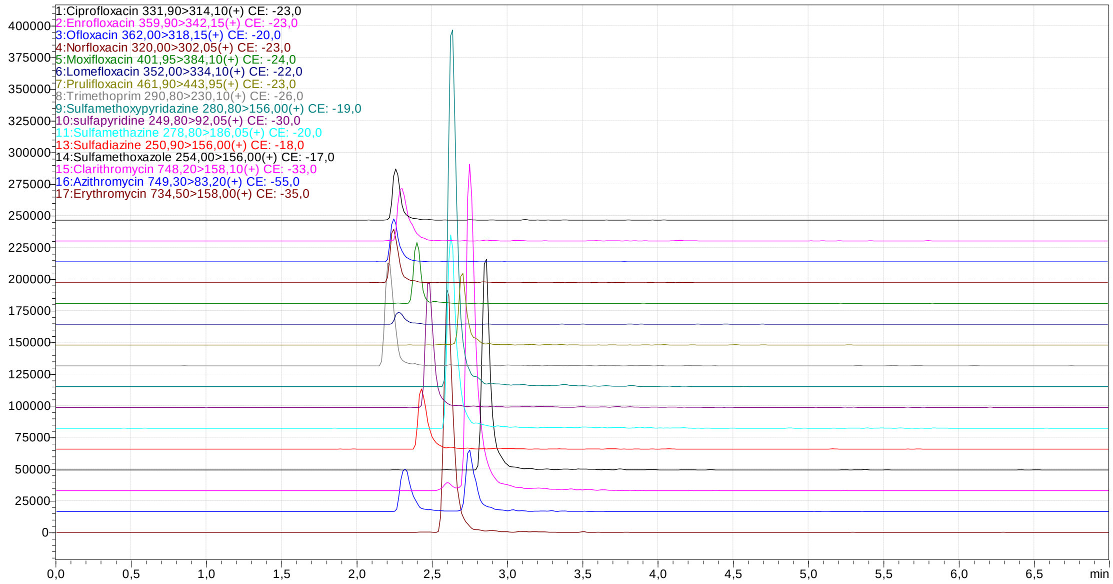


SPE extraction (Paíga et al., 2017)

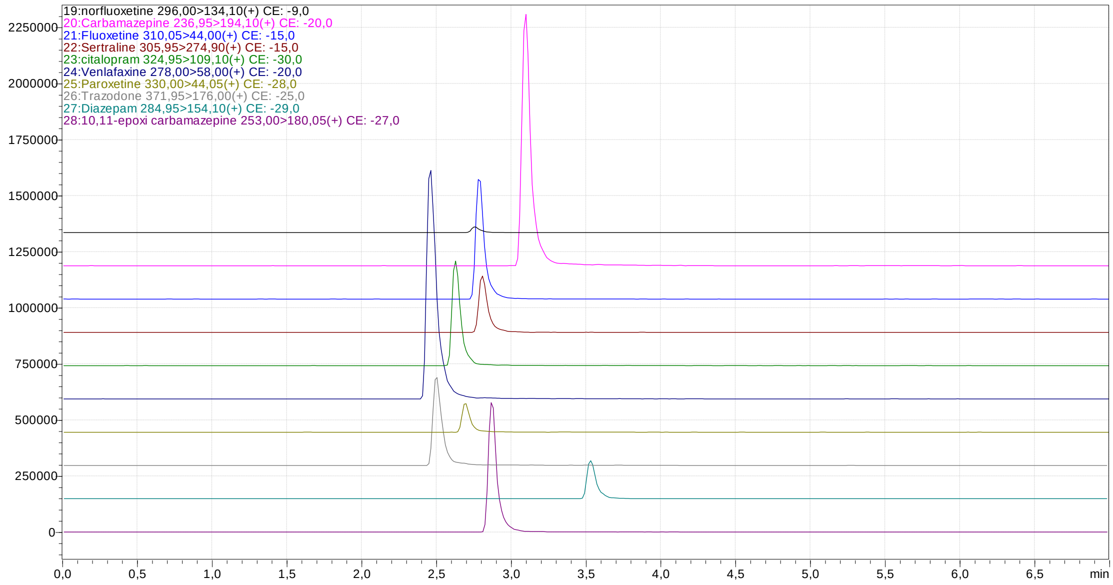
QuEChERS methodology (Santos et al., 2016)

Figure SM1. Schematic SPE and QuEChERS methodologies for the extraction of the pharmaceuticals under study in river water and sediment samples.

a) Antibiotics



b) Psychiatric drugs



Note: The overlap of the twenty-seven pharmaceuticals would be barely perceptible in the chromatogram, so the pharmaceuticals were divided into two chromatograms separating them by the therapeutic class.

Figure SM2. Overlay chromatogram for a) antibiotics and b) psychiatric drugs in a standard mixture with a concentration of 500 µg/L in each pharmaceutical.

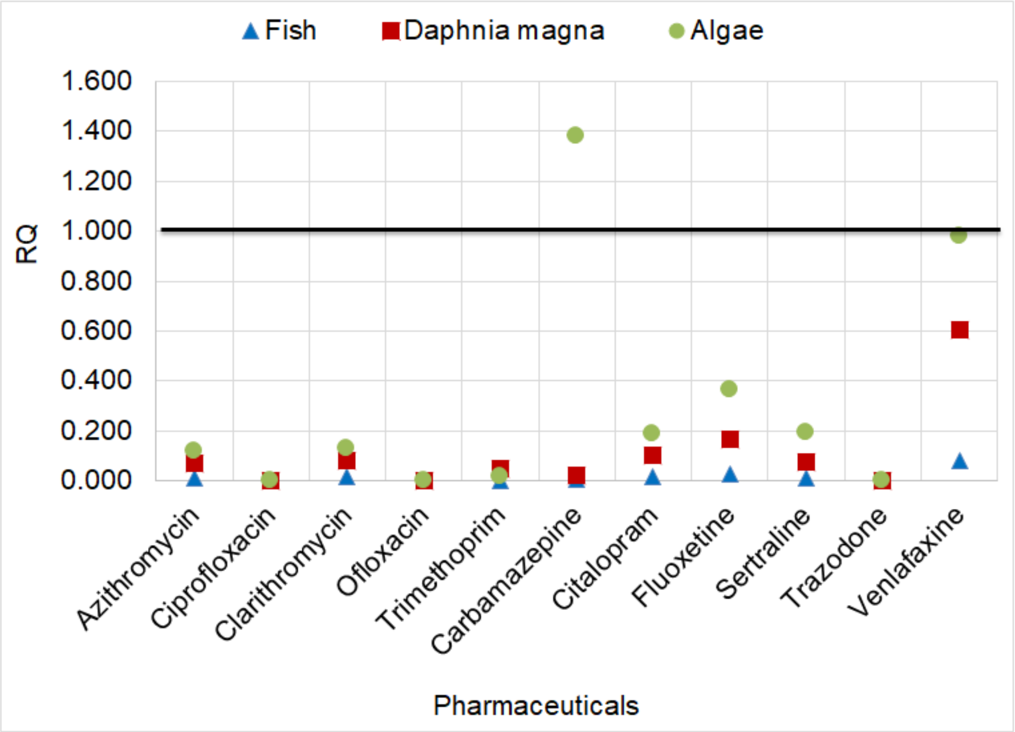


Figure SM3. The risk quotients (RQ) for different trophic levels (algae, Daphnia magna, and fish) of antibiotics and psychiatric drugs in the surface waters. Bold line marks risk quotient equal to one.

CHAPTER 4 GLYPHOSATE, AMPA AND GLUFOSINATE OCCURRENCE IN WATERS AND SEDIMENTS – WORLD ASSESSMENT

As previously mentioned in Chapter 2, glyphosate has been the subject of legal controversy in recent years concerning its safety and potential link to cancer (Novotny, 2022). In 2015, the International Agency for Research on Cancer (IARC), of the World Health Organization (WHO), classified glyphosate as "probably carcinogenic to humans" based on studies that showed an association between glyphosate exposure and an increased risk of non-Hodgkin's lymphoma. This classification led to a series of lawsuits against the manufacturers of glyphosate-based herbicides, most notably Monsanto (now owned by Bayer). However, the US Environmental Protection Agency (EPA) and other regulatory agencies have generally affirmed that glyphosate is safe when used according to label instructions and have not restricted its use. Despite the possibility of posing a risk to the environment and to human and animals health, the European Commission (EC) recently renewed the use of glyphosate-based herbicides until December 15 of, 2023, approving a one-year extension on the previous five-year authorization (European Commission, 2017).

On the other hand, the use of glufosinate is already banned in Europe since 2020 (European Commission, 2020a, 2022a). Considering the alleged reprotoxicity, among other tested risks to human health related to the exposure to glufosinate, in 2017, the French Health and Environment Regulator (ANSES) had already withdrawn the selling authorization for this product in the French market, that included all the plant protection products containing glufosinate (ANSES, 2017).

After their application to the soil/plant, they tend to degrade rapidly into their degradation products. Glyphosate is degraded, mostly by microbial action, taking the form of sarcosine acid and aminomethylphosphonic acid (AMPA), the last being its main metabolite and highly persistent in the environment (Stephen O. Duke, 2020).

The first published study on glyphosate monitoring in groundwater dates back to 1996 (Smith *et al*., 1996) and in surface water to 1998 (Skark *et al*., 1998), this last reporting also AMPA's contamination. Since then, concern about contamination by these compounds has been growing over the years, coupled with an increase of environmental sampling studies.

To assess and evaluate glyphosate, AMPA, and glufosinate world's environmental contamination, the published studies between January 1, 2018, and March 30, 2023, including glyphosate, AMPA, and glufosinate monitoring in water (surface and groundwater) and sediments were analyzed. An extensive search on academic databases, such as Scopus, Web of Science, Science Direct, PubMed, Research Gate, and Google Scholar, was conducted using the combination of the following keywords: “glyphosate”, “glufosinate”, “aminomethylphosphonic acid”, or “AMPA” with “river”, "water resource", “riverside”, "hydrographic basin", “watercourse”, “freshwater”, “river basin”, “stream”, “tributary”, “lake”, “pond”, “groundwater”, “surface water”, “creeks”, “wetland”. After removing duplicates, the publications screening was performed by examining the entire content of the articles and gathering the relevant information (e.g., concentrations, analytical methods, number of samples, detection frequency) of the three compounds under study. Articles presenting model-based predictions of contaminations without information on the measured occurrences of compounds were excluded.

Ninety-four publications were selected through more than 1 000 analyzed articles; the information contained therein is reviewed below.

4.1 Limits and threshold for Glyphosate, AMPA, and Glufosinate in water

In order to analyze the concentrations of glyphosate, AMPA, and glufosinate found in waters and sediments around the world, a summary of the relevant legislation is of utmost importance. The applicable legislation to contaminations associated to these pollutants differs widely from country to country. Additionally, the same country may have different limit values depending on the type of water (drinking water, surface water, or groundwater). The restrictions can be targeted to individual and specified compounds, any pesticide individually, or even the sum of all pesticides found.

The Figure 4.1 shows the maximum glyphosate concentration values allowed in water intended for human consumption established for some countries by current legislation.

In Europe, the Council Directive 98/83/EC on the quality of water intended for human consumption provides a limit of 0.1 μg L^{-1} (maximum individual value) to groundwater contamination by “*pesticides and their relevant metabolites, degradation and reaction products”* and of 0.5 μg L^{-1} to the sum of all individual pesticides. Additionally, the directive states that “only those pesticides which are likely to be present in a given supply need be monitored“, leaving it unclear which compounds need to be monitored (European Commission, 1998). The European Union (EU) countries apply this directive and its amendments. Additionally, some EU countries have adapted their legislation based on European directives, as is the case of France, where in addition to the 0.1 μg L^{-1} defined for groundwater, it also defines environmental quality standards (EQS) to be taken into account in the assessment of the ecological status of continental surface waters (not intended for drinking water production) of 28 μg L^{-1} for glyphosate and 452 μg L^{-1} for AMPA. Also, propose a maximum acceptable value of 70 μg L^{-1} for glyphosate and 45200 μg L^{-1} for AMPA. For marine water establish an environmental guide value of 5.6 μg L^{-1} and 45 μg L^{-1} for glyphosate and AMPA, respectively with a maximum acceptable concentration value of 14 μg L^{-1} and 4520 μg L^{-1}, respectively (Ministre de l'écologie du développement durable et de l'énergie, 2015; Portail Substaces Chimiques, 2020).

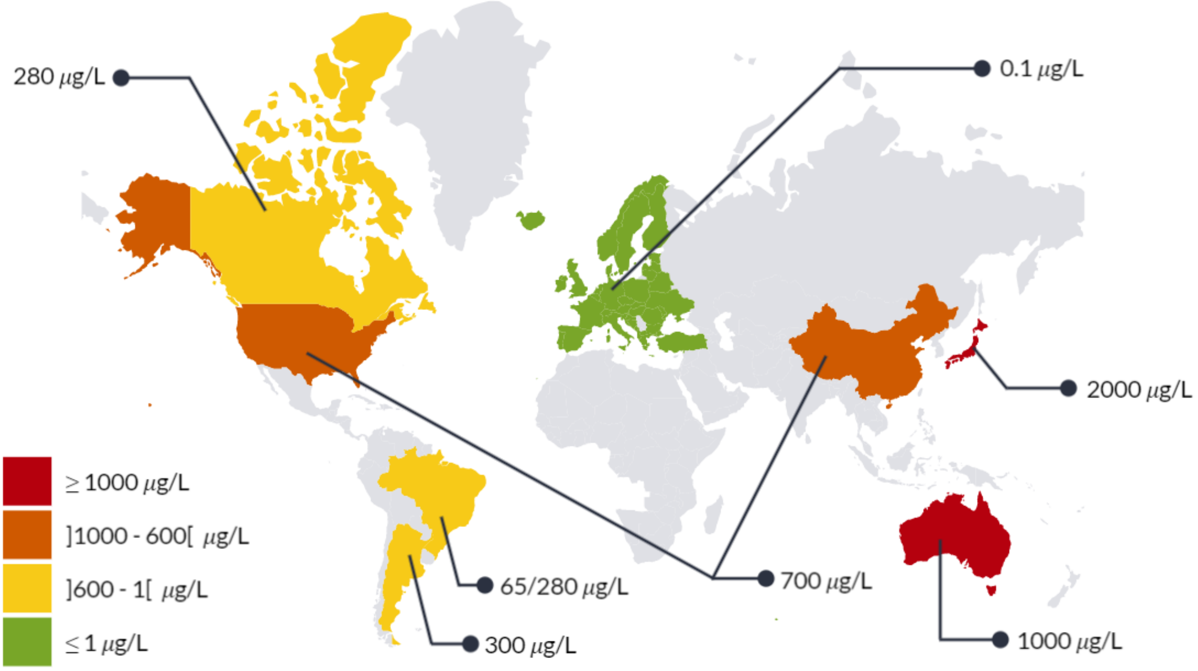


Figure 4.1 - Legal limits for glyphosate residues in water intended for human consumption (developed by the author).

In the USA, Environmental Protection Agency (EPA) national primary drinking water regulations also considered glyphosate in the list of organic contaminants in drinking water with a maximum contamination level of 700 μg L^{-1} (EPA, 2009).

Canada guidelines fixed the maximum acceptable concentration of glyphosate in drinking water of 280 μg L^{-1} (Health Canada, 2022). Argentina established similar drinking water quality guideline levels for glyphosate, namely 300 μg L^{-1} and a quality guide level for aquatic biota protection of 240 μg L^{-1}, both expressed as glyphosate isopropylamine (Subsecretaria de Recursos Hídricos de la Nación, 2003).

Regarding Australian regulation, recommended maximum level for glyphosate presence in water is 1000 μg/L. In this case, the legislated values are not generalized to all pesticides but are individualized considering their characteristics and potential presence in the environment (NHMRC & NRMMC, 2011).

In China, water bodies are divided into five classes according to the utilization purposes and protection objectives: class I refers to spring water and national nature reserves; class II and III are the first and second classes of protected areas for centralized sources of drinking water, for aquatic species and swimming areas; class IV refers to water areas for industrial and non-direct exposure recreation uses; and class V is mainly applicable to the water bodies for agricultural use and landscape (Asian Development Bank, 2016). Also, groundwater is similarly classified in the Standard for groundwater quality (General Administration of Quality Supervision, 2017). Environmental Quality Standards for Surface Water apply to the different classes of surface water. GB 5749-2006, the standards for drinking Water Quality concerning drinking water sources (class II and III), presents a limit especially to glyphosate, of 700 μg L^{-1} (Ministry of Health of China, 2006).

Japan legislation exhibits one of the highest limit values for glyphosate concentration in water, of 2 000 μg L^{-1}. This legal framework is the particularity that the indicated limit refers to the sum of glyphosate and AMPA's concentration. Additionally, in 2014 a review of the legislation included the addition of a maximum concentration value for glufosinate contamination of 20 μg L^{-1} (Ministry of Health Labor and Welfare of Japan, 2003).

In Brazil, there are two distinct limits for the contamination of water intended for human consumption. The first is presented in the applicable legislation for surface waters which, similarly to China, presents a five-class categorization taking into account the surface water destination: special class, water intended for drinking water supply, with disinfection as well as the preservation of the natural balance of aquatic communities and environments; class 1, intended for drinking water supply, after simplified treatment, as well as the protection of aquatic communities, recreational activities of primary contact (e.g. swimming, diving) and irrigation of raw and direct consumption vegetables; class 2, destined for the drinking water supply, after conventional treatment as well as the protection of aquatic communities, recreational activities of primary contact and the irrigation of vegetables, fruit plants among others with which the public may have direct contact; class 3, destined for the drinking water supply, after conventional or advanced treatment, irrigation and recreational activities of secondary contact; and class 4, destined for navigation; and for landscape harmony. For classes 1 and 2, the limit value for glyphosate concentration is 65 μg L^{-1}, and for class 3, 280 μg L^{-1} (CONAMA, 2005). For water intended for human consumption supplied from an alternative water supply system or solution, it is established a different limit of 500 μg L^{-1} not only for glyphosate concentration in water but for the sum of glyphosate and AMPA's concentration (Ministério da Saúde, 2017).

Given the evident differences found in the maximum limits for glyphosate and AMPA in water intended for human consumption and, in some cases, the absence of any one or all three in their legal documents associated with water quality, several authors refer to the importance and urgency of revise the current legal limits of glyphosate, AMPA and glufosinate in surface and groundwaters for human and aquatic biota protection (Campanale *et al*., 2021; D. M. de Oliveira *et al*., 2023; Z. Li, 2018; Z. Li & Fantke, 2022).

4.2 Pre-treatment, extraction, and analysis

Accurate measurement of glyphosate, AMPA, and glufosinate concentrations in environmental samples is essential for quantitative exposure assessments. However, the unique chemical properties of these compounds, such as high-water solubility, low solubility in organic solvents and volatilization, absence of chromophores or fluorophores, ionic character and their preference for forming complexes turns extraction and quantification into a challenging process (EFSA, 2005, 2015; Valle *et al*., 2019).

Reviewing the analytical methods applied in the environmental monitoring of waters and sediments contamination by glyphosate, AMPA, and glufosinate published between January 2018 and March 2023 worldwide, it can be seen that the most applied detection methods can be divided into three main categories: high-performance, ultra-performance or Ultra-High-Performance liquid chromatography (HPLC, UPLC or UHPLC) (Alonso *et al*., 2022; Lajmanovich *et al*., 2023; López-Vázquez *et al*., 2023; Raby *et al*., 2022; Rodríguez-Bolaña *et al*., 2023; Suciu *et al*., 2023; Natalia Veronica Van Opstal *et al*., 2023), gas-chromatography (GC) (Donald *et al*., 2018; Rezaei Kalantary *et al*., 2022; Tongo *et al*., 2022), and enzyme-linked immunosorbent assay (ELISA) (Horn *et al*., 2019; Melendez-Pastor *et al*., 2021; Reynoso *et al*., 2020; Welch *et al*., 2019). Figure 4.2 resumes all analytical methods used in the studies and shows that high-performance (HPLC – 38%) and ultra-performance or Ultra-High-Performance (UHPLC/UPLC-36%) liquid chromatography were the most applied methodologies, followed by LC (7%), ELISA (4%) and gas chromatography (GC-3%).

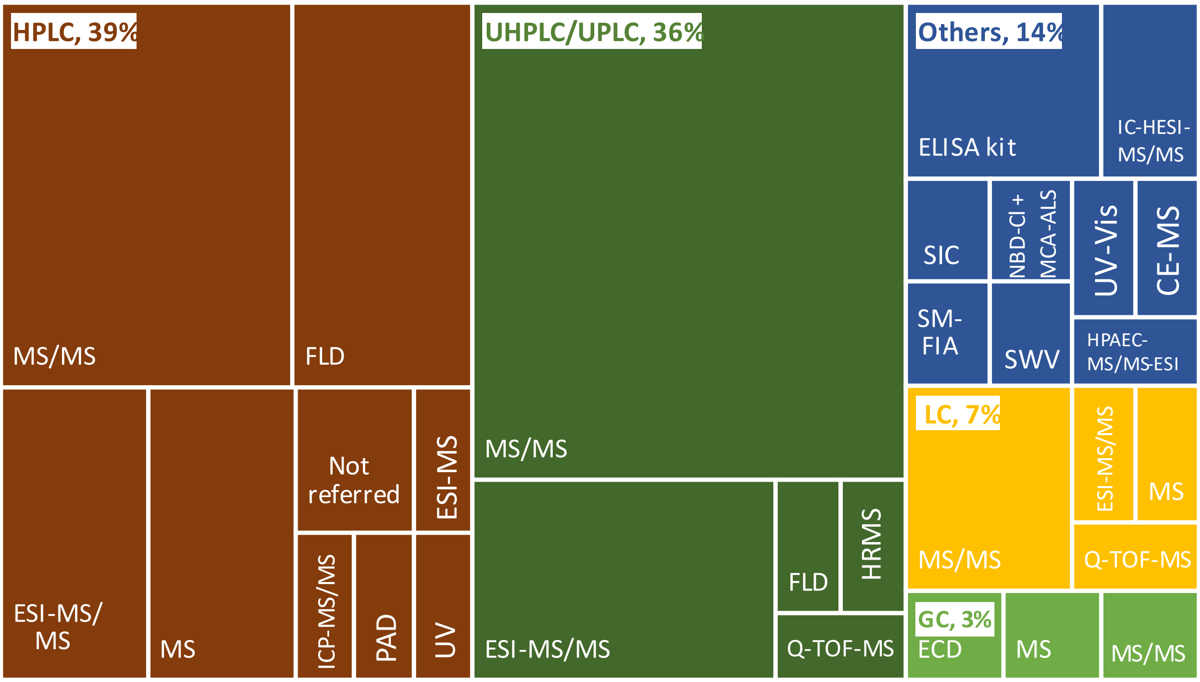


Figure 4.2 - Analytical technics applied in the studied publications (2018-2023) (developed by the author).

Some studies have shown that ELISA is an accurate and cost-effective method for measuring glyphosate in surface water, with a minimum detection limit of 0.05 µg/L (Melendez-Pastor *et al.*, 2021; Reynoso *et al.*, 2020; Welch *et al.*, 2019). However, the use of ELISAs to measure environmental levels of glyphosate has not yet been fully validated. Combining immunoassays with chromatography and HPLC for confirmation offers a cost-effective way to increase spatial and temporal sampling. As more evidence emerges regarding the accuracy and precision of glyphosate ELISAs, their use is expected to increase *(Reynoso et al.*, 2020).

Although the results obtained using ELISA to glyphosate analysis presented negligible bias relative to an analysis by LC-MS/MS, the AMPA and glufosinate are not measured by this method (Mahler *et al.*, 2017).

In the water matrix, the higher values presented as LOD were 490 μg/L (Lima *et al.*, 2022), followed by 43 μg/L (A. L. Pérez *et al.*, 2019), 28 μg/L (Álvarez Bayona *et al.*, 2022), and 5.1 μg/L (Oliveira Pereira *et al.*, 2019). Only the first one is above the limit value stipulated for the country where the study was conducted (Brazil: maximum of 65/280 μg/L (CONAMA, 2005)). On the other hand, the lowest LOD values used were 0.00003 μg/L (Tongo *et al.*, 2022) and 0.0007 μg/L (Vu *et al.*, 2021), obtained by GC-ECD and UPLC-MS/MS, respectively. As shown in Figure 4.3, only 40% of the studies present LOD values <0.1 μg/L, the maximum permissible value for individual pesticide water contaminations in the European Union (European

Commission, 1998). Regarding quantification, the minimum quantified values (LOQ) were 0.0024 μg/L (Vu *et al*., 2021), 0.0025 μg/L (Campanale *et al*., 2022; Pires *et al*., 2023) and 0.005 μg/L (Huntscha *et al*., 2018; Suciu *et al*., 2023), by UPLC-MS/MS, LC-MS/MS, and UHPLC-ESI-MS/MS and HPLC-MS/MS. About 25% of the studies reviewed had only one of the limit values (LOD or LOQ).

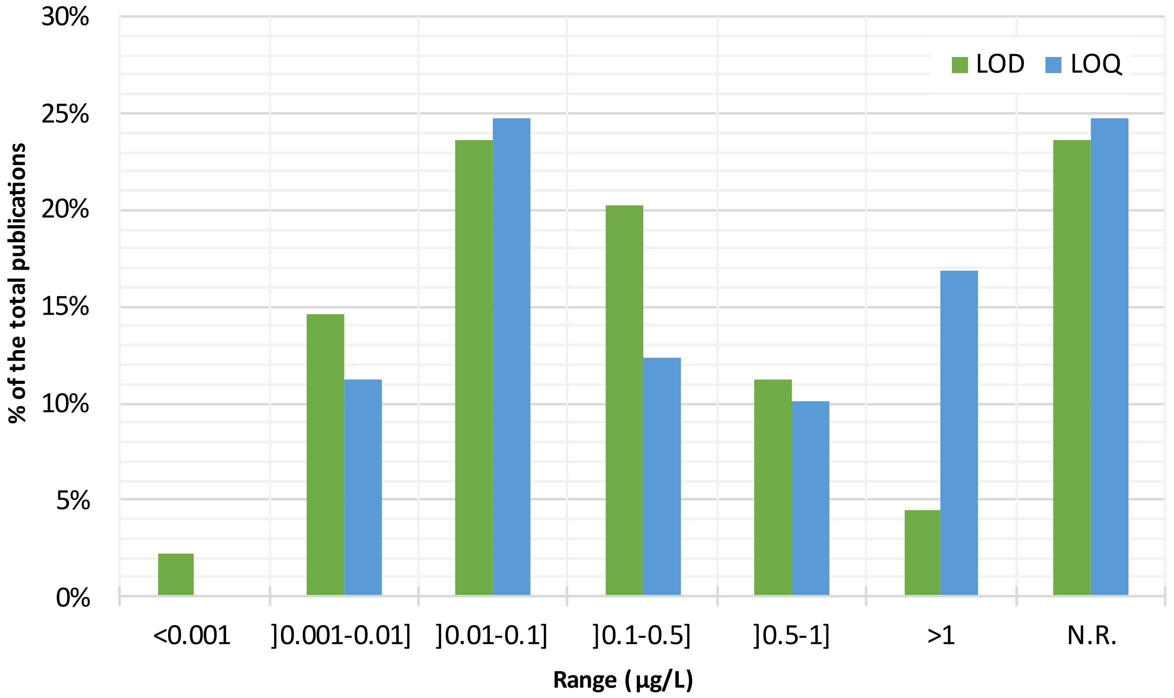


Figure 4.3 - Percentage of publications within each of the six ranges of LOD and LOQ values, referring to water matrix analysis (developed by the author).

Referring to sediments, the maximum LOD values presented were 10 μg/kg (Wimmer *et al*., 2022), 5 μg/kg (B. Yan *et al*., 2022), and 3 μg/kg (Bonansea *et al*., 2018). Concerning the lowest LOD values used, 0.00021 μg/kg (Rahman *et al*., 2019), 0.007 μg/kg (Tongo *et al*., 2022), and 0.01 μg/kg (Gunarathna *et al*., 2018; Materu *et al*., 2021) were reported, quantified by HPLC-UV, GC-ECD, and HPLC-MS. The lower LOQ for sediments analysis was 0.1 μg/kg (Gunarathna *et al*., 2018; Mac Loughlin *et al*., 2022a) and de maximum was 30 μg/kg (Wimmer *et al*., 2022).

Concerning the sample pre-treatment, among the studies reviewed, 48% performed derivatization, of which 83% used the agent FMOC-Cl (at different concentrations) and 56% used borate buffer. Other derivatization reagents used were ninhydrin and sodium molybdate (Álvarez Bayona *et al*., 2022) and 2-mercaptoethanol (OPA-MCE) (Oliveira Pereira *et al*., 2019). As an advantage of this method over the one employing FMOC-Cl, this last author mentions that the reaction is faster and may be assembled online with the separation methodology.

Furthermore, the excess of reagent doesn't need to be separated prior to the chromatographic analysis (Oliveira Pereira *et al*., 2019). Different derivatization reaction periods were used, ranging from 10 min (Pinto *et al*., 2018) to 24h (Montiel-León *et al*., 2019; Okada *et al*., 2018; D. J. Pérez *et al*., 2021; Rahman *et al*., 2019), with "overnight period" being the most applied. In some cases, the control of the reaction temperature was also mentioned (Campanale *et al*., 2022; Montiel-León *et al*., 2019). 11% of the studies referred that derivatization was not performed/required, or that direct analysis was operated.

Regarding the extraction methods, used in 34% of the studies, in 84%, SPE was applied as the extraction technique (of which 15% used SPE-online). Other extraction methods mentioned were droplet/dispersive liquid-liquid microextraction (Pinto *et al*., 2018; Rezaei Kalantary *et al*., 2022), the addition of dichloromethane (Álvarez Bayona *et al*., 2022; Castro Berman *et al*., 2018; Mac Loughlin *et al*., 2022b), lyophilization (De María *et al*., 2021; Pires *et al*., 2020), and trisodium phosphate (Na_3PO_4) (Wimmer *et al*., 2022) and tripotassium phosphate (K_3PO_4) (D. J. Pérez *et al*., 2021) addition. In 10% of the publications, no derivatization and/or extraction method was mentioned.

4.3 Environmental monitoring

Among the 94 studies reviewed, all analyzed the presence of glyphosate in the environment. 66 publications also reported on AMPA and 19 also looked for glufosinate.

Surface water was the most monitored matrix during the studied period, representing 91% of all the analyzed samples, followed by groundwater samples (7%) and sediments (1%) (Figure 4.4).

Of all the samples analyzed, in 54% and 43% glyphosate and AMPA, respectively, were investigated and only in 3% glufosinate was searched.

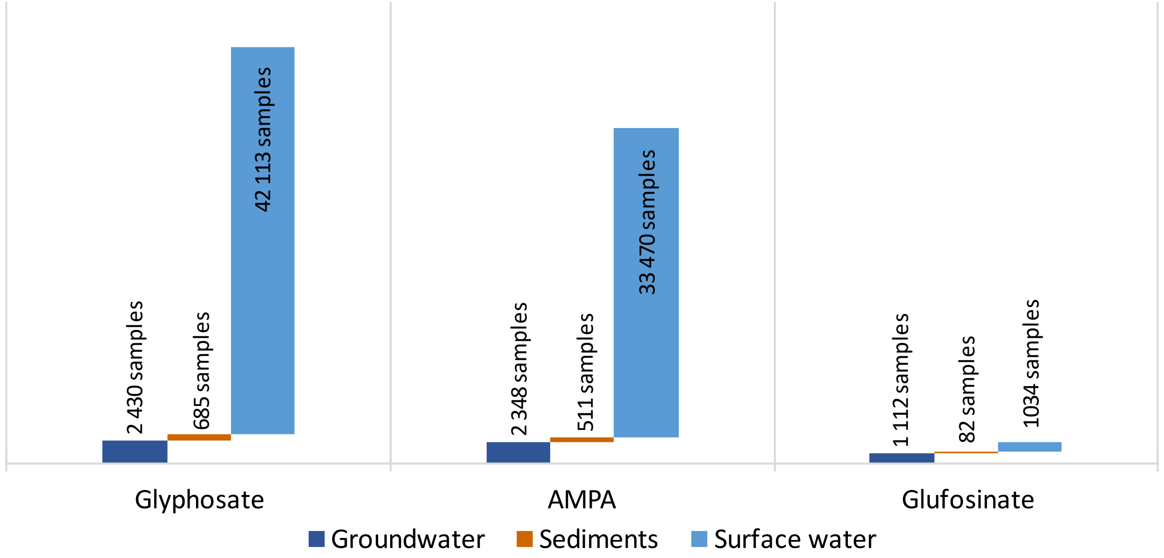


Figure 4.4 - Number of samples analyzed by type and compound (developed by the author).

Referring to the publications and samples in which glyphosate was assessed (Figure 4.5), France exhibits the higher samples/publication ratio, substantially influenced by one study that use an extensive dataset of measurements from the French Office for Biodiversity, with more than 24 000 samples (Carles *et al.*, 2019), followed by Japan (2 346 samples/publication) and Italy (average of 1 127 samples/publication). Argentina was the country with the higher frequency of studies publication, but a minor 64 samples/publication ratio.

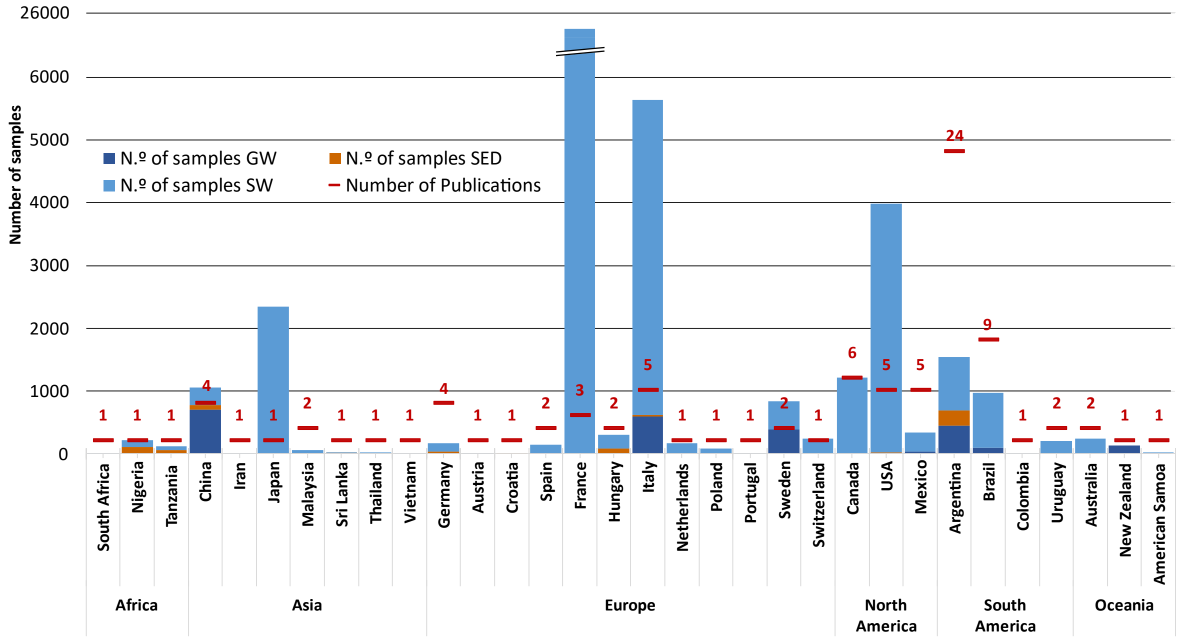


Figure 4.5 - Groundwater (GW), surface water (SW), and sediment (SED) samples analyzed for glyphosate contamination by continent and country and the number of publications that include glyphosate monitoring in the study period (developed by the author).

The continent with the largest number of samples analyzed for glyphosate is Europe, with 32692 samples analyzed, and the American continent, with 5 538 samples analyzed in North America and 2 722 in South America (Figure 4.5). Referring to the total samples tested by country, France (25 099 samples) and Italy stand out, followed by the USA and Japan.

The European countries with higher number of samples analyzed concerning glyphosate are consistent with the glyphosate rate of application. France has been the country in Europe with the highest use of glyphosate (about 20% of total sales in Europe in the year 2017 (C. Antier *et al.*, 2020)), leading to increased concern about its potential presence in the environment. The same can be pointed out for Italy as it accounted for 8% of total glyphosate sales in Europe in the same year (C. Antier *et al.*, 2020).

Regarding the analysis of AMPA, Europe continues to be the continent with the largest number of samples analyzed (27 884) followed by America, with 4524 samples in North America and 2 334 samples in South America (Figure 4.6).

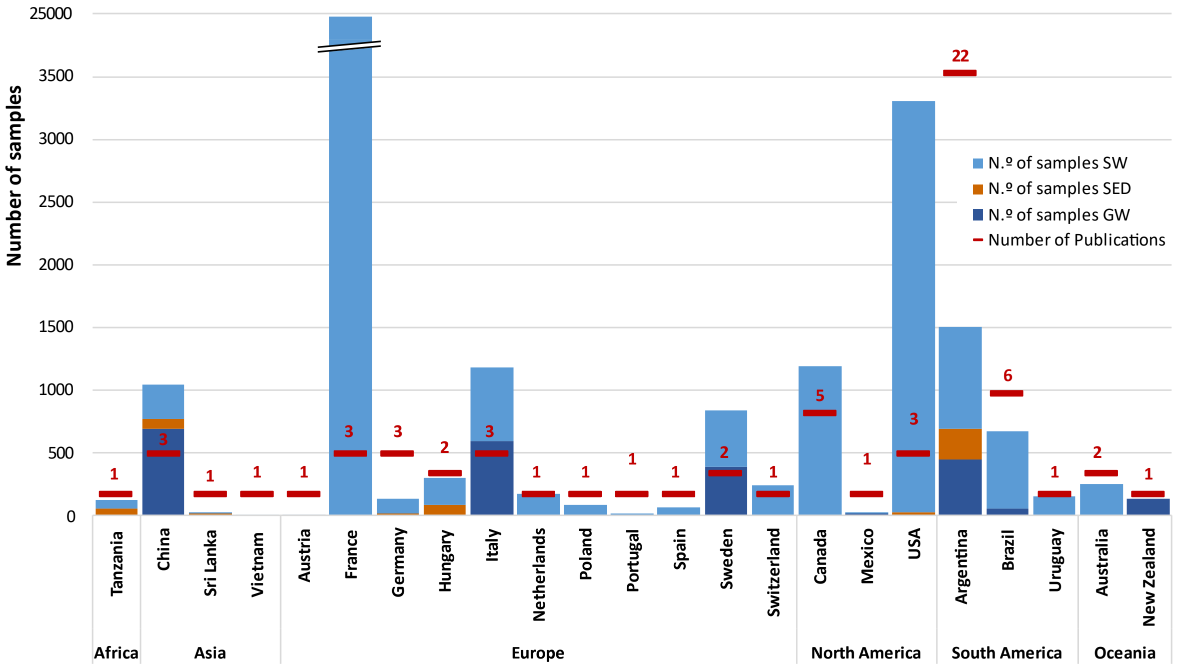


Figure 4.6 - Groundwater (GW), surface water (SW), and sediment (SED) samples analyzed for AMPA contamination by continent and country, and number of publications that include AMPA monitoring in the study period (developed by the author).

For AMPA assessment, France presented, once again, the higher samples/publication ratio, influenced by the same study (Carles *et al.*, 2019), followed by USA, with a ratio of 1 101 samples/publication, Sweden (422 samples/publication) and Italy (394 samples/publication).

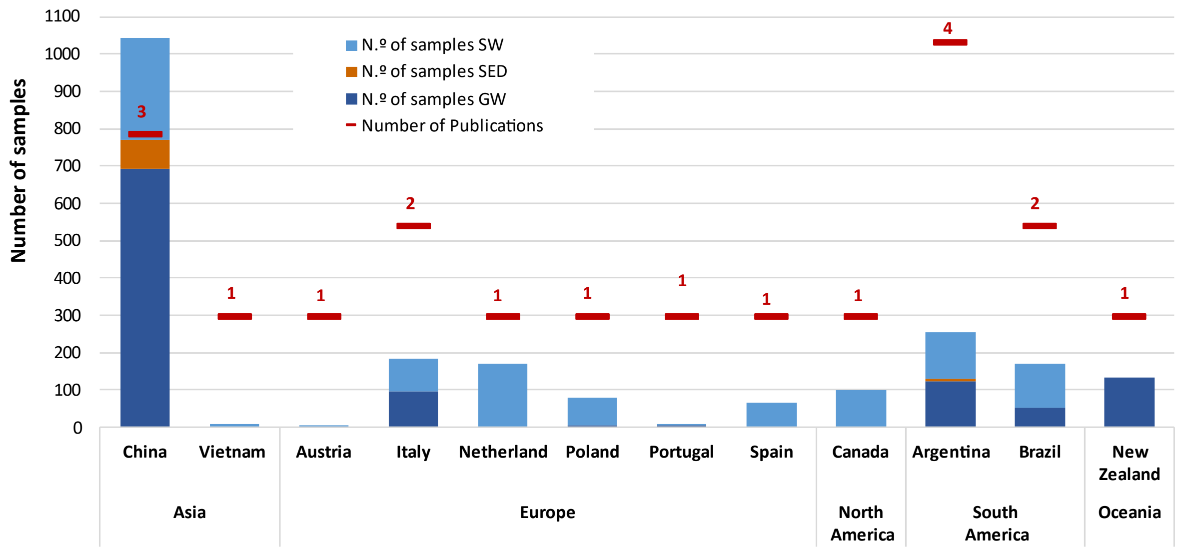


Figure 4.7 - Groundwater (GW), surface water (SW), and sediment (SED) samples analyzed for glufosinate contamination by continent and country, and number of publications that include glufosinate monitoring in the study period (developed by the author).

China was the country that stood out when it comes to monitoring glufosinate in environmental samples, followed by Argentina by far (Figure 4.7). In Europe, and even though the use of glufosinate is banned since 2020 (European Commission, 2020a, 2022a), a total of 512 samples were analyzed, conveying a correct approach to ensure vigilance regarding the possible persistence of this compound.

Within the analyzed period, 2022 was the year with more published studies regarding glyphosate monitoring in surface water, ground water and sediments (22%) followed by 2021 (21%) and 2020 (20%) (Figure 4.8).

The year 2021, although it was not the year with the highest number of publications, was the one in which, along with 2022, a greater number of different countries have published (13 countries/year). Argentina stood out greatly from the rest of the countries regarding the number of publications, totaling 24 publications in the five years and 3 months analyzed, representing, on average, one publication every 3 months. Next was Brazil, with 9 publications in the same period, with an average of one publication every 7 months and Canada, with 6 publications, and an average of one publication every 11 months.

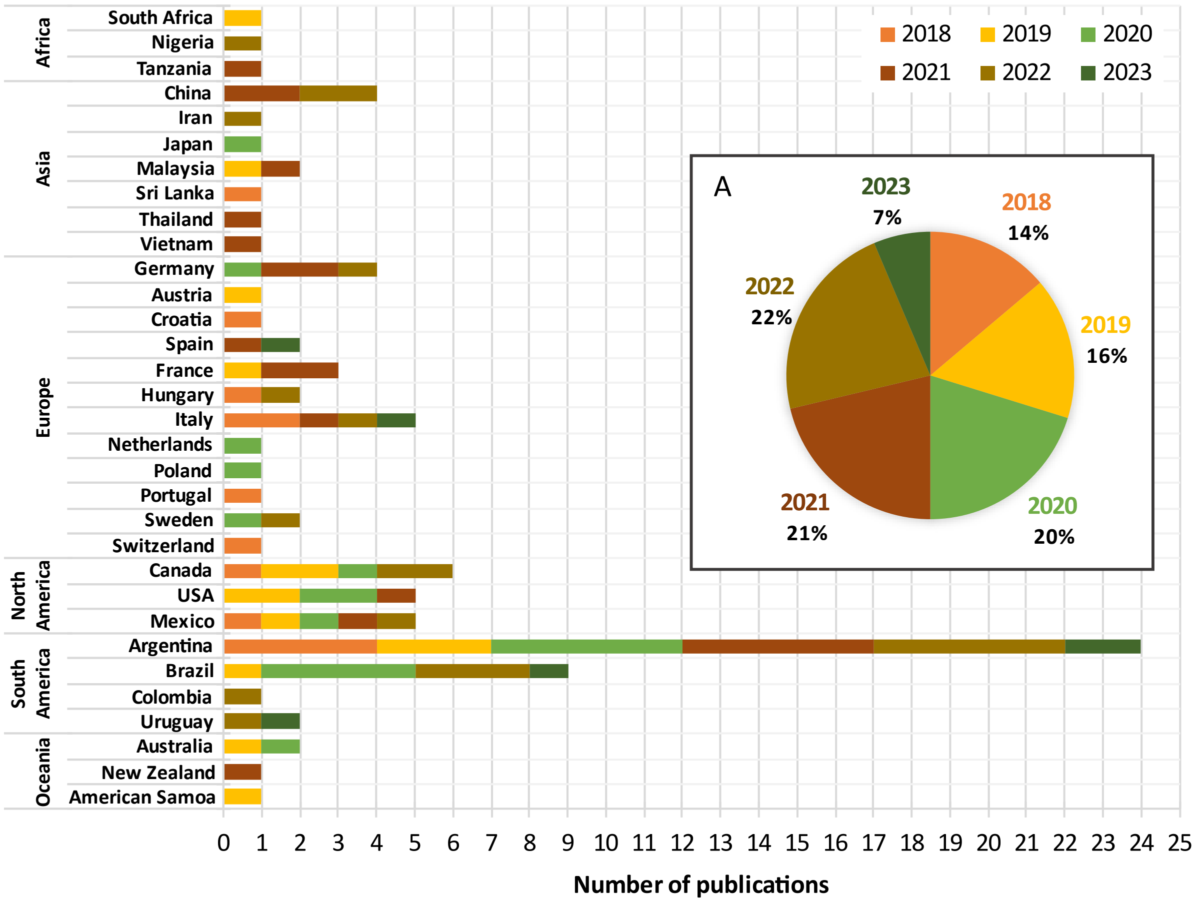


Figure 4.8 - Number of publications by country between 2018 and 2023. A) Percentage of the total publications by year (developed by the author).

4.4 Glyphosate, AMPA and glufosinate in water and sediments

The rate and level of glyphosate, AMPA, and glufosinate contamination of water and sediment reported in the articles published from January 1, 2018 to March 31, 2023 were analyzed. Regarding the percentage of contaminated samples (concentration >LOD), in Figure 4.9 it can be seen that surface water samples show a higher frequency of contamination by compounds such as glyphosate and AMPA, with an average detection percentage of 70% and 87%, respectively, in the analyzed publications. As for glufosinate, the percentage of contaminated surface water samples is much lower, around 6%.

For groundwater, the rate of contaminated samples is much lower for all three substances (Figure 4.9). The glyphosate and AMPA contaminations show a similar rate of about 18% and 16%, respectively, and the contamination of the samples analyzed with glufosinate was almost zero (0,7%).

In the studied sediment samples, the detection percentage of the analytes was very similar, 44% for glyphosate, 56% for AMPA and 52% for glufosinate.

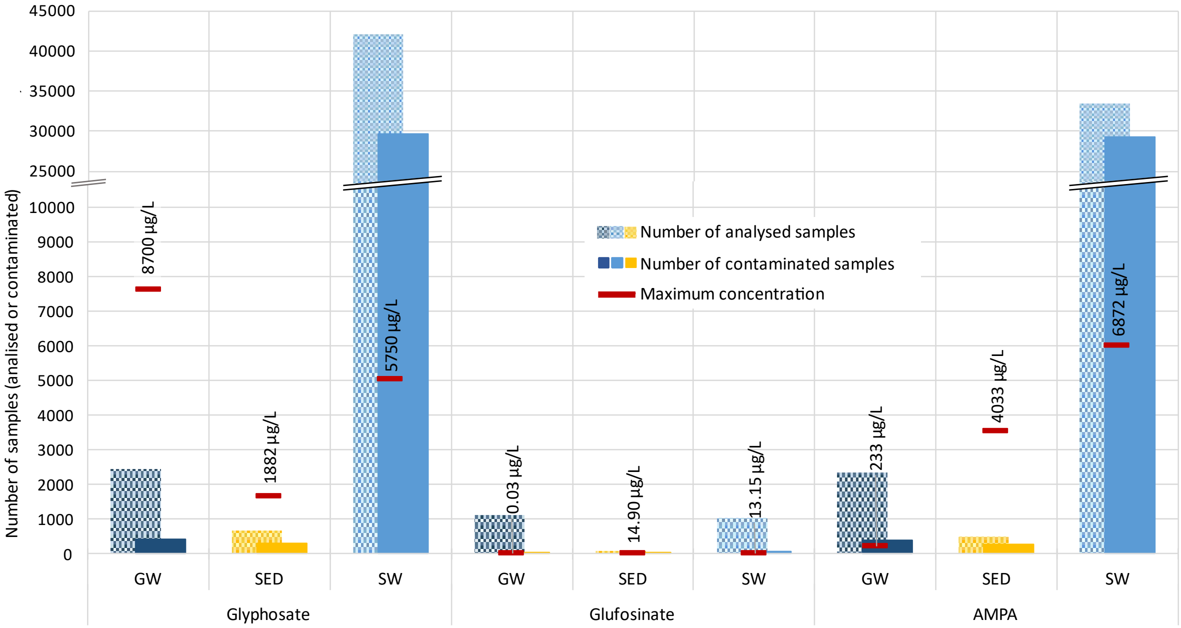


Figure 4.9 - Number of analyzed samples and contaminated (>LOD) by matrix type (GW, Groundwater; SED, Sediments; or SW, Surface water). Red lines represent the maximum reported concentration in each matrix (developed by the author).

The maximum contaminant concentration found in surface water was 6 872 µg/L, 5 750 µg/L, and 13.15 µg/L for AMPA, glyphosate and glufosinate, respectively. In groundwater, where contamination was expected to be lower, the maximum values found were 8 700 µg/L for glyphosate, higher than that found in surface water, and 233 µg/L and 0.03 µg/L for AMPA and glufosinate, respectively. For sediments, the maximum concentrations found were 1 882 µg/kg, 4 033 µg/kg and 14.9 µg/kg for glyphosate, AMPA and glufosinate.

In Figure 4.10, the maximum glyphosate concentration found in each country is presented taking into account each of the sample types: surface water, groundwater, and sediments.

As shown in Figure 4.10, the maximum glyphosate concentration in surface water was detected in Minas Gerais, Brazil, where 5750 µg/L glyphosate concentration was spotted in a low-order stream (Lima *et al.*, 2022). Contrary to what might be expected, the maximum concentration was found in a stream with more urban influence than in streams with agricultural influence, namely with glyphosate-based herbicides (GBH). The results suggested that the lower concentrations found in agricultural-influenced streams (still well above the legal limit, with an average of 970 µg/L and a detection frequency of 60%) were due to the tendency of glyphosate to adsorb into the soil, particularly in acidic soils such as the situation under study (Lima *et al.*, 2022). In the same survey, the highest groundwater contamination by glyphosate found in the published studies under review was also discovered (8700 µg/L). The sampling in which these results were obtained was done during the rainy season, in January.

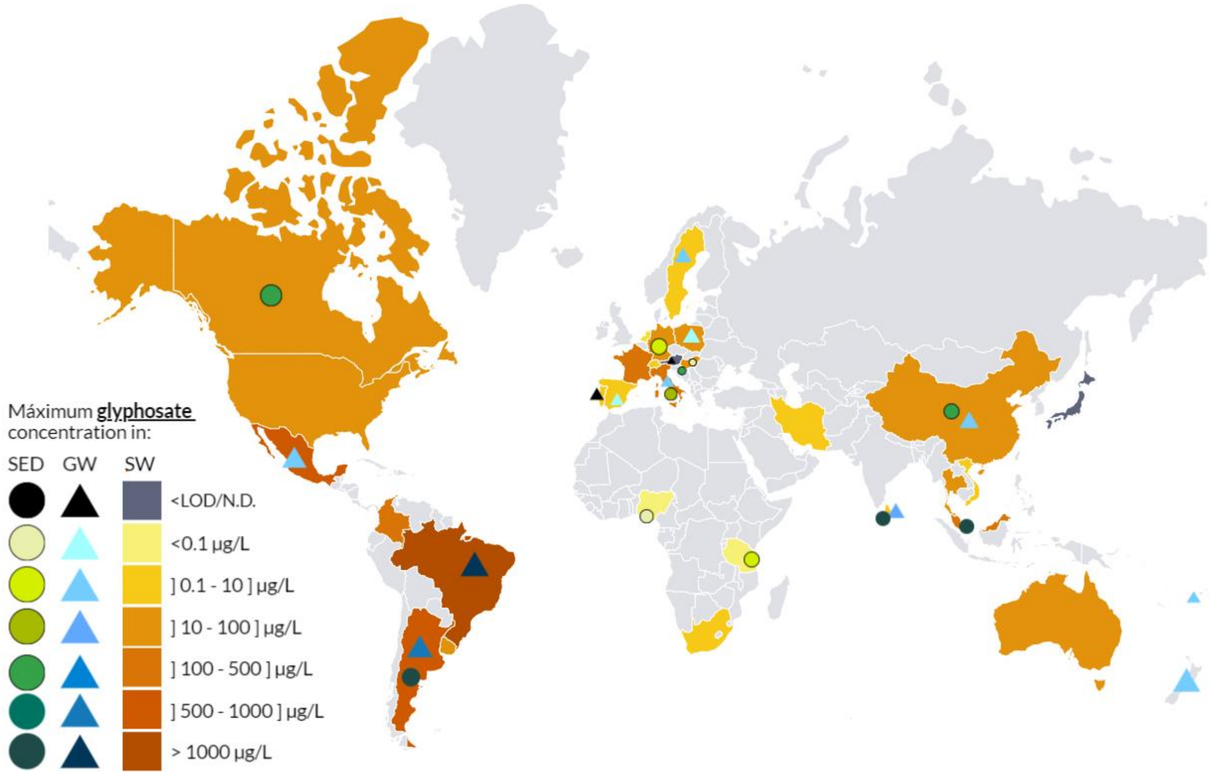


***Figure 4.10** - Maximum glyphosate concentration found in each country reported in the published studies for surface water (SW) - country color (no publications in surface water - light gray); Groundwater (GW) - circles; and sediments (SED) - triangles (µg/kg) (developed by the author).*

The second highest glyphosate concentration found in surface waters in the period under review was in Buenos Aires, Argentina, with a value of 590 µg/L and was measured in an agricultural pond about 15 days after glyphosate was applied to nearby maize crop field (Brodeur *et al*., 2021).

Concerning groundwater, the second higher glyphosate concentration was detected in an area cultivated in the city of Córdoba, Argentina (825 µg/L), but with low representativity, since it was the only sample analyzed (A. L. Pérez *et al*., 2019). A higher concentration of glyphosate in sediments was also found in Cordoba, in the Suquía river basin, with a value of 1882 µg/kg (Bonansea *et al*., 2018). A similar maximum concentration was also reported by Rahman *et al*. (2019) in Malaysia (1800 µg/kg), by Mac Loughlin *et al*. (2022b) in Buenos Aires, Argentina (1147 µg/kg), and by Gunarathna *et al*. (2018) in Sri Lanka, Asia (of 1011 µg/kg).

In Figure 4.10, the maximum AMPA and glufosinate concentration found in each country is presented for surface water, groundwater, and sediments.

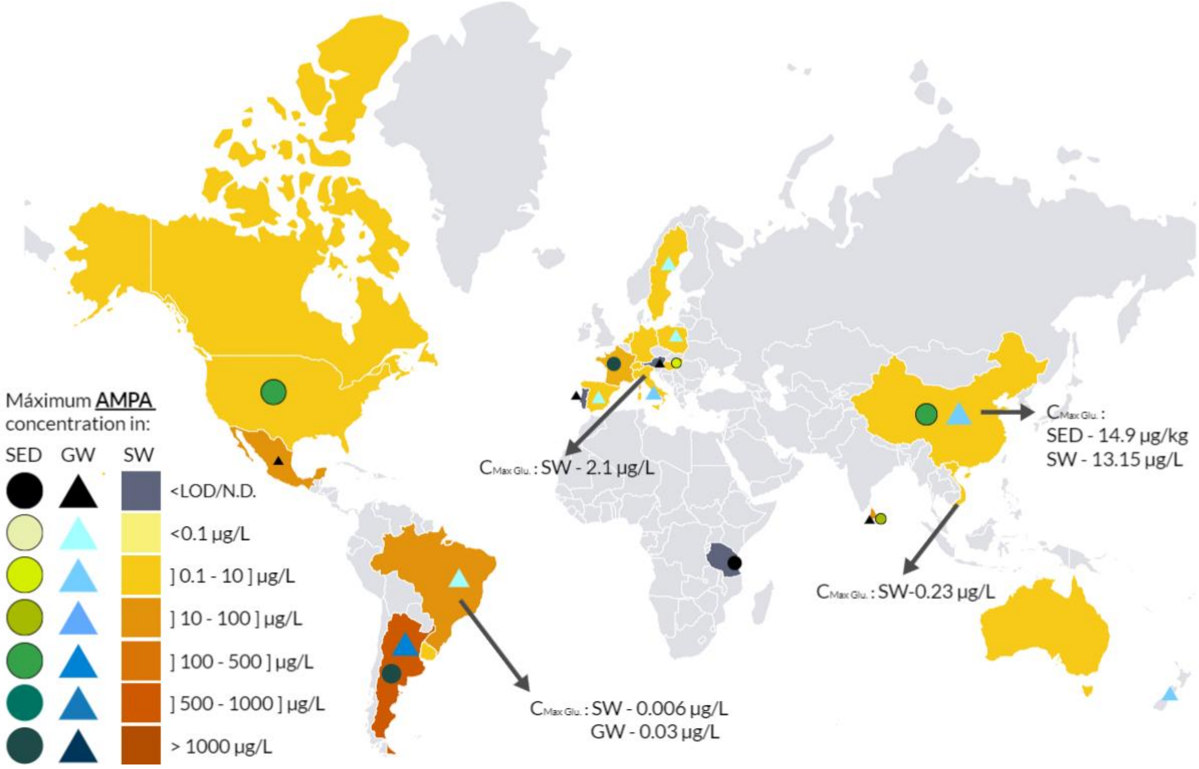


Figure 4.11 - Maximum AMPA concentration found in each country reported in the published studies for surface water (SW) - country color (no publications in surface water - light gray); Groundwater (GW) - circles; and sediments (SED) - triangles (µg/kg); $C_{Max.Glu}$- Maximum glufosinate concentration (developed by the author).

As can be seen by comparing Figure 4.10 and Figure 4.11, most of the maximum values observed for glyphosate in water and sediment were higher than for AMPA in the same country. Additionally, the number of countries studied was lower for AMPA and glufosinate than for glyphosate.

Maximum AMPA concentration in surface water was detected in Entre Rios, Argentina, where 6872 µg/L were identified in Parana and Gualeguay River basins (Suárez *et al.*, 2021). Argentina was, also, the country with the highest AMPA contamination in groundwater, with 233 µg/L detected in Santa Fé (Vera-Candioti *et al.*, 2021), and in sediments, 4033 µg/kg, identified in Buenos Aires (Mac Loughlin *et al.*, 2022b).

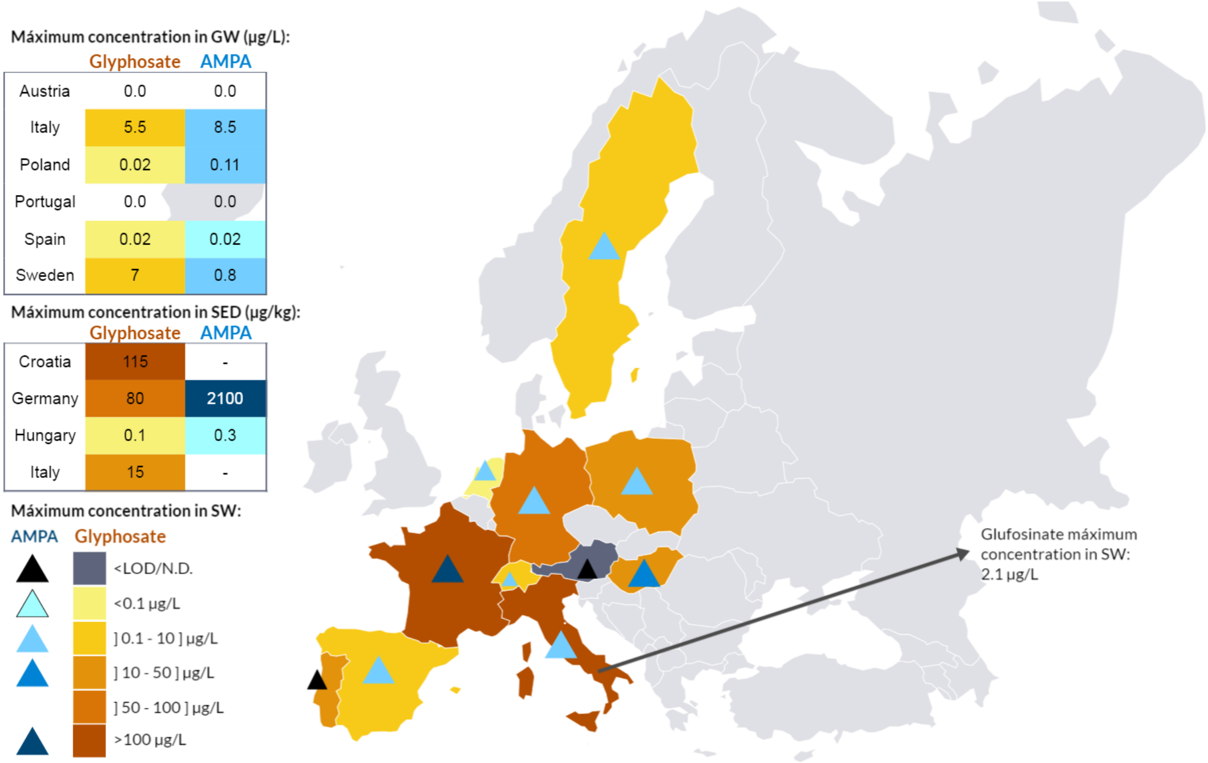
Despite the various monitoring studies carried out, glufosinate was never detected in Argentina (Demonte *et al.*, 2018; Lajmanovich *et al.*, 2023; Natalia Veronica Van Opstal *et al.*, 2023; Natalia Verónica Van Opstal *et al.*, 2022), Austria (Lajin & Goessler, 2019), Canada (Donald *et al.*, 2018), Netherland (Geerdink *et al.*, 2020), Poland (Pazikowska-Sapota *et al.*, 2020), Spain (López-Vázquez *et al.*, 2023), Portugal (Pinto *et al.*, 2018), and New Zeeland (Close *et al.*, 2021).

Sediments were the environmental matrix associated with the highest detected concentration of glufosinate (14.9 μg/kg). These results were found by Yan *et al*. (2022) in Hubei, China, that also reported high detection rates, of almost 100% in all studied locations and sampling campaigns (May, July, and October), for AMPA and an average superior to 80% for glyphosate detection rate in sediments (B. Yan *et al*., 2022).

Only one survey reported values of glufosinate above the detection limit in Europe and that was in the Veneto region, Italy, where a maximum concentration of 2.1 µg/L (with an average of 0.1 µg/L) was detected in waters from Venice lagoon. The other four surveys with glufosinate values quantified above 0.1 µg/L were performed in Asia, three of them in China, with maximum reported values of 13.15 µg/L (Geng *et al*., 2021), 6.13 µg/L (B. Yan *et al*., 2022), and 0.5 µg/L (Lin *et al*., 2022). The first one was registered in a scan through 196 surface water samples of 10 provinces in China that also showed that the detection rate of glufosinate was 2.6% in surface water and 0% in the 694 groundwater samples tested. On the other hand, for glyphosate and AMPA, the study reported maximum concentrations of 32.49 µg/L, 10.31 µg/L (frequency of detection 14.3% and 15.8%) in surface water, and 2.09 µg/L, 5.13 µg/L (frequency of detection 1.01%, 0.86%), respectively (Geng *et al*., 2021).

The other survey reporting values of glufosinate above the detection limit is Asia was found in the Red River Delta region, Vietnam, with 0.23 µg/L of glufosinate in surface water, but with a low detection frequency and short sample representativity once the sample analysis was performed to validate a purification/extraction methodology (Vu *et al*., 2021).

In European countries (Figure 4.12), where genetically modified crops are not authorized and recommendations are to reduce the use of glyphosate, the maximum stated concentration in surface water was 111 µg/L and 145 µg/L (average concentrations of 0.24 and 0.55 µg/L in the same survey) for glyphosate and AMPA, respectively (Carles *et al*., 2019), both found in France. Values of 108 µg/L (Di Guardo & Finizio, 2018), 1.4 µg/L (Masiol *et al*., 2018) and 2.1 µg/L (Masiol *et al*., 2018) were found as maximum concentrations of glyphosate, AMPA, and glufosinate, respectively, in Italy surface waters. In Germany, maximum concentrations of 58 µg/L and 5.5 µg/L for glyphosate and AMPA were detected (Tauchnitz *et al*., 2020). In groundwater, the higher glyphosate concentrations were about 10 times lower, with 7 µg/L found in Sweden (Cederlund, 2022), followed by Italy, where maximum concentrations of 5.5 µg/L and 8.5 µg/L for glyphosate and AMPA, respectively were found in wells located near a farmyard and used for irrigation and/or preparation of plant protection products mixtures (Suciu *et al*., 2023).



Máximum concentration in GW (µg/L):

	Glyphosate	AMPA
Austria	0.0	0.0
Italy	5.5	8.5
Poland	0.02	0.11
Portugal	0.0	0.0
Spain	0.02	0.02
Sweden	7	0.8

Máximum concentration in SED (µg/kg):

	Glyphosate	AMPA
Croatia	115	-
Germany	80	2100
Hungary	0.1	0.3
Italy	15	-

Figure 4.12 - Maximum glyphosate, AMPA and glufosinate concentrations found in European countries reported in the published studies for surface water (SW) - country color (no publications in surface water -light gray.); Groundwater (GW) - fist table; and sediments (SED) - second table (developed by the author).

Germany presented the higher sediment contamination in Europe (Figure 4.12), of 2100 µg/kg of AMPA, the same location where 80 µg/kg was the maximum concentration of glyphosate in the same matrix (Wimmer *et al.*, 2022). In Croatia, a maximum glyphosate concentration of 115.3 µg/kg was found in the Sava River, in a sampling location less polluted concerning to the remaining 428 organic contaminants surveyed in the same study but considered one of the most toxic (Babić *et al.*, 2018).

Analyzing the maximum detected values of glyphosate contamination of surface water, groundwater and sediments reported in years prior to the period analyzed here (before the year 2018), the following are noteworthy:

- Sasal *et al.*, (2017) performed a study in Entre Ríos, Argentina, with a network of 311 monitoring points and 703 surface water samples analyzed during three sampling periods, and reported a maximum glyphosate concentration of 105000 µg/L. On average, the results of the three sampling periods found that more than 70% of the samples showed values below 0.1 µg/L (Sasal *et al.*, 2017).
- In surface waters from an agricultural area in Colombia, 2777 µg/L was the highest glyphosate concentration found by Alza-Camacho *et al.*, (2016).

- In river sediments, the maximum concentration of 3294 and 7219 μg/kg for glyphosate and AMPA, was found by (Primost *et al.*, 2017). Additionally, in this survey, the suspended particulate matter (SPM) was studied and maximum concentrations of 584 µg/kg and 475 µg/kg of glyphosate and AMPA, respectively, were found. Lower detection frequency was observed in surface water (27 e 55%) with maximum concentrations of water of 1.80 µg/L and 1.90 µg/L of glyphosate and AMPA, revealing that SPM analysis would be also sensitive for these contaminants search in the aquatic ecosystem.

4.5 Presence of glyphosate, AMPA and glufosinate in other matrixes

In the analyzed studies associated with the monitoring of water and sediments, the analysis of contamination by the same compounds was sometimes carried out in other matrices. Yan *et al*. (2022) reported that bioaccumulation of AMPA in crabs, fish, and crayfish was higher than glyphosate and glufosinate, and that tissues with a lower metabolic rate (e.g. muscle and brain) have a lower bioaccumulation potential. On the other hand, organs with more intense metabolic activities (e.g. intestine and liver), accumulated higher levels of these herbicides. The higher solubility of glyphosate in water and the fact of being insoluble in most organics can hinder the absorption by the gastrointestinal tract of animals and make it quickly excreted by the intestines without metabolism, leading to less accumulation in other organs. (B. Yan *et al*., 2022)

Also, Tongo *et al*. (2022) found out that, although not detected in any of the 108 surface water samples analyzed in Nigeria and detected at low concentrations (average 0.0093 μg/kg) in sediments, glyphosate showed a strong potential to bioaccumulate and biomagnify along the trophic levels (Tongo *et al*., 2022).

Lajmanovich *et al*. (2023) investigated the presence of glyphosate, AMPA, and glufosinate in river fish, discovering very high concentrations and detection frequencies of glyphosate - 187 µg/kg (detection frequencies of 93.75%) and AMPA - 3116 µg/kg (DF 100%), and glufosinate 677 µg/kg (detection frequencies of 50%). In fish viscera samples, lower values were found but also with high detection frequencies (75, 100 and 12.5% for glyphosate, AMPA and glufosinate) (Lajmanovich *et al*., 2023).

Fernandes *et al*. (2019) monitored the glyphosate and AMPA residues presence in epilithic biofilms occurring in the Guaporé River fluvial network, in Brazil, throughout a year and reported that the maximum concentrations in fall and spring, respectively, fluctuated from

250 µg/kg to 305 µg/kg for glyphosate and from 670 µg/kg to 400 µg/kg for AMPA. Also concluded that their presence was strongly influenced by the number of herbicide applications and the access and protection of the collecting point (G. Fernandes *et al*., 2019).

Some studies investigate glyphosate and AMPA presence in water and sediments and in water suspended particulate matter (SPM). A survey of five sampling points along the Suquía River basin (Córdoba, Argentina), with 60 samples taken, compares the presence of glyphosate and AMPA in water and SPM in the water. The concentrations varied significantly between the different environmental matrices, with levels ranging from 12 to 20 times higher in sediment and SPM compared to water, and being more frequently detected (Bonansea *et al*., 2018).

Another findings in Argentina, this time in Buenos Aires, reported a maximum concentration of glyphosate in the soluble and particulate phases of 17.0 μg/L and 35620 μg/kg for glyphosate, and 4.5 μg/L and 19586 μg/kg for AMPA, respectively. Given these results, the study states that both compounds have an affinity for the particulate phase, additionally evidenced by the experimental K_d values reported. However, despite the partitioning, the soluble fraction contributed significantly more to the total weight load in the studied water body, representing over 90% of the average value (Mac Loughlin *et al*., 2020).

4.6 Study and analysis of higher mobility pathways

In agricultural regions, agrochemicals can easily contaminated water bodies via overspray, spray drift, and surface run-off. Aiming to assess the hydrogeological factors, namely groundwater flow, recharge, discharge and deep, that affect the occurrence of glyphosate and AMPA in water sources, Lutri *et al*. (2020) performed a detailed hydrogeological and hydrodynamic characterization of its study agrosystem in Córdoba, Argentina. Additionally, completed its survey with an assessment of glyphosate and AMPA contamination in surface water and groundwater at the same location. With it, it sought to better understand glyphosate AMPA's transport and fate and AMPA into aquatic systems. Glyphosate was detected in 66% of surface water samples and 15.8% of groundwater samples. In contrast, AMPA was found in 33% of surface water samples and 15.8% of groundwater samples. The presence of these compounds was most strongly associated with areas characterized by shallow water tables, low hydraulic conductivity in the aquifer, low hydraulic gradient, and very low flow velocity. Notably, the study found that groundwater samples had higher glyphosate and AMPA levels than surface water samples (streams), which may be due to their greater dilution capacity. The detection of these compounds in the unconfined aquifer, less exposed to pollution due to the soil and the unsaturated zone protection, highlighted the potential for long-term contamination of groundwater resulting from the prolonged use of glyphosate under prevailing agricultural practices, exceeding the degradation potential of the soil and unsaturated zone (Lutri *et al*., 2020).

As Lutri *et al*. (2020), which concluded that the shallow water table depth could act as a key factor influencing the frequency of glyphosate and AMPA detection in groundwater, Mas *et al*. (2020), in their work in Argentina found a higher detection frequency of 27% for glyphosate and 46% for AMPA in hand-dug wells with a shallow water table than in boreholes (17% for glyphosate and 11% for AMPA) where the water table was deeper than 50 m. The referred higher detection frequency could also be influenced by the local soil type that, with its fine-textured and well-structured characteristics, could enhance the preferential flow and become an important pathway (Mas *et al*., 2020). The findings emphasize the significance of exploring the link between the depth of the water table and the identification of glyphosate and AMPA in groundwater.

Field experiments that evaluate the water contamination caused by glyphosate application can provide important insights into the behavior of glyphosate and its degradation product AMPA in soil and groundwater. Mencaroni *et al*. (2022) conducted a field experiment in the Prosecco wine production area in northeastern Italy, aiming to investigate the dynamics of glyphosate and AMPA in the local soil and water. Two monitoring sites were established and equipped with two soil-water monitoring stations. Soil and water samples were collected and analyzed for glyphosate and AMPA concentrations. Glyphosate dissipation time of 36±8 days in soils was found, and full dissipation only occurred after 6 months. However, AMPA dissipation dynamics were longer, and full dissipation was only verified after almost 300 days. The study has also shown that the main enhancers of glyphosate adsorption to soil were clays, and iron and aluminum oxides chelated to soil organic matter. These compounds possibly acted as cation bridges leading to low glyphosate mobility. Moreover, both compounds were detected mainly after substantial rainfall events at 70 cm depth, bypassing the well-structured soil conditions in intermediate layers and showing a reduced soil-filtering capacity during this extreme rain events that could increase groundwater vulnerability to contamination (Mencaroni *et al*., 2022).

In another field trial, Mencaroni *et al*. (2023) studied the impact of adopting conservation agriculture during the transition period on glyphosate and AMPA dynamics under different shallow water table conditions, in a set of eight lysimeters. In addition, it examined the interactions between these molecules and the surrounding soil and water, associated with their dissipation and formation processes, as well as their adsorption on soil particles and transport to groundwater. Once again, they concluded that the sorption of glyphosate in the soil is primarily influenced by clay minerals, soil organic carbon, phosphate content, and the amount of aluminum and iron present in all crop and water management systems tested. However, the adoption of conservation practices did have an impact on glyphosate concentration in the soil profile. The presence of a shallow water table was found to influence glyphosate transport in the vadose zone. Its detection in groundwater suggests that it can rapidly move through preferential pathways, posing a threat to groundwater quality in agricultural lands. In contrast, the absence of AMPA in the groundwater indicates a different adsorption and transport mechanism compared to glyphosate. Overall, their findings emphasize the importance of adopting sustainable agricultural practices to mitigate the environmental impact of glyphosate and its potential to contaminate groundwater resources (Mencaroni *et al.*, 2023).

Lima *et al.* (2022) also studied the environmental mobility of glyphosate in a Southeast Brazilian catchment by monitoring surface runoff from experimental agricultural soil plots with known glyphosate applications and monitoring water samples from several low-order streams of the same basin. Glyphosate showed considerable environmental mobility in surface runoff, streams, and drinking water resources. Its leaching was slow due to sorption to soil particles (enhanced by the local acidic soils, also referred by (Garba, Samsuri, *et al.*, 2018)), resulting in delayed peaks in runoff experiments and stream monitoring. Glyphosate pollution patterns were influenced by rainfall regime and flow rate when contamination sources were close to collection sites, and spray dates were known. However, glyphosate concentrations showed high temporal and spatial variation in streams in agricultural and urban areas, with no apparent patterns apart from the observed land-use effects (Lima *et al.*, 2022).

Concerning water physicochemical characteristics and constituents, according to the findings of the study conducted by Carles *et al.*, (2019), phosphorus, besides playing a crucial role in river eutrophication, can also hinder the complete degradation of glyphosate by biofilms and promote the accumulation of AMPA in river water. Moreover, the study highlights the role of biofilms and rivers’ trophic status in evaluating the fate and persistence of glyphosate (Carles *et al.*, 2019).

Therefore, it is essential to consider several factors to accurately evaluate the impact of glyphosate on river ecosystems and groundwater.

4.7 Glyphosate, AMPA and glufosinate contamination sources

Several authors have mentioned the significant impact of urban areas on water contamination by glyphosate and AMPA (e.g., application of glyphosate on weed control, domestic gardens and horticulture, and industry) (Di Guardo & Finizio, 2018; G. Fernandes *et al*., 2019; Lima *et al*., 2022; Okada *et al*., 2020; Tauchnitz *et al*., 2020; Wirth *et al*., 2021).

Wastewater treatment plants (WWTPs) have been identified as a source of herbicide contamination in surface water. Studies have shown that WWTP effluent can contain significant amounts of herbicides. The levels of herbicides in surface waters close to WWTPs are higher than those in surface waters further away, indicating the significant impact of WWTPs on herbicide contamination (Tóth *et al*., 2022). Strategies to reduce herbicide contamination from WWTPs may include better treatment technologies and the implementation of best management practices to reduce herbicide use in the surrounding areas (Rezaei Kalantary *et al*., 2022).

In a three-year study, Tóth *et al*., (2022) investigated more than 450 pesticide compounds in the Lake Balaton in Hungary and its sub-catchment area. The detected compounds were associated with their persistent or escalating use in agricultural and domestic activities in the region, and a representative impact of the WWTP effluent in the intricate dynamics of pesticide loads and its potential impact on Lake Balaton's water quality was discovered. The treated effluent produced at the WWTP presented, in all seasons, the highest diversity in pesticide composition and represented the major point source for pesticide load in the studied water body (Tóth *et al*., 2022).

Likewise, related to the influence of WWTP in surface water contaminations, Wirth *et al*. (2021) reported a higher concentration of glyphosate and AMPA near the WWTP outlet to Warnow River, Germany, that apparently caused an increase in their concentration at the sampling points collected downstream. These concentrations were almost 4 and 16 times higher than the concentrations of the samples taken upstream for glyphosate and AMPA, respectively. AMPA is also a metabolite of various industrial organophosphonates, such as the ones used in the textile industry as detergents. The significantly higher concentration of AMPA in the wastewater treatment plant (WWTP) area compared to glyphosate could be associated with the fact that some of the detected AMPA could be originated from industrial sources rather than from glyphosate degradation (Wirth *et al*., 2021).

On the contrary, Rezaei Kalantary *et al*., (2022) reported a WWTP 100% removal efficiency of most of the studied OCPs, namely glyphosate. Additionally refers that the major part of studied pesticides removal occurred in coagulation-flocculation and rapid sand filtration units (87%) due to the hydrophobic nature of pesticides and the use of granular activated carbon in the filtration unit (Rezaei Kalantary *et al*., 2022).

Di Guardo & Finizio, (2018) studied a new risk management methodology for pesticide surface water bodies contamination in the Lombardy region, Italy, using glyphosate as a case study and its historical monitoring data from national monitoring plans of pesticide residues in surface water. One of the results was a risk analysis on the selected monitoring stations describing locations where mitigation actions are recommended. The classification as risk or high risk of glyphosate contamination of many surface water monitoring stations was associated with a non-agricultural use of glyphosate, since they are localized in highly urbanized areas, near railways or major roads.

An investigation of the possible glyphosate groundwater contamination associated with its wide application through European railways for controlling vegetation growing on its tracks was developed in Sweden by Cederlund (2022). Glyphosate, along with AMPA, was spotted in 16% and 14%, respectively, of the groundwater samples taken from wells located underneath the tracks. In those sampling sites, the EU groundwater quality standard of 0.1 µg/L was exceeded in 6% and 4% of the cases for glyphosate and AMPA, respectively. Limited glyphosate and AMPA horizontal spread in the groundwater zone was identified, as only 1–3% of the groundwater samples taken from outside the track area had detectable amounts of the two contaminants (Cederlund, 2022).

The wells from several farmyards showed the highest rates and concentrations of glyphosate and AMPA, in contrast with those from vineyards, which presented comparatively lower levels of these substances. This observation suggests that improper or non-agricultural use of glyphosate may occur in farmyards, such as in yard cleaning activities (Suciu *et al*., 2023).

On the other hand, the occurrence and concentration of glyphosate, AMPA, and glufosinate in sediments around Lake Honghu in Hubei province, China, were referred by Yan *et al*. (2022) as being reflective of the intensity of agricultural practices in the surrounding areas. Additionally, regarding river sediments, their findings suggested that these are an important reservoir for both glyphosate and its metabolite and were also the matrix associated with the highest detected concentration of glufosinate. The study's results also demonstrate that the average glyphosate and metabolite concentrations in sediment are roughly half of the average concentrations observed in soil (B. Yan *et al*., 2022).

A survey carried out on 119 farmers in the Cienega region, Mexico, revealed that the most frequently used pesticides (paraquat from bipyridyls class (31.95%), followed by organophosphates class (28.87%) within which glyphosate and glufosinate) were some of the predominant pesticides detected in surface water near the working areas of the surveyed farmers (Silva-Madera *et al*., 2021).

These findings underscore the need for proper and responsible use of glyphosate and other chemicals in agriculture to minimize their impact on human health and the environment. In short, when examining publications on glyphosate monitoring in water and sediments, France demonstrated the highest samples/publication ratio, followed by Japan and Italy. Argentina had the highest frequency of publication studies but a lower samples/publication ratio. The monitoring of AMPA in water and sediments also showed higher publication frequency in Argentina, while France once again had the highest samples/publication ratio, followed by the USA, Sweden, and Italy. China had a significantly larger number of monitored glufosinate samples compared to other countries with publications on this compound. Regarding maximum contaminant concentrations, surface water exhibited values of 6 872 µg/L, 5 750 µg/L, and 13.15 µg/L for AMPA, glyphosate, and glufosinate, respectively. Groundwater recorded maximum values of 8 700 µg/L for glyphosate, 233 µg/L for AMPA, and 0.03 µg/L for glufosinate. Sediments had maximum concentrations of 1 882 µg/kg, 4 033 µg/kg, and 14.9 µg/kg for glyphosate, AMPA, and glufosinate, respectively. Surprisingly, the maximum glyphosate concentration was higher in groundwater than in surface water, although the frequency of detection was much higher in surface water (70%) compared to groundwater (18%). For AMPA and glufosinate, the detection frequency in surface waters was 87% and 6%, while in groundwater, it was 16% and 0.7%, respectively. South American countries displayed the highest maximum detected concentrations for glyphosate and AMPA, while sediments were the environmental matrix with the highest detected concentration of glufosinate. In Europe, France had the highest maximum concentrations in surface waters, followed by Italy and Germany. In groundwater, glyphosate concentrations were approximately 10 times lower, with the highest levels found in Sweden, followed by Italy. Germany and Croatia reported the maximum concentrations found in sediments. Several factors were identified as drivers for the presence of these compounds in surface water, sediments, and groundwater. These factors include overspray, spray drift, surface runoff, shallow water tables, low hydraulic conductivity in aquifers, low hydraulic gradient, very low flow velocity, soil type, and its chemical composition. Potential sources of contamination mentioned were persistent and increasing applications in agricultural and domestic activities, WWTPs, and improper use.

CHAPTER 5 EVALUATION OF THE ADSORPTION POTENTIAL OF BIOCHARS PREPARED FROM FOREST AND AGRI-FOOD WASTES FOR THE REMOVAL OF FLUOXETINE

This chapter intend to assess the application the proposed treatment technologies – adsorption – to water contaminated with residues of the antidepressant fluoxetine. This study was performed by applying batch and column adsorption experiments onto biochars with different source feedstocks. Its development seeks to understand and optimize this treatment technology towards its implementation, for example, in a wastewater treatment facility, minimizing the entry of this contaminant in surface waters and, consequently, its propagation.

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Evaluation of the adsorption potential of biochars prepared from forest and agri-food wastes for the removal of fluoxetine

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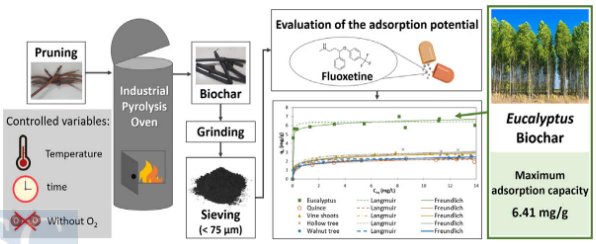
G R A P H I C A L A B S T R A C T



Abstract

Twelve biochars from forest and agri-food wastes (pruning of Quercus ilex, Eucalyptus grandis, Pinus pinaster, Quercus suber, Malus pumila, Prunus spinosa, Cydonia oblonga, Eriobotrya japonica, Juglans regia, Actinidia deliciosa, Citrus sinensis and Vitis vinifera) were investigated as potential low-cost and renewable adsorbents for removal of a commonly used pharmaceutical, fluoxetine. Preliminary adsorption experiments allowed to select the most promising adsorbents, Quercus ilex, Cydonia oblonga, Eucalyptus, Juglans regia and Vitis vinifera pruning material. They were characterized by proximate, elemental and mineral analysis, thermogravimetric analysis, Fourier transform infrared spectroscopy, determination of specific surface area and pH at the point of zero charge. Batch and equilibrium studies were performed, and the influence of pH was evaluated. The equilibrium was reached in less than 15 min in all systems. The maximum adsorption capacity obtained was 6.41 mg/g for the Eucalyptus biochar, which also demonstrated a good behavior in continuous mode (packed column).

Keywords: anti-depressant pharmaceutical; biochar; column experiments; kinetics and equilibrium; waste valorization.

Abbreviations: EA, elemental analysis; FLX, fluoxetine; FTIR, Fourier transform infrared spectroscopy; HPLC-FLD, high-performance liquid chromatography with fluorescence detection; RMSE, root mean square error; RPM, rotation per minute; SD, standard deviation; TGA, Thermogravimetric analysis.

5.1 Introduction

Pharmaceutical products and their active compounds are among the most found environmental contaminants, being characterized by their persistency and biological activity (Biel-Maeso *et al.*, 2018). Their appearance in the environment depends on several factors, such as the consumption by human population and animals and the removal efficiency in wastewater treatment plants (WWTP), being spotted in aquatic environment and soil (Biel-Maeso *et al.*, 2018; Paula Paíga *et al.*, 2019). Fluoxetine (FLX) is an anti-depressant pharmaceutical widely used to treat depression (Silva *et al.*, 2014). Since only a fraction of this compound is metabolized by human body, much of it (and its metabolites) may end up in domestic wastewaters. As the conventional wastewater treatment systems are not specifically designed for the removal of pharmaceutical active compounds, it is crucial to develop remediation strategies.

Since FLX was designed to produce a specific pharmacological response, it presents a certain chemical stability which is related with its insufficient removal in municipal WWTP and limited environmental degradation (Silva *et al*., 2012). This compound is relatively recalcitrant to hydrolysis, photolysis, and biodegradation (Redshaw *et al*., 2008).

An effective tertiary treatment for removal of pharmaceuticals is adsorption (Cobas *et al*., 2016; Andreia Silva *et al*., 2018), however, its use has been limited as the adsorbent material can represent a high operational cost for wastewater treatment systems. Therefore, there is a need to search for cheaper alternatives. Recently, biochar materials have been shown to be promising solutions owing to their low cost, and high adsorption efficiency (Ahmed *et al*., 2016; F. R. Oliveira *et al*., 2017; Rosales *et al*., 2017).

Many agricultural and industrial activities generate large quantities of biomass wastes. Biochar production from these wastes is currently one of the most innovative fields of research (F. R. Oliveira *et al*., 2017; Tripathi *et al*., 2016; Turk Sekulić *et al*., 2018). Biochar is a carbonaceous solid material obtained by pyrolysis of several feedstocks, including lignocellulosic wastes, such as wood, pruning's, leaves, grass or other biomass from forest and agricultural origin. The main chemical and physical properties of biochars towards their application as adsorbent material are their relatively high porosity and specific surface area, high surface charge and high-water holding capacity (F. R. Oliveira *et al*., 2017; Turk Sekulić *et al*., 2018).

Several authors have reported that the use of biochars for the removal of toxic substances from industrial wastewaters represents an effective and affordable method, especially in what concerns small volumes of highly concentrated liquid waste streams (F. R. Oliveira *et al*., 2017). Moreover, they can also improve physical, chemical, and biological properties of soils (Bis *et al*., 2018; Fryda & Visser, 2015; Laghari *et al*., 2016; Lehmann *et al*., 2011; F. Liao *et al*., 2018; Yu *et al*., 2019). The properties of biochars depend on the type of feedstock used and the pyrolysis settings, such as the residence time, temperature, heating rate, and reactor type (Bis *et al*., 2018; Yu *et al*., 2019). Depending on the target pollutant, biochar and activated carbon efficiencies might be comparable. However, biochar production is eco-friendly and less expensive than the typical activated carbons that require costly and energy consuming activation processes (Ahmed *et al*., 2016).

The present work aims to investigate the effectiveness of FLX adsorption capacity by different biochars produced from forest and agri-food wastes, namely pruning of several forest trees, orchard trees and vineyards. Usually, these types of wastes are characterized concerning their bioactivities for further application in the food, pharmaceutical and/or cosmetic industries (Moreira *et al*., 2017, 2018). According to authors' knowledge, there are no published reports on their use for biochar production and subsequent application for removal of FLX from aqueous solutions. With this purpose, twelve biomass wastes, namely pruning from *Quercus ilex L.* (hollow tree), Eucalyptus grandis W. Hill ex Maiden (eucalyptus), *Pinus pinaster Ainton*. (pine), *Quercus suber L*. (cork tree), *Malus pumila Mill.* (apple tree), Prunus spinosa L. (blackberry tree), *Cydonia oblonga Mill.* (quince), *Eriobotrya japonica* (Thunb.) Lindl (medlar tree), Juglans regia L. (walnut tree), Actinidia deliciosa Liang & Ferguson (kiwi shrub), Citrus sinensis (L.) Osbeck (orange tree) and Vitis vinifera L. (vine), were submitted to pyrolysis under the same controlled conditions (temperature, oxygen and residence time). After the preliminary assays to evaluate the biochars' uptake capacity for FLX, five materials were selected and studied in detail, namely for physico-chemical parameters, kinetic and equilibrium assays in batch mode. Continuous studies in packed column were also carried out for the best adsorbent (eucalyptus biochar) to demonstrate its efficacy under dynamic conditions.

Ex situ thermal processes for adsorbent regeneration are highly efficient, but the number of regeneration cycles is reduced, especially for small particles, as is the case of biochars. Electrochemical regeneration processes may be an interesting alternative to be studied, that can be performed in situ.

5.2 Materials and methods

5.2.1 Chemicals

FLX hydrochloride (> 98%) was purchased from Sigma-Aldrich (Steinheim, Germany). A FLX stock standard solution (1000 mg/L) was prepared by dissolving an appropriate amount of the reagent in methanol and stored at - 20 °C in a dark glass vial. Dilutions of this solution were prepared with HPLC-grade water, obtained from purification of deionized water in a Simplicity 185 system (Millipore, Molsheim, France). Hydrochloric acid and sodium hydroxide (purity > 99.0%), used for pH adjustments, were obtained from VWR. HPLC-gradient grade acetonitrile and formic acid (HCCOH, purity 99–100%), used for the preparation of HPLC eluents, were from VWR Chemicals BDH Prolabo, PA, USA.

5.2.2 Biochar preparation

Twelve different types of biomass wastes from different vegetal species, namely pruning from *Quercus ilex* L. (hollow tree), *Eucalyptus grandis* W. Hill ex Maiden (eucalyptus), *Pinus* *pinaster* Ainton. (pine), *Quercus suber* L. (cork tree), *Malus pumila* Mill. (apple tree), *Prunus spinosa* L. (blackberry tree), *Cydonia oblonga* Mill. (quince), *Eriobotrya japonica* (Thunb.) Lindl (medlar tree), *Juglans regia* L. (walnut tree), *Actinidia deliciosa* Liang & Ferguson (kiwi shrub), *Citrus sinensis* (L.) Osbeck (orange tree) and *Vitis vinifera* L. (vine), were kindly provided by Ibero Massa Florestal Company (Portugal) and used to produce the biochars. The different biomass wastes were pyrolyzed in an industrial oven from Ibero Massa Florestal (Portugal): 8 hours of heating time, 14 hours of holding at 500 ºC and cooling for 18 hours until room temperature. The pyrolysis was made without any gas supply (nitrogen or carbon dioxide). There is a minimum volume of air remaining between the biomass pieces, just after closing the oven that is consumed immediately when the temperature increases. Therefore, the process undergoes in the absence of molecular oxygen, being present only the oxygen constituting the biomass.

Prior to use, the obtained biochars were grounded in a cutting mill (Type GBA 0301, Ferrari) and sieved to obtain a material of a uniform particle size. The fraction with a particle diameter < 75 μm was selected for the experiments.

5.2.3 Biochar characterization

The characterization of biochars was only performed for the selected biochars, based on their FLX adsorption capacity, namely *Quercus ilex* L. (hollow tree), *Cydonia oblonga* Mill. (quince), *Eucalyptus grandis* W. Hill ex Maiden (eucalyptus), *Juglans regia* L. (walnut tree) and *Vitis vinifera* L. (vine) pruning material.

The laser diffraction method was applied to perform the granulometric analyses using a Mastersizer Hydro 2000G (Malvern Instruments, UK), a laser diffraction granulometer attached to a dispersion unit, capable to analyze particle sizes between 20 nm and 2 mm. The refractive index for the dispersed phase was 2.42 and the particle absorption index was 1. The amount of sample used to the analysis was such that the value of obscurance fell within the range of 10-20%. The continuous phase was water with a refractive index of 1.330, the pump speed was set at 1250 rpm and the stirrer speed at 600 rpm, ensuring homogenization.

Elemental analysis (quantification of carbon, hydrogen, nitrogen and sulphur contents) was performed in an Elemental Analyzer Thermo Finnigan - CE Instruments, model Flash EA 1112 CHNS series, based on sample combustion dynamics. The proximate analysis that included the quantification of moisture content, volatile matter and ashes followed the ASTM D1762 standard, which is specifically designed for wood charcoal.

Thermogravimetric analysis (TGA) was performed in a Setaram Labsys EVO equipment, between room temperature and 850 °C, with a heating rate of 5 °C/min, under argon atmosphere.

Fourier transform infrared spectroscopy (FTIR) analyses were performed in a Perkin-Elmer – Spectrum 1000 spectrophotometer, using the potassium bromide (KBr) disc method (biochar:KBr ratio of around 1:200). The spectra were recorded from 400 to 4000 cm^{-1} with the resolution of 1 cm^{-1}.

The pH at the point of zero charge (pH_{pzc}) for the selected biochars was determined according to the following methodology (Carabineiro *et al*., 2012): 0.1 g of biochar was added to 20 mL of 0.1 M NaCl solutions with initial pH values between 2.0 and 12.0 (pH adjustment was performed with solutions of NaOH or HCl with concentrations of 0.01 to 1 M); the mixtures were stirred for 24 h and the final pH was measured; pH_{pzc} value corresponds to the plateau of the curve pH_{final} *vs* $pH_{initial}$.

The determination of the mineral content was performed according to the European Standard EN 15290 (2011) on samples previously digested (3 mL H_2O_2 30% v/v + 8 mL HNO_3 65% v/v + 2 mL HF 40% v/v) in a microwave station (Milestone Ethos 1600 Microwave Labstation) followed by neutralization (20 mL H_3BO_3 4% w/v); the acidic solutions were analysed by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) (Horiba Jobin-Yvon equipment) for the quantification of the most common chemical elements in biochars: Ca, K, Na, Fe, Mg, Al, Cr, Ni, Cu, Zn.

Textural parameters such as apparent surface area (S_{BET}) and total pore volume (V_{total}) were evaluated from the adsorption of N_2 at 77 K (ASAP 2010 Micromeritics equipment) by using the single point method at the relative pressure of P/Po = 0.3; all samples were previously outgassed overnight, under vacuum, at 150 °C before analysis.

5.2.4 Preliminary adsorption assays

Preliminary adsorption studies were performed in the twelve different biochars by placing 0.25 g of each biochar in 25 mL of solution containing 20 mg/L of FLX in Erlenmeyer flasks; the flasks were closed and magnetically stirred at 400 rpm (Multistirrer 15, Velp Scientifica) for 2 hours at room temperature (25 °C) without pH adjustment. At the end of the experiments, an aliquot of the final solutions were immediately centrifuged (Heraeus Fresco 21 Microcentrifuge, Thermo Scientific, USA) at 14500 rpm, for 10 minutes, at 4 ºC, which ensure that all solid is separated from the supernatant (Piccirillo *et al*., 2017). The supernatant was analyzed by HPLC to determine the final concentration of the FLX, as described in Section 2.9. In parallel, blank assays were prepared with the same FLX concentration and without biochar. The assays were performed in triplicate, and the results were expressed as mean and standard deviation (SD). The percentage of adsorbate removal (*R*, %) was calculated from the equation (1):

$$R = \frac{(C_0 - C_f)}{C_0} \times 100 \qquad (1)$$

where C_0 and C_f (mg/L) represent the initial and final concentration of the FLX (determined by HPLC) after 2 hours stirring.

5.2.5 Kinetic assays

For the kinetic experiments, 0.75 g of biochar in 250 mL of solution containing 20 mg/L of FLX were used and stirred at 400 rpm (VMS – C7 advanced, VWR) during 60 min at room temperature. The contact time was chosen taking in consideration the results obtained in previous kinetic studies with biochars. An aliquot of 1 mL was collected every minute, centrifuged and analyzed as described in Section 2.4 in order to determine the remaining concentration of FLX in solution along time.

The mass of FLX adsorbed per gram of adsorbent (q_t, mg/g) was calculated according to equation (2):

$$q_t = (C_0 - C_e) \times \frac{V}{m} \qquad (2)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of FLX, *V* (L) is the volume of the FLX solution and *m* (g) is the mass of biochar.

The pH was recorded (Consort pH Meter model C861, Belgium) during the experiments.

5.2.6 Effect of pH

The effect of initial pH was evaluated only for the three most promising biochars, namely for hollow tree, eucalyptus and vine. For this purpose, 0.04 g of eucalyptus and 0.08 g of hollow tree or vine were placed in flasks with 25 mL of a 20 mg/L aqueous solution of FLX. The pH in each suspension was adjusted in a range from 4 to 7 by using 0.01 mol/L HCl or 0.1 mol/L NaOH solutions. The flasks were stirred at 400 rpm (Multistirrer 15, Velp Scientifica) for 120 minutes, although it was known that equilibrium was reached in less than 15 min. Samples of 1 mL were collected and centrifuged at time 0, 15 and 120 minutes, the pH was measured and the FLX concentration was determined as described in Section 2.4. A blank test (without the addition of biochar) was done for each pH investigated.

Additionally, another assay was also carried out to evaluate the pH influence, where the biochar and water were in contact for 2 hours allowing the leaching of species that could interfere with the pH value of the solution. Then, the pH solution was adjusted to 7.0 and let stand for 1 hour. Only after these steps, the FLX was added, and the assay was conducted.

5.2.7 Equilibrium assays

Adsorption isotherms were obtained by using different quantities of the adsorbent, ranging from 10 to 400 mg, in flasks with 25 mL of a 20 mg/L aqueous solution of FLX. The mixtures were stirred (Multistirrer 15, Velp Scientifica) for 15 minutes (time enough to reach equilibrium) at room temperature. Then, samples were centrifuged and FLX concentration was determined as described in Section 2.4.

Two commonly used adsorption isotherm models, Langmuir and Freundlich, were used to adjust the experimental values.

The Langmuir's model assumes a monolayer adsorption over an energetically homogeneous adsorbent surface. It does not take into consideration interactions between adsorbed molecules and is represented by equation (3) (Langmuir, 1918):

$$q_e = \frac{(Q_m .\ k_L .C_e)}{(1+ k_L .C_e)} \tag{3}$$

where C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), K_L is the Langmuir equilibrium constant related to the energy of adsorption (L/mg), and Q_m is the maximum adsorption capacity (mg/g), which in this model should corresponds to a monolayer coverage of the adsorbent surface.

Freundlich´s isotherm is an empirical model that assumes the existence of heterogeneous adsorption centers on the surface of the adsorbent. It is represented by the equation (4) (Freundlich, 1907):

$$q_e = K_F .C_e^{1/n} \tag{4}$$

where K_F is the Freundlich isotherm constant [(mg/g) (L/mg)$^{1/n}$)], and n (dimensionless) is the Freundlich exponent which describes the strength of adsorption. Typically, $1/n$ value ranges between 0 and 1, and if $1/n$ is closer to 0, the adsorption intensity is higher.

Isotherm parameters, correlation coefficients (r^2) and root mean square error (RMSE) for Langmuir and Freundlich models were obtained by Microsoft Excel for Windows 2010 with XLSTAT Version 2018.7.

5.2.8 Column assays

A glass column (Omnifit) (15 cm maximum height and 2.5 cm of internal diameter) and a peristaltic pump (Gilson, Minipuls 3) were used. The column was filled up with 4.0 g (15 mL) of biochar eucalyptus and 50.6 g (25 mL) of washed silica sand. The sand was used as dispersive material, half of it was placed below and the other half above the biochar. A continuous down-flow rate of 2.033 mL/min was employed. The assays were performed at room temperature and a 20 mg/L aqueous solution of FLX was used. Samples were periodically taken from the outflow, and they were analyzed as described in Section 2.9.

Three models, namely Thomas's, Yoon-Nelson's and Yan's models, were used to adjust the experimental data.

The Thomas's model is one of the most widely used column performance models which allows to predict the relationship between concentration and time, and is represented by equation (5) (Thomas, 1944):

$$\frac{C}{C_0} = \frac{1}{1+exp\left(\frac{k_{Th}Q_0 m}{F} - k_{Th}C_0 t\right)} \tag{5}$$

Where C_0 is the initial concentration of FLX, C is the FLX concentration at time t (mg/L), Q_0 is the maximum adsorption capacity of the adsorbent (mg/g), m is the amount of adsorbent (g), F is the flow rate (mL/min), t is the time of assay (min) and k_{Th} is the Thomas' model constant (mL/mg.min).

The Yan's model (Equation 6) is more accurate than Thomas' model as it helps to overcome some of the drawbacks, such as predicting the initial concentration with respect to time zero, and describing the breakthrough curves in fixed-bed columns (G. Yan *et al.*, 2001).

$$\frac{C}{C_0} = 1 - \frac{1}{1+\left(\frac{C_0 F t}{1000 Q_0 m}\right)^a} \tag{6}$$

where a is the Yan's model constant.

The Yoon-Nelson's model (Equation 7) doesn't require neither detailed data about characteristics of adsorbate, the type of adsorbent, nor physical proportions of the adsorption bed (Yoon & Nelson, 1984).

$$\frac{C}{C_0} = \frac{Exp\,[k(t-\tau)]}{1+Exp\,[k(t-\tau)]} \qquad (7)$$

Being k the Yoon-Nelson's model constant (min^{-1}) and τ the time (min) required for 50% adsorbate breakthrough.

5.2.9 Determination of fluoxetine concentration

The concentration of FLX was measured by a high-performance liquid chromatography with fluorescence detection (HPLC-FLD), using a Shimadzu LC Prominence system (Shimadzu Corporation, Kyoto, Japan) equipped with a LC-20AB pump, a DGU-20A5 degasser, a SIL-20A autosampler, a CTO-20AC column oven, and a RF-10A-XL fluorescence detector (FLD). The control of the chromatographic system and the acquisition and processing of chromatographic data were made using LC solution version 1.25 SP2 software. The separation was achieved with a Luna C_{18} column (150 mm x 4.6 mm, 5 µm) from *Phenomenex,* using the method described by Silva *et al*., (2019). FLX quantification was carried out using external calibration. For that, different concentrations (ranging from 2.5 to 20000 µg/L) were prepared in water from the respective stock solution (1000 mg/L prepared in methanol), and FLX limits of detection and quantification were 386 and 1285 µg/L, respectively. The concentration of FLX found in each sample, resulting from triplicate injections, was expressed as mg/L.

As in many studies in literature, this study was made in concentrations higher than environmental levels in order to study the process with more accuracy and precision, since it is known that adsorption is a quite efficient process even at low concentration levels (Mohanty *et al*., 2006).

5.3 Results and discussion

5.3.1 Preliminary adsorption assays

In this study, twelve different biochars prepared from forest and agri-food wastes were tested to evaluate their removal efficiency for the pharmaceutical compound FLX from aqueous solutions. Concerning the results obtained in the preliminary batch assays, it was found that the produced biochars reached a pharmaceutical removal ranging from 36% for pine to 100% for eucalyptus residues, respectively. These differences are related with the different physical (e.g. granulometry, specific surface area and pore size distribution) and chemical (e.g. type and abundance of functional groups present in the surface of the adsorbent) properties of the prepared biochars. These preliminary data enabled to select the produced biochars with the highest removal capacity, namely hollow tree, quince, eucalyptus, walnut tree and vine, in order to be subsequently fully characterized.

5.3.2 Biochar characterization

A detailed physico-chemical characterization was carried out for each selected biochar in order to understand their adsorption behavior.

Proximate and elemental analyses, and mineral composition of biochars are reported in Table 5.1.

Table 5.1 - Proximate and elemental analyses, and mineral composition of the selected biochars; the values presented correspond to the mean of replicates and respective standard deviation, except for elemental analysis.

Biochar source	**Eucalyptus**	**Hollow tree**	**Quince**	**Vine**	**Walnut tree**
Proximate analysis (% ar[a])					
Moisture	9.67 ± 0.10	5.40 ± 0.34	6.20 ± 0.18	4.32 ± 0.00	4.93 ± 0.04
Volatile matter	7.76 ± 0.15	18.2 ± 0.3	15.8 ± 0.6	16.9 ± 0.2	15.9 ± 0.4
Ashes	1.67 ± 0.09	4.55 ± 0.22	5.05 ± 0.39	5.90 ± 0.19	4.87 ± 0.46
Fixed carbon[b]	80.90 ± 0.01	71.85 ± 0.40	72.95 ± 0.30	72.88 ± 0.01	74.30 ± 0.01
Elemental analysis (% dbc)					
C	83.61	79.47	79.92	80.31	81.58
O[d]	12.75	13.79	12.86	11.13	10.79
H	1.56	1.88	1.55	1.73	2.12
N	0.41	0.31	0.62	0.93	0.64
S	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Mineral analysis (mg/kg db[d])					
Ca	3349 ± 107	19181 ± 1794	9947 ± 241	13236 ± 252	14710 ± 107
K	1944 ± 20	10599 ± 831	14437 ± 522	18469 ± 480	8922 ± 196
Na	1882 ± 43	209 ± 18	278 ± 8	376 ± 35	1425 ± 111
Fe	1407 ± 13	305 ± 17	1296 ± 15	748 ± 37	313 ± 11
Mg	1279 ± 10	2462 ± 211	2792 ± 18	2587 ± 130	2158 ± 29
Al	367 ± 21	127 ± 1	184 ± 3	333 ± 1	357 ± 43
Cr	208 ± 2	56 ± 18	265 ± 2	158 ± 13	64 ± 15
Ni	125 ± 5	43 ± 3	149 ± 0	114 ± 34	54 ± 3
Cu	87 ± 1	39 ± 5	101 ± 2	92 ± 5	87 ± 5
Zn	7.49 ± 0.74	7.91 ± 0.32	68.4 ± 0.3	77.6 ± 0.3	68.2 ± 1.3

[a]ar: as-received basis; [b]calculated as: 100 – (Moisture + Volatile matter + Ashes); [c]db: dry basis;

[d]calculated as: 100 - (C + H + N + S + Ashes); values are means ± standard deviations.

A relevant characteristic shown by these biochars was the high fixed carbon content. The prepared biochars are mainly composed by carbon (higher than 79% w/w for all biochars) and oxygen, with small amounts of hydrogen (less than 2.12% w/w) and nitrogen (less than 0.93% w/w). Ash content was low for all the biochar samples (less than 6% w/w). Sulfur is below 0.01% w/w in all the produced biochars. Regarding the mineral composition, Ca was the major element in all produced biochars, except for quince and vine, which presented higher levels of K. On the other hand, the lowest element content in biochars was found to be Zn, except for walnut tree which presented lower levels of Ni. The total mineral content of the analyzed chemical elements from vine biochar was 3.4-fold higher, if compared to the eucalyptus biochar, which presented the smallest mineral content (10655 *vs* 36191 mg/kg, in dry basis, for eucalyptus and vine, respectively). Eucalyptus biochar presents the lowest content of volatile matter, which may indicate that pyrolysis was able to convert more organic matter of this material, when compared with the other biochars, contributing to an increase of its porosity and specific surface area.

Table 5.2 summarizes the results of textural characterization, namely the specific surface area and pore volume, which influence the adsorptive capacity of the produced biochars, and pH_{pzc}. It is clear that eucalyptus biochar has the larger BET surface area and pore volume. The granulometric results obtained allow to verify that, although sieved to 75 μm, the materials still have particles with higher diameters, which may indicate elongated geometries. Table 5.2 reports the particle size distribution for the selected biochars, and it can be observed that 50% of particles have a diameter lower than 27 μm, which will influence the FLX adsorption.

Table 5.2 - Textural characteristics and pH_{pzc} of the selected biochars.

Biochar source	**Surface area (m^2/g)**	**Total pore volume (cm^3/g)**	**Particle size distribution (μm)**			**pH_{pzc}**
			D10	**D50**	**D90**	
Eucalyptus	335	0.17	3.87	13.54	53.96	9.75
Hollow tree	207	0.10	4.30	19.25	59.53	9.59
Quince	230	0.12	4.34	27.26	84.93	9.75
Vine	62	0.03	3.72	14.18	72.63	9.61
Walnut tree	219	0.11	3.79	15.60	66.06	9.85

The obtained FTIR spectra presented a very similar pattern for all the biochars. Peaks appearing at 3 440 cm^{-1} attributed to the O-H stretching vibration (Coates, 2006; Qian *et al.*, 2013) were identified, which in this case is related to the water present in samples, since they were not dried before FTIR analysis. The minor bands at 2 921 cm^{-1} and 2 853 cm^{-1}, more significant for vine, correspond to the stretching of C–H for aliphatic (alkane/alkyl) groups; the bands at 1 633 cm^{-1} and 1 385 cm^{-1} can be attributed to C=C and to methyl group ($-CH_3$) stretching vibration, respectively (Coates, 2006; Qian *et al.*, 2013). The bands at 1 454 cm^{-1} and at 877 cm^{-1}, more evident in hollow tree, can be assigned to aromatic ring stretch (C=C-C) and to aromatic C-H out-of-plane bend.

Thermogravimetric studies were carried out for the selected biochars to evaluate their thermal stability. The obtained results reveal that all samples are quite stable up to 600 °C, presenting mass losses lower than 10% w/w, which was expected as pyrolysis occurred at 500

°C. Above this temperature, eucalyptus biochar presented a rather insignificant degradation up to 850 °C with a total mass loss of around 8% w/w. Hollow tree biochar presented the higher mass loss at 850 °C (14% w/w). These results indicated that these biochar samples can be thermally regenerated/activated without a significant mass loss.

The pH_{pzc} is a very important parameter characterizing the acid-base behavior of the solids at which the net surface charge of the adsorbent becomes electrically neutral. The adsorbent surface tends to be negatively charged at $pH > pH_{pzc}$ and tends to attract cations, while at $pH < pH_{pzc}$ tends to be positively charged attracting anions from the solution (Sayğılı *et al.*, 2015). The experimental results of pH_{pzc} (Table 5.2) demonstrate the basic character of the produced biochars ($pH_{pzc} > 9$ for all biochars). These results agree with the overall literature about biochars that typically indicate basic properties (Ahmad *et al.*, 2014; Bis *et al.*, 2018; El-Naggar *et al.*, 2019) for this type of materials.

5.3.3 Kinetic assays

The effect of contact time on adsorption was determined in order to characterize the equilibrium adsorption time for the five selected biochars. This assay gives information about the rate at which the retention takes place and the minimum contact time required to reach the equilibrium (Sardella *et al.*, 2015). As it can be seen from Figure 5.1A, the FLX removal is very fast in the first minute of the adsorption assay. After the first fifteen minutes of the assay, the equilibrium was achieved for all the studied adsorbents. Thus, the contact time was fixed at this value for the following batch adsorption experiments. Moreover, the performed kinetic studies (Figure 5.1A) show that the amount of FLX adsorbed per gram of adsorbent is very similar for all the tested materials except for eucalyptus, which presents a much higher FLX adsorption capacity (5.74 vs 2.79 mg/g for eucalyptus and quince, respectively). This difference could be related with the fact that this material presents the highest total volume of pores and the highest specific surface area, at least 100 m^2/g higher than the other studied biochars, therefore more sites are available for the FLX adsorption.

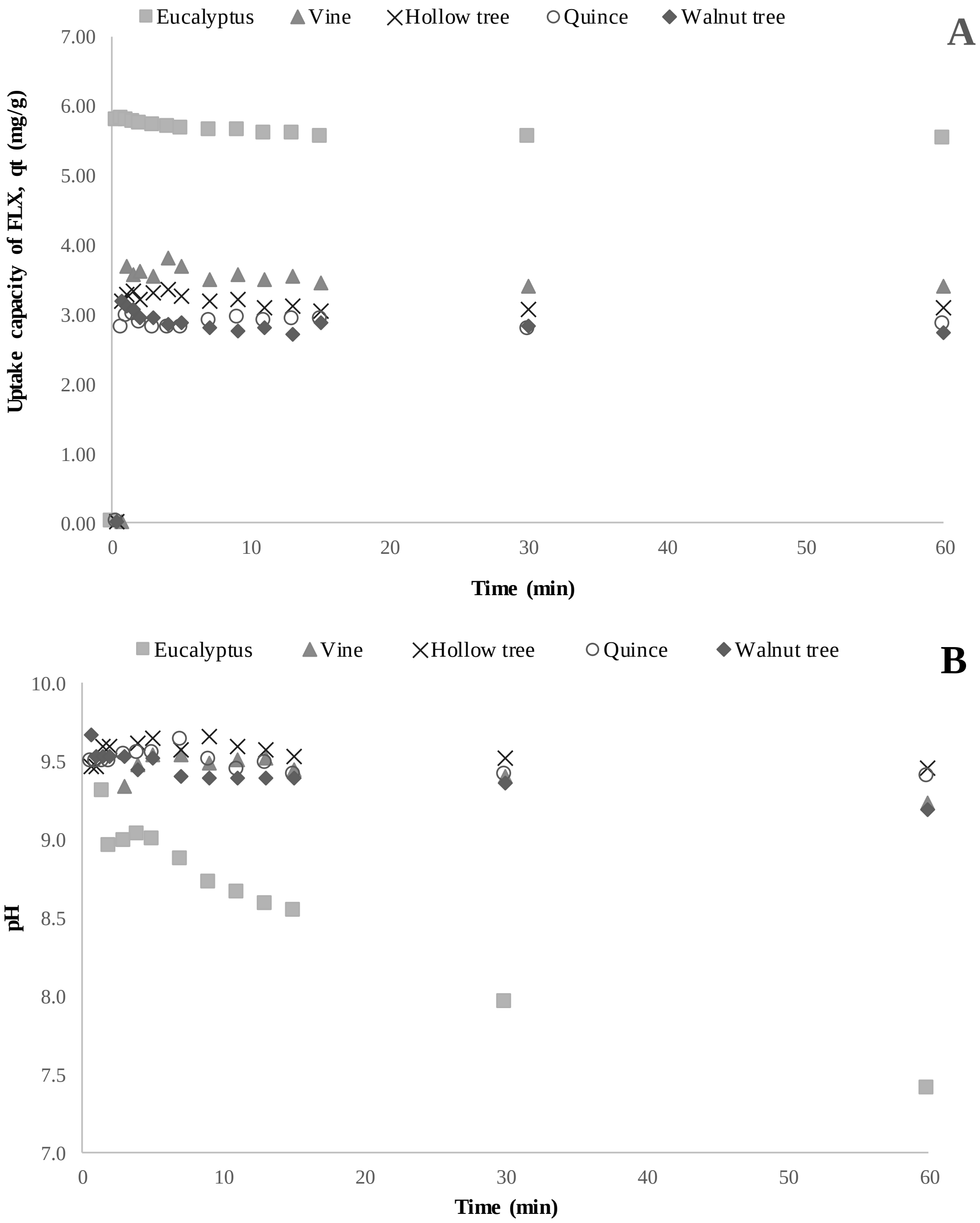


Figure 5.1 - Uptake capacity of FLX (A) and pH evolution (B) during kinetic experiments for the five selected biochars.

Additionally, the evolution of pH during the contact time was also measured (Figure 5.1B). The pH of the original solution of FLX (before adding the biochars) was 6.5. During the kinetic assays, the pH variation (Figure 5.1B) was not significant and converged to the pH_{pzc} values for all biochars, except for eucalyptus biochar, which showed a decrease from 9.30 to 7.40 during the 60 minutes of experiment. It suggests that it may occur an interaction biochar/adsorbate that originates neutral or moderately acid products.

5.3.4 pH studies

The effect of pH on the removal of FLX was investigated only for the three most promising biochars, namely eucalyptus, hollow tree and vine, in the range between 4.0 and 7.0. The selection was made considering the results obtained in the preliminary adsorption assays, as well as the information from the kinetic studies (Figure 5.1A), which showed that the highest uptake capacity of fluoxetine was obtained for eucalyptus, hollow tree and vine. Regarding the pH range, it was selected considering that in wastewater treatment plants the pH values allowed by biological treatments and permitted for discharge are near neutral. Despite the efforts to perform pH studies at values above the range tested (7.0-9.0), it was impossible to maintain the FLX solution pH value (blank) in the adjusted initial pH after 120 min. In fact, as it can be seen from Figure 5.2A analysis, for all blank assays, a decrease was noticed during the experiment, which was higher for higher initial pH values, namely for 7.0 a decrease of 0.9 units in the blank test was observed, except for pH 5.0 for which no significant variation was observed. The initial pH of the systems biochar/FLX in aqueous solution was adjusted to 4, 5, 6 or 7, as in the blank tests, but after 1 min changes were already noticed (Figure 5.2A) and final pH values (at 120 min) converged to 6.50 - 6.78 for eucalyptus and to 7.75 - 8.72 for hollow tree and vine, regardless of the initial pH. Although it was expected an increase of the pH towards the pH_{pzc} during the experiment, this was only observed in the first minutes (Fig. 2A, measurement at 1 min) and then a decrease was observed, which might be attributed to the behavior of FLX in aqueous solution as detected in the blank assays. This decrease was more significant in the eucalyptus biochar, as verified in the kinetic experiment probably due to its higher specific surface area (Table 5.2) that favors the interaction of the biochar surface and FLX.

Fig. 2B presents the effect of initial pH, ranging from 4.0 to 7.0, on the amount of FLX adsorbed per gram of adsorbent (q_e, mg/g). In the case of hollow tree and vine, it can be observed that the amount of FLX adsorbed was not influenced by pH. On the contrary, for eucalyptus, the FLX adsorption capacity increased at least 5.9 times, between pH 4.0 and 7.0, reaching a maximum value of 8.23 mg/g at an initial pH of 7.0. The pH is one of the most important factors on the adsorption process, affecting not only the solvent chemistry but also the surface binding sites of the adsorbent (Demiral & Güngör, 2016; Sardella *et al.*, 2015; Turk Sekulić *et al.*, 2018), which could explain the obtained differences for the FLX adsorption. In fact, the pH solution can control the electrostatic interactions between the adsorbent and the adsorbate (Özçimen & Ersoy-Meriçboyu, 2009). The differences observed between FLX adsorption at different pH values could be related with the electrostatic interaction between the net surface charge of the adsorbent and the electric charge of FLX molecules. Once the pKa of FLX is 9.8, for all pH values studied (pH < pK_a), the molecules were mainly protonated, increasing the net positive charge with the decrease of pH (Silva *et al.*, 2019).

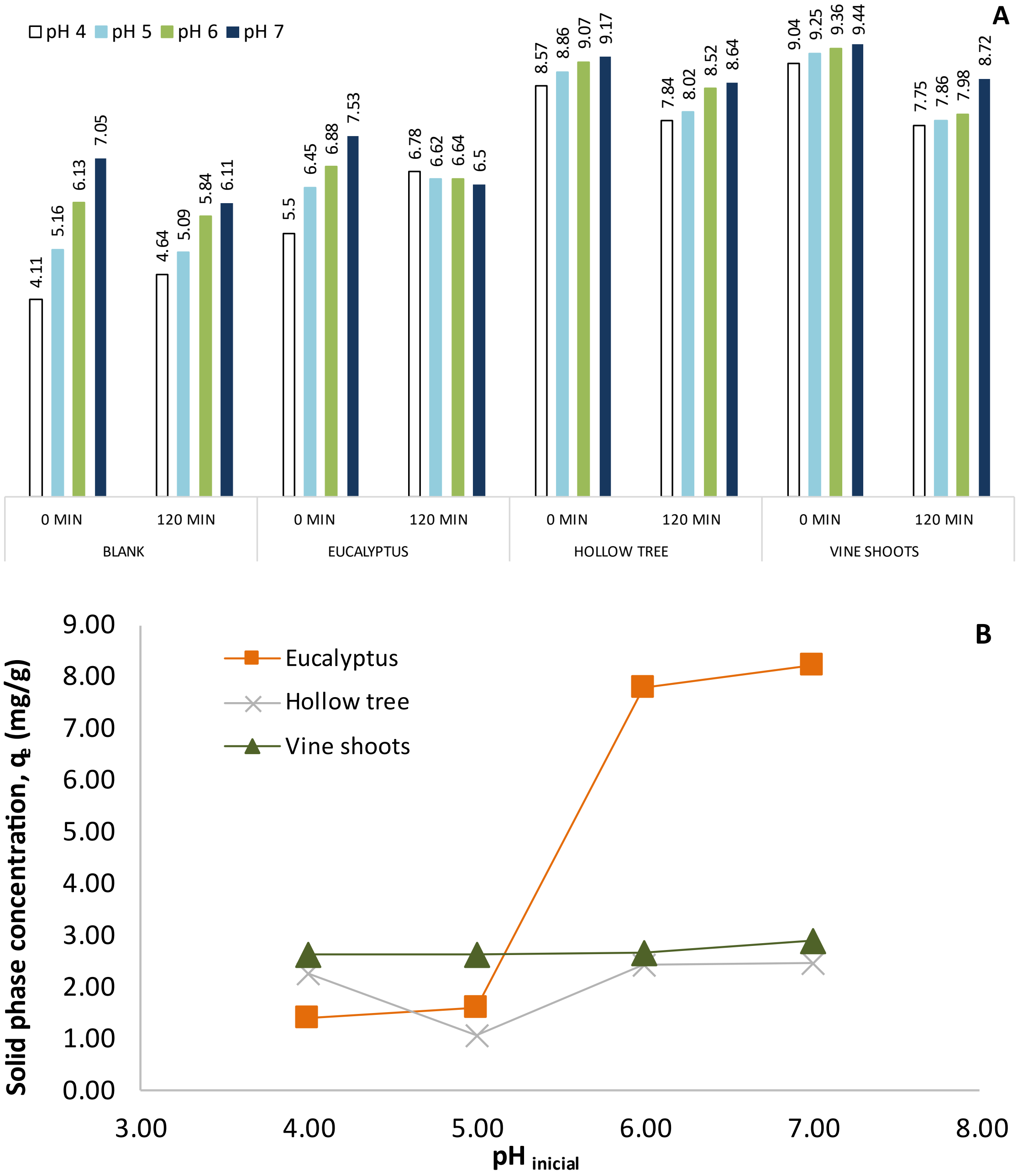


Figure 5.2 - Effect of biochar material on pH values at the beginning and end of the experiment (A) and effect of initial pH (B) on FLX adsorption for the three most promising adsorbents, namely eucalyptus, hollow tree and vine.

Regarding the biochars tested, all the pH_{pzc} values were above 9.59 (Table 5.2), which means that in the pH range of the experiments (5.5 to 9.5) the biochars should be positively charged (pH < pH_{pzc}) contributing to the electrostatic repulsion between the adsorbent and the adsorbate. This repulsion increases as the pH decreases, since 2 units below the pK_a FLX should be positively charged and the same occurs for biochars 2 units below the pH_{pzc} (Andreia

Silva *et al*., 2019). The maximum electrostatic repulsion should occur below pH 7, but this was not the main factor that influenced the adsorption, since the best results were obtained for eucalyptus biochar near this pH value.

Other factors should also be considered, namely the direct interaction of the pharmaceutical with the surface functional groups on the biochar surface, to explain the increase of adsorption capacity of eucalyptus biochar at initial pH in the range 6.0 to 7.0. From the functional groups identified in the FTIR of this biochar, there are no groups with marked acidic or alkaline characteristics that could be involved in the adsorption process. However, some functional groups on the biochar surface become deprotonated when pH increases and therefore negatively charged, thus favoring adsorption of the pharmaceutical compound (Andreia Silva *et al*., 2019).

Additionally, another assay was also carried out to evaluate the pH influence, where the pH adjustment was made after leaching of the biochars and FLX solution was added just before the experiment. In this case, no variations of pH values were noticed during the experiment: the initial and final pH values were, respectively, 6.96 and 7.09 for eucalyptus, 7.76 and 7.75 for hollow tree and 7.60 and 7.68 for vine. Concerning the amount of FLX adsorbed, no considerable improvements were observed compared to the values obtained in the above-mentioned pH study (7.21, 2.66 and 3.01 mg/g for eucalyptus, hollow tree, and vine biochars, respectively).

5.3.5 Adsorption isotherms

Adsorption isotherms are very important to understand how the molecules or ions of FLX interact with surface sites of the biochars selected. Therefore, the correlation of experimental data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of its extent (Demiral & Güngör, 2016).

The results of the equilibrium studies for the five selected biochars together with the fitted models are presented in Figure 5.3A. The estimated models' parameters, correlation coefficients and RMSE are gathered in Table 5.3. A comparative analysis of the statistical parameters shows that the Freundlich's model (Table 5.3), which presented the smallest values of RMSE and the greatest values of r^2, was the best fit although Langmuir model could also fit the equilibrium results. These results suggest that the biochars tested have heterogeneous adsorption sites, which are favorable for adsorption phenomenon (Cobas *et al*., 2016; Turk Sekulić *et al*., 2018). Additionally, the obtained results led to the conclusion that eucalyptus is the most efficient FLX adsorbent, as the maximum Langmuir monolayer adsorption capacity (Q_m) is at least 2-fold higher than for the other biochars. On the other hand, the biochar walnut tree was characterized by the lowest adsorption capacity (2.30 mg/g). Concerning the Freundlich's parameters, K_F, which represents the tendency of the adsorbent to adsorb, was found to decrease in the sequence eucalyptus > hollow tree > vine > walnut tree > quince, which agrees with the results revealed by Langmuir's model. The parameter n, which characterizes the ability of the FLX to be adsorbed, presented values higher than 1, indicating favorable adsorption of FLX for all the investigated biochars. These results confirm the ones obtained with the kinetic study, in which eucalyptus biochar performed better. The best textural properties presented by this material (Table 5.2) played the major role on FLX removal.

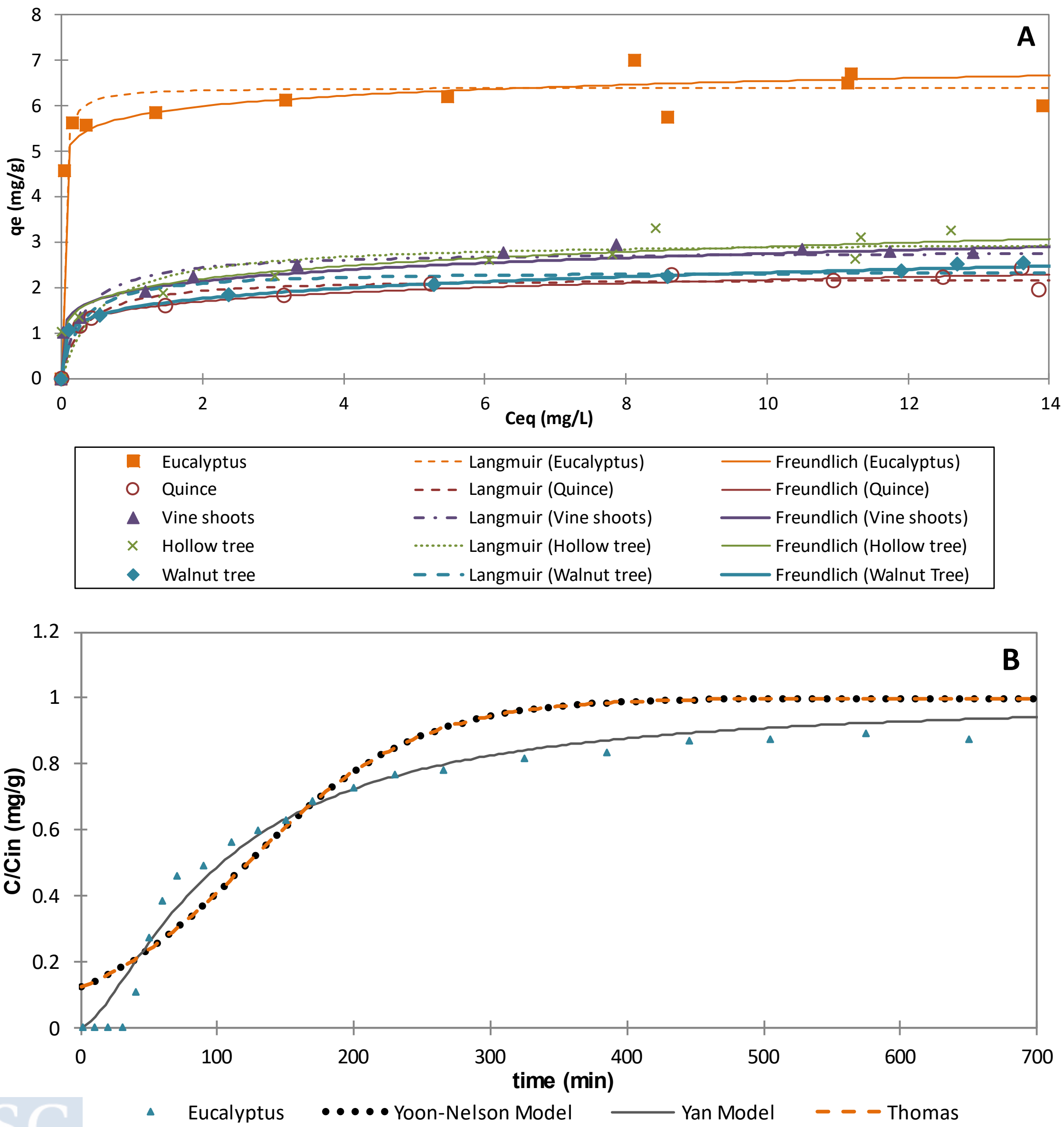


Figure 5.3 - Experimental results and fitted models for equilibrium batch (A) and continuous (packed column) studies (B).

Several studies have been conducted using different types of adsorbents for FLX removal (Jaria *et al.*, 2015; Andreia Silva *et al.*, 2019), although only one study was found regarding the use of biochars prepared from fishbones (Piccirillo *et al.*, 2017). In the present study the adsorption capacity of the majority biochars tested was found to be lower than the adsorption capacity reported by Piccirillo *et al.* (2017). These authors employed higher pyrolysis temperatures (ranging from 600 to 1 000 °C) and the highest adsorption capacity was obtained at 1 000 °C (55.87 mg/g). Comparing the obtained Q_m values for similar pyrolysis temperatures, in the present study it was obtained a maximum adsorption capacity of 6.41 mg/g for eucalyptus at 500 °C, which is 2.5 times higher than the value obtained with fishbones biochar at 600 °C (2.52 mg/g). Despite of the lower adsorption capacity when compared to commercially available adsorbents (Jaria *et al.*, 2015; Andreia Silva *et al.*, 2019), this study demonstrated that the investigated biochars could be considered as promising alternative low-cost materials for the removal of FLX from aqueous solutions.

Table 5.3 - Langmuir and Freundlich isotherm parameters for fluoxetine adsorption

Biochar source	**Langmuir model**				**Freundlich model**			
	K_L (L/mg)	Q_m (mg/g)	r^2	RMSE	K_F ([(mg/g) (L/mg)$^{1/n}$)]	*n*	r^2	RMSE
Eucalyptus	45.37	6.41	0.93	0.51	5.77	18.29	0.95	0.44
Hollow tree	1.87	3.04	0.88	0.43	1.95	5.79	0.94	0.25
Quince	3.41	2.21	0.95	0.17	1.53	6.53	0.96	0.14
Vine	3.38	2.80	0.93	0.29	1.93	6.47	0.96	0.19
Walnut tree	3.85	2.37	0.94	0.22	1.56	5.76	0.99	0.07

5.3.6 Column adsorption assay

To evaluate the behaviour of the most promising biochar, produced from eucalyptus biomass wastes, in a continuous adsorption process, experimental assays were performed using a fixed-bed column. To the best of authors' knowledge, this is the first continuous study in packed column using biochars for the adsorption of FLX.

In this experiment, FLX reached the saturation after approximately 10 h (Figure 5.3B). Three models, namely Yoon-Nelson's, Thomas's and Yan's were selected to be fitted to the experimental, which are represented in Figure 5.3B. The parameters, the correlation coefficients as well as RMSE obtained for each model were determined (Table 5.4).

The Thomas model is usually employed to estimate the extent and rate constant of sorption and assumes that the external and internal mass transfer resistances are not limiting steps (Martínez-lladó *et al.*, 2011). The Yoon and Nelson (1984) model was only used as a descriptive model. Yoon-Nelson's and Thomas's models presented the same parameters and therefore the same fitted curve. Yan's model can overcome the Thomas model deficiency in predicting the concentration at initial times and provide a more accurate description of the different parts of the breakthrough curve (G. Yan *et al.*, 2001; G. Yan & Viraraghavan, 2001), what justifies its better performance (higher correlation coefficient, 0.974, and lower RMSE, 0.056).

Table 5.4 - Parameters for the Yoon-Nelson, Thomas and Yan models for the adsorption of FLX onto eucalyptus biochar in a fixed-bed column.

Model	**Parameters**	**Eucalyptus biochar**
Yoon-Nelson	k_{YN} (min^{-1})	0.016
	τ_{YN} (min)	122.081
	RMSE	0.124
	r^2	0.900
Thomas	k_{TH} (mL/(mg min))	0.629
	q_{TH} (mg/g)	1.57
	RMSE	0.124
	r^2	0.900
Yan	a_{Ya}	1.454
	q_{Ya} (mg/g)	1.322
	RMSE	0.056
	r^2	0.974

The adsorption capacity predicted by this model for eucalyptus in the column (1.3 mg/g) was 5 times lower than the predicted by the Langmuir isotherm (6.4 mg/g). The amount of FLX adsorbed during the column experiment (estimated by numerical integration of the area above the breakthrough curve) reached the level of 4.3 mg/g, which is in accordance with the value predicted by the Langmuir isotherm considering that the estimation of the capacity based in experimental values was underestimated (the saturation of the adsorbent was not achieved, only 89% was reached). The breakthrough for 50% removal can be estimated as 90 minutes for eucalyptus biochar.

5.4 Conclusions

The present study demonstrated that biochars prepared from different forest/agri-food wastes could be used as effective adsorbents for FLX removal, with adsorption capacities ranging from 2.21 to 6.41 mg/g (Langmuir model) for the five selected biochars, eucalyptus biochar presented the highest adsorption capacity, followed by hollow tree, vine, walnut tree and quince. Adsorption kinetics was fast (less than 15 min). Additionally, column adsorption assays demonstrated good performance of this low-cost adsorbent in continuous mode, showing that eucalyptus biochar can be effectively used as renewable alternative for FLX removal. Future studies on life cycle assessment and cost analysis will be performed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2019.121973.

Appendix A. Supplementary data

Table 1S. Langmuir and Freundlich isotherm model parameters for fluoxetine adsorption in biochars from different feedstocks

Biochar feedstocks	**Pyrolysis operating conditions**				**Adsorption Assay conditions**	**Langmuir parameters**		**Freundlich parameters**		**Reference**
	T (°C)	**Residence time (h)**	**Inert gas Flow**	**Other**		K_L (L/mg)	Q_m (mg/g)	K_F ($mg^{1-1/n}$. $L^{1/n}$. g^{-1})	n	
Eucalyptus *(Eucalyptus)*	500	24	Recirculation of pyrolysis gas	Industrial oven	400 rpm, room temperature	45.37	6.41	5.77	18.29	This study
Quince *(Cydonia oblonga*)						3.41	2.21	1.53	6.53	
Vine (*Vitaceae*)						3.38	2.80	1.93	6.47	
Holm oak *(Quercus ilex)*						1.87	3.04	1.95	5.79	
Walnut Tree (*Juglandaceae*)						3.85	2.37	1.56	5.76	
Fishbones	600	1	N_2 - 100 m/min	Temperature ramp of 5 °C/min	70 rpm, 30 °C, pH 8	-	2.52	0.78	-	(Piccirillo *et al.*, 2017)
	700					-	18.18	5.14	-	
	800					-	33.22	7.59	-	
	900					-	34.48	8.64	-	
	1000					-	55.87	12.53	-	

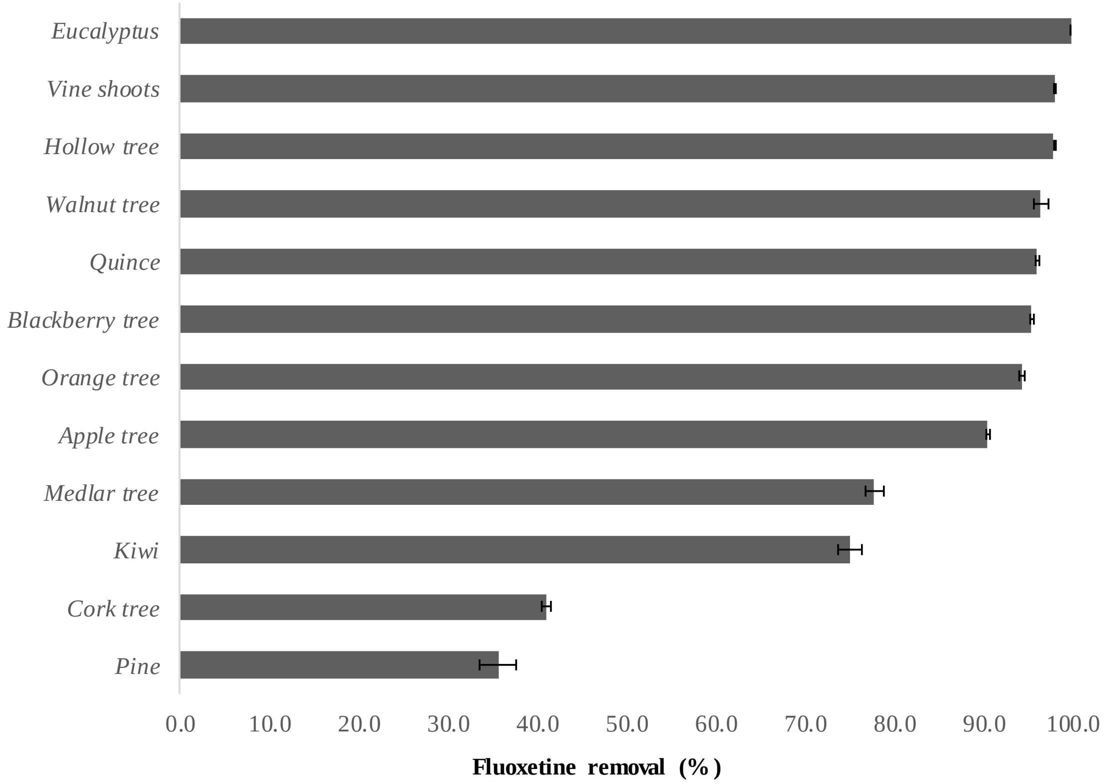

Figure 1S. Fluoxetine removal (%) for twelve different biochars prepared from forest and agri-food wastes in batch assays.

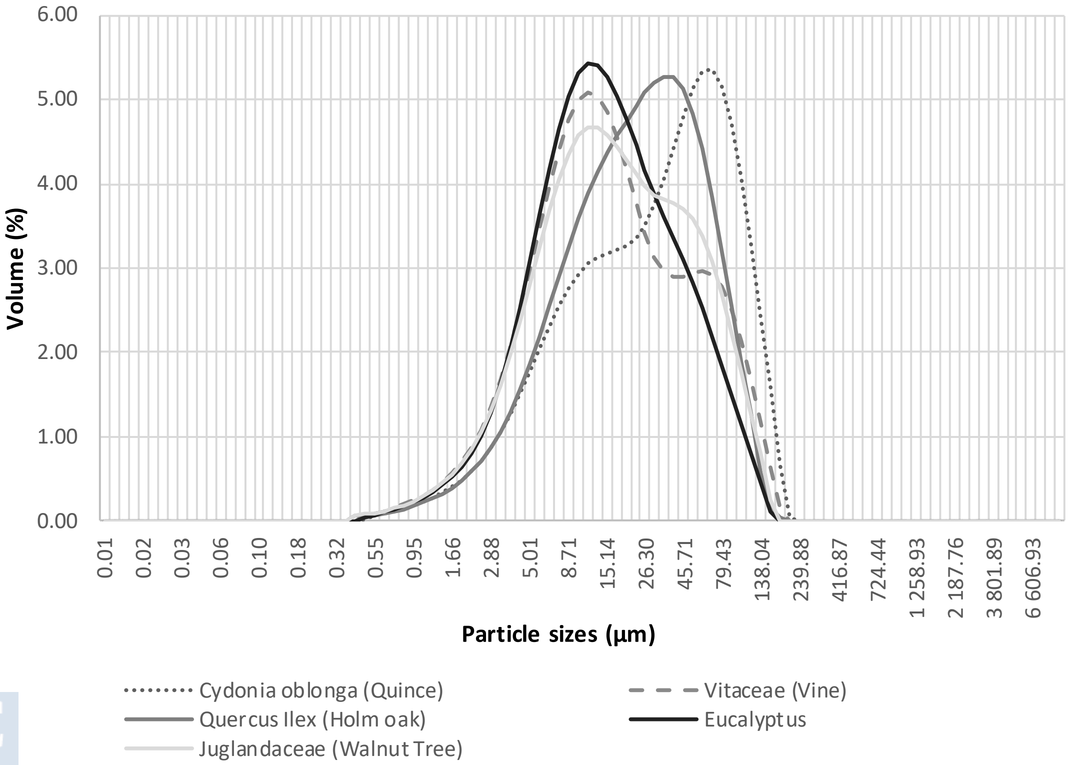

Figure 2S. Particle size distribution for the selected biochars.

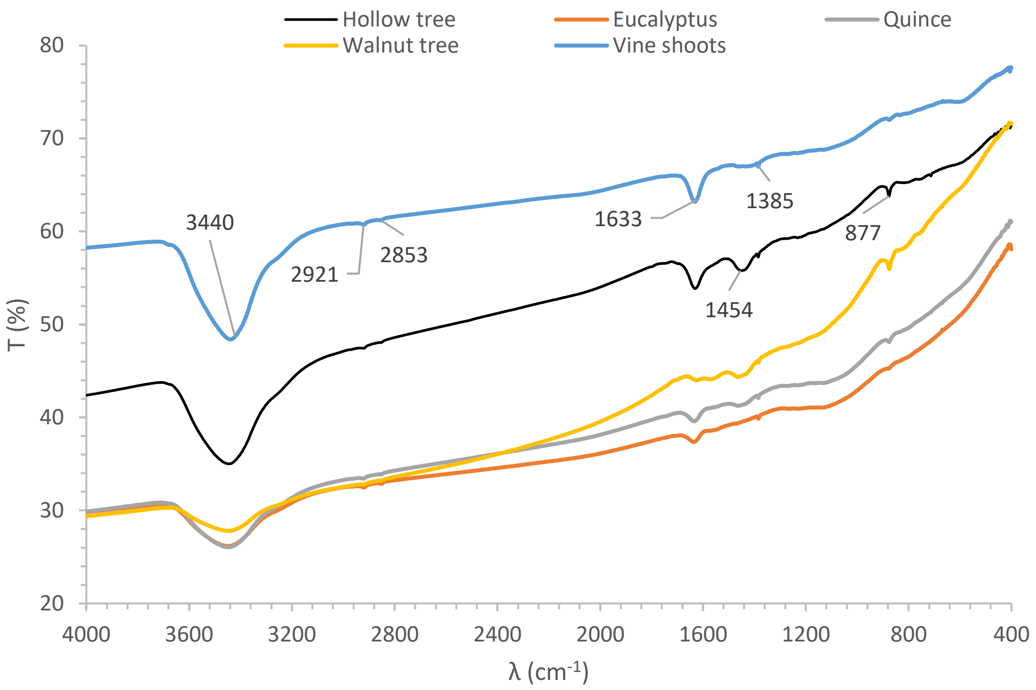

Figure 3S. FTIR spectra of the selected biochars, namely eucalyptus, hollow tree, quince, vine and walnut tree.

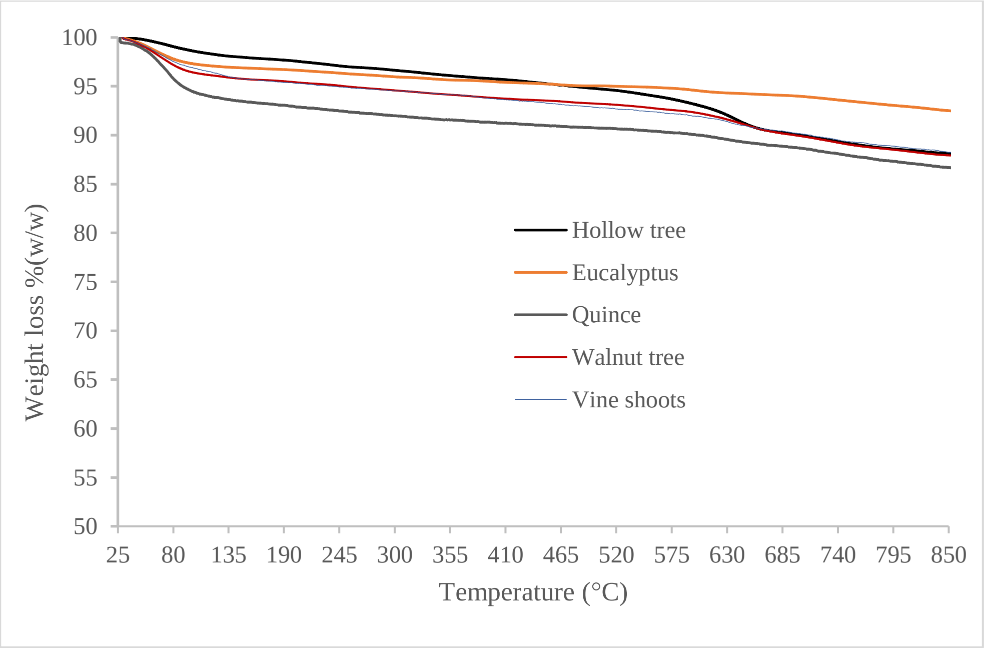

Figure 4S. Thermogravimetric analysis of the selected biochars, namely eucalyptus, hollow tree, quince, vine and walnut tree.

CHAPTER 6 INFLUENCE OF ADSORBENT MATERIAL AND ITS CHARACTERISTICS ON THE GLYPHOSATE, AMPA AND GLUFOSINATE REMOVAL

This chapter assesses the application of the same treatment technologies – adsorption – but applied to water contaminated with herbicides glyphosate (alongside with its degradation product, AMPA) and glufosinate. The adsorbent materials tested were biochar's from different sources, soils and tailor-made Technosols. Batch adsorption experiments were performed and the influence of characteristics as solution pH and point zero charge pH of the adsorbents were accomplished.

Its development pursues to study and adjust this treatment technology considering its implementation, for example, in soil, where the herbicides are normally applied, allowing minimizing the entry of this contaminants into surface and groundwater and, consequently, its propagation. Understanding what the most important characteristics to consider in the construction of a tailor-made Technosol is, in addition, an objective of the work presented, since it is a more complete remediation technology, which can include not only adsorption but also other types of treatment such as the degradation of adsorbed compounds through the inclusion of materials capable of developing it.

A paper from this study will be submitted for publication:

- Maria João Fernandes, Paula Paíga, Sónia Figueiredo, Felipe Macías, Cristina Delerue-Matos. "Influence of adsorbent material and its characteristics on the glyphosate, AMPA and glufosinate removal". Bioresource Technology (2023) (under review).

Abstract

The widespread use of pesticides is an ingrained practice fostered by intensive agriculture to achieve efficient and sustainable production. The exposure level of humans and animals and the hazardous effects of these compounds is largely documented. Glyphosate and glufosinate, two broad-spectrum, non-selective, organophosphorus herbicides, and aminomethylphosphonic acid (AMPA), the primary metabolite of glyphosate, are three of these compounds of concern. Adsorption is a process that may prevent the uncontrolled migration and availability of pesticides in soil. The selection of the adsorbent material is of serious concern, and characteristics such as low-cost, sustainable, non-toxic, and high sorption capacity are essential attributes to be considered. Laboratory batch assays were conducted to investigate the adsorption kinetics and equilibrium of glyphosate, AMPA, and glufosinate onto three different materials: biochars, soils, and tailor-made Technosols (TMT). Moreover, the pH influence in the adsorption process was also studied. The equilibrium was reached in 14 h and 72 h in natural soils and Technosols, respectively. The maximum adsorption capacity obtained for glyphosate was 10.84 mg g^{-1} onto soils. On the other hand, for AMPA, the highest value was 15.08 mg g^{-1} for the adsorption onto TMT. The results revealed that natural soils and TMT can be used as effective, low-cost, and sustainable adsorbents to remove glyphosate and AMPA from aqueous solutions. TMT can prevent the migration of these pesticides and allow their remediation.

Keywords: Adsorption; Biochar, Characterization; Contaminated soils, Herbicide; Waste valorization;

Abbreviations: TMT, Technosol; AMPA, Aminomethylphosphonic acid; HPLC-FLD, High-performance liquid chromatography with fluorescence detection; SEE, standard error of estimate; RPM, Rotation per minute; SD, Standard deviation;

6.1 Introduction

The use of pesticides is a deep-rooted practice for plant protection and to achieve efficient and productive crops, demanded by intensive agriculture (McGinley *et al.*, 2022). According to Eurostat, between 2011 and 2020, Europe’s total annual pesticide sales increased by 4.4% (from 386 999 to 404 179 tonnes), reaching a peak of 439,790 in 2016. In 2020, almost 34% of the employed pesticides were herbicides (Eurostat, 2022)

Glyphosate (N-(phosphonomethyl) glycine) is an active ingredient in numerous commercial broad-spectrum, non-selective, organophosphate herbicides and is by far the most used pesticide worldwide (IARC, 2017; Kumari *et al*., 2016). Essential amino acids production required for the weed photosynthetic processes is blocked by this herbicide, which inhibits the synthesis of enolpyruvylshikimic phosphate (C. Zhou *et al*., 2020). It is applied for agronomic purposes, including weed control, crop desiccation, ending cover crops/grassland, or renewing permanent grassland and urban weed control (Clémentine Antier *et al*., 2020). Its widespread use can be related to several characteristics such as high efficacy, broad spectrum, and low cost, combined with the introduction of genetically engineered glyphosate-tolerant crops (Fogliatto *et al*., 2020). Aminomethylphosphonic acid (AMPA) is a glyphosate primary metabolite and was 3 to 6 times more resistant to degradation, being an emergent environment concern (Grandcoin *et al*., 2017; Sun *et al*., 2019).

Similarly to glyphosate in chemical structure and use, glufosinate-ammonium is a nonselective, foliar-applied herbicide that inhibits a key enzyme (*glutamine synthetase*) involved in plant nitrogen assimilation (Takano & Dayan, 2020). Although the market share of glufosinate-resistant crops is smaller, when compared to glyphosate-resistant crops, mainly due to the higher cost and weaker performance as a wide-ranging herbicide, glufosinate is largely applied to maize, cotton, canola, and soybean fields infested with glyphosate-resistant weeds (S. O. Duke & Dayan, 2011; C. Zhou *et al*., 2020).

Environmental Protection Agency (EPA) national primary drinking water regulations already presented glyphosate in the list of organic contaminants in drinking water with a maximum contaminant level of 700 μg L^{-1} (EPA, 2009). In Europe, the Commission Directive (EU) 2015/1787, containing the established limit to water intended for human consumption, refers to "*pesticides and their relevant metabolites, degradation and reaction products*", establishing a maximum individual value of 0.1 μg L^{-1} and a limit the total value of 0.5 μg L^{-1}. It is also mentioned that "*only those pesticides which are likely present in a given supply need be monitored*" (European Commission, 2015a).

The presence of these compounds has been reported in a variety of studies, including in soils (Battaglin *et al*., 2014; V. Silva *et al*., 2019), water/groundwater (Geng *et al*., 2021; Grandcoin *et al*., 2017; Medalie *et al*., 2020; Poiger *et al*., 2017; Van Bruggen *et al*., 2018), and air (Ramirez-Haberkon, Aimar, *et al*., 2021; Ramirez-Haberkon, Aparicio, *et al*., 2021). Additionally, they have also been found in grains and commercial food products (Bou-Mitri *et al*., 2022; Y. Liao *et al*., 2018; J. Xu *et al*., 2019), human urine (Bootsikeaw *et al*., 2021; Campbell *et al*., 2022; Connolly *et al*., 2020; Grau *et al*., 2022; Nova *et al*., 2020; Ospina *et al*., 2022; Schütze *et al*., 2021) and blood (Gillezeau *et al*., 2019), and maternal milk (Camiccia *et al*., 2022), revealing the level of exposure to which humans and animals have been subjected.

The toxic effects of glyphosate, AMPA and glufosinate on mammalian and aquatic organisms have been the focus of research studies. Glyphosate and glufosinate-ammonium are linked with unwanted effects on mammalian development (EFSA, 2005, 2015). Furthermore, the glyphosate contribution to the potential chronic toxicity in aquatic organisms was recently assessed (Bonansea *et al*., 2018; D. J. Pérez *et al*., 2021). Lethal and genotoxic effects (e.g. in zebrafish larvae) (de Brito Rodrigues *et al*., 2019) were related to glyphosate and AMPA exposure as well as stimulation of harmful algal growth (Dabney & Patiño, 2018) and impaired tadpole motility (Agostini *et al*., 2020). Also, immunotoxicity, increased levels of oxidative stress and deformities in zebrafish embryos (Xiong *et al*., 2019) were associated with glufosinate exposure. Additionally, glyphosate's potential to cause an increased prevalence of respiratory diseases and symptoms (Seesen & Sapbamrer, 2020) and perturbations of the reproductive system at distinct levels (from hormonal pathway disruption to potential teratogenicity) has been described in humans. Moreover, severe mammary, hepatic and kidney hormone-dependent disturbances, altered reproductive behavior, and tumor-promoting effect (hemangiosarcoma, adenomas, kidney, and liver tumors, malignant lymphomas, skin keratoacanthomas, and basal cell tumors) in rats were also reported (Ojelade *et al*., 2022; Portier, 2020; Séralini *et al*., 2014). Despite the evidence of posing a risk to the environment and also human and animals health, the European Commission (EC) recently renewed the use of glyphosate-based herbicides until December 15 of 2023, approving a one-year extension on the previous five-year authorization (European Commission, 2022b).

Depending on environmental conditions, including soil characteristics such as temperature, moisture, type, binding extent, endogenous microbial populations and activity, and phosphate levels, glyphosate persistence in the soil varies extensively, with a half-life ranging between 1 and 215 days (Al-Rajab & Hakami, 2014; Muñoz *et al*., 2021; Zhelezova *et al*., 2017). AMPA, which is more persistent in soil and water, presents a half-life between 23 and 958 days (Bento *et al*., 2016, 2017; Spengler *et al*., 2021; Yang *et al*., 2015). Oppositely, glufosinate ammonium presents low persistence in soil, with a half-life between 6 and 20 days. Additionally, a high persistence is described in water, with a half-life of more than 300 days (National Center for Biotechnology Information, 2023a). Therefore, developing methodologies for the remediation of environmental contaminations in soil and water by the referred compounds is of utmost importance. Several remediation technologies have been studied and developed, namely bioremediation (Zhan *et al*., 2018), advanced oxidation (Feng *et al*., 2020; Kudzin *et al*., 2019), and adsorption (Feng *et al*., 2020; Ighalo *et al*., 2021; Mojiri *et al*., 2020).

Adsorption to a solid (adsorbent) is an interface process that may involve physical interactions (electrostatic forces) and chemical bonds in and therefore attaches species (adsorbates) from the gas or liquid phase. Consequently it significantly affects the transfer and availability of pesticides in soil, being one of the main processes of controlling pesticide leaching and reducing the ability of their migration and the potential to contaminate surface waters or groundwater (Sidoli *et al.*, 2016). It is extensively used in large-scale wastewater treatments due to its simple layout, and high efficiency along with use of low-cost and non-toxic adsorbents. The removal of glyphosate from an aqueous environment by adsorption has been investigated, evaluating the use of a wide variety of materials as adsorbents (e.g., activated carbon, biochar, chitin, and chitosan, and minerals such as zeolite, goethite and clay soils) (Herath *et al.*, 2016; Nourouzi *et al.*, 2012; Rissouli *et al.*, 2017; Vasiljević *et al.*, 2019). The selection of the adsorbent material is of high concern, with characteristics such as low-cost, sustainable, non-toxic, and high sorption capacity as important attributes to consider.

Biochar is a solid and stable porous material with high carbon content, manufactured through pyrolysis/carbonization of biomass under a limited or absent oxygen environment and moderate temperature conditions (< 700 °C). It is an attractive solution to be implemented as a soil amendment, as well as for removing pollutants from aqueous environments. Its use presents itself as a tool for environmental management, acting in soil improvement, waste treatment, climate change mitigation, and energy production (Ahmad *et al.*, 2014; Lehmann & Stephen, 2009; N. Li *et al.*, 2022; McGinley *et al.*, 2022; Rajapaksha *et al.*, 2014). Recent studies demonstrated that its application enhances the physicochemical and biological properties of soils, such as water and nutrient retention capacity, soil structure, microbial population, and activity (Ahmad *et al.*, 2014; El-Naggar *et al.*, 2019; Goldan *et al.*, 2022). Besides being economically attractive (e.g., low-cost feedstock and energy generation), the production of biochar from biomass also allows by-product/waste valorization, heat, and gases capture to energy carriers production (electricity, bio-oil, or hydrogen) (Lehmann, 2007), carbon sequestration, and soil fertility improvement (Ahmad *et al.*, 2014; McGinley *et al.*, 2022). The feedstock selection can largely influence the properties of the biochar, as well as the production process conditions, namely temperature range, heating rate, pressure, and residence time (El-Naggar *et al.*, 2019; K. Weber & Quicker, 2018). Forest and agro-food residues, animal manure, *algae*, paper mill waste, municipal solid waste, and sewage sludge are raw materials that can be used to produce biochar (Alazaiza *et al.*, 2023; Coimbra *et al.*, 2015; M. J. Fernandes *et al.*, 2019; Goldan *et al.*, 2022; N. Li *et al.*, 2022; Lonappan *et al.*, 2018; Lu *et al.*, 2018; Saiz-Rubio *et al.*, 2019). Biochar materials are largely used as adsorbents due to their high adsorption capacity for distinct contaminants associated with their high surface area and porosity (nano, micro, meso, and macropores), ion exchange capacity, and pH (Herath *et al*., 2016; Mojiri *et al*., 2020). In addition, the biochars used for the adsorption of contaminants can promote other benefits for the environment in which they are applied (e.g., soil), such as improved fertility (e.g., through the addition or/and immobilization of nutrients and water retention ability), soil correction, carbon storage, and enhanced biodiversity (Cha *et al*., 2016; Hedde *et al*., 2019; Macías & Arbestain, 2010). The mixture of various materials can be an advantage to achieve these benefits, as is the case of tailor-made Technosols (TMT) (Ruiz *et al*., 2020).

The preparation of TMT currently represents a challenge in the rehabilitation of soil and water (Macías & Arbestain, 2010; E. S. Santos *et al*., 2017). Technosols are anthropogenic soils, significantly dominated or strongly influenced by human-made material (bricks, glass, slag, household garbage, mine waste, etc.) (IUSS Working Group WRB, 2015). Constructed TMTs are engineered soils which combine anthropogenic materials derived from human activities with other additives to obtain the desired characteristics. They replicate functions of natural soil and can be used to provide several soil functions and ecosystem services, such as suitable conditions for plant growth/production (food and biomass), soil remediation, carbon sequestration, restoring water bodies and degraded or polluted areas, groundwater recharge and ecosystem biodiversity (Arán *et al*., 2018; Barredo *et al*., 2020; Camps Arbestain *et al*., 2008). Besides the attractive advantages and usefulness, TMTs are an economically feasible method of re-using waste products or waste-derived materials, such as sludges, fly ashes, organic compost, biochar, foundry sand, and construction residues. Simultaneously, its production and use promote the recycling of essential nutrients and the stabilization of organic matter (OM) present in such materials (Barredo *et al*., 2020; Camps Arbestain *et al*., 2008), following the principles of a circular economy. When applied, TMT progresses through natural processes of pedogenesis, showing a high capacity for retention, immobilization, and decomposition of contaminants (Barredo *et al*., 2020; Macías & Arbestain, 2010). To date, few studies have been carried out regarding the adsorption of glyphosate, AMPA, and glufosinate in soils and biochar, and there are no studies on the adsorption of these compounds in TMT (H. A. Pereira *et al*., 2021). This study aimed to analyze the adsorption of glyphosate, AMPA, and glufosinate-ammonium from aqueous solutions onto various materials, namely soils, biochar from several feedstocks, and TMTs. High-performance liquid chromatography with fluorescence detection (HPLC-FLD) was used to quantify the tested contaminants. The comparison between the adsorption in the different matrices could illustrate the potential role that TMT and/or biochar may play in controlling the environmental behavior of these contaminants. Understanding the main characteristics of these materials as sorbents will contribute to the development of TMT for the remediation of contaminated sites.

6.2 Materials and methods

6.2.1 Chemicals and reagents

Standards of glyphosate (purity 99.5% HPLC), aminomethylphosphonic acid (AMPA) (purity 99.0%), and glufosinate-ammonium (purity 97.9% HPLC) were acquired from Sigma-Aldrich (Germany). A Simplicity 185 system was used for ultra-pure water production (Millipore resistivity of 18.2 MΩ.cm). The glyphosate, AMPA, and glufosinate-ammonium solutions were prepared daily using polypropylene volumetric flasks at a concentration of 12.5 mg L^{-1} by dissolving 12.5 mg of each reagent in 1 L of ultra-pure water. Hydrochloric acid (HCl) and sodium hydroxide (NaOH, purity > 99.0%), used for pH adjustments, were obtained from VWR (France). The stock solution (3.75 mM) of 9-fluorenylmethyl chloroformate (FMOC-Cl) (purity 99.0%, Sigma-Aldrich (Germany) was daily prepared to dissolve 19.4 g in 20 mL of acetonitrile (HPLC grade, purchased from VWR, France). Borate buffer solution (Borax, 25 mM $Na_2B_40_7·10H_2O$, pH = 9) was prepared by dissolving 4.77 g of sodium tetraborate decahydrate (Sigma-Aldrich, Germany) in 500 mL of ultra-pure water and pH was adjusted with NaOH. Methanol (Honeywell, Riedel-de Haën) was purchased from VWR, and 5mM ammonium hydrogen carbonate (purity 99.0%, Alfa Aesar) at pH 9 was acquired from Thermo Fisher Scientific (Germany). The eluents used in the chromatographic analysis were filtered through a 0.22 µm nylon membrane filter 47 mm (Fioroni Filters) using a Dinko D-95 vacuum pump and degassed for 15 min in an ultrasonic bath (Selecta P).

6.2.2 Adsorbent Materials Preparation/Source

Forty-one samples of three types of materials were tested – biochar, soil, and TMTs. The tested biochars, produced from different raw materials and kindly provided by (Saiz-Rubio *et al.*, 2019), result from a variety of feedstocks: acacia (*Acacia melanoxylon*) trunk divided in sapwood (BAcSw-3) and heartwood (BAcHw-2), eucalyptus branches (BEu-2), pine sawdust (BSd-1), pine bark (BPb), olive pomace compost (BOpc), rice husk (BRh), corncob (BCc1 and BCc-2), and German crushed wood chips (BSdG). Biochar samples production methodology is briefly described: produced in an experimental unit of biomass pyrolysis under oxygen-limited conditions in which the temperature ranged from 300 and 600°C and the residence time between 1.5 and 6 h.

Eight soil samples were collected in northern Spain, in a primarily granitic area near Santiago de Compostela (references and qualifiers presented in Table 6.2).

The TMTs used in this study were produced from industrial and agro-industrial waste, namely mine sediment, sawdust biomass, sludge from wastewater treatment, organic compost, ash, and sand (references and qualifiers presented in Table 6.3). They were gently supplied by CVAN (Centro de Valorización Ambiental del Norte, Touro, Spain).

6.2.3 Adsorbent Materials Characterization

Biochars were already characterized by Saiz-Rubio *et al.*, 2019 and their main characteristics are presented in table S1 (supplementary material). Relatively to soils and TMTs, its main physicochemical properties are shown in table S2 and S3 (supplementary material). Applied methodologies are briefly described: pH (H_2O, KCl, NaF, and H_2O_2) was measured in a suspension of soil or TMT in deionized water/KCl 0,1 M (1:5, w/v), in NaF (1:50, w/v), and in H_2O_2 15% pH 5.5 (1:20, w/v); organic matter (OM) was determined by loss-in-ignition in which a sample of 5 g of dried soil/TMT was placed at 400 °C for 4 h; electric conductivity (EC) was measured in a suspension of soil or TMT in deionized water (1:5, w/v); phosphorus (P) and total P content were determined by the molybdenum blue method after wet acid digestion (Olsen *et al.*, 1954), extracted with sodium bicarbonate 0.5 M and determined by colorimetry; equilibrium ions (Cl^-, F^-, SO_4^{2-}, PO_4^{3-}, NO_2^-, NO_3, NH_4^+), Fe, and aluminum were determined by selective extraction using acid ammonium oxalate (Blakemore, 1983), sodium pyrophosphate (Bascomb, 1968) and citrate bicarbonate dithionite (Mehra & Jackson, 1960). Also, cation exchange capacity, metals, and metalloids (microwave digestion following EPA method 3051 and ICP-MS analysis (U.S. EPA, 2007)) were determined.

The pH at the point of zero charges (pH_{pzc}) was determined for the selected adsorbents following the methodology used by Rivera-Utrilla *et al.*, 2001: a mass of 0.15 g of adsorbent was added to 50 mL of 0.01 M NaCl solution with initial pH values between 1.0 and 12.0. The pH adjustments were performed with solutions of NaOH 0.01 mol L^{-1} or HCl 1 M. The mixtures were stirred for 24h, and the final pH was quantified. After, pH_{final} vs $pH_{initial}$ were plotted and the pH_{pzc} value was determined by the intersection of this curve with the line $pH_{final} = pH_{initial}$.

6.2.4 Batch adsorption assays

6.2.4.1 Preliminary assays

Batch adsorption trials were carried out to assess the potential of each one of the forty-one materials to adsorb the selected herbicides and metabolite. This preliminary adsorption assay was executed with the intent of selecting the best adsorbent materials in each category. This study was performed by adding 0.1 g of each material (biochar, soil, and TMTs) and 25 mL of a 12.5 mg L^{-1} solution of glyphosate, AMPA, and glufosinate-ammonium in a plastic Erlenmeyer. All mixtures were shaken using a magnetic stirrer (WITEG, MS-MP8, Germany) at a speed of 400 rpm for 2 h at room temperature (25°C) without any pH adjustment. The influence of the agitation (type and velocity) was previously tested, and no significant differences were verified. Nevertheless, slightly faster adsorption was confirmed when magnetic bar stirring was used (data not shown). In all assays, blank tests were performed in parallel, using only the contaminated solution, without the adsorbent material addition. After 2 h of agitation, 1 mL aliquot was taken and immediately submitted to a 10 min 14 500 rpm centrifugation, at 4 °C, (Heraeus Fresco 21 Microcentrifuge, Thermo Scientific, USA). The supernatant obtained was transferred to another centrifugation tube and centrifuged again, ensuring that all solids were separated from the supernatant. All samples were derivatized before their injection for analysis using HPLC (Shimadzu Corporation, Kyoto, Japan), as described in section 2.6. The quantity of glyphosate adsorbed (C_S; g kg^{-1}) was calculated from the adsorbent dry weight (m_s) and the difference between the solution concentration (g L^{-1}) at the equilibrium (C_e) and the blank solution concentration (g L^{-1}).

All the adsorption experiments were conducted in duplicate. It must be highlighted, and as reported in several studies, highly polar pesticides, such as glyphosate, AMPA, and glufosinate, tend to attach to the active sites of glass surfaces. Thus, to prevent this phenomenon, the assays were performed using only plastic material (Campanale *et al*., 2021; Koskinen *et al*., 2016). Druart *et al*., 2011 reported losses of 20%, 25%, and 23% for glyphosate, glufosinate, and AMPA, respectively, when glassware was not previously silanized. The pH was recorded (Consort pH Meter model C861, Belgium) at the beginning and end of the experiments.

The removal efficiency by the adsorbent materials (removal %) was calculated from the equation (1):

$$\text{Removal \%} = \frac{(C_0 - C_f)}{C_0} \times 100 \qquad (1)$$

where C_0 and C_f (mg L^{-1}) correspond to the initial and final concentration of the contaminants after 2 hours stirring.

6.2.4.2 Kinetic assays

Kinetic batch adsorption assays were executed to study the equilibration time and adsorption rate of glyphosate, AMPA, and glufosinate onto the previously selected adsorbents. In addition, it was also attempted to understand the most relevant adsorption mechanisms of the tested adsorbate/adsorbent pairs. For the kinetic experiments, a ratio of 1 g adsorbent to 250 mL of adsorbate was applied, using a solution containing 12.5 mg L^{-1} of each contaminant (3.125 mg contaminant/g adsorbent). Plastic Erlenmeyer's flasks were used. The mixtures were continuously agitated using a magnetic stirrer at a speed of 400 rpm, for 24 h (for soils) and 170 h (for TMTs), at room temperature (25°C) without pH adjustment. Simultaneously, a blank assay was performed, in which the contaminated solution was placed in the same experimental conditions as the other experiments but without adding adsorbent, allowing the consideration of losses that may occur without being associated with adsorption, to measure the reference concentration. To determine the adsorption rate over time, samples of 1 mL were collected in predetermined intervals of time from the first 20 s of the assay until 24 h for soils (31 samples) and 170 h for TMTs (39 samples). The aliquots were centrifuged, derivatized and analyzed as described in Section 2.6 to determine the remaining concentration of contaminants over time.

The mass of contaminants adsorbed per gram of adsorbent (q_t, mg g^{-1}) was calculated according to equation (2):

$$q_t = (C_0 - C_e) \times \frac{V}{m} \tag{2}$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of the contaminant, respectively, V (L) is the volume of the solution and m (g) is the mass of adsorbent.

Four commonly used kinetic models, the pseudo-first-order (S.K. Lagergren, 1898), pseudo-second-order (Ho & McKay, 1999), Elovich (Low, 1960) and Weber and Morris intraparticle diffusion (W. Weber & Morris, 1963) models (see Supplementary Material - Equations (1)–(4)) were selected to fit the experimental kinetic results, using XLSTAT.

6.2.4.3 Equilibrium assays

The equilibrium adsorption isotherms of the selected adsorbents were determined by varying the amount of adsorbent (0.03 to 0.15 g) and placing it in contact with the 25 mL of the glyphosate, AMPA, and glufosinate solution (12.5 mg L^{-1} of each reagent) during 14 h. The equilibrium concentration in the solution was measured as described in Section 2.6. All tests were carried out in duplicate. Langmuir and Freundlich isotherm models were selected to fit the experimental values as well as the Sips model, using XLSTAT (see Supplementary Material - Equations (5)–(7)). Also, the dimensionless constant separation factor (R_L), an important characteristic of a Langmuir isotherm and originally defined by (K. R. Hall *et al.*, 1966) was calculated according to equation (3):

$$R_L = \frac{1}{1+K_L C_0} \tag{3}$$

where K_L is the Langmuir constant (mg g^{-1}) and C_0 is the initial concentration of adsorbate (mg g^{-1}).

6.2.5 pH influence

The effect of initial pH on the adsorption of the studied contaminants was evaluated in batch studies, by adjusting the pH of the contaminated solutions using concentrated HCl and NaOH in the range of 1.0–12.0 and glyphosate, AMPA, and glufosinate concentrations of 12.5 mg L^{-1} of each reagent, a 25 mL solution volume and an adsorbent mass of 0.6 g.

6.2.6 Determination of glyphosate, AMPA, and glufosinate

HPLC-FLD was used for chromatographic analysis of glyphosate, AMPA, and glufosinate. Chromatographic separation was accomplished using a Gemini® 3 µm NX-C18 110 Å (100 mm × 4.6 mm) column from Phenomenex in a Shimadzu LC Prominence system (Shimadzu Corporation, Kyoto, Japan) at 30 ^{o}C. The chromatograph was equipped with a DGU-20A5R degasser, a LC 20AD pump, a SIL 20AHT autosampler, a fluorescence detector (RF-10AXL), and a CBM-20A system controller. The injected volume was 20 µL and LabSolution software version 5.82 (Shimadzu, Kyoto, Japan) was used for control and data processing. The emission/excitation wavelength used was 315/270 nm.

The study compounds are polar and extremely soluble in water, thus, derivatization should be performed for chromatographic analyses (Meyer *et al.*, 2009). The derivatization and chromatography procedure were followed by the authors Garba *et al.*, 2018; Hanke *et al.*, 2008; Ramirez *et al*., 2014; Silva *et al*., 2018 and the application note of Phenomenex (Trass, 2014). Nevertheless, some changes were made, as described in the following paragraph.

The mobile phase consisted of the solvent's ammonium hydrogen carbonate (A), acetonitrile (B), and methanol (C). Different mobile phases comprising several combinations of the mentioned eluents were tested, as also different flow rates were evaluated to provide more effective separation using isocratic and gradient elution. The program starts with an isocratic elution with 80%:10%:10% (A:B:C, v/v/v) during 2 min. After a linear gradient was performed and 5%:40%:55% (A:B:C, v/v/v) was reached in 4 min. The proportions of the eluents were maintained for 6 min, and the chromatographic program returned to the initial proportions of the eluents in 3 min. The total time of analysis was 25 min. A flow rate of 0.6 mL/min was used. The retention times of the studied compounds were 2.481, 8.741, and 9.728 min for glyphosate, glufosinate, and AMPA, respectively.

The linearity of the method was established by setting calibration curves using linear regression analysis. For all compounds, good fits were found ($R > 0.999$).

To the derivatization 1 mL of 25 mM borate buffer at pH 9 and 0.5 mL of 3.75 mM FMOC-Cl were added to a plastic 15 mL falcon, followed by 0.5 mL of solution. Then, the falcon was mixed for 60 minutes (100 rpm) at room temperature using an orbital mixer (HulaMixer™ Sample Mixer, from Thermo Fisher Scientific)

6.3 Results and discussion

6.3.1 Adsorbent Materials Characterization

The adsorbent's chemical characteristics can positively or negatively affect the adsorption of the compounds under study. Organic matter, P_{Olson}, clay, iron, and aluminum oxides content were associated with changes in the soil adsorption capacity. High values of OM (in particular humic substances) were reported to be promoters of part of the glyphosate sorption, especially in sandy soils, mainly through the hydrogen bonding interaction (Albers *et al*., 2009; E. Pereira *et al*., 2019). Also, the adsorption has improved with the increase of the iron and aluminium oxides and clay concentration in soils (E. Pereira *et al.*, 2019). Glyphosate complexation through a cation-exchange reaction between cations released from the clays with solution protons has been referred to as an adsorption mechanism. It was additionally reported that pH variations affect the adsorption of both glyphosate and AMPA by changing their ionic state and the available amorphous oxide surface sorption sites (Gerónimo *et al*., 2018; Sidoli *et al*., 2016).

Characteristics of the biochar, soils, and TMTs are listed in Tables S6.1, S6.2, and S6.3. For the studied biochars, pH values varied between 5.50 and 10.50, and a high variation of macronutrient values and trace metals between them was observed. The studied soils were mainly characterized by low pH values (4.58-4.97), OM between 9% and 27%, low CE (32.01-82.01), and high Fe_{ox}, Fe_{dith}, $Al_{ox,}$ and Al_{dith}. Tested TMT presented different pH values, between 4.10 and 9.01, and OM content ranging 7% to 82%. TMT CE was always higher than in soils, with values within 193 and 5180 µS cm^{-1}. The redox potential values are between 128 and 366 mV, values associated with moderately reduced soils (Macías & Arbestain, 2010).

Referring to their classification, Aluminic Umbrisols (S4A, 11B, 13A), Ferrasols derived from amphibolites (high content of Mg^{2+} and Fe^{2+}) (S9B), Háplic Umbrisols (1Ah and 2Ah) and Andic and Ferralic Leptosols (referred as Andic and Ferralic) were tested. Umbrisols are characterized by a significant accumulation of OM in the mineral surface soil and a low base saturation. Leptosol contain a fine soil over continuous rock and soil extremely rich in coarse fragments. Ferrasols have a diffuse horizon boundary, a clay accumulation dominated by low-activity clays (mainly kaolinite) and a high content of sesquioxides. With good permeability and stable microstructure, these soils present a low available water storage capacity.

TMTs and soils with distinct properties (defined by their qualifiers) were tested, namely as Arenic Calcic Technosol (TMT 1), Aluandic Technosol (TMT 2), Andic Eutric Technosol (TMT 3, G, I, J, K, L, M, Q, R and S), Reductic Eutric Technosol (TMT 4 and A), Dystric Technosol (TMT B and D), Calcic Technosol (TMT C), Andic Technosol (TMT E and F), Eutric Technosol (TMT H and O), Ferric Technosol (TMT N) and Reductic Andic Technosol (TMT P) (see Table 6.3). Dystric qualifier is used to soils with an effective base saturation (EBS)[1] of less than 50% and eutric refers to soils with 50% or more EBS (Kubotera *et al.*, 2020). Andic properties are associated with the manifestation of short-range-order minerals and/or organo-metallic complexes, with low bulk density and high phosphate retention (≥ 85%). Eutrophic qualifier refers to soils with predominant reactive organic-aluminic complex. On the other hand, reductic soils are characterized by high OM or low redox potential, with high tendency to reduce the oxygen levels from the soil. This anaerobic conditions are mostly caused by gaseous emissions (e.g. methane, carbon dioxide) or by liquid intrusions other than water, e.g. gasoline (IUSS Working Group WRB, 2015). Ferralic horizon consists of mineral material, a texture class of sandy loam or finer, with a relatively low cation exchange capacity of < 16 $cmol_c$ kg^{-1} clay and a sum of exchangeable bases plus exchangeable Al of < 12 $cmol_c$ kg^{-1} clay. Calcic soils present a horizon

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[1] EBS is the ratio of exchangeable bases (Ca + Mg + K + Na) to effective cation exchange capacity (Ca + Mg + K + Na + Al) (IUSS Working Group WRB, 2015)

with accumulations of primary and secondary carbonates in the fine earth fraction. Umbric present a texture class of loamy sand or coarser, with low base saturation and moderate to high content of OM. Finally, Arenic qualifier refers to a horizon with a texture class of sand or loamy sand (IUSS Working Group WRB, 2015).

6.3.2 Batch adsorption assays

6.3.2.1 Preliminary

Adsorption studies offer know-how on the behavior of compounds, providing insights into their mobility and transfer in ecosystems (Skeff *et al*., 2018). The preliminary batch assays were performed using the three types of adsorbents: biochars, soils, and TMT. With the exception of the biochars, which were tested only with the granulometry < 50 μm, all the materials were tested in two granulometries: < 2 mm and < 50 μm. Regarding the results obtained, it was found that glyphosate, glufosinate, and AMPA were poorly adsorbed by all analyzed biochar samples (Table 6.1). Graphical representation with standard deviations is presented in Figure S6.1 of the Appendix A. Supplementary data.

Table 6.1 - Glyphosate, AMPA and glufosinate removal by the tested biochars (<50 μm refers to biochar granulometry)

		Removal (%)		
Biochar	**Reference**	**Glyphosate**	AMPA	Glufosinate
		<50 μm	**<50 μm**	**<50 μm**
Eucalyptus	Beu-2	24.5	0.0	6.0
Corncob 1	BCc-1	16.4	0.0	3.6
Corncob 2	BCc-2	16.5	0.0	4.9
Acacia bark	BAcSw-3	0.0	0.0	0.0
Acacia heartwood	BAcSw-2	0.0	0.0	0.0
Compost	BOpc	0.3	3.4	0.0
Rice husk	BRh	8.8	3.0	7.0
Pine Bark	BPb	6.6	0.4	3.9
Wood chip	BSdG	10.5	3.0	6.9
Pine sawdust	BSd-1	15.9	3.8	12.4

Eucalyptus biochar presented this group most efficient glyphosate adsorption, with 24.5% of removal efficiency. For glufosinate and AMPA, on the other hand, it was the pine sawdust biochar that showed the higher removal efficiency of 12.4% and 3.8%, respectively. These results are in accordance with the ones obtained by Hall *et al*., 2018, which refer that glyphosate adsorption on biochar is low (< 5% removal) for the biochar produced under 500 ºC, although it may be enhanced by increasing the biochar production temperature (Hall *et al.*, 2018).

Concerning the tested soils, as can be observed in Table 6.2 (graphical representation with standard deviations is presented in Figure S6.2 of the Appendix A. Supplementary data), high adsorption of glyphosate and AMPA was obtained (maximum of 93.9% and 90.7%), in contrast to glufosinate, for which 6.2% removal was not exceeded. The soil S9B < 50 μm presented the best adsorption performance for all the contaminants, 93.9%, 6.2%, and 90.7% for glyphosate, glufosinate, and AMPA. Soil 1Ah also presented 90.7% of AMPA adsorption but lower values for the other two compounds.

Table 6.2 - Glyphosate, AMPA and glufosinate removal by the tested soils (<2 mm and <50 µm refers to soil granulometry)

		Removal (%)					
Soil	**Reference Soil Groups and qualifiers**	**Glyphosate**		**AMPA**		**Glufosinate**	
		<2mm	**<50 µm**	**<2mm**	**<50 µm**	**<2mm**	**<50 µm**
S9B	Ferrasol*	88.8	93.9	84.7	90.7	4.2	6.2
S4A	Aluminic Umbrisols	72.3	88.2	73.0	89.4	2.6	4.3
11B	Aluminic Umbrisols*	67.9	81.5	51.4	69.3	3.6	4.5
13A	Aluminic Umbrisols	75.2	82.6	78.1	86.1	3.6	3.7
Andic	Andic Leptosols	52.5	41.4	79.5	69.3	0.9	1.3
Ferrálic	Ferralic Leptosols	24.3	24.1	27.8	29.0	0.0	0.0
1Ah	Háplic Umbrisols	56.8	78.4	68.8	90.7	1.1	3.3
2Ah	Háplic Umbrisols	45.7	78.5	51.5	85.9	1.6	3.3

* derived from amphibolites

For most of the natural soils tested, there were no significant differences in the adsorption by soils with granulometry < 50 μm and < 2 mm.

Table 6.3 show the removal capacity of the tested TMTs concerning glyphosate, AMPA and glufosinate (graphical representation with standard deviations is presented in Figure S6.3 of the Appendix A. Supplementary data). Among the 46 samples of tested TMTs (23 of each granulometry), and comparing the two granulometries, the lower granulometry materials were, in general, the ones that presented the highest adsorption rates. Lower grain size contributes to faster kinetics and to higher specific area and therefore to higher adsorption capacities. Arenic Calcic Technosol (TMT 1), Aluandic Technosol (TMT 2), Andic Eutric Technosol (TMT 3) and Reductic Eutric Technosol (TMT 4) with <50 μm were the TMTs with best removal performance, with removal % ranging 61.6 to 78.8 % for glyphosate and 28.4 to 83.1% for AMPA. It should also be noted that in this preliminary test, it can be seen that there is some discrepancy between the % removal of glyphosate and AMPA by the same technosol, and this difference is more evident than in natural soils (Table 6.2).

Table 6.3 - Glyphosate, AMPA and glufosinate removal by the tested TMTs (<2 mm and <50 μm refers to TMT granulometry)

		Removal (%)					
Technosol	Reference Soil Groups and qualifiers	Glyphosate		AMPA		Glufosinate	
		<2mm	<50 μm	<2mm	<50 μm	<2mm	<50 μm
TMT 1	**Arenic Calcic Technosol**	**3.3**	**61.6**	**63.6**	**83.1**	**0.0**	**2.4**
TMT 2	**Aluandic Technosol**	**1.9**	**78.8**	**56.2**	**74.5**	**1.8**	**3.6**
TMT 3	**Andic Eutric Technosol**	**2.2**	**67.9**	**24.1**	**30.6**	**0.0**	**0.0**
TMT 4	**Reductic Eutric Technosol**	**66.2**	**74.3**	**23.4**	**28.4**	**0.0**	**0.0**
TMT A	**Reductic Eutric Technosol**	**0.3**	**0.0**	**3.1**	**6.5**	**0.5**	**0.0**
TMT B	**Dystric Technosol**	**1.6**	**0.0**	**11.2**	**14.3**	**0.0**	**0.0**
TMT C	**Calcic Technosol**	**0.0**	**23.9**	**10.8**	**17.3**	**0.0**	**1.1**
TMT D	**Dystric Technosol**	**0.0**	**9.0**	**11.4**	**13.1**	**0.2**	**0.0**
TMT E	**Andic Technosol**	**0.0**	**36.6**	**12.0**	**10.7**	**2.8**	**0.0**
TMT F	**Andic Technosol**	**0.0**	**9.3**	**3.8**	**0.6**	**0.0**	**0.0**
TMT G	**Andic Eutric Technosol**	**0.0**	**12.2**	**1.7**	**4.1**	**0.0**	**0.0**
TMT H	**Eutric Technosol**	**1.5**	**39.4**	**8.6**	**17.7**	**0.0**	**0.0**
TMT I	**Andic Eutric Technosol**	**0.2**	**21.3**	**15.0**	**17.6**	**0.0**	**0.0**
TMT J	**Andic Eutric Technosol**	**25.3**	**29.5**	**17.8**	**21.8**	**0.3**	**0.0**
TMT K	**Andic Eutric Technosol**	**18.1**	**24.0**	**10.7**	**13.8**	**0.0**	**0.0**
TMT L	**Andic Eutric Technosol**	**2.4**	**30.9**	**6.6**	**7.5**	**0.0**	**0.0**
TMT M	**Andic Eutric Technosol**	**0.9**	**47.1**	**12.8**	**22.1**	**0.0**	**0.0**
TMT N	**Ferric Technosol**	**1.3**	**44.5**	**24.7**	**33.3**	**0.4**	**0.9**
TMT O	**Eutric Technosol**	**12.3**	**16.0**	**6.2**	**9.5**	**0.0**	**0.0**
TMT P	**Reductic Andic Technosol**	**0.6**	**40.8**	**8.9**	**13.0**	**0.0**	**0.2**
TMT Q	**Andic Eutric Technosol**	**19.8**	**26.1**	**6.8**	**10.5**	**0.6**	**2.2**
TMT R	**Andic Eutric Technosol**	**13.3**	**26.7**	**4.1**	**8.3**	**0.4**	**0.0**
TMT S	**Andic Eutric Technosol**	**2.2**	**34.5**	**6.6**	**10.2**	**0.0**	**0.0**

The adsorption percentages of the adsorbents that stood out in each type are presented in Figure 6.1. As can be seen in the figure, there is a large discrepancy between glyphosate and AMPA removal by biochars when compared to natural soils and TMTs. On the other hand, biochars were the materials that showed the best ability to remove glufosinate. Regarding the soils and technosols presented in the figure, for the conditions used in the preliminary test (contact time 2 hours and 0.1 g of adsorbent to 25 mL of a 12.5 mg L^{-1} of glyphosate, AMPA and glufosinate solution) the soils showed higher removal/adsorption efficiency.

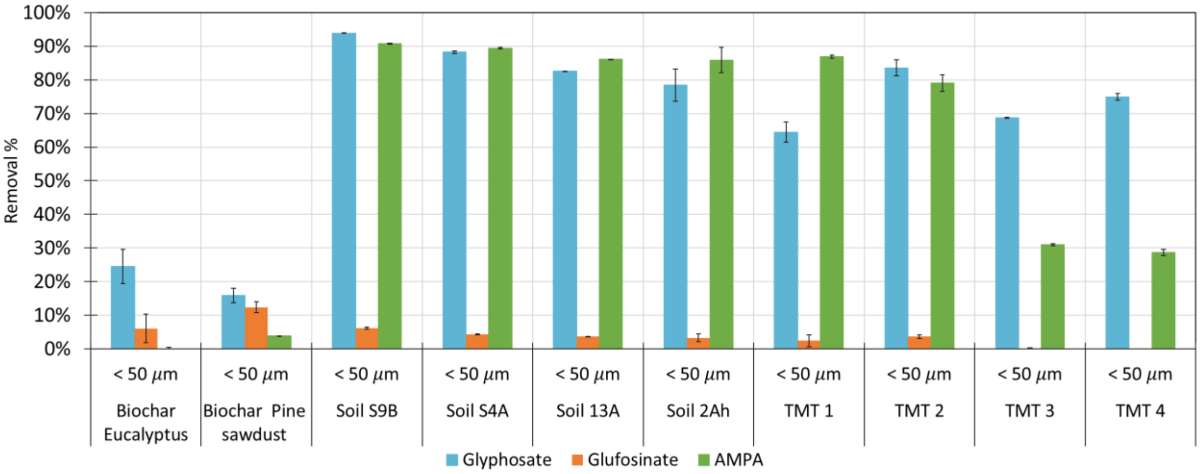

Figure 6.1 - Glyphosate, glufosinate and AMPA adsorption by ten of the seventy-two tested materials. Error bars correspond to the standard deviation of six replicates.

The results regarding different removal efficiencies are presented in a boxplot graph in Figure 6.2, where samples were grouped according to their type (biochar, soil, and TMT) and their granulometry (< 2 mm and < 50 μm).

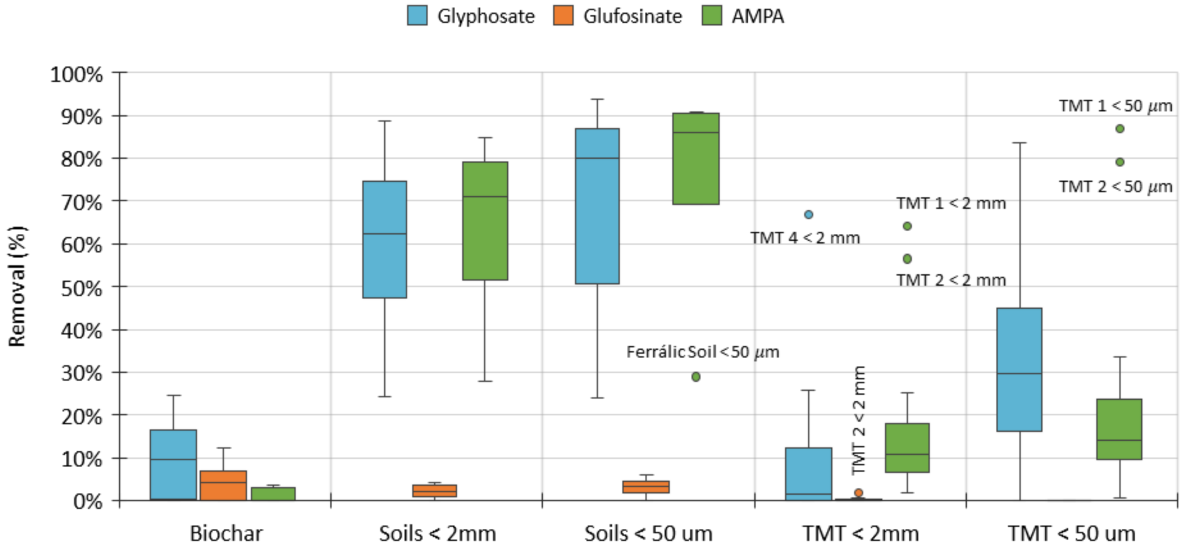

Figure 6.2 - Boxplot of the adsorption (%) for the samples grouped as biochar (< 50 µm), soil (< 2 mm and < 50 µm), and TMT (< 2 mm and < 50 µm). The line within the box indicates the median value. The lower limit of the box demonstrates the first quartile (Q1), and the upper limit indicates the third quartile (Q3). The "moustaches" indicate the minimum and maximum values, excluding outliers. Outliers are shown as circles with the sample tag (<1.5 times of the length of the interquartile range from the lower and higher edges of the box).

Once again, it is possible to see that the tested biochars presented, overall, a lower adsorption capacity but, regarding glyphosate, it was similar to the TMTs with higher granulometry (< 2 mm). In general, soils showed a superior adsorption capacity. According to the results obtained, the impact of the adsorbent granulometry in the adsorption is higher in TMTs than in soils. The outliers presented in the boxplot are materials that, because of their properties and characteristics, have better or worse adsorption capacity that the majority of the adsorbents from the same group. Since TMTs are mixtures of distinct materials, and therefore each TMT has a unique constitution, it is normal to find some heterogeneity of results for the Technosol group.

6.3.2.2 Kinetics

Kinetic studies offer significant data associated with the adsorption pathways and combined information regarding the adsorption mechanism involved. Also giving information about the rate at which the adsorbate retention takes place and the minimum contact time required to reach the equilibrium. Only the highest performance adsorbents from the preliminary adsorption tests were assessed namely: soils S9B, S4A, 13A, and 2Ah and TMTs 1, 2, 3, and 4.

The amounts of glyphosate and AMPA adsorbed at time t (q_t, mg g^{-1}) between 0 and 24 h (soils) and between 0 and 170 h (TMTs) are shown in Figure 6.3. Also, the fittings with the kinetic models are presented. The kinetic parameters calculated for the pseudo-first order, pseudo-second order, Elovich, and Weber and Morris (intraparticle diffusion) models are presented in Table 6.4. The correlation coefficients (r^2) were assessed to verify the compliance between experimental and model data and the SEE values.

The concentration of glufosinate in the aqueous phase remained practically constant during the 14 h (soils) and 170 h (TMTs), which demonstrates that the adsorption in the studied adsorbents was not significant (test t-student, $p > 0.05$; see supplementary material). This was also reported by Skeff *et al*., 2018 relative to the adsorption of glufosinate by Baltic Sea sediments.

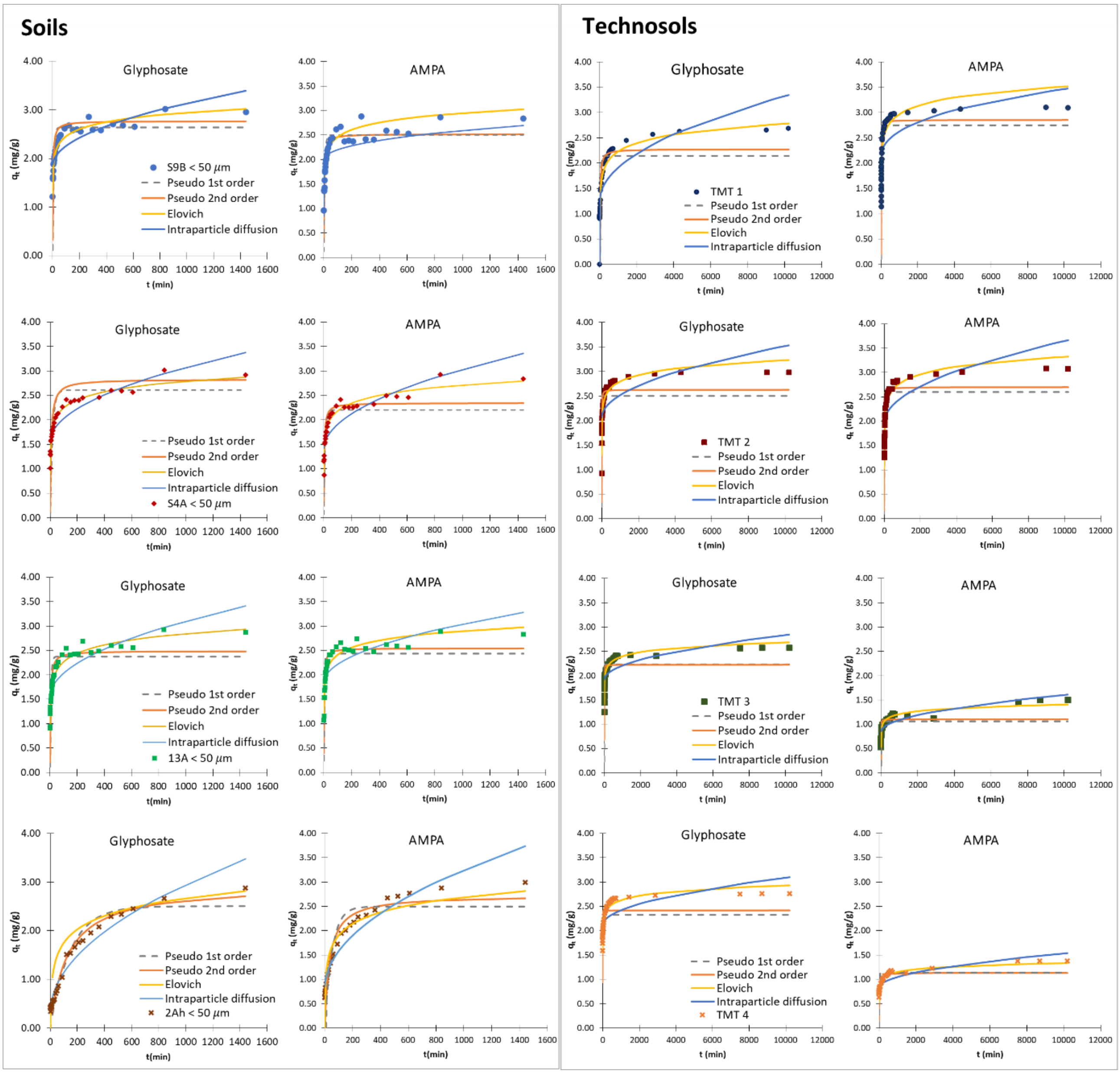

Figure 6.3 - Glyphosate and AMPA adsorption kinetics in soils S9B, S4A, 13A and 2Ah (graphics on the left) and in TMTs 1 to 4 (graphics on the right), and pseudo-second-order, pseudo-first-order, Elovich models, and Weber and Morris fitted to kinetic data.

Table 6.4 - Predicted kinetics parameters from nonlinear analysis of pseudo-first order, pseudo-second order, Elovich and Weber and Morris models, and experimental q_e values.

	Glyphosate								AMPA							
	Soils				TMT				Soils				TMT			
	S9B	S4A	13A	2Ah	1	2	3	4	S9B	S4A	13A	2Ah	1	2	3	4
$q_{e\ experimental}$ (mg g^{-1})	2.95	2.92	2.87	2.87	2.68	2.99	2.58	2.76	2.84	2.84	2.83	2.99	3.10	3.07	1.50	1.38
Pseudo-first order																
q_e (mg g^{-1})	2.64	2.61	2.37	2.51	2.15	2.50	2.23	2.33	2.50	2.20	2.44	2.50	2.75	2.60	1.06	1.14
k_1 (min^{-1})	0.13	0.06	0.16	0.01	0.04	0.31	0.33	2.48	0.15	0.10	0.31	0.02	0.12	0.12	0.44	0.06
r^2	0.801	0.803	0.803	0.967	0.768	0.587	0.728	0.617	0.841	0.803	0.795	0.903	0.805	0.729	0.578	0.613
SEE	0.441	0.524	0.346	0.240	0.417	0.450	0.308	0.320	0.353	0.436	0.316	0.383	0.400	0.416	0.187	0.279
Pseudo-second order																
q_e (mg g^{-1})	2.77	2.83	2.49	2.95	2.27	2.62	2.23	2.41	2.52	2.35	2.55	2.73	2.85	2.70	1.10	1.14
k_2 (g mg^{-1} min^{-1})	0.14	0.05	0.11	0.00	0.03	0.17	0.59	0.79	0.17	0.15	0.21	0.01	0.08	0.07	0.55	0.06
r^2	0.859	0.844	0.887	**0.973**	0.830	0.730	0.825	0.742	0.879	0.829	0.896	**0.928**	0.884	0.832	0.702	0.711
SEE	0.302	0.421	0.245	**0.198**	0.341	0.356	0.202	0.265	0.241	0.287	0.215	**0.302**	0.287	0.311	0.156	0.274
Elovich																
α (mg.g^{-1}.min^{-1})	238	36	21	0.32	3.2	559	36111	66380	81	30	199	0.92	70	70	151	203
β (g mg^{-1})	4.73	4.29	3.98	2.50	4.25	5.32	8.14	7.63	4.46	4.35	4.75	2.93	4.24	4.50	11.93	12.82
r^2	**0.971**	**0.971**	**0.974**	0.820	**0.936**	**0.935**	**0.984**	**0.981**	**0.934**	**0.962**	**0.950**	0.920	**0.947**	**0.969**	**0.968**	**0.968**
SEE	**0.107**	**0.111**	**0.113**	0.462	**0.173**	**0.163**	**0.060**	**0.071**	**0.165**	**0.125**	**0.144**	0.243	**0.171**	**0.121**	**0.050**	**0.047**
Intraparticle diffusion																
k_{id} ([mg.g^{-1}] min$^{0.5}$)	0.04	0.05	0.05	0.08	0.02	0.01	0.01	0.01	1.46	0.05	0.04	0.08	1.90	0.02	0.01	0.01
C (mg g^{-1})	1.85	1.55	1.54	0.36	1.26	2.06	1.91	2.11	0.00	1.39	1.83	0.81	0.00	1.96	0.85	0.82
r^2	0.824	0.880	0.799	0.950	0.698	0.676	0.779	0.782	0.735	0.836	0.755	0.924	0.666	0.680	0.837	0.850
SEE	0.263	0.227	0.309	0.195	0.378	0.365	0.224	0.242	0.336	0.376	0.316	0.236	0.432	0.388	0.112	0.102

The adsorption kinetics could be divided into two distinct stages, the first characterized by an accelerated adsorption process followed by a period of slow adsorption. Within the first 10 min of contact time, reasonably fast glyphosate and AMPA adsorption were observed in soils, resulting in more than 50% removal for both contaminants, except for soil 2Ah that presented a slower initial adsorption rate (14% and 29% of glyphosate and AMPA in the first 10 min). This was followed by a slow adsorption rate reaching the equilibrium after 14 h (24h for 2Ah), achieving 2.87 to 3.02 mg g^{-1} (87.9 – 94.2%) and 2.86 to 2.99 mg g^{-1} (93.1% – 94.2%) of maximum glyphosate and AMPA adsorption, respectively. In some cases, adsorption rates after 14 h increased slightly. Thus, since no significant differences in standard deviations were observed between 14 h and 24 h, the first was selected as the equilibrium time. The adsorption of the two compounds, glyphosate and AMPA, was similar among all soils, except for 2Ah, which showed slightly higher adsorption for AMPA.

On the other hand, the adsorption kinetics of the two compounds was distinct concerning TMT. Although the adsorption kinetics can also be divided into two phases, the adsorption percentage at the end of the first phase is lower than in soils. Comparing the first 10 minutes of the assay, only TMT 2 achieved more than 50% removal for both contaminants. During the same contact time, TMT 1 only exceeded 50% removal for AMPA and TMT 3 and 4 for glyphosate. Additionally, regarding the amount adsorbed in each TMT, it was found that TMT 1 and 2 showed higher adsorption capacities for AMPA than for glyphosate, unlike the other TMT. In TMT 3 and 4, despite presenting similar adsorption profiles over time, a higher adsorption rate was observed for glyphosate compared to AMPA. The adsorption equilibrium of glyphosate and AMPA was reached in 72 h, achieving 2.48 to 2.98 mg g^{-1} (74.6 – 93.9%) and 1.29 to 3.07 mg g^{-1} (39.3 – 93.7%) of maximum glyphosate and AMPA adsorption, respectively. Once again, in some samples, adsorption rates after 72 h increased slightly. Thus, since no significant differences in standard deviations were observed between 72 h and 170 h, the first was selected as the equilibrium time.

The results for soils are comparable to the reported by Ghavamifar *et al.*, 2023 and Dotor-Robayo *et al.*, 2022, which obtained equilibrium times of 12 h and 24 h, respectively. Regarding the other adsorbents, similar equilibrium times have been reported for coconut shell-activated carbon and wood biochar (Dissanayake Herath *et al.*, 2019) and lower values for biochar derived from rice husk (Herath *et al.*, 2016).

Concerning the glyphosate adsorption capacity, Dotor-Robayo *et al.*, 2022 obtained around 75% to 95% for the three tested soils concerning an initial ratio of 0.0017 mg of glyphosate/g soil. Also, Ghavamifar *et al.*, 2023 accomplished around 75% of glyphosate adsorption concerning an initial ratio of 200 mg of glyphosate/g soil.

The calculated equilibrium adsorption values, q_e, using the pseudo-second-order model are closer to the experimental results than the pseudo-first-order (Table 6.4), as expected because the r^2 of the pseudo-second-order model was always higher than the one pseudo-first-order model, also being the most suitable model to describe the adsorption of both compounds in the 2Ah soil, suggesting that the adsorption on active sites is preponderant indicating the chemical reaction as the primary rate-limiting step (Caceres-Jensen *et al.*, 2019; Wang & Guo, 2020b). The Elovich model presented the best fit for all the other assays (for glyphosate and AMPA), suggesting that the surface chemistry of the adsorbent material is the major promoter of adsorption in the tested materials. The highest values for β and α constants were observed on TMT 3 and 4, indicating an initial mass transfer contribution through the vacant sites.

Although the intraparticle diffusion model was not the best fit for any of the studied systems, it showed relatively high r^2 values in soils (0.755 to 0.950) with maximum values (0.950 and 0.924 for glyphosate and AMPA adsorption, respectively) for the 2Ah soil. For this, when a plot of q_t against $t^{1/2}$ was performed (Figure 6.4), two linear regions were observed, proposing that the adsorption process is controlled by a multistep mechanism (Caceres-Jensen *et al*., 2019; Dissanayake Herath *et al*., 2019; Tran *et al*., 2017).

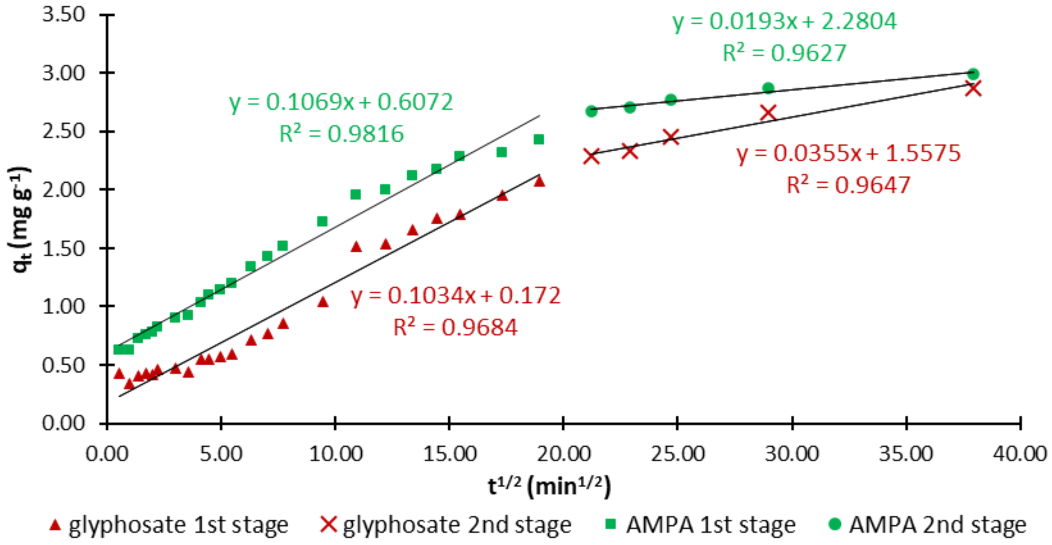

Figure 6.4 - Soil 2Ah glyphosate and AMPA adsorption data represented as q_t plotted against $t^{1/2}$ to intraparticle diffusion model analysis.

The interception of the linearized model with the axis is largely associated with the boundary layer thickness and proportional to the constant *C*, representing the initial adsorption on external sites (Caceres-Jensen *et al*., 2019; Wang & Guo, 2020b). As in this study C presented, for 2Ah soil values higher than 0, it is plausible to assume that the external mass transfer across the boundary layer controlled by liquid film diffusion was preponderant to the glyphosate and AMPA removal during the first stage (Caceres-Jensen *et al*., 2019).

6.3.2.3 Equilibrium

The adsorption contact times of 14 h and 72 h for soils and TMTs, respectively, defined in the kinetic assay (see 3.2.1), were considered as the equilibrium times for the three soils (S9A, 13A, and S4A), and two TMTs (TMT 1 and TMT 2) that showed the highest adsorption efficiencies for glyphosate and AMPA.

The relationship involving the amount of glyphosate adsorbed per unit of adsorbent mass, and an adsorption isotherm model usually describes the concentration of a remaining substance at equilibrium. Fittings of the Langmuir, Freundlich, and Sips models to the experimental data are presented with the experimental results in Figure 6.5. The estimated values of equilibrium model parameters, the correlation coefficient (r^2) values, and the Sum of squared errors (SSE) are summarized in Table 6.5.

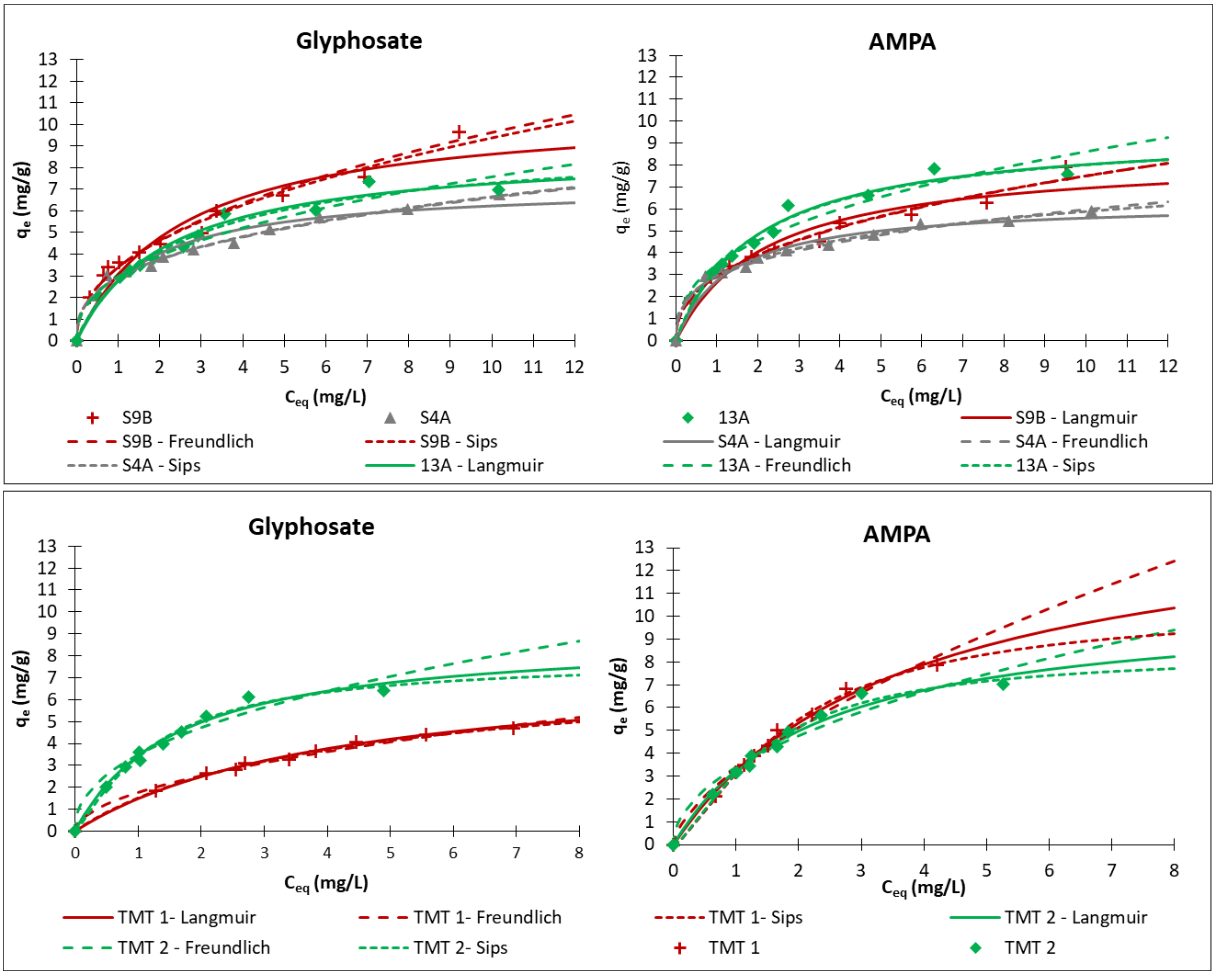

Figure 6.5 - Glyphosate and AMPA adsorption isotherms for three soils (S9B, 13A, and S4A) and two TMTs (1 and 2).

Table 6.5 - Parameters of equilibrium models (± SD) for glyphosate and AMPA adsorption onto soils (S9B, 13A, and S4A) and TMTs (1 and 2)

	Glyphosate					AMPA				
	S9B	13A	S4A	TMT 1	TMT 2	S9B	13A	S4A	TMT 1	TMT 2
Langmuir										
q_m	10.84 ± 1.14	8.83 ± 0.45	7.24 ± 0.42	7.71 ± 0.51	8.94 ± 0.54	8.46 ± 0.71	9.58 ± 0.44	6.31 ± 0.24	15.08 ±1.11	10.52 ± 0.80
K_L	0.40 ± 0.10	0.46 ± 0.06	0.63 ± 0.11	0.24 ± 0.03	0.62 ± 0.08	0.46 ± 0.11	0.51 ± 0.06	0.76 ± 0.10	0.27 ±0.03	0.45 ± 0.07
r^2	0.943	0.976	0.958	**0.996**	0.985	0.945	**0.982**	0.972	0.993	0.982
SEE	0.701	0.336	0.394	**0.099**	0.254	0.524	**0.327**	0.247	0.204	0.304
R_L	0.107	0.149	0.107	**0.329**	0.120	0.121	0.136	0.099	**0.266**	0.157
Freundlich										
K_F	3.40 ± 0.12	2.96 ± 0.15	2.95 ± 0.07	1.77 ± 0.08	3.49 ± 0.20	2.93 ± 0.13	3.48 ± 0.21	2.92 ± 0.07	3.31 ± 0.15	3.41 ± 0.20
n	2.21 ± 0.11	2.46 ± 0.19	2.83 ± 0.12	1.93 ± 0.12	2.28 ± 0.29	2.45 ± 0.16	2.53 ± 0.25	3.21 ± 0.14	1.57 ± 0.11	2.05 ± 0.23
r^2	**0.985**	0.960	**0.992**	0.992	0.957	**0.983**	0.957	0.991	0.981	0.953
SEE	0.319	0.374	**0.173**	0.135	0.428	0.304	0.536	0.142	0.339	0.484
Sips										
q_{mLF}	11.87 ±1.23	9.66 ± 1.88	10.37 ± 1,52	7.80 ± 1.68	7.84 ± 0.83	14.96 ±1,76	9.81 ± 1.28	14.14 ± 7.81	10.49 ± 0.83	8.36 ± 0.75
K_{LF}	0.41 ± 0.04	0.40 ± 0.10	0.39 ± 0.02	0.24 ± 0.05	0.77 ± 0.16	0.24 ± 0.02	0.51 ± 0.10	0.26 ± 0.18	0.42 ± 0.05	0.60 ±0.09
n_{LF}	0.78 ± 0.08	0.89 ± 0.21	0.62 ± 0.04	0.96 ± 0.17	1.23 ± 0.21	0.58 ± 0.05	0.95 ± 0.17	0.4 ± 0.1	1.38 ± 0.13	1.42 ± 0.22
r^2	0.954	**0.977**	0.984	0.996	**0.987**	0.974	0.982	**0.993**	**0.997**	**0.988**
SEE	0.342	0.338	0.174	0.101	**0.243**	0.291	0.328	**0.144**	**0.141**	**0.245**

q_m (mg.g^{-1}); K_L (L.g^{-1}); K_F ((mg.g^{-1}(mg.L^{-1})$^{-1/n}$))

The adsorption data fitted well to Freundlich, Langmuir, and Sips isotherm models with high regression coefficients (r^2 between 0.943 and 0.997). Experimental data of the adsorption onto TMT are better described for the Sibs model ($r^2 > 0.987$), except for glyphosate in TMT 1, which presents the same r^2 for both Langmuir and Sips models but a lower SSE for the first. Concerning soil adsorption data, the Freundlich model had a slightly better fit for S9B (glyphosate and AMPA) and for S4A (glyphosate) comparing r^2, suggesting the possible occurrence of multilayer physical type of adsorption by heterogeneous surfaces (Skeff *et al.*, 2018; Wang & Guo, 2020a). AMPA adsorption by S4A, despite presenting a higher r^2 (0.993 and 0.991) for the Sips model, had a lower SEE relative to the fit with the Langmuir model. The same happened with the results of AMPA adsorption in 13A, which showed an equal r^2 for the Sips and Langmuir model adjustment, but a lower SEE for the Langmuir model fit (Table 6.5).

The maximum adsorption capacity (q_m) calculated from the Langmuir model was 10.84 mg g^{-1} to glyphosate (soil S9B) and 15.08 mg g^{-1} to AMPA (TMT 1). Similar q_m values are described for glyphosate adsorption in soils, namely 1.85 to 7.8 mg g^{-1} by (E. Pereira *et al.*, 2019) and 0.389 mg g^{-1} by Ghavamifar *et al.*, 2023.

R_L values between 0 and 1 were calculated, indicating that the adsorption of glyphosate and AMPA onto all tested adsorbents is a viable and favorable process (K. R. Hall *et al.*, 1966; Herath *et al.*, 2016).

Analyzing Freundlich model parameter n, and according to Giles *et al.*, 1974 classification, since 1/n is always under the de unit, the isotherms exhibited an L-type, proposing that the adsorption sites were not homogeneously distributed, disposing of different adsorption energies. The higher energy sites are where the adsorption first happened. In the sequence, adsorption increases at the lower energy sites (Giles *et al.*, 1974; Herath *et al.*, 2016). K_F values ranged from 1.77 to 3.49 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} for glyphosate and 2.92 to 3.41 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} for AMPA adsorption. In general, they are slightly higher than others reported in the literature, namely 0.642 to 1.36 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} (E. Pereira *et al.*, 2019), 0.074 to 0.45 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} (Gros *et al.*, 2017), 0.044 to 0.249 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} (Autio *et al.*, 2004), 0.032 to 0.540 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} (Sidoli *et al.*, 2016), 0.101 to 0.414 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} (Okada *et al.*, 2016), 0.158 to 0.396 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} (Padilla & Selim, 2019), and 0.093 to 2.754 $\mu g^{1-1/n}$ $L^{1/n}$ g^{-1} (Báez *et al.*, 2015) to glyphosate. Concerning AMPA, 0.033 to 0.392 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} (Sidoli *et al.*, 2016) and 0.038 to 1.517 $\mu g^{1-1/n}$ $L^{1/n}$ g^{-1} (Báez *et al.*, 2015) were also reported.

The Sips model, a hybrid model combining the Langmuir and Freundlich models, is proposed to describe the heterogeneous or homogeneous adsorption systems. At low adsorbate concentration, it reduces to Freundlich isotherm model. Also, a monolayer adsorption capacity specification of the Langmuir isotherm could be anticipated at high adsorbate concentration. Adsorption affinity between adsorbate and the sorption site could be defined by K_{LF}, and the degree of surface non-homogeneity illustrated by the parameter n_{LF} (Mohan *et al.*, 2011; Taleghani *et al.*, 2020). When n_{LF} value diverges from 1, this variation will be higher for a very heterogeneous system. This model, which fits several of the results obtained, as described above, led to values of n_{LF} between 0.62 and 1.23 to glyphosate and between 0.40 and 1.42 to AMPA, which could propose that the adsorbents surfaces are heterogeneous and that this surface heterogeneity was beneficial for the adsorption of glyphosate and AMPA (Mohan *et al.*, 2011; Wang & Guo, 2020a).

6.3.3 pH influence

Adsorptive attributes such as solubility, molecular size, and pKa are extremely important to understanding the adsorption process and nature. The solubility characterizes the hydrophobic interactions, the molecular size adjusts the availability to the adsorbent pores, and the dissociation of the adsorbate species is described by its pK_a and governed by the pH of the solution (Mojiri *et al.*, 2020). Consequently, the study of the pH influence is considered a key factor during adsorption because it affects the dissociation state of the adsorbate, the functional groups of glyphosate, AMPA, glufosinate, and the ones present at the adsorbent's surface, as well as the surface charge of the adsorbents, altering chemical properties and interaction mechanisms (Mojiri *et al.*, 2020). Thus, the effect of initial pH on the adsorption of glyphosate and AMPA were tested.

The pH_{pzc} was determined for the adsorbents with the higher adsorption rates among the tested soils and TMTs (soils: S9B, S4A, and 13A; TMT: 2, 3, and 4) and for the less efficient adsorbents between the TMTs, namely TMTs A to G (Figure 6.6), to better understand its influence in the adsorption process.

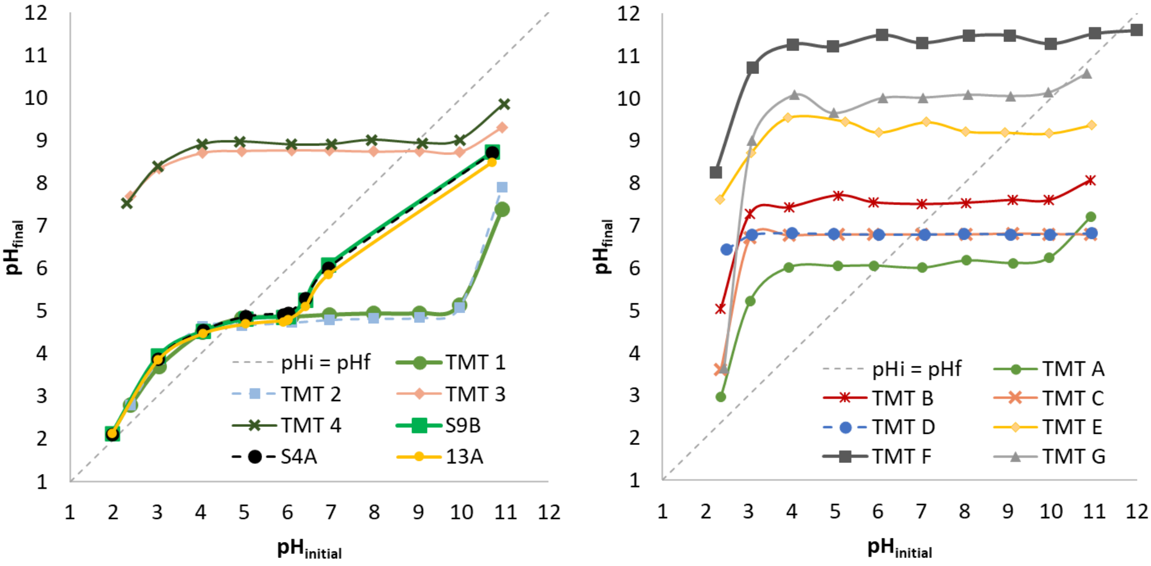

Figure 6.6 - pH_{PZC} of the best-studied adsorbents (soils S9B, S4A, and 13A; TMTs 1 to 4) - left; and the low-rate adsorption TMTs (A to G) - right.

All soils presented a pH_{PZC} of approximately 4.9, as well as TMTs 1 and 2. This is, apparently, the most beneficial pH_{PZC} to the adsorption of glyphosate and AMPA (considering no pH adjustments).

The glyphosate molecule is a zwitterion and can take over other ionic states, depending on the pH in which the adsorption process occurs, since it presents four dissociation equilibrium constants. Glyphosate exhibit four distinct dissociation constants, the first two (pKa_1 and pKa_2) associated with a first proton in phosphonic and carboxyl groups, and pKa_3 and pKa_4 with a proton in phosphonic group and amino groups, respectively (values presented in Table 6.6). Consequently, with increasing pH, the net molecule charge tends to be more negative (Dotor-Robayo *et al.*, 2022; Sidoli *et al.*, 2016). Since different pK_a are reported in the literature for glyphosate, in the present study, the discussion was based on the values reported by Dotor-Robayo *et al.*, 2022 and presented in Table 6.6.

Table 6.6 - Dissociation equilibrium constants (pK_a) of glyphosate, AMPA, and glufosinate

	Glyphosate[1]	**AMPA[2]**	**Glufosinate[3]**
pK_{a1}	0.8	1.8	2.0
pK_{a2}	2.3	5.4	2.9
pK_{a3}	5.6	10.0	9.8
pK_{a4}	11.0	–	–

[1] (Dotor-Robayo *et al.*, 2022)

[2] (Sidoli *et al.*, 2016)

[3] (Takano & Dayan, 2020)

The pH_{pzc} can help to understand the influence of pH on the adsorption process. When the pH is higher than the pH_{pzc}, negative charges dominate the adsorbent material surfaces. Thus, the increasing pH raises the density of negative charge sites in the adsorbent surface, simultaneously with the increase in negative charges on glyphosate, resulting in adsorption disfavor (Sidoli *et al.*, 2016). Otherwise, the positively charged surface soils or TMT (when pH is under pH_{pzc}) and the negatively charged groups of glyphosate molecules (pH>2,9) form electrostatic attractions, resulting in increased adsorption of glyphosate onto the particles. The impact of the pH variation on the AMPA adsorption process is similar since its ionization state is controlled by three pK_a values comparable to those of glyphosate (Table 6.6). No significant differences were found in the adsorption of glufosinate on any of the adsorbents with the change in pH.

The maximum glyphosate adsorption in soils and TMT occurred at the pH range of 2 – 4, at which glyphosate dissociates into its ionic form, as presented in Figure 6.7, with dominant glyphosate net charge of -1. Then, since the density of the adsorbent positively charged surface declines, a dramatic reduction of the glyphosate adsorption occurred due to the repulsive force between the yet negatively charged glyphosate molecules and negatively charged adsorbate (Herath *et al.*, 2016). The same was reported by several authors (Gimsing *et al.*, 2004; Okada *et al.*, 2016; Skeff *et al.*, 2018).

During the batch adsorption assay, performed with no pH adjustments (described in section 6.3.2), it was possible to measure the natural pH value of the adsorbent/solution mixture for the best adsorbents (ranging from 3.95 to 4.03). Comparing the results, all measured pH values were below the adsorbent pH_{pzc}. Thus, during the adsorption processes, their surface was positively charged, exhibiting mainly strong electrostatic interactions with negatively charged groups of glyphosate molecules, predominant at that same pH (Figure 6.7).

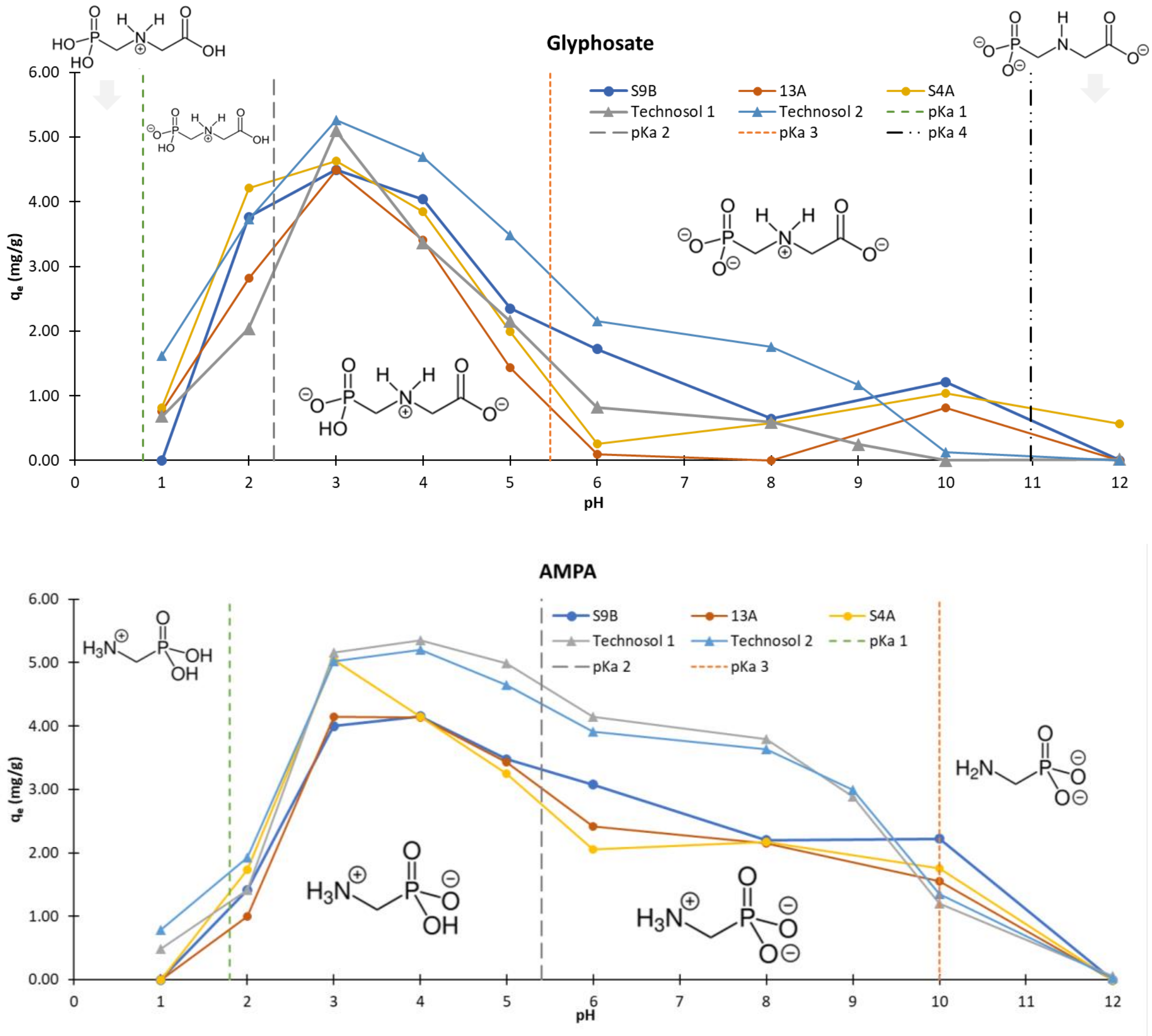

Figure 6.7 - Effects of pH on the adsorption of glyphosate (top) and AMPA (bottom) onto the tested soils and TMT, corresponding dissociation equilibrium constants (pK_a), and consequent most abundant molecular forms.

For the five adsorbents, there was an enhance in adsorption within pH 1 and 3. As all five materials presented a pH_{PZC} of approximately 4.9, this increase was expected considering the positively charged surface and the loss of the proton associated with the carboxyl group (pKa_2) in the case of glyphosate and the phosphonic group (pKa_1) in the case of AMPA. Then there was a gradual reduction between pH 3 and pH 6, more pronounced for glyphosate than for AMPA. Between pH 6 and 10 the adsorption of glyphosate on the various adsorbents tested was significantly lower with exception of TMT 1 that only reduce for pH higher than 10, achieving adsorption values close to zero. On the other hand, for AMPA the reduction in the adsorption by TMTs only occurs with more pronounced effect from pH higher than 9, keeping constant adsorption values between pH 6 and 10 for the remaining adsorbents. For all the adsorbents, between pH 10 and 12 there was a marked decrease to values close to zero (except for glyphosate adsorption onto soil S4A that, at pH 12, is slightly higher than the others).

6.3.4 Discussion

Concerning the tested natural soils, S9B, a Ferrasols derived from amphibolites (high content of Mg^{2+} and Fe^{2+}) described by its clay accumulation dominated by low-activity clays (mainly kaolinite) and a high content of sesquioxides, as aluminium oxide Al_2O_3 and phosphorus (III) oxide P_4O_6, presented the best results in glyphosate and AMPA adsorption.

Referring to TMT, greatest results were obtained by TMT 1 and 2 applications. TMT 1 was generally formed by a Calcic Arenosol, providing characteristics as coarse texture, generally high permeability and low water and nutrient storage capacity, with accumulations of secondary carbonates (calcic carbonates) in the fine earth fraction. On the other hand, Arenosols facilitate cultivation, rooting and harvesting of root and tuber crops (IUSS Working Group WRB, 2015). TMT 2 was mostly produced with an Aluandic Andosol. Andosols are typically dark soils, generally fertile, with a strong phosphate fixation (caused by active Al and Fe). These Technosols are described by an accumulation of stable organomineral complexes, which Al complexed by organic acids prevailing, with an extremely acid to acid reaction and a blackish color (Aluandic qualifier) (IUSS Working Group WRB, 2015).

Aluminic Umbrisols (A4A and S13A) also shown good adsorption capacity, probably associated to their significant accumulation of OM and amorphous iron and aluminium oxides.

Referring to pH influence in the adsorption process, at extremely low pH levels (<0.8 and 1.8), glyphosate and AMPA acquire a positive charge due to the protonation of their amino group. At slightly higher pH values, glyphosate achieves a neutral charge at pH <2.3, while AMPA reaches a neutral charge at pH <5.4. As the pH continues to increase, both herbicides exhibit negative charges. The fact that glyphosate is a zwitterion in aqueous solutions may have facilitated its adsorption on adsorbents with pH_{pzc} lower than the pH values of the solution where the glyphosate molecule becomes predominantly negative (i.e., where the surface charge and predominant glyphosate charge are both negative) due to the presence of positive and negative charges on different parts of the molecule, and thus can interact electrostatically with positively and negatively charged surfaces. On the other hand, glyphosate's zwitterionic nature in the environment leads to the formation of glyphosate-metal complexes. It readily forms complexes with various divalent and trivalent cations such as calcium, magnesium, copper, and iron leading to the reduction of its bioavailability for microbial degradation, thereby increasing its persistence (Ulrich & Ferguson, 2021).

For the five adsorbents for which the influence of solution pH on the adsorption of glyphosate and AMPA was tested, all with pH_{PZC} of approximately 4.9, there was an increase in adsorption between pH 1 and pH 3, as expected considering the loss of the proton associated with the carboxyl group (pKa_2) in the case of glyphosate and the phosphonic group (pKa_1) in the case of AMPA and the predominant positively charged adsorbent surface. Subsequently, there was a gradual decrease in the adsorption between pH 3 and pH 6 (more pronounced for glyphosate than for AMPA). Between pH 6 and 10 the adsorption of glyphosate onto the various adsorbents tested was already significantly lower (except for TMT 1 that only reduce at pH higher than 10, reaching adsorption values close to zero). On the other hand, for AMPA the adsorption reduction by the TMTs only occurs with more pronounced effect from pH 9 onwards, continuing constant between pH 6 and 10 for the remaining adsorbents. For all the adsorbents, between pH 10 and 12 there was a marked decrease to values close to zero (except for glyphosate adsorption onto soil S4A that, at pH 12, was slightly higher than the others). Is important to highlight that, as presented in Figure 6.7, AMPA adsorption onto soils and TMTs occurred at the pH range between 2 and 5, at which AMPA most abundant ionic form is neutral and adsorbents surfaces were positively charged.

Therefore, the complexation with aluminum, iron, and organometallic complexes, which form a strong, irreversible bond with phosphates, increased the adsorption onto some of the tested materials. Thus, soil containing higher amorphous iron and aluminium oxides, OM content and low pH were positively correlated with enhanced glyphosate and AMPA adsorption, as also mentioned by other authors (Gunarathna *et al*., 2018; Mencaroni *et al*., 2022, 2023).

6.4 Conclusions

This study investigated the adsorption behavior of glyphosate, AMPA, and glufosinate onto a set of materials, including biochars, soils, and TMTs. The results revealed variable adsorption performance for the three compounds across the tested samples. In the preliminary experiments, it was possible to see that the three compounds were poorly adsorbed by all tested biochar samples, with maximum removal of 25%, 12% and 4% for glyphosate, AMPA and glufosinate, respectively. These results were mostly attributed to the temperature at which biochar was produced (> 500 ºC), in accordance with the obtained by other researchers (Hall *et al.*, 2018). In contrast, tested soils exhibited high adsorption capacity, particularly for glyphosate and AMPA, with preliminary assays showing maximum removal percentages of 94% and 91%, respectively. However, glufosinate adsorption did not exceed 6% removal. For TMTs maximum adsorption values of 79% and 83% for glyphosate and AMPA, respectively, were achieved, whereas glufosinate exhibited notably low adsorption with a maximum removal of only 3%. Furthermore, smaller grain sizes were associated with enhanced adsorption performances when comparing with the same soil or TMT with higher grain size. The adsorption kinetics for these compounds were relatively slower compared to fluoxetine adsorption onto the biochars, with complete adsorption of glyphosate and AMPA occurring in 14 hours for soils and 72 hours for TMT, consistent with reported literature. The Langmuir model analysis indicated a maximum adsorption capacity of 10.84 mg/g for glyphosate (soil S9B) and 15.08 mg/g for AMPA (TMT 1). These findings suggest that natural soils and TMTs can serve as effective, cost-efficient, and sustainable adsorbents for removing glyphosate and AMPA from aqueous solutions. Moreover, the selection of sustainable materials, rich in Al and Fe oxides, high clay content, and OM should be prioritized for TMT production. The development and production of tailor-made Technosols presents an innovative and integrated solution to enhance natural resource quality, promote sustainability reducing waste generation through its reuse, and remediating contaminated areas.

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Appendix A. Supplementary data

Table S6.1 - Physical and chemical properties of biochars

Sample	T (ºC) ***	Physico-chemical											Proximate analysis and TGA				Macronutrients content of biochar (g kg^{-1})							Trace metal content (mg kg^{-1})							Water holding Capacity (Hydrological behavior)	
		pH	% C	% N	% H	% S	%Ash	%O	%C$_{inorg}$	O/C$_{org}$	H/C$_{org}$	C/N	% Moisture	%Volatile matter	%Ash	%Fix C	P	Ca	Mg	Na	K	Fe	Al	Co	Cr	Cu	Mn	Ni	Pb	Zn	Field capacity ****	Wilting point****
Beu-2*	500	9.4	79.0	0.6	1.9	0.036	3.8	14.7	0.36	0.14	0.30	163	2.41	22.17	3.92	73.91	1.25	23.26	1.07	0.34	3.08	0.99	0.5	< 5	10	20	138	26	< 25	42	176.81 ± 34.71	96.53 ±23.92
BCc-1*	500	9.7	77.2	0.8	2.1	0.032	6.3	13.6	0.09	0.13	0.33	117	3.49	16.03	9.09	74.88	2.31	1.64	1.4	0.17	17.12	3.98	1.07	< 5	46	22	78	140	< 25	440	153.28 ± 3.26	138.25 ±0.86
BCc-2*	500	9.8	80.2	0.5	2.5	0.030	5.1	11.7	0.05	0.11	0.37	208	4.94	15.78	5.33	78.9	2.78	1.3	0.63	0.19	21.84	5.2	0.4	< 5	62	15	68	79	< 25	620	121.07 ± 3.8	108.85 ±2.97
BAcSw-3**	300	7.6	69.7	0.6	4.3	0.004	3.5	22.0	0.28	0.24	0.75	140	2.09	39.63	2.88	57.49	0.62	14.82	0.76	0.78	3.02	0.13	<0,05	< 5	< 5	< 5	26	< 5	< 25	781	86.23 ± 15.57	67.76 ±13.43
BAcSw-2*	350	7.1	70.0	0.7	3.9	0.021	3.6	21.9	0.59	0.24	0.67	119	2.72	37.31	3.62	59.06	0.77	2.04	1.04	0.89	3.69	0.04	<0,05	< 5	< 5	< 5	27	< 5	< 25	885	93.54 ± 56.38	68.96 ± 43.44
BOpc**	450	9.9	28.6	1.6	1.8	0.139	49.3	18.7	1.66	0.52	0.78	21	2.65	29.41	49.49	21.1	3.84	124.2	8.6	3.38	24	10.78	11.8	11	25	60	234	28	39	76	63.26 ± 1.54	47.3 ± 1.76
BRh*	600	8.4	49.6	2.3	1.5	0.358	23.3	23.0	0.05	0.35	0.36	25	4.25	16.67	38.66	44.66	17.22	21.14	8.4	4.7	35.92	3.7	0.84	< 5	25	108	800	24	< 25	400	128.17 ± 1.55	96.16 ± 1.36
BPb*	550	8.8	88.7	0.6	1.0	0.059	4.4	5.2	0.15	0.04	0.14	167	2.58	14.91	2.82	82.27	0.48	11.62	1.28	0.66	2.9	0.54	0.9	< 5	8	9	61	9	< 25	400	125.82 ± 21.21	115.56 ±18.88
BSdG*	450	10.5	73.0	1.0	2.7	0.100	20.2	3.0	0.20	0.03	0.45	88	2.09	22.26	11.15	66.59	6.7	20.8	5.4	1.8	15.5	2.54	0.56	< 5	23	55	446	20	< 25	860	nd	nd
BSd-1**	300	5.5	65.8	0.7	5.0	0.065	0.7	27.7	0.12	0.32	0.92	107	2.39	52.1	1.37	46.53	0.4	4.34	0.46	0.27	1.61	0.46	0.44	< 5	< 5	< 5	85	< 5	< 25	265	131.57 ± 50.59	84.02 ±4.44

* H/Corg ≤ 0,7 - classified as biochar
** H/Corg > 0,7 – classified as Pyrogenic carbonaceous materials (PCM)
*** Production temperature
**** % dry sample

nd – not determined

Table S6.2 - Physical and chemical properties of soils

	pH		pH H_2O_2 15%						MO	C.E.	Elementar Analysis		Equilibrium ions							Cation exchange capacity					Selective extractions*					
Sample	H_2O	KCl	2´	30´	60´	120´	240´	360´			P Total	P Olsen	Cl^-	F^-	SO_4^{2-}	PO_4^{3-}	NO_2^-	NO_3^-	NH_4^+	Al	Ca	Mg	Na	K	Fe_{py}	Al_{py}	Fe_{ox}	Al_{ox}	Fe_{dith}	Al_{dith}
									%	µS cm^{-1}	mg L^{-1}		mg L^{-1}							cmol(+)·Kg^{-1}					mg Kg^{-1}		mg Kg^{-1}		mg Kg^{-1}	
S4 A[a]	4.97	4.34	5.47	5.31	5.11	4.71	4.31	4.14	16%	56.52	467	2.02	0.46	0.02	1.32	0.03	0.03	0.44	0.34	2.00	0.09	0.25	0.07	0.33	2343	8576	6772	18456	13885	11650
S13 A[b]	4.58	4.33	5.42	5.34	5.14	4.78	4.42	4.23	27%	82.01	610	1.09	0.32	0.02	0.52	0.03	0.03	2.76	0.54	3.47	0.04	0.08	0.07	0.10	5488	16456	8657	21159	68117	19990
S9 B[c]	4.85	4.48	5.50	5.07	4.59	4.24	3.97	3.89	23%	60.42	646	0.03	0.89	0.01	1.22	0.03	0.03	0.33	0.34	2.30	0.02	0.06	0.07	0.07	4203	13830	7374	20264	29787	21405
S11 B[d]	4.77	4.30	5.44	5.45	5.31	5.16	4.74	4.52	12%	32.58	602	1.30	0.24	0.01	0.93	0.03	0.03	0.09	0.32	3.16	0.01	0.03	0.05	0.04	7137	11355	5703	8666	51038	9679
2Ah	nd	nd	nd	nd	nd	nd	nd	nd	10%	32.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
1Ah	nd	nd	nd	nd	nd	nd	nd	nd	18%	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Andic	nd	nd	nd	nd	nd	nd	nd	nd	26%	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Ferrálic	nd	nd	nd	nd	nd	nd	nd	nd	9%	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd – not determined

*Fe_{py} and Al_{py} –present in organic complexes, and non-crystalline hydrous oxides, extracted using sodium pyrophosphate (Bascomb, 1968); Fe_{ox} and Al_{ox} – amorphous oxy-hydroxides, extracted using acid ammonium oxalate (Blakemore, 1983); Fe_{dith} and Al_{dith} – Crystallized oxy-hydroxides, extracted using citrate bicarbonate dithionite (Mehra & Jackson, 1960)

[a] NaF 2’- 11.21 and NaF 30’- 11.42

[b] NaF 2’- 11.37 and NaF 30’- 11.55

[c] NaF 2’- 11.36 and NaF 30’- 11.55

[d] NaF 2’- 11.28 and NaF 30’- 11.48

Table S6.3 - Physical and chemical properties of Technosols

Sample	Physico-chemical						
	pH H_2O	pH KCl	MO %	C.E. µS cm^{-1}	Redox mV	C %	N %
TMT 1	4.35	4.49	9%	211	263	3.69	0.22
TMT 2	4.10	4.01	14%	193	366	5.74	0.43
TMT 3	7.33	6.82	19%	2840	194	6.29	0.13
TMT 4	7.67	7.11	7%	1913	199	6.47	0.1
TMT A	6.15	6.74	82%	1620	201	37.78	2.02
TMT B	7.57	7.04	22%	1219	172	13.09	1.09
TMT C	7.70	7.56	27%	2440	240	10.87	1.18
TMT D	7.85	7.56	25%	2600	153	12.94	0.96
TMT E	7.81	6.90	9%	483	196	3.85	0.23
TMT F	9.01	8.72	23%	5180	128	11.45	0.81
TMT G	8.16	7.32	8%	416	207	3.4	0.21
TMT N	nd	nd	9%	nd	nd	nd	nd
TMT H	nd	nd	14%	nd	nd	nd	nd

nd – not determined

Table S6.3 - (continuation)

Sample	Metals and metalloids																							
	Li	Be	V	Cr	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Mo	Cd	Cs	Ba	Hg	Tl	Pb	Mg	Si	Ca	Mn	Fe
	mg kg^{-1}																							
TMT 1	69.66	2.02	44.65	42.24	8.04	22.68	17.69	60.29	48.10	4.10	93.70	27.88	2.17	0.05	21.44	54.48	0.07	0.55	33.62	5987	1835	694	99	291
TMT 2	37.24	1.85	111.35	74.18	29.75	59.05	63.75	118.18	6.53	3.65	53.68	7.82	1.85	0.15	9.19	151.73	0.11	0.74	22.47	8819	1737	699	114	2242
TMT 3	14.60	0.58	496.60	53.22	5.47	196.78	89.81	254.30	6.34	0.02	98.88	733.50	15.30	0.34	6.25	265.29	0.11	0.29	28.99	11958	1790	142776	98	5098
TMT 4	8.70	0.44	375.94	38.53	7.19	230.23	118.49	423.50	5.90	0.27	22.26	798.35	9.41	0.79	1.18	253.00	0.09	0.28	28.03	14940	1999	247258	105	6497
TMT A	2.94	0.06	21.35	nd	1.06	4.97	36.14	27.14	1.42	1.22	1.38	71.95	0.97	0.19	0.32	14.20	0.04	0.03	10.67	1888	602	26444	107	318
TMT B	34.02	1.58	42.46	nd	12.78	26.77	240.36	560.48	28.04	3.53	29.97	116.39	3.88	0.69	5.79	152.11	0.33	0.26	53.71	14028	1491	42068	101	668
TMT C	21.30	0.72	72.17	102.17	11.04	37.24	110.66	207.11	12.89	4.60	35.08	124.13	5.49	0.50	4.75	213.45	0.16	0.33	20.38	6872	1116	12259	88	339
TMT D	35.92	1.22	58.08	89.89	11.02	25.13	154.66	294.03	24.79	2.82	28.93	115.31	2.59	0.46	5.71	118.67	0.22	0.23	41.49	9493	1015	40236	82	490
TMT E	17.44	0.77	337.58	166.20	29.57	115.83	71.62	127.30	6.52	2.26	52.86	306.38	3.40	0.23	4.48	138.41	0.06	0.23	10.94	8185	1466	41992	99	2176
TMT F	17.17	0.75	328.08	89.69	5.43	85.27	88.78	252.56	14.98	3.79	20.97	348.09	5.67	0.76	3.08	139.76	0.16	0.21	21.43	7084	1088	58289	82	2385
TMT G	14.71	0.51	94.34	nd	10.07	33.15	214.43	140.52	6.62	9.66	36.04	125.07	5.76	0.22	4.11	200.31	0.04	0.13	15.62	10686	1089	25722	88	1136
Ferrálic	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TMT H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd – not determined

Kinetic assays

Pseudo-first order model (Lagergren, 1898):

$$q_t = q_e(1 - e^{(-k_1 \cdot t)}) \tag{1}$$

Pseudo-second order model (Ho, 2004):

$$q_t = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)} \tag{2}$$

where: *t* is the equilibrium time (min); q_t is the amount of herbicide adsorbed at time *t* (mg g^{-1}); q_e is the adsorption capacity at equilibrium (mg g^{-1}); and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first order and pseudo-second order kinetic rate constants.

Elovich (Low, 1960):

$$q_t = {}^{1}\!/_{\beta} \ln(\alpha\beta) + \left({}^{1}\!/_{\beta}\right) \ln t \tag{3}$$

Weber and Morris intraparticle diffusion models:

$$q_t = k_{id} t^{0.5} + C \tag{4}$$

where: α is the Elovich constant related to the initial sorption rate ($mg.g^{-1}.min^{-1}$); β is the Elovich sorption constant, related to the desorption rate; C is the thickness of the adsorption boundary layer diffusion effects; and k_{id} represents the rate constant for intraparticle diffusion (mg g^{-1} $min^{-0.5}$).

Langmuir:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

Freundlich :

$$q_e = K_F {C_e}^{1/n} \tag{6}$$

Sips (Saadi *et al.*, 2015):

$$q_e = \frac{q_{mLF}(K_{LF} C_e)^{n_{LF}}}{1 + (K_{LF} C_e)^{n_{LF}}} \tag{7}$$

where: q_e is the quantity of herbicide adsorbed per gram of media (mg g^{-1}); q_m is the maximum adsorption capacity (mg g^{-1}); K_L is the Langmuir constant, correlated to the affinity between herbicide and the media (l mg^{-1}); C_e is the concentration of herbicide in the liquid phase at equilibrium (mg l^{-1}); K_F is the Freundlich adsorption capacity factor (mg g^{-1}(mg $l^{-1})^{-1/n}$); 1/n is the intensity parameter; q_{mLF} is the Sibs maximum adsorption capacity (mg g^{-1}); K_{LF} is the Sips constant, correlated to the affinity between herbicide and the media (l mg^{-1}); n_{LF} is the intensity parameter;

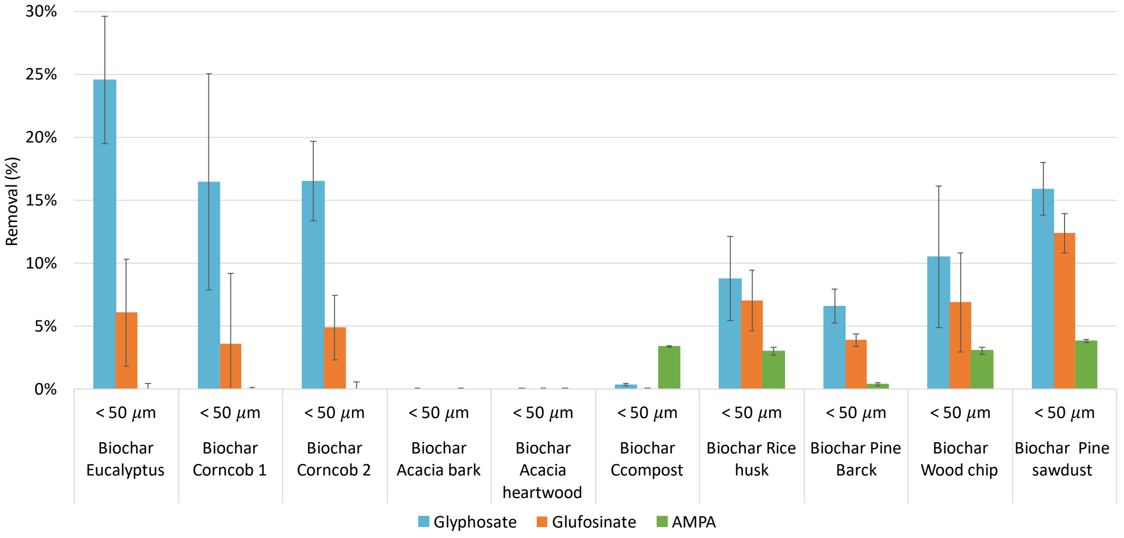


Fig. S6.1 - Glyphosate, glufosinate and AMPA adsorption by biochar materials. Error bars correspond to the standard deviation of six replicates.

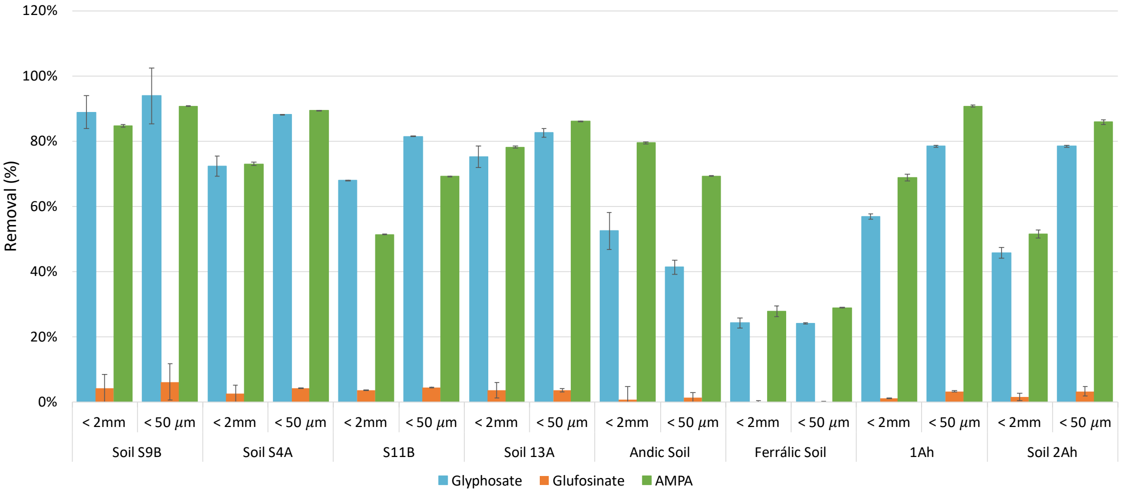


Fig. S6.2- Glyphosate, glufosinate and AMPA adsorption by natural soil. Error bars correspond to the standard deviation of six replicates.

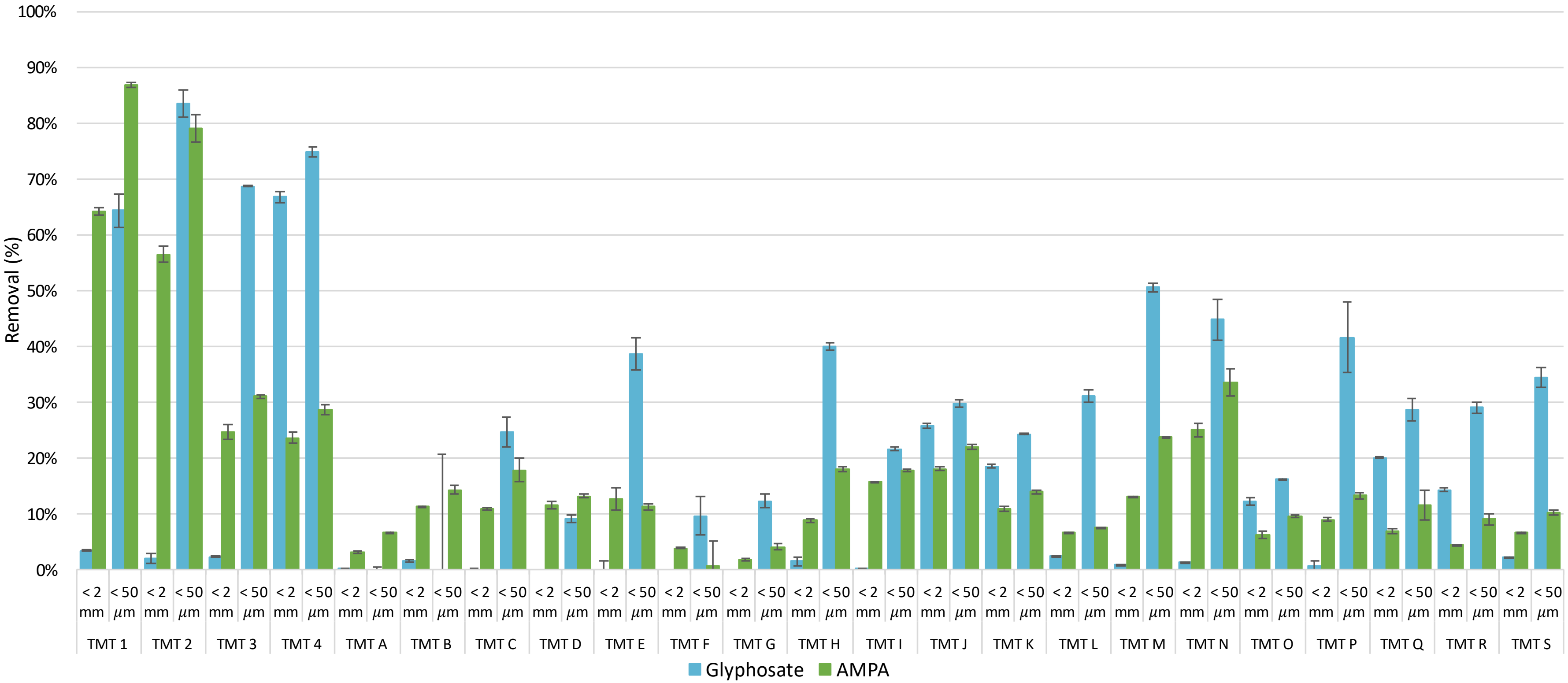


Fig. S6.3- Glyphosate and AMPA adsorption by TMTs. Error bars correspond to the standard deviation of six replicates.

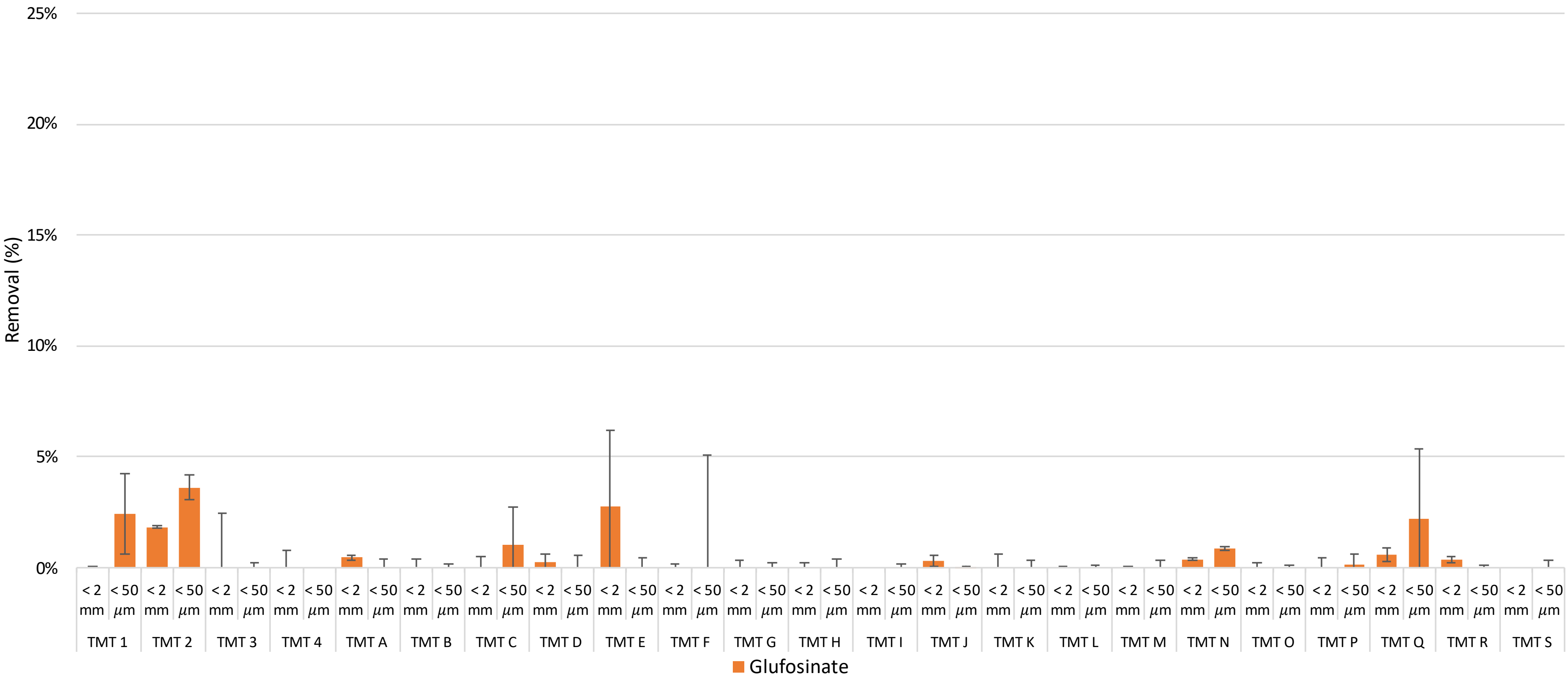


Fig. S6.4 - Glufosinate adsorption by TMTs. Error bars correspond to the standard deviation of six replicates.

CHAPTER 7 GENERAL CONCLUSIONS

7.1 Main outcomes of the thesis

Pharmaceuticals and pesticides are increasingly recognized as chemicals of concern. This perception is associated with the major growth in its use, as well as their known negative effects on soil and aquatic species and respective ecosystems, as well as potential impact on human health. Moreover, these chemicals have been found to be prevalent in various environmental compartments, in substantial quantities and high frequency. Therefore, as a first approach to the problem, antibiotics and antidepressants presence was monitored in two rivers in northern Portugal. Water samples and sediment samples (from the top layer, within 0 and 2 cm depth, and bottom layer within 2 and 10 cm) were collected along the Douro and Leça rivers (Porto, Portugal). Samples were characterized and analyzed for seventeen antibiotics and ten antidepressants. A higher concentration of pharmaceuticals was observed in samples from the Leça River compared to those from the Douro River. In Douro water samples, only two psychiatric drugs, carbamazepine, and fluoxetine, were detected. However, thirteen out of twenty-seven pharmaceuticals, including six antibiotics and seven psychiatric drugs, were found in the Leça River water samples. Of particular note, azithromycin was the pharmaceutical found at the highest concentration, in the Leça River samples, with the values of 2.82 μg/L. It was measured in a sampling point located near a WWTP effluent discharge, that could explain the higher concentrations found. Regarding the detection frequency, fluoxetine was the most frequently detected pharmaceutical in water samples. Additionally, carbamazepine and venlafaxine were found to pose a potential risk to algae in the Leça River water. Concerning sediments samples, within the analyzed antibiotics only sulfamethoxypyridazine was found in Douro sediment and azithromycin in Leça sediment, both in the top sediment layer. Also, psychiatric drugs were found in the collected samples: four in Douro sediment and six in Leça sediments. Comparing the concentration found in the top and bottom sediment layers in each sampling point, in Douro River venlafaxine, the only quantified pharmaceutical, presented a higher concentration in the bottom zone which could be correlated with its migration through the soil. In Leça sediments, higher concentrations were found in the top layer which could be associated with recent pollution events in the studied area. The review of some monitoring studies reported in the literature showed that only a few included sediment analysis, while most of them presented solely water sample analysis (especially for psychiatric drugs). Thus, and when comparing the obtained results and those reported in the literature, it was not possible to identify a consistent contamination pattern or associate the sediments contamination with the migration of the contaminants from the water. Nevertheless, it was possible to notice that higher concentrations of these contaminants were observed at sampling locations following the WWTP discharges.

In addition, a literature search was performed on water and sediment contamination with glyphosate, AMPA, and glufosinate to assess the mobility of these compounds after use. To assess and evaluate world's environmental contamination by the referred substances, the published studies during the last five years including monitoring of glyphosate, AMPA, and glufosinate concentrations in water (surface and groundwater) and sediments were analyzed. The applicable legislation to contaminations associated to these pollutants differs widely from country to country. Additionally, the same country may have different limit values depending on the type of water (drinking water, surface water, or groundwater). The restrictions can be targeted to individual and specified compounds, any pesticide individually, or even the sum of all pesticides found. Europe holds the lowest legal limit for glyphosate residues in water intended for human consumption (0.1 μg/L) and Japan the highest (2 000 μg/L). The most applied detection method was HPLC and MS/MS. Referring to the detection limits stablished in the analyzed studies, only 40% of the studies present LOD values <0.1 μg/L, the maximum permissible value for individual pesticide water contaminations in the European Union. Concerning the sample pre-treatment, among the studies reviewed the most referred was "overnight" derivatization, with the agent FMOC-Cl and borate buffer. The extraction was mostly performed throughout SPE. Referring publications of glyphosate monitoring in water and sediments, France was the country with the higher samples/publication ratio, followed by Japan and Italy. Argentina was the country with the higher frequency of studies publication, but a lower samples/publication ratio. It was found that the European countries that have a higher number of samples analyzed for glyphosate levels tend to correspond with the increased rate of glyphosate application. Publications of AMPA monitoring in water and sediments, were also more frequent in Argentina, but France was, once again, the country with the higher samples/publication ratio, followed by USA, Sweden, and Italy. The number of glufosinate monitored samples was largely higher in China that in the rest of the countries with publications about this compound.

The maximum contaminant concentration found in surface water was 6 872 µg/L, 5750 µg/L, and 13.15 µg/L for AMPA, glyphosate and glufosinate, respectively. In groundwater, maximum values of 8 700 µg/L for glyphosate, and 233 µg/L for AMPA and 0.03 µg/L for glufosinate were found. For sediments, the maximum concentrations found were 1 882 µg/kg, 4 033 µg/kg and 14.9 µg/kg for glyphosate, AMPA and glufosinate. Although the maximum glyphosate concentration, contrary to what was expected, was higher in groundwater than in surface water, the frequency of detection was much higher in surface water (70%) compared to groundwater (18%). Referring AMPA and glufosinate, the detection frequency in surface waters was 87% and 6% and in groundwater of 16% and 0.7%, respectively. South America countries presented the highest values of maximum detected concentration for glyphosate and AMPA. Sediments were the environmental matrix with the highest detected concentration of glufosinate. In Europe, France was the country where maximum concentrations were found in surface waters, followed by Italy and Germany. In groundwater, the higher glyphosate concentrations were about 10 times lower, with its maximum found in Sweden, followed by Italy. Germany and Croatia presented the maximum concentration found in sediments. Several factors were mentioned as drivers of the spread of these compounds to surface water, sediments, and groundwater, namely overspray, spray drift, surface run-off, shallow water tables, low hydraulic conductivity in the aquifer, low hydraulic gradient, very low flow velocity, soil type and its chemical constitution. As potential contamination sources, the persistent and escalating application in agricultural and domestic activities, WWTP and improper use were referred.

Therefore, and in view of the documented contamination associated with the compounds under study, it is essential to determine remediation technologies, designed not only to remediate contaminated sites but also to reduce their mobility, preventing water and soil contamination, and reducing health problems associated with these compounds' ingestion. Thus, fluoxetine, glyphosate, AMPA, and glufosinate adsorption onto different materials was investigate. Firstly, twelve biochars produced from different forest/agri-food wastes were tested as adsorbents for fluoxetine removal from water. The obtained adsorption capacities ranged from 2.21 to 6.41 mg/g (according with Langmuir model) for the five selected biochars, and eucalyptus biochar presented the highest adsorption capacity, followed by hollow tree, vine, walnut tree and quince. Adsorption kinetics was fast, with total adsorption in less than 15 min. The column adsorption experiments exhibited a good performance of eucalyptus biochar in continuous mode, indicating that it can be successfully used as renewable alternative for fluoxetine removal.

Glyphosate, AMPA and glufosinate adsorption onto a total of forty-one samples of three different materials, biochars, soils, and tailor-made Technosols (TMT), was tested. Regarding the results obtained, it was concluded that the three compounds were poorly adsorbed by all analyzed biochar samples, with maximum removal of 25%, 12% and 4 % for glyphosate, AMPA and glufosinate, respectively. These results were mostly associated with the biochar production temperature. Concerning the tested soils, high adsorption for glyphosate and AMPA was obtained (maximum of 94% and 91% in the preliminary assays), in contrast to glufosinate, for which 6% removal was not exceeded. For TMTs maximum adsorption values of 79% and 83% for glyphosate and AMPA, respectively, were achieved. Once again, glufosinate stood out for its low adsorption values, with a maximum of 3% of removal. Furthermore, smaller grain sizes were associated with enhanced adsorption performances when comparing with the same soil or TMT with higher grain size. Adsorption kinetics was not so fast as for fluoxetine adsorption, with total adsorption occurring in 14 h onto soils and 72 h onto TMTs. Similar equilibrium times have been reported in literature. The maximum adsorption capacity (according with Langmuir model) was 10.84 mg/g to glyphosate (soil S9B) and 15.08 mg/g to AMPA (TMT 1). The results revealed that natural soils and TMT can be used as effective, low-cost, and sustainable adsorbents to remove glyphosate and AMPA from aqueous solutions, and that materials with high Al and Fe oxides, clay content and OM should be selected to the TMT production. Tailor-made Technosol production will allow the development of an innovative and integrated solution that contributes to improving the quality of natural resources, sustainability, reducing waste production, and restoring contaminated areas.

7.2 Future research recommendations

Despite the results obtained in the developed monitoring study, more contamination search needs to be performed in different dimension river courses, in sediments and in soil.

Thus, concerning glyphosate, AMPA, glufosinate and fluoxetine contaminated soils and water remediation, and although several other studies have been developed in recent years, there are still aspects that require further research and investigation, essential to the development of better and more suitable remediation techniques.

Firstly, the accurate identification of source of pollution is essential, thus, samples need to be collected in other locations as rural area, industrialized area, and near possible contamination sites. Associated with its fate and transport, it is important to improve the understanding of how these compounds behaves in contaminated water, sediments and soil, its persistence, mobility, and interactions. This knowledge can help determine the extent of contamination and which remediation techniques would be most effective.

Also, a deep understanding of the ecological and human health effects associated with their contamination is essential. More and systematic toxicity studies on soil organisms, animals, and plants are needed to assess environmental risks.

Glyphosate, AMPA and glufosinate, due to their distinct chemical characteristics, including their high-water solubility, limited solubility in organic solvents, and low volatilization, combined with the absence of chromophores or fluorophores, ionic nature, and preference for complex formation, render the extraction and quantification processes highly challenging for expert researchers in the field. Thus, time spending, complex and expensive analytical methodologies are normally applied, compromising frequent monitoring surveys of these compounds. Therefore, improving detection and monitoring techniques in soils, sediments and water is crucial for assessing necessity and the effectiveness of remediation strategies. This may involve the development of sensitive and accurate methods to quantify these compounds in different matrix types.

Considering the various situations in which adsorption can be applied, namely in water treatment in WWTP or in soil treatment (in situ application), it would be interesting to study the reaction of the treatment system to possible environmental variations encountered as well as to changes in contaminant load and in the form of contamination.

Regarding the materials tested for the adsorption process, further study of the feedstock life cycle, used in the production of biochar and Technosols, as well as the impact of their production process against the benefits arising from their use still needs to be carried out.

Additionally, a cost benefit analysis must be undertaken. Also, a column adsorption experiments for the best glyphosate and AMPA adsorbents is recommended.

The design and production of a technosol based on the results obtained in this thesis and its application as an adsorbent, not only in water but also in soils contaminated with glyphosate and AMPA would be a very important next step.

Regarding the adsorption of fluoxetine in biochars, it would be interesting to study the regeneration and reuse of the most efficient biochar.

The study of other remediation techniques applied in association with adsorption, namely biodegradation, phytoremediation, and photodegradation, evaluating the effectiveness of each technique combination in soil and water remediation, should be performed.

Most of the existing remediation studies have focused on laboratory-scale or small contaminated areas. Hence, there is a need for research that addresses the remediation of glyphosate, AMPA and glufosinate-contaminated soils and water on a larger scale, considering technical, economic, and environmental feasibility.

Thus, in terms of conclusions, it can be inferred that there is a wide range of potential contaminants present in the environment, either directly utilized by humans or generated through decomposition or metabolization upon ingestion. The increasing sophistication of analytical techniques enables the detection of trace quantities, facilitating the study of early-stage health effects and the assessment of compound ecotoxicity across different trophic levels. Awareness campaigns and international policies have contributed to mitigating certain environmental calamities, not preventing, however, that these contaminants continue to be detected. Moreover, some contaminants are persistence, demanding the treatment and remediation of various environmental compartments. Significant progress has been made, with different options available depending on the type and levels of contamination, the specific compartment under consideration, and the available financial resources. Nonetheless, much work remains, as each contaminant or group of contaminants requires laboratory-scale exploration and even pilot-scale investigations due to the complex nature of the environment, which is influenced by diverse factors. The field encompassing this thesis is thus an area of active development. While substantial advancements have already been achieved, there is still much to be accomplished. It is hoped that this dissertation has contributed to a small advance in science and can serve as a foundation for further advanced studies. The work is not finished; opened doors for everything that remained to be done.

REFERENCES

Açikkol, M., & Salkim, D. (2010). GC-MS analysis of fluoxetine and its active metabolite norfluoxetine in human urine. *Marmara Pharmaceutical Journal*, *14*(2), 98–103. https://doi.org/10.12991/201014456

Acuña, V., von Schiller, D., García-Galán, M. J., Rodríguez-Mozaz, S., Corominas, L., Petrovic, M., Poch, M., Barceló, D., & Sabater, S. (2015). Occurrence and in-stream attenuation of wastewater-derived pharmaceuticals in Iberian rivers. *Science of the Total Environment*, *503–504*, 133–141. https://doi.org/10.1016/j.scitotenv.2014.05.067

Aghababaei, A., Borugadda, V. B., Dalai, A., & Niu, C. H. (2023). An investigation on adsorption of carbamazepine with adsorbents developed from flax shives: Kinetics, mechanisms, and desorption. *Chemical Engineering Research and Design*, *189*, 138–155. https://doi.org/10.1016/j.cherd.2022.11.008

Agostini, M. G., Roesler, I., Bonetto, C., Ronco, A. E., & Bilenca, D. (2020). Pesticides in the real world: The consequences of GMO-based intensive agriculture on native amphibians. *Biological Conservation*, *241*(November 2019), 108355. https://doi.org/10.1016/j.biocon.2019.108355

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S. S., & Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, *99*, 19–23. https://doi.org/10.1016/j.chemosphere.2013.10.071

Ahmed, M. B., Zhou, J. L., Ngo, H. H., Guo, W., & Chen, M. (2016). Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresource Technology*, *214*, 836–851. https://doi.org/10.1016/j.biortech.2016.05.057

Al-Rajab, A. J., & Hakami, O. M. (2014). Behavior of the non-selective herbicide glyphosate in agricultural soil. *American Journal of Environmental Sciences*, *10*(2), 94–101. https://doi.org/10.3844/ajessp.2014.94.101

Alazaiza, M. Y. D., Albahnasawi, A., Eyvaz, M., Maskari, T. Al, Nassani, D. E., Amr, S. S. A., Abujazar, M. S. S., & Bashir, M. J. K. (2023). An Overview of Green Bioprocessing of Algae-Derived Biochar and Biopolymers: Synthesis, Preparation, and Potential Applications. *Energies*, *16*(791), 1–23. https://doi.org/https://doi.org/10.3390/en16020791

Albers, C. N., Banta, G. T., Hansen, P. E., & Jacobsen, O. S. (2009). The influence of organic matter on sorption and fate of glyphosate in soil - Comparing different soils and humic substances. *Environmental Pollution*, *157*(10), 2865–2870. https://doi.org/10.1016/j.envpol.2009.04.004

Alcántara-de la Cruz, R., Cruz-Hipolito, H. E., Domínguez-Valenzuela, J. A., & De Prado, R. (2021). Glyphosate ban in Mexico: potential impacts on agriculture and weed management. *Pest Management Science*, *77*(9), 3820–3831.

https://doi.org/10.1002/ps.6362

Alonso, B., Griffero, L., Bentos Pereira, H., Pareja, L., & Pérez Parada, A. (2022). Determination of glyphosate and AMPA in freshwater and soil from agroecosystems by 9-fluorenylmethoxycarbonyl chloride derivatization and liquid chromatography - fluorescence detection and tandem mass spectrometry. *MethodsX*, *9*, 101730. https://doi.org/10.1016/j.mex.2022.101730

Álvarez Bayona, M. A., Maturana Córdoba, A., Gallardo Amaya, R. J., & Muñoz Acevedo, A. (2022). Occurrence of glyphosate in surface and drinking water sources in Cúcuta, Norte de Santander, and its removal using membrane technology. *Frontiers, Environmental Science*, *10*(941836), 1–18. https://doi.org/10.3389/fenvs.2022.941836

Alza-Camacho, W. R., García-Colmenares, J. M., & Chaparro-Acuña, S. P. (2016). *Voltammetric Quantification of Paraquat and Glyphosate in Surface Waters*. *17*(3), 331–345. https://doi.org/https://doi.org/10.21930/rcta.vol17_num3_art:510

Amalina, F., Krishnan, S., Zularisam, A. W., & Nasrullah, M. (2023). Biochar and sustainable environmental development towards adsorptive removal of pollutants: Modern advancements and future insight. *Process Safety and Environmental Protection*, *173*(March), 715–728. https://doi.org/10.1016/j.psep.2023.03.069

Andrade, V. S., Gutierrez, M. F., Regaldo, L., Paira, A. R., Repetti, M. R., & Gagneten, A. M. (2021). Influence of rainfall and seasonal crop practices on nutrient and pesticide runoff from soybean dominated agricultural areas in Pampean streams, Argentina. *Science of the Total Environment*, *788*, 147676. https://doi.org/10.1016/j.scitotenv.2021.147676

ANSES. (2017). *ANSES withdraws marketing authorisation for Basta F1, a plant protection product containing glufosinate*. https://www.anses.fr/en/content/anses-withdraws-marketing-authorisation-basta-f1-plant-protection-product-containing

Antier, C., Andersson, R., Auskalnienė, O., Barić, K., Baret, P., Besenhofer, G., Calha, I., Carrola Dos Santos, S., De Cauwer, B., Chachalis, D., Dorner, Z., Follak, S., Forristal, D., Gaskov, S., Gonzalez Andujar, J. L., Hull, R., Jalli, H., Kierzek, R., Kiss, J., … Wirth, J. (2020). A survey on the uses of glyphosate in European countries. In *INRAE*. https://doi.org/https://doi.org/10.15454/A30K-D531

Antier, Clémentine, Kudsk, P., Reboud, X., Ulber, L., Baret, P. V., & Messéan, A. (2020). Glyphosate use in the European agricultural sector and a framework for its further monitoring. *Sustainability (Switzerland)*, *12*(14), 1–22. https://doi.org/10.3390/su12145682

Arán, D., Antelo, J., Fiol, S., & Macías, F. (2018). Immobilization of phosphate by a Technosol spolic silandic: kinetics, equilibrium and dependency on environmental variables. *Journal of Soils and Sediments*, *18*(9), 2914–2923. https://doi.org/10.1007/s11368-018-1970-y

Arán, D., Santos, E. S., Abreu, M. M., & Macías, F. (2017). *Chemical and ecotoxicity evaluation of tailings rehabilitated using Technosol*. *19*, 17270.

Ardelean, M., Pode, R., Schoonman, J., Pop, A., & Manea, F. (2017). Fast simultaneous electrochemical detection of tetracycline and fluoxetine in water. *WIT Transactions on Ecology and the Environment*, *216*, 213–220. https://doi.org/10.2495/WS170201

Asian Development Bank. (2016). *Addressing Water Security in the People's Republic of China: The 13th Five-Year Plan (2016-2020) and Beyond*. https://www.adb.org/sites/default/files/institutional-document/200481/water-security-prc.pdf

Ata, Ş., Berber, M., Çabuk, H., & Akyüz, M. (2015). Optimization of Magnetic Extraction by Experimental Design Methodology for the Determination of Antidepressants in Biological Samples. *International Journal of Dairy Technology*, *7*(15), 6231–6242. https://doi.org/10.1111/j.1471-0307.1961.tb00962.x

Australian Government. (2013). *Guideline for groundwater quality protection in Australia: National Water Quality Managemennt Strategy*. https://www.waterquality.gov.au/sites/default/files/documents/guidelines-groundwater-quality-protection.pdf

Autio, S., Siimes, K., Laitinen, P., Rämö, S., Oinonen, S., & Eronen, L. (2004). Adsorption of sugar beet herbicides to Finnish soils. *Chemosphere*, *55*(2), 215–226. https://doi.org/10.1016/j.chemosphere.2003.10.015

Babić, S., Barišić, J., Stipaničev, D., Repec, S., Lovrić, M., Malev, O., Martinović-Weigelt, D., Čož-Rakovac, R., & Klobučar, G. (2018). Assessment of river sediment toxicity: Combining empirical zebrafish embryotoxicity testing with in silico toxicity characterization. *Science of the Total Environment*, *643*, 435–450. https://doi.org/10.1016/j.scitotenv.2018.06.124

Báez, M. E., Espinoza, J., Silva, R., & Fuentes, E. (2015). Sorption-desorption behavior of pesticides and their degradation products in volcanic and nonvolcanic soils: interpretation of interactions through two-way principal component analysis. *Environmental Science and Pollution Research*, *22*(11), 8576–8585. https://doi.org/10.1007/s11356-014-4036-8

Baldissarelli, D. P., Vargas, G. D. L. P., Korf, E. P., Galon, L., Kaufmann, C., & Santos, J. B. (2019). Remediation of soils contaminated by pesticides using physicochemical processes: A brief review. *Planta Daninha*, *37*, 1–13. https://doi.org/10.1590/S0100-83582019370100054

Barredo, O., Vilela, J., Garbisu, C., Besga, G., Alkorta, I., & Epelde, L. (2020). Technosols made from urban and industrial wastes are a good option for the reclamation of abandoned city plots. *Geoderma*, *377*(June), 114563. https://doi.org/10.1016/j.geoderma.2020.114563

Bascomb, C. L. (1968). Distribution of pyrophosphate-extractable iron and organic carbon in soils of various groups. *Journal of Soil Science*, *19*(2), 251–268. https://doi.org/https://doi.org/10.1111/j.1365-2389.1968.tb01538.x

Battaglin, W. A., Meyer, M. T., Kuivila, K. M., & Dietze, J. E. (2014). Glyphosate and its degradation product AMPA occur frequently and widely in U.S. soils, surface water, groundwater, and precipitation. *Journal of the American Water Resources Association*, *50*(2), 275–290. https://doi.org/10.1111/jawr.12159

Beckie, H. J., Flower, K. C., & Ashworth, M. B. (2020). Farming without glyphosate? *Plants*, *9*(1). https://doi.org/10.3390/plants9010096

Benbrook, C. M. (2016). Trends in glyphosate herbicide use in the United States and globally. *Environmental Sciences Europe*, *28*(1), 1–15. https://doi.org/10.1186/s12302-016-0070-0

Bento, C. P. M., Commelin, M. C., Baartman, J. E. M., Yang, X., Peters, P., Mol, H. G. J., Ritsema, C. J., & Geissen, V. (2018). Spatial glyphosate and AMPA redistribution on the soil surface driven by sediment transport processes – A flume experiment. *Environmental Pollution*, *234*, 1011–1020. https://doi.org/10.1016/j.envpol.2017.12.003

Bento, C. P. M., Goossens, D., Rezaei, M., Riksen, M., Mol, H. G. J., Ritsema, C. J., & Geissen, V. (2017). Glyphosate and AMPA distribution in wind-eroded sediment derived from loess soil. *Environmental Pollution*, *220*, 1079–1089. https://doi.org/10.1016/j.envpol.2016.11.033

Bento, C. P. M., Yang, X., Gort, G., Xue, S., van Dam, R., Zomer, P., Mol, H. G. J., Ritsema, C. J., & Geissen, V. (2016). Persistence of glyphosate and aminomethylphosphonic acid in loess soil under different combinations of temperature, soil moisture and light/darkness. *Science of the Total Environment*, *572*, 301–311. https://doi.org/10.1016/j.scitotenv.2016.07.215

Beretta, M., Britto, V., Tavares, T. M., da Silva, S. M. T., & Pletsch, A. L. (2014). Occurrence of pharmaceutical and personal care products (PPCPs) in marine sediments in the Todos os Santos Bay and the north coast of Salvador, Bahia, Brazil. *Journal of Soils and Sediments*, *14*(7), 1278–1286. https://doi.org/10.1007/s11368-014-0884-6

Bertram, M. G., Ecker, T. E., Wong, B. B. M., O’Bryan, M. K., Baumgartner, J. B., Martin, J. M., & Saaristo, M. (2018). The antidepressant fluoxetine alters mechanisms of pre- and post-copulatory sexual selection in the eastern mosquitofish (Gambusia holbrooki). *Environmental Pollution*, *238*, 238–247. https://doi.org/10.1016/j.envpol.2018.03.006

Bhat, S. A., Qadri, H., Cui, G., & Li, F. (2020). Remediation of Pesticides Through Microbial and Phytoremediation Techniques. In G. Qadri, H., Bhat, R., Mehmood, M., Dar (Ed.), *Fresh Water Pollution Dynamics and Remediation* (pp. 235–245). Springer. https://doi.org/10.1007/978-981-13-8277-2_13

Biel-Maeso, M., Corada-Fernández, C., & Lara-Martín, P. A. (2018). Monitoring the occurrence of pharmaceuticals in soils irrigated with reclaimed wastewater. *Environmental Pollution*, *235*, 312–321. https://doi.org/10.1016/j.envpol.2017.12.085

Bilias, F., Nikoli, T., Kalderis, D., & Gasparatos, D. (2021). Towards a soil remediation strategy using biochar: Effects on soil chemical properties and bioavailability of potentially toxic elements. *Toxics*, *9*(8). https://doi.org/10.3390/toxics9080184

Bis, Z., Kobyłecki, R., Ścisłowska, M., & Zarzycki, R. (2018). Biochar – Potential tool to combat climate change and drought. *Ecohydrology and Hydrobiology*, *18*(4), 441–453. https://doi.org/10.1016/j.ecohyd.2018.11.005

Blakemore, L. (1983). Acid oxalate-extractable iron, aluminium and silicon. *ICOMAND (International Committee on the Classification of Andisols) Circular Letter No. 5, Appendix 1*.

Bonansea, R. I., Filippi, I., Wunderlin, D. A., Marino, D. J. G., & Amé, M. V. (2018). The fate of glyphosate and AMPA in a freshwater endorheic basin: An ecotoxicological risk assessment. *Toxics*, *6*(1), 1–13. https://doi.org/10.3390/toxics6010003

Bootsikeaw, S., Kongtip, P., Nankongnab, N., Chantanakul, S., Sujirarat, D., Mahaboonpeeti, R., Khangkhun, P., & Woskie, S. (2021). Urinary glyphosate biomonitoring of sprayers in vegetable farm in Thailand. *Human and Ecological Risk Assessment*, *27*(4), 1019–1036. https://doi.org/10.1080/10807039.2020.1797471

Borova, V. L., Maragou, N. C., Gago-Ferrero, P., Pistos, C., & Thomaidis, N. S. (2014). Highly sensitive determination of 68 psychoactive pharmaceuticals, illicit drugs, and related human metabolites in wastewater by liquid chromatography-tandem mass spectrometry. In *Analytical and Bioanalytical Chemistry* (Vol. 406, Issue 17, pp. 4273–4285). https://doi.org/10.1007/s00216-014-7819-3

Bou-Mitri, C., Mekanna, A. N., Dagher, S., Moukarzel, S., & Farhat, A. (2022). Occurrence and exposure to glyphosate present in bread and flour products in Lebanon. *Food Control*, *136*, 108894. https://doi.org/10.1016/J.FOODCONT.2022.108894

Bozkaya-Schrotter, B., Dainies, C., Lescourret, A. S., Bignon, A., Breant, P., & Schrotter, J. C. (2008). Treatment of trace organics in membrane concentrates I: Pesticide elimination. *Water Science and Technology: Water Supply*, *8*(2), 223–230. https://doi.org/10.2166/ws.2008.056

Brodeur, J. C., Poletta, G. L., Simoniello, M. F., Carriquiriborde, P., Cristos, D. S., Pautasso, N., Paravani, E., Poliserpi, M. B., D'Andrea, M. F., Gonzalez, P. V., Aca, V. L., & Curto, A. E. (2021). The problem with implementing fish farms in agricultural regions: A trial in a pampean pond highlights potential risks to both human and fish health. *Chemosphere*, *262*. https://doi.org/10.1016/j.chemosphere.2020.128408

Bunting, S. Y., Lapworth, D. J., Crane, E. J., Grima-Olmedo, J., Koroša, A., Kuczyńska, A., Mali, N., Rosenqvist, L., van Vliet, M. E., Togola, A., & Lopez, B. (2021). Emerging organic compounds in European groundwater. *Environmental Pollution*, *269*. https://doi.org/10.1016/j.envpol.2020.115945

Caceres-Jensen, L., Rodríguez-Becerra, J., Sierra-Rosales, P., Escudey, M., Valdebenito, J., Neira-Albornoz, A., Dominguez-Vera, V., & Villagra, C. A. (2019). Electrochemical method to study the environmental behavior of Glyphosate on volcanic soils: Proposal of adsorption-desorption and transport mechanisms. *Journal of Hazardous Materials*, *379*. https://doi.org/10.1016/j.jhazmat.2019.120746

Calvo-Flores, F. G., Isac-Garcéa, J., & Dobado, J. A. (2017). Overview of Pharmaceutical Products as Emerging Pollutants. In J. A. D. Francisco G. Calvo-Flores, Joaquín Isac-García (Ed.), *Emerging Pollutants: Origin, Structure, and Properties* (First Edit, pp. 57–101). Wiley-VCHVerlag GmbH& Co. KGaA. https://doi.org/10.1002/9783527691203.ch4

Camiccia, M., Candiotto, L. Z. P., Gaboardi, S. C., Panis, C., & Kottiwitz, L. B. M. (2022). Determination of glyphosate in breast milk of lactating women in a rural area from Paraná state, Brazil. *Brazilian Journal of Medical and Biological Research*, *55*, 1–7. https://doi.org/10.1590/1414-431X2022e12194

Campanale, C., Massarelli, C., Losacco, D., Bisaccia, D., Triozzi, M., & Uricchio, V. F. (2021). The monitoring of pesticides in water matrices and the analytical criticalities: A review. *TrAC - Trends in Analytical Chemistry*, *144*, 116423. https://doi.org/10.1016/j.trac.2021.116423

Campanale, C., Triozzi, M., Massarelli, C., & Uricchio, V. F. (2022). Development of a UHPLC-MS/MS method to enhance the detection of Glyphosate, AMPA and Glufosinate at sub-microgram / L levels in water samples. *Journal of Chromatography A*, *1672*(463028), 1–11. https://doi.org/10.1016/j.chroma.2022.463028

Campbell, G., Mannetje, A., Keer, S., Eaglesham, G., Wang, X., Lin, C. Y., Hobson, P., Toms, L. M., Douwes, J., Thomas, K. V., Mueller, J. F., & Kaserzon, S. (2022). Characterization of glyphosate and AMPA concentrations in the urine of Australian and New Zealand populations. *Science of the Total Environment*, *847*(April), 157585. https://doi.org/10.1016/j.scitotenv.2022.157585

Camps Arbestain, M., Madinabeitia, Z., Anza Hortalà, M., Macías-García, F., Virgel, S., & Macías, F. (2008). Extractability and leachability of heavy metals in Technosols prepared from mixtures of unconsolidated wastes. *Waste Management*, *28*(12), 2653–2666. https://doi.org/10.1016/j.wasman.2008.01.008

Carabineiro, S. A. C., Thavorn-Amornsri, T., Pereira, M. F. R., Serp, P., & Figueiredo, J. L. (2012). Comparison between activated carbon, carbon xerogel and carbon nanotubes for the adsorption of the antibiotic ciprofloxacin. *Catalysis Today*, *186*(1), 29–34. https://doi.org/10.1016/j.cattod.2011.08.020

Carazo-Rojas, E., Pérez-Rojas, G., Pérez-Villanueva, M., Chinchilla-Soto, C., Chin-Pampillo, J. S., Aguilar-Mora, P., Alpízar-Marín, M., Masís-Mora, M., Rodríguez-Rodríguez, C. E., & Vryzas, Z. (2018). Pesticide monitoring and ecotoxicological risk assessment in surface water bodies and sediments of a tropical agro-ecosystem. *Environmental Pollution*, *241*, 800–809. https://doi.org/10.1016/j.envpol.2018.06.020

Carles, L., Gardon, H., Joseph, L., Sanchís, J., Farré, M., & Artigas, J. (2019). Meta-analysis of glyphosate contamination in surface waters and dissipation by biofilms. *Environment International*, *124*(November 2018), 284–293. https://doi.org/10.1016/j.envint.2018.12.064

Castrejón-Godínez, M. L., Tovar-Sánchez, E., Valencia-Cuevas, L., Rosas-Ramírez, M. E., Rodríguez, A., & Mussali-Galante, P. (2021). Glyphosate pollution treatment and microbial degradation alternatives, a review. *Microorganisms*, *9*(11), 1–21. https://doi.org/10.3390/microorganisms9112322

Castro Berman, M., Marino, D. J. G., Quiroga, M. V., & Zagarese, H. (2018). Occurrence and levels of glyphosate and AMPA in shallow lakes from the Pampean and Patagonian regions of Argentina. *Chemosphere*, *200*, 513–522. https://doi.org/10.1016/j.chemosphere.2018.02.103

Cederlund, H. (2022). Environmental fate of glyphosate used on Swedish railways — Results from environmental monitoring conducted between 2007–2010 and 2015–2019. *Science of the Total Environment*, *811*, 152361. https://doi.org/10.1016/j.scitotenv.2021.152361

Cela-Dablanca, R., Álvarez-Rodríguez, E., Fernández-Sanjurjo, M. J., Arias-Estévez, M., Santás-

Miguel, V., Fernández-Calviño, D., & Núñez-Delgado, A. (2023). Biotic and Abiotic Contamination Due to Emerging Pollutants in Sewage Sludge and Soils: A Country-Based Perspective. In A. Núñez-Delgado & M. Arias-Estévez (Eds.), *Emerging Pollutants in Sewage Sludge and Soils. The Handbook of Environmental Chemistry, vol. 114* (pp. 1–17). Springer International Publishing. https://doi.org/10.1007/698_2022_846

Cerqueira, M. B. R., Guilherme, J. R., Caldas, S. S., Martins, M. L., Zanella, R., & Primel, E. G. (2014). Evaluation of the QuEChERS method for the extraction of pharmaceuticals and personal care products from drinking-water treatment sludge with determination by UPLC-ESI-MS/MS. *Chemosphere*, *107*, 74–82. https://doi.org/10.1016/j.chemosphere.2014.03.026

Cha, J. S., Park, S. H., Jung, S. C., Ryu, C., Jeon, J. K., Shin, M. C., & Park, Y. K. (2016). Production and utilization of biochar: A review. *Journal of Industrial and Engineering Chemistry*, *40*, 1–15. https://doi.org/10.1016/j.jiec.2016.06.002

Chambers, E., Wagrowski-Diehl, D. M., Lu, Z., & Mazzeo, J. R. (2007). Systematic and comprehensive strategy for reducing matrix effects in LC/MS/MS analyses. *Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences*, *852*(1–2), 22–34. https://doi.org/10.1016/j.jchromb.2006.12.030

Chen, J., Zhang, D., Zhang, H., Ghosh, S., & Pan, B. (2017). Fast and slow adsorption of carbamazepine on biochar as affected by carbon structure and mineral composition. *Science of the Total Environment*, *579*, 598–605. https://doi.org/10.1016/j.scitotenv.2016.11.052

Chen, L., Lang, H., Liu, F., Jin, S., & Yan, T. (2018). Presence of Antibiotics in Shallow Groundwater in the Northern and Southwestern Regions of China. *Groundwater*, *56*(3), 451–457. https://doi.org/https://doi.org/10.1111/gwat.12596

Chen, Y., Yu, K., Hassan, M., Xu, C., Zhang, B., Gin, K. Y. H., & He, Y. (2018). Occurrence, distribution and risk assessment of pesticides in a river-reservoir system. *Ecotoxicology and Environmental Safety*, *166*(August), 320–327. https://doi.org/10.1016/j.ecoenv.2018.09.107

Cheng, Y.-L., Lee, C.-Y., Huang, Y.-L., Buckner, C. A., Lafrenie, R. M., Dénommée, J. A., Caswell, J. M., Want, D. A., Gan, G. G., Leong, Y. C., Bee, P. C., Chin, E., Teh, A. K. H., Picco, S., Villegas, L., Tonelli, F., Merlo, M., Rigau, J., Diaz, D., … Mathijssen, R. H. J. (2011). Advances in Analytical Methods for Organophosphorus Pesticide Detection. In Dr. Margarita Stoytcheva (Ed.), *Pesticides in the Modern World - Trends in Pesticides Analysis* (Vol. 11, Issue tourism, pp. 93–142). InTech. http://www.intechopen.com/books/pesticides-in-the- modern-world-trends-in-pesticides-analysis/advances-in-analytical-methods-for-organophosphorus-pesticide- detection

Christine Veyrac. (2021). *Données de vente de produits phytopharmaceutiques 2011 à 2019*. https://agreste.agriculture.gouv.fr/agreste-web/disaron/Chd2104/detail/;jsessionid=daf4e526f7e9400ffe6cde2a3e95.stats-prod-glassfish-7.zsg.agri-20000

ClinCalc DrugStats Database. (2023). *Fluoxetine - Drug Usage Statistics, United States, 2013 - 2020*. https://clincalc.com/DrugStats/Drugs/Fluoxetine

Close, M. E., Humphries, B., & Northcott, G. (2021). Outcomes of the first combined national survey of pesticides and emerging organic contaminants (EOCs) in groundwater in New Zealand 2018. *Science of the Total Environment*, *754*, 142005. https://doi.org/10.1016/j.scitotenv.2020.142005

Coates, J. (2006). Interpretation of Infrared Spectra, A Practical Approach. *Encyclopedia of Analytical Chemistry*, 1–23. https://doi.org/10.1002/9780470027318.a5606

Cobas, M., Meijide, J., Sanromán, M. A., & Pazos, M. (2016). Chestnut shells to mitigate pesticide contamination. *Journal of the Taiwan Institute of Chemical Engineers*, *61*, 166–173. https://doi.org/10.1016/j.jtice.2015.11.026

Coimbra, R. N., Calisto, V., Ferreira, C. I. A., Esteves, V. I., & Otero, M. (2015). Removal of pharmaceuticals from municipal wastewater by adsorption onto pyrolyzed pulp mill sludge. *Arabian Journal of Chemistry*. https://doi.org/10.1016/j.arabjc.2015.12.001

CONAMA. (2005). Resolução Conama N° 357, de 17 de Março De 2005, que dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências. *Diário Oficial Da União*, *053*, 58–63. file:///C:/Users/Maria João Fernandes/Dropbox/My PC (DESKTOP-3F0ETAE)/Downloads/Resolução Conama nº 357.pdf

Connolly, A., Koslitz, S., Bury, D., Brüning, T., Conrad, A., Kolossa-Gehring, M., Coggins, M. A., & Koch, H. M. (2020). Sensitive and selective quantification of glyphosate and aminomethylphosphonic acid (AMPA) in urine of the general population by gas chromatography-tandem mass spectrometry. *Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences*, *1158*(August), 122348. https://doi.org/10.1016/j.jchromb.2020.122348

Correia, D., Domingues, I., Faria, M., & Oliveira, M. (2023). Effects of fluoxetine on fish: What do we know and where should we focus our efforts in the future? *Science of the Total Environment*, *857*(159486), 17. https://doi.org/10.1016/j.scitotenv.2022.159486

Cruzeiro, C., Amaral, S., Rocha, E., & Rocha, M. J. (2017). Determination of 54 pesticides in waters of the Iberian Douro River estuary and risk assessment of environmentally relevant mixtures using theoretical approaches and Artemia salina and Daphnia magna bioassays. *Ecotoxicology and Environmental Safety*, *145*(July), 126–134. https://doi.org/10.1016/j.ecoenv.2017.07.010

Dabney, B. L., & Patiño, R. (2018). Low-dose stimulation of growth of the harmful alga, Prymnesium parvum, by glyphosate and glyphosate-based herbicides. *Harmful Algae*, *80*(November), 130–139. https://doi.org/10.1016/j.hal.2018.11.004

Dalbosco, T., Cadore, J. S., Pezzini, A., Lazzari, N. M. G. B., Giubel, G. O. M., Lazzari, T., Barbizan, L. D., Novello, D. T., & Brião, V. B. (2023). Removal of fluoxetine from water by nanofiltration and reverse osmosis. *Revista Ambiente & Água - An Interdisciplinary Journal of Applied Science*, *18*(e2885), 445–458. https://doi.org/doi:10.4136/ambi-agua.2885

de Brito Rodrigues, L., Gonçalves Costa, G., Lundgren Thá, E., da Silva, L. R., de Oliveira, R., Morais Leme, D., Cestari, M. M., Koppe Grisolia, C., Campos Valadares, M., & de Oliveira, G. A. R. (2019). Impact of the glyphosate-based commercial herbicide, its components and its metabolite AMPA on non-target aquatic organisms. *Mutation Research - Genetic Toxicology and Environmental Mutagenesis*, *842*(July 2018), 94–101. https://doi.org/10.1016/j.mrgentox.2019.05.002

de Farias, N. O., Oliveira, R., Sousa-Moura, D., de Oliveira, R. C. S., Rodrigues, M. A. C., Andrade, T. S., Domingues, I., Camargo, N. S., Muehlmann, L. A., & Grisolia, C. K. (2019). Exposure to low concentration of fluoxetine affects development, behaviour and acetylcholinesterase activity of zebrafish embryos. *Comparative Biochemistry and Physiology Part - C: Toxicology and Pharmacology*, *215*(August 2018), 1–8. https://doi.org/10.1016/j.cbpc.2018.08.009

De María, M., Silva-Sanchez, C., Kroll, K. J., Walsh, M. T., Nouri, M. Z., Hunter, M. E., Ross, M., Clauss, T. M., & Denslow, N. D. (2021). Chronic exposure to glyphosate in Florida manatee. *Environment International*, *152*, 106493. https://doi.org/10.1016/j.envint.2021.106493

de Oliveira, D. M., Agostinetto, L., & Siegloch, A. E. (2023). Comparison of the drinking water standard for pesticides of the Brazil with other countries. *Heliyon*, *9*(3), e13783. https://doi.org/10.1016/j.heliyon.2023.e13783

de Oliveira Santos, A. D., do Nascimento, M. T. L., Sanson, A. L., dos Santos, R. F., Felix, L. C., da Silva de Freitas, A., Hauser-Davis, R. A., da Fonseca, E. M., Neto, J. A. B., & Bila, D. M. (2022). Pharmaceuticals, natural and synthetic hormones and phenols in sediments from an eutrophic estuary, Jurujuba Sound, Guanabara Bay, Brazil. *Marine Pollution Bulletin*, *184*(September). https://doi.org/10.1016/j.marpolbul.2022.114176

de Souza, R. M., Seibert, D., Quesada, H. B., de Jesus Bassetti, F., Fagundes-Klen, M. R., & Bergamasco, R. (2020). Occurrence, impacts and general aspects of pesticides in surface water: A review. *Process Safety and Environmental Protection*, *135*, 22–37. https://doi.org/10.1016/j.psep.2019.12.035

Demiral, H., & Güngör, C. (2016). Adsorption of copper (II) from aqueous solutions on activated carbon prepared from grape bagasse € r. *Journal of Cleaner Production*, *124*, 103–113. https://doi.org/10.1016/j.jclepro.2016.02.084

Demonte, L. D., Michlig, N., Gaggiotti, M., Adam, C. G., Beldoménico, H. R., & Repetti, M. R. (2018). Determination of glyphosate, AMPA and glufosinate in dairy farm water from Argentina using a simplified UHPLC-MS/MS method. *Science of the Total Environment*, *645*, 34–43. https://doi.org/10.1016/j.scitotenv.2018.06.340

DGAV. (2021). *Relatório de vendas de produtos fitofarmacêuticos de 2019*. https://www.dgav.pt/medicamentos/conteudo/produtos-fitofarmaceuticos/divulgacao/informacoes-sobre-vendas-de-produtos-fitofarmaceuticos/

Di Guardo, A., & Finizio, A. (2018). A new methodology to identify surface water bodies at risk by using pesticide monitoring data: The glyphosate case study in Lombardy Region (Italy). *Science of the Total Environment*, *610–611*, 421–429. https://doi.org/10.1016/j.scitotenv.2017.08.049

Diaz-Camal, N., Cardoso-Vera, J. D., Islas-Flores, H., Gómez-Oliván, L. M., & Mejía-García, A. (2022). Consumption and ocurrence of antidepressants (SSRIs) in pre- and post-COVID-19 pandemic, their environmental impact and innovative removal methods: A review. *Science of the Total Environment*, *829*. https://doi.org/10.1016/j.scitotenv.2022.154656

Didoné, E. J., Minella, J. P. G., Tiecher, T., Zanella, R., Prestes, O. D., & Evrard, O. (2021). Mobilization and transport of pesticides with runoff and suspended sediment during flooding events in an agricultural catchment of Southern Brazil. *Environmental Science and Pollution Research*, *28*(29), 39370–39386. https://doi.org/10.1007/s11356-021-13303-z

Dissanayake Herath, G. A., Poh, L. S., & Ng, W. J. (2019). Statistical optimization of glyphosate adsorption by biochar and activated carbon with response surface methodology. *Chemosphere*, *227*, 533–540. https://doi.org/10.1016/j.chemosphere.2019.04.078

Donald, D. B., Cessna, A. J., & Farenhorst, A. (2018). Concentrations of Herbicides in Wetlands on Organic and Minimum-Tillage Farms. *Journal of Environmental Quality*, *47*(6), 1554–1565. https://doi.org/10.2134/jeq2018.03.0100

Dotor-Robayo, M. Y., Guerrero-Dallos, J. A., & Martínez-Cordón, M. J. (2022). Influence of monoammonium phosphate on glyphosate adsorption-desorption in tropical soils: Effect of the order of sorbate additions. *Chemosphere*, *303*(January). https://doi.org/10.1016/j.chemosphere.2022.135030

Druart, C., Delhomme, O., De Vaufleury, A., Ntcho, E., & Millet, M. (2011). Optimization of extraction procedure and chromatographic separation of glyphosate, glufosinate and aminomethylphosphonic acid in soil. *Analytical and Bioanalytical Chemistry*, *399*(4), 1725–1732. https://doi.org/10.1007/s00216-010-4468-z

Duke, S. O., & Dayan, F. E. (2011). Bioactivity of Herbicides. In *Comprehensive Biotechnology, Second Edition* (Second Edi, Vol. 4, pp. 23–35). Elsevier B.V. https://doi.org/10.1016/B978-0-08-088504-9.00273-7

Duke, Stephen O. (2020). Glyphosate: Environmental fate and impact. *Weed Science*, *68*(3), 201–207. https://doi.org/10.1017/wsc.2019.28

Ebele, A. J., Abou-Elwafa Abdallah, M., & Harrad, S. (2017). Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. *Emerging Contaminants*, *3*(1), 1–16. https://doi.org/10.1016/j.emcon.2016.12.004

Ebele, A. J., Oluseyi, T., Drage, D. S., Harrad, S., & Abou-Elwafa Abdallah, M. (2020). Occurrence, seasonal variation and human exposure to pharmaceuticals and personal care products in surface water, groundwater and drinking water in Lagos State, Nigeria. *Emerging Contaminants*, *6*, 124–132. https://doi.org/10.1016/j.emcon.2020.02.004

EFSA. (2005). Conclusion regarding the peer review of the pesticide risk assessment of the active substance. *EFSA Journal*, *3*(8), 1–81. https://doi.org/10.2903/j.efsa.2005.32ar

EFSA. (2015). Conclusion on the peer review of the pesticide risk assessment of the active substance glyphosate. *EFSA Journal*, *13*(11), 107. https://doi.org/10.2903/J.EFSA.2015.4302

EFSA. (2023). *Glyphosate*. https://www.efsa.europa.eu/en/topics/topic/glyphosate#published-on-this-topic

El-Naggar, A., Lee, S. S., Rinklebe, J., Farooq, M., Song, H., Sarmah, A. K., Zimmerman, A. R., Ahmad, M., Shaheen, S. M., & Ok, Y. S. (2019). Biochar application to low fertility soils: A review of current status, and future prospects. *Geoderma*, *337*(May 2018), 536–554. https://doi.org/10.1016/j.geoderma.2018.09.034

Elfikrie, N., Ho, Y. Bin, Zaidon, S. Z., Juahir, H., & Tan, E. S. S. (2020). Occurrence of pesticides in surface water, pesticides removal efficiency in drinking water treatment plant and potential health risk to consumers in Tengi River Basin, Malaysia. *Science of the Total Environment*, *712*. https://doi.org/10.1016/j.scitotenv.2020.136540

EPA. (2009). *National Primary Drinking Water Regulations*. https://www.epa.gov/sites/production/files/2016-06/documents/npwdr_complete_table.pdf

Espinoza-Montero, P. J., Vega-Verduga, C., Alulema-Pullupaxi, P., Fernández, L., & Paz, J. L. (2020). Technologies employed in the treatment of water contaminated with glyphosate: A review. *Molecules*, *25*(23), 1–26. https://doi.org/10.3390/molecules25235550

European Commission. (1998). Council Directive 98/83/EC on the quality of water intended for human consumption. *Official Journal of the European Communities*, *L0083*, 1–36. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:01998L0083-20151027&from=EN

European Commission. (2000). Directive 2000/60/EC of 23 October 2000 establishing a framework for Community action in the field of water policy. *Official Journal of the European Communities*, *L 327*, 1–93. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A02000L0060-20141120

European Commission. (2006). Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. *Official Journal of the European Union*, *L 372*, 19–31. https://doi.org/10.5040/9781782258674.0025

European Commission. (2008). Directive 2008/105/EC of 16 December 2008 on environmental quality standards in the field of water policy. *Official Journal of the European Union*, *L 348*, 84–97.

European Commission. (2013). Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013. *Fundamental Texts On European Private Law*, *L 226*, 1–17. https://doi.org/https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32013L0039

European Commission. (2014). Commission Directive 2014/80/EU, amending Annex II to Directive 2006/118/EC of the European Parliament and of the Council on the protection ofgroundwater against pollution and deterioration. *Official Journal of the European Union*, *L 182*, 52–55.

European Commission. (2015a). Commission Directive (EU) 2015/1787 amending Annexes II and III to Council Directive 98/83/EC on the quality of water intended for human consumption. *Official Journal of the European Union*, *L 260*, 6–17.

European Commission. (2015b). Commission Implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of t. *Official Journal of European Union L 78*, *L 78*, 40–42. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv%3AOJ.L_.2015.078.01.0040.01.ENG

European Commission. (2017). Commission implementing regulation (EU) 2017/2324 of 12 December 2017 renewing the approval of the active substance glyphosate in accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council concerning the placing of plant pr. *Official Journal of the European Union*, *L 333*, 10–16. https://webarchive.nationalarchives.gov.uk/eu-exit/20200124174550/https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32017R2324

European Commission. (2018). Commission Implementing Decision (EU) 2018/840 of 5 June 2018 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament. *Official Journal of the European Union*, *L 141*, 9–12. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32018D0840

European Commission. (2020a). Commission delegated Regulation 2020/1068 amending Annexes I and V to Regulation (EU) No 649/2012 of the European Parliament and of the Council concerning the export and import of hazardous chemicals. *Official Journal of the European Union*, *L 234*, 1–7. https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/start/screen/active-substances/details/79

European Commission. (2020b). Commission Implementing Decision (Eu) 2020/1161 of 4 August 2020 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. *Official Journal of the European Union*, *L 257*, 32–35. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2020.257.01.0032.01.ENG&toc=OJ:L:2020:257:TOC

European Commission. (2022a). Commission Implementing Regulation (EU) 2022/801 of 20 May 2022 amending Implementing Regulation (EU) No 540/2011 to update the list of active substances approved or deemed to have been approved under Regulation (EC) No 1107/2009 of the European Parliamen. *Official Journal of the European Union*, *L143*, 7–10. https://eur-lex.europa.eu/eli/reg_impl/2022/801/oj

European Commission. (2022b). *Glyphosate*. https://food.ec.europa.eu/plants/pesticides/approval-active-substances/renewal-approval/glyphosate_en

European Commission. (2023). *Glyphosate*. https://food.ec.europa.eu/plants/pesticides/approval-active-substances/renewal-approval/glyphosate_en#status-of-glyphosate-in-the-eu

European Environment Agency. (2019). The European environment - state and outlook 2020. Knowledge for transition to a sustainable Europe. In *European Union* (Vol. 60, Issue 6). European Environment Agency. https://doi.org/10.15196/TS600305

European Standard. (2011). EN15290:2011 – Solid biofuels – Determination of major elements – Al, Ca, Fe, Mg, P, K, Si, Na and Ti. *European Committee for Standardization*.

Eurostat. (2022). *Pesticide sales*. Eurostat. https://ec.europa.eu/eurostat/databrowser/view/aei_fm_salpest09/default/table?lang=e

Evagelista, P. A., Vilca, F. Z., Pimpinato, R. F., & Tornisielo, V. L. (2020). Optimization of a methodology for simultaneous determination of four antidepressants present in fresh water by high efficiency liquid chromatography. *Revista Eletrônica Em Gestão, Educação e Tecnologia Ambiental*, *24*, e8. https://doi.org/10.5902/2236117062663

Fabbri, D., Pizzol, R., Calza, P., Malandrino, M., Gaggero, E., Padoan, E., & Ajmone-Marsan, F. (2021). Constructed technosols: A strategy toward a circular economy. *Applied Sciences (Switzerland)*, *11*(8). https://doi.org/10.3390/app11083432

FAO. (2022). *FAOSTAT: Pesticides Use*. License: CC BY-NC-SA 3.0 IGO. https://www.fao.org/faostat/en/#data/RP

Federal Office of Consumer Protection and Food Safety. (2021). *Sales quantities of active substances in plant protection products from 1987 to 2021 (in German)*. https://www.bvl.bund.de/EN/Tasks/04_Plant_protection_products/01_ppp_tasks/02_ppp_AuthorisationReviewActSub/03_ppp_DomesticSalesExport/PPP_domesticSales_and_Export_node.html

Fehsenfeld, T. (2015). *The Effect of Soil Type on Migration of Pharmaceuticals and Personal Care Products (PPCPs) Through Cape Cod Soils*. https://www.mbl.edu/ses/files/2016/02/Theo_ProjectPaperFinalforweb.pdf

Feng, D., Soric, A., & Boutin, O. (2020). Treatment technologies and degradation pathways of glyphosate: A critical review. *Science of the Total Environment*, *742*, 140559. https://doi.org/10.1016/j.scitotenv.2020.140559

Fernandes, G., Aparicio, V. C., Bastos, M. C., De Gerónimo, E., Labanowski, J., Prestes, O. D., Zanella, R., & dos Santos, D. R. (2019). Indiscriminate use of glyphosate impregnates river epilithic biofilms in southern Brazil. *Science of the Total Environment*, *651*, 1377–1387. https://doi.org/10.1016/j.scitotenv.2018.09.292

Fernandes, M. J., Moreira, M. M., Paíga, P., Dias, D., Bernardo, M., Carvalho, M., Lapa, N., Fonseca, I., Morais, S., Figueiredo, S., & Delerue-Matos, C. (2019). Evaluation of the adsorption potential of biochars prepared from forest and agri-food wastes for the removal of fluoxetine. *Bioresource Technology*, *292*(August), 121973. https://doi.org/10.1016/j.biortech.2019.121973

Ferreiro, D. A. (2017). *Recuperación de suelos contaminados con aniones potencialmente tóxicos y metales pesados mediante Tecnosoles y biocarbones adsorbentes* [Universidade de Santiago de Compostela]. http://hdl.handle.net/10347/16427

Fogliatto, S., Ferrero, A., & Vidotto, F. (2020). Current and future scenarios of glyphosate use in Europe: Are there alternatives? In D. L. Sparks (Ed.), *Advances in Agronomy* (1st ed., Vol. 163, pp. 219–278). Elsevier Inc. https://doi.org/10.1016/bs.agron.2020.05.005

Freundlich, H. (1907). Über die Adsorption in Lösungen. *Zeitschrift Für Physikalische Chemie*, *57U*, 385. https://doi.org/doi:10.1515/zpch-1907-5723

Fryda, L., & Visser, R. (2015). Biochar for Soil Improvement: Evaluation of Biochar from Gasification and Slow Pyrolysis. *Agriculture (Switzerland)*, *5*(4), 1076–1115. https://doi.org/10.3390/agriculture5041076

Garba, J., Saiful, M., & Hamdani, A. (2018). Simplified method for derivatization of extractable glyphosate and aminomethylphosphonic acid and their determination by high performance liquid chromatography Environmental Research & Technology. *Environmental Research & Technology*, *1*(2), 19–30.

Garba, J., Samsuri, A. W., Othman, R., & Ahmad Hamdani, M. S. (2018). Adsorption-desorption and leaching potential of glyphosate and aminomethylphosphonic acid in acidic Malaysian soil amended with cow dung and rice husk ash. *Environmental Monitoring and Assessment*, *190*(11). https://doi.org/10.1007/s10661-018-7034-3

Gasco Cavero, S., García-Gil, A., Cruz-Pérez, N., Martín Rodríguez, L. F., Laspidou, C., Contreras-Llin, A., Quintana, G., Díaz-Cruz, S., & Santamarta, J. C. (2023). First emerging pollutants profile in groundwater of the volcanic active island of El Hierro (Canary Islands). *Science of the Total Environment*, *872*(October 2022). https://doi.org/10.1016/j.scitotenv.2023.162204

Geerdink, R. B., Hassing, M., Ayarza, N., Bruggink, C., Wielheesen, M., Claassen, J., & Epema, O. J. (2020). Analysis of glyphosate, AMPA, Glufosinate and MPPA with ION chromatography tandem mass spectrometry using A membrane suppressor in the ammonium form application to surface water of low to moderate salinity. *Analytica Chimica Acta*, *1133*, 66–76. https://doi.org/10.1016/j.aca.2020.05.058

General Administration of Quality Supervision, I. and Q. of the P. (2017). Standard for groundwater quality (GB/T 14848-2017). *National Standard of the People's Republic of China*, 1–22. https://www.chinesestandard.net/PDF.aspx/GBT14848-2017

Geng, Y., Jiang, L., Zhang, D., Liu, B., Zhang, J., Cheng, H., Wang, L., Peng, Y., Wang, Y., Zhao, Y., Xu, Y., & Liu, X. (2021). Glyphosate, aminomethylphosphonic acid, and glufosinate ammonium in agricultural groundwater and surface water in China from 2017 to 2018: Occurrence, main drivers, and environmental risk assessment. *Science of the Total Environment*, *769*, 144396. https://doi.org/10.1016/j.scitotenv.2020.144396

Gerónimo, E. De, Aparicio, V. C., & Costa, J. L. (2018). Glyphosate sorption to soils of Argentina. Estimation of affinity coefficient by pedotransfer function. *Geoderma*, *322*, 140–148. https://doi.org/10.1016/j.geoderma.2018.02.037

Ghavamifar, S., Naidu, R., Mozafari, V., & Li, Z. (2023). Can calcite play a role in the adsorption of glyphosate? A comparative study with a new challenge. *Chemosphere*, *311*(P1), 136922. https://doi.org/10.1016/j.chemosphere.2022.136922

Giles, C. H., Smith, D., & Huitson, A. (1974). A General Treatment and Classification of the Solute Adsorption Isotherm. *Journal of Colloid and Interface Science*, *47*(3), 755–765. https://doi.org/https://doi.org/10.1016/0021-9797(74)90252-5

Gillezeau, C., Van Gerwen, M., Shaffer, R. M., Rana, I., Zhang, L., Sheppard, L., & Taioli, E.

(2019). The evidence of human exposure to glyphosate: A review. *Environmental Health: A Global Access Science Source*, *18*(1), 1–14. https://doi.org/10.1186/s12940-018-0435-5

Gimsing, A. L., Borggaard, O. K., & Bang, M. (2004). Influence of soil composition on adsorption of glyphosate and phosphate by contrasting Danish surface soils. *European Journal of Soil Science*, *55*(1), 183–191. https://doi.org/10.1046/j.1365-2389.2003.00585.x

Glinski, D. A., Purucker, S. T., Van Meter, R. J., Black, M. C., & Henderson, W. M. (2018). Analysis of pesticides in surface water, stemflow, and throughfall in an agricultural area in South Georgia, USA. *Chemosphere*, *209*, 496–507. https://doi.org/10.1016/j.chemosphere.2018.06.116

Goldan, E., Nedeff, V., Barsan, N., Culea, M., Tomozei, C., Panainte-Lehadus, M., & Mosnegutu, E. (2022). Evaluation of the Use of Sewage Sludge Biochar as a Soil Amendment—A Review. *Sustainability (Switzerland)*, *14*(9). https://doi.org/10.3390/su14095309

Gomes, A. I., Pires, J. C. M., Figueiredo, S. A., & Boaventura, R. A. R. (2014). Optimization of River Water Quality Surveys by Multivariate Analysis of Physicochemical, Bacteriological and Ecotoxicological Data. *Water Resources Management*, *28*(5), 1345–1361. https://doi.org/10.1007/s11269-014-0547-9

Gomes, M. P., Brito, J. C. M., Vieira, F., Kitamura, R. S. A., & Juneau, P. (2022). Emerging Contaminants in Streams of Doce River Watershed, Minas Gerais, Brazil. *Frontiers in Environmental Science*, *9*(January), 1–11. https://doi.org/10.3389/fenvs.2021.801599

Grandcoin, A., Piel, S., & Baurès, E. (2017). AminoMethylPhosphonic acid (AMPA) in natural waters: Its sources, behavior and environmental fate. *Water Research*, *117*, 187–197. https://doi.org/10.1016/j.watres.2017.03.055

Grau, D., Grau, N., Gascuel, Q., Paroissin, C., Stratonovitch, C., Lairon, D., Devault, D. A., & Di Cristofaro, J. (2022). Quantifiable urine glyphosate levels detected in 99% of the French population, with higher values in men, in younger people, and in farmers. *Environmental Science and Pollution Research*, *29*(22), 32882–32893. https://doi.org/10.1007/s11356-021-18110-0

Grilli, E., Vigliotti, R. C., Fiorentino, A., Scognamiglio, M., Rossetti, L., Nogueira, T. A. R., Jani, A. D., Abreu-Junior, C. H., Ribeiro Roder, L., Ganga, A., & Capra, G. F. (2023). Constructed Technosols as a Soil Rebuilding Technique to Reclaim Abandoned Limestone Quarries in the Mediterranean Region: A Field Study. *Sustainability*, *15*(6), 5036. https://doi.org/10.3390/su15065036

Gros, P., Ahmed, A., Kühn, O., & Leinweber, P. (2017). Glyphosate binding in soil as revealed by sorption experiments and quantum-chemical modeling. *Science of the Total Environment*, *586*, 527–535. https://doi.org/10.1016/j.scitotenv.2017.02.007

Gunarathna, S., Gunawardana, B., Jayaweera, M., Manatunge, J., & Zoysa, K. (2018). Glyphosate and AMPA of agricultural soil, surface water, groundwater and sediments in areas prevalent with chronic kidney disease of unknown etiology, Sri Lanka. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, *53*(11), 729–737. https://doi.org/10.1080/03601234.2018.1480157

Guo, M., Song, W., & Tian, J. (2020). Biochar-Facilitated Soil Remediation: Mechanisms and Efficacy Variations. *Frontiers in Environmental Science*, *8*(October). https://doi.org/10.3389/fenvs.2020.521512

Hall, K. E., Spokas, K. A., Gamiz, B., Cox, L., Papiernik, S. K., & Koskinen, W. C. (2018). Glyphosate sorption/desorption on biochars – interactions of physical and chemical processes. *Pest Management Science*, *74*(5), 1206–1212. https://doi.org/10.1002/ps.4530

Hall, K. R., Eagleton, L. C., Acrivos, A., & Vermeulen, T. (1966). Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Industrial and Engineering Chemistry Fundamentals*, *5*(2), 212–223. https://doi.org/10.1021/i160018a011

Hanke, I., Singer, H., & Hollender, J. (2008). Ultratrace-level determination of glyphosate, aminomethylphosphonic acid and glufosinate in natural waters by solid-phase extraction followed by liquid chromatography-tandem mass spectrometry: Performance tuning of derivatization, enrichment and detection. *Analytical and Bioanalytical Chemistry*, *391*(6), 2265–2276. https://doi.org/10.1007/s00216-008-2134-5

Hawash, H. B., Moneer, A. A., Galhoum, A. A., Elgarahy, A. M., Mohamed, W. A. A., Samy, M., El-Seedi, H. R. M. S. G., Mubarak, M. F., & F.Attia, N. (2023). Occurrence and spatial distribution of pharmaceuticals and personal care products (PPCPs) in the aquatic environment, their characteristics, and adopted legislations. *Journal of Water Process Engineering*, *52*(December 2022), 103490. https://doi.org/10.1016/j.jwpe.2023.103490

Health Canada. (2022). Guidelines for Canadian Drinking Water Quality—Summary Tables. *Healthy Environments and Consumer Safety Branch*, 1–42. https://doi.org/10.1021/ba-1987-0214.ch035

Hedde, M., Nahmani, J., Séré, G., Auclerc, A., & Cortet, J. (2019). Early colonization of constructed Technosols by macro-invertebrates. *Journal of Soils and Sediments*, *19*(8), 3193–3203. https://doi.org/10.1007/s11368-018-2142-9

Herath, I., Kumarathilaka, P., Al-Wabel, M. I., Abduljabbar, A., Ahmad, M., Usman, A. R. A., & Vithanage, M. (2016). Mechanistic modeling of glyphosate interaction with rice husk derived engineered biochar. *Microporous and Mesoporous Materials*, *225*, 280–288. https://doi.org/10.1016/j.micromeso.2016.01.017

Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, *34*(5), 451–465. https://doi.org/10.1016/S0032-9592(98)00112-5

Hoerlein, G. (1994). Glufosinate (phosphinothricin), a natural amino acid with unexpected herbicidal properties. *Reviews of Environmental Contamination and Toxicology*, *138*, 73–145. https://doi.org/10.1007/978-1-4612-2672-7_4

Horn, S., Pieters, R., & Bøhn, T. (2019). A first assessment of glyphosate, 2,4-D and Cry proteins in surface water of South Africa. *South African Journal of Science*, *115*(9–10), 1–7. https://doi.org/10.17159/sajs.2019/5988

Huhn, C. (2018). More and enhanced glyphosate analysis is needed. *Analytical and Bioanalytical Chemistry*, *410*(13), 3041–3045. https://doi.org/10.1007/s00216-018-1000-3

Huntscha, S., Stravs, M. A., Bühlmann, A., Ahrens, C. H., Frey, J. E., Pomati, F., Hollender, J., Buerge, I. J., Balmer, M. E., & Poiger, T. (2018). Seasonal Dynamics of Glyphosate and AMPA in Lake Greifensee: Rapid Microbial Degradation in the Epilimnion during Summer. *Environmental Science and Technology*, *52*(8), 4641–4649. https://doi.org/10.1021/acs.est.8b00314

IARC. (2017). Some organophosphate insecticides and herbicides. In *Monographs on the evaluation of carcinogenics risks to humans.* (Vol. 112, p. 451). International Agency for Research on Cancer. http://monographs.iarc.fr/ENG/Publications/corrigenda.php

IBAMA. (2022). *Painel de Informações sobre a Comercialização de Agrotóxicos e Afins no Brasil – série histórica 2009 - 2021*. Instituto Brasileiro Do Meio Ambiente e Dos Recursos Naturais Renováveis (IBAMA). https://www.gov.br/ibama/pt-br/assuntos/quimicos-e-biologicos/agrotoxicos/paineis-de-informacoes-de-agrotoxicos/paineis-de-informacoes-de-agrotoxicos#Painel-comercializacao

Ighalo, J. O., Ajala, O. J., Adeniyi, A. G., Babatunde, E. O., & Ajala, M. A. (2021). Ecotoxicology of glyphosate and recent advances in its mitigation by adsorption. *Environmental Science and Pollution Research*, *28*(3), 2655–2668. https://doi.org/10.1007/s11356-020-11521-5

Ishfaq Showket Mir, Monaza Rashid, Javeed Ahmad Khan, & Bisma Yousuf. (2022). Emerging Pollutants- A review of current understanding and future scenario. *World Journal of Advanced Research and Reviews*, *16*(2), 074–088. https://doi.org/10.30574/wjarr.2022.16.2.1119

IUSS Working Group WRB. (2015). World reference base for soil resources 2014, update 2015 - International soil classification system for naming soils and creating legends for soil maps. In *World Soil Resources Reports No. 106.* https://doi.org/10.1017/S0014479706394902

Jaria, G., Calisto, V., Gil, M. V., Otero, M., & Esteves, V. I. (2015). Removal of fluoxetine from water by adsorbent materials produced from paper mill sludge. *Journal of Colloid and Interface Science*, *448*, 32–40. https://doi.org/10.1016/j.jcis.2015.02.002

Jelić, A., Gros, M., Petrovic, M., Ginebreda, A., & Barceló, D. (2012). Occurrence and Elimination of Pharmaceuticals During Conventional Wastewater Treatment. *Emerging and Priority Pollutants in Rivers. The Handbook of Environmental Chemistry*, *19*, 1–24. https://doi.org/10.1007/978-3-642-25722-3

Jia, G., Xu, J., Long, X., Ge, S., Chen, L., Hu, D., & Zhang, Y. (2019). Enantioselective Degradation and Chiral Stability of Glufosinate in Soil and Water Samples and Formation of 3-Methylphosphinicopropionic Acid and N-Acetyl-glufosinate Metabolites. *Journal of Agricultural and Food Chemistry*, *67*(41), 11312–11321. https://doi.org/10.1021/acs.jafc.9b01028

K'oreje, K. O., Vergeynst, L., Ombaka, D., De Wispelaere, P., Okoth, M., Van Langenhove, H., & Demeestere, K. (2016). Occurrence patterns of pharmaceutical residues in wastewater, surface water and groundwater of Nairobi and Kisumu city, Kenya. *Chemosphere*, *149*, 238–244. https://doi.org/10.1016/j.chemosphere.2016.01.095

Kairigo, P., Ngumba, E., Sundberg, L. R., Gachanja, A., & Tuhkanen, T. (2020). Occurrence of antibiotics and risk of antibiotic resistance evolution in selected Kenyan wastewaters, surface waters and sediments. *Science of the Total Environment*, *720*, 137580. https://doi.org/10.1016/j.scitotenv.2020.137580

Karungamye, P., Rugaika, A., Mtei, K., & Machunda, R. (2022). The pharmaceutical disposal practices and environmental contamination: A review in East African countries. *HydroResearch*, *5*, 99–107. https://doi.org/10.1016/j.hydres.2022.11.001

Khan, A. H., Aziz, H. A., Khan, N. A., Hasan, M. A., Ahmed, S., Farooqi, I. H., Dhingra, A., Vambol, V., Changani, F., Yousefi, M., Islam, S., Mozaffari, N., & Mahtab, M. S. (2022). Impact, disease outbreak and the eco-hazards associated with pharmaceutical residues: a Critical review. *International Journal of Environmental Science and Technology*, *19*(1), 677–688. https://doi.org/10.1007/s13762-021-03158-9

Khan, Afzal Husain, Khan, N. A., Zubair, M., Azfar Shaida, M., Manzar, M. S., Abutaleb, A., Naushad, M., & Iqbal, J. (2022). Sustainable green nanoadsorbents for remediation of pharmaceuticals from water and wastewater: A critical review. *Environmental Research*, *204*, 112243. https://doi.org/https://doi.org/10.1016/j.envres.2021.112243

Kocadal, K., Alkas, F. B., Battal, D., & Saygi, S. (2022). A review on advances and perspectives of glyphosate determination: challenges and opportunities. *Archives of Environmental Protection*, *48*(3), 89–98. https://doi.org/10.24425/aep.2022.142693

Kock, A., Glanville, H. C., Law, A. C., Stanton, T., Carter, L. J., & Taylor, J. C. (2023). Emerging challenges of the impacts of pharmaceuticals on aquatic ecosystems: A diatom perspective. *Science of The Total Environment*, *878*(February), 162939. https://doi.org/10.1016/j.scitotenv.2023.162939

Koskinen, W. C., Marek, L. J., & Hall, K. E. (2016). Analysis of glyphosate and aminomethylphosphonic acid in water, plant materials and soil. *Pest Management Science*, *72*(3), 423–432. https://doi.org/10.1002/ps.4172

Kosma, C. I., Kapsi, M. G., Konstas, P. S. G., Trantopoulos, E. P., Boti, V. I., Konstantinou, I. K., & Albanis, T. A. (2020). Assessment of multiclass pharmaceutical active compounds (PhACs) in hospital WWTP influent and effluent samples by UHPLC-Orbitrap MS: Temporal variation, removals and environmental risk assessment. *Environmental Research*, *191*(August), 110152. https://doi.org/10.1016/j.envres.2020.110152

Kotwani, A., Joshi, J., & Kaloni, D. (2021). Pharmaceutical effluent: a critical link in the interconnected ecosystem promoting antimicrobial resistance. *Environmental Science and Pollution Research*, *28*(25), 32111–32124. https://doi.org/10.1007/s11356-021-14178-w

Kubotera, H., Yamaguchi, N., & Kusaba, T. (2020). New definition of the qualifiers for Dystric and Eutric should be noted for the classification of Andosols with WRB2014. *Soil Science and Plant Nutrition*, *66*(4), 593–601. https://doi.org/10.1080/00380768.2020.1783699

Kudsk, P., & Mathiassen, S. K. (2020). Pesticide regulation in the European Union and the glyphosate controversy. *Weed Science*, *68*(3), 214–222. https://doi.org/10.1017/wsc.2019.59

Kudzin, M. H., Zylla, R., Mrozinska, Z., & Urbaniak, P. (2019). 31 P NMR investigations on roundup degradation by AOP procedures. *Water (Switzerland)*, *11*(2). https://doi.org/10.3390/w11020331

Kumari, K. G. I. D., Moldrup, P., Paradelo, M., Elsgaard, L., & de Jonge, L. W. (2016). Soil Properties Control Glyphosate Sorption in Soils Amended with Birch Wood Biochar. *Water, Air, and Soil Pollution*, *227*(6). https://doi.org/10.1007/s11270-016-2867-2

Kurakalva, R. M., & Aradhi, K. K. (2022). Occurrence and distribution of HCHs and DDTs in surface water and groundwater from the Gajulamandyam region along the Swarnamukhi river basin, Andhra Pradesh, India. *International Journal of Environmental Analytical Chemistry*, *102*(18), 6955–6969. https://doi.org/10.1080/03067319.2020.1818735

la Cecilia, D., & Maggi, F. (2020). Influential sources of uncertainty in glyphosate biochemical degradation in soil. *Mathematics and Computers in Simulation*, *175*(xxxx), 121–139. https://doi.org/10.1016/j.matcom.2020.01.003

Laghari, M., Naidu, R., Xiao, B., Hu, Z., Mirjat, M. S., Hu, M., Kandhro, M. N., Chen, Z., Guo, D., Jogi, Q., Abudi, Z. N., & Fazal, S. (2016). Recent developments in biochar as an effective tool for agricultural soil management: a review. *Journal of the Science of Food and Agriculture*, *96*(15), 4840–4849. https://doi.org/10.1002/jsfa.7753

Lajin, B., & Goessler, W. (2019). Direct speciation analysis of organophosphorus environmental pollutants in water by HPLC-ICPMS/MS. *Talanta*, *196*(December 2018), 357–361. https://doi.org/10.1016/j.talanta.2018.12.075

Lajmanovich, R. C., Repetti, M. R., Cuzziol Boccioni, A. P., Michlig, M. P., Demonte, L., Attademo, A. M., & Peltzer, P. M. (2023). Cocktails of pesticide residues in Prochilodus lineatus fish of the Salado River (South America): First record of high concentrations of polar herbicides. *Science of the Total Environment*, *870*(October 2022). https://doi.org/10.1016/j.scitotenv.2023.162019

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, *40*(9), 1361–1403. https://doi.org/10.1021/ja02242a004

Lapworth, D. J., Baran, N., Stuart, M. E., & Ward, R. S. (2012). Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. *Environmental Pollution*, *163*, 287–303. https://doi.org/10.1016/j.envpol.2011.12.034

Lehmann, J. (2007). Bio-energy in the black. *Frontiers in Ecology and Environment*, *5*(7), 381–387.

Lehmann, J., Rillig, M. C., Thies, J., Masiello, C. A., Hockaday, W. C., & Crowley, D. (2011). Biochar effects on soil biota - A review. *Soil Biology and Biochemistry*, *43*(9), 1812–1836. https://doi.org/10.1016/j.soilbio.2011.04.022

Lehmann, J., & Stephen, J. (2009). Biochar for environmental management : science and technology. In J. Lehmann & S. Joseph (Eds.), *Biochar for Environmental Management*. Earthscan.

Li, N., He, M., Lu, X., Yan, B., Duan, X., Chen, G., Wang, S., & Hou, L. (2022). Municipal solid waste derived biochars for wastewater treatment: Production, properties and applications. *Resources, Conservation and Recycling*, *177*(135), 106003. https://doi.org/10.1016/j.resconrec.2021.106003

Li, S., Shi, W., Li, H., Xu, N., Zhang, R., Chen, X., Sun, W., Wen, D., He, S., Pan, J., He, Z., & Fan, Y. (2018). Antibiotics in water and sediments of rivers and coastal area of Zhuhai City, Pearl River estuary, south China. *Science of the Total Environment*, *636*, 1009–1019. https://doi.org/10.1016/j.scitotenv.2018.04.358

Li, X., He, F., Wang, Z., & Xing, B. (2022). Roadmap of environmental health research on emerging contaminants: Inspiration from the studies on engineered nanomaterials. *Eco-Environment & Health*, *1*(3), 181–197. https://doi.org/10.1016/j.eehl.2022.10.001

Li, Y., Wang, F., Lin, Q., Deng, P., Zhang, Y., & Hu, D. (2022). The fate and behavior of glufosinate-enantiomers and their metabolites in open-field soil and weeds. *Arabian Journal of Chemistry*, *15*(11), 104191. https://doi.org/10.1016/j.arabjc.2022.104191

Li, Z. (2018). A health-based regulatory chain framework to evaluate international pesticide groundwater regulations integrating soil and drinking water standards. *Environment International*, *121*(August), 1253–1278. https://doi.org/10.1016/j.envint.2018.10.047

Li, Z., & Fantke, P. (2022). Toward harmonizing global pesticide regulations for surface freshwaters in support of protecting human health. *Journal of Environmental Management*, *301*(October 2021), 113909. https://doi.org/10.1016/j.jenvman.2021.113909

Liang, X., Chen, B., Nie, X., Shi, Z., Huang, X., & Li, X. (2013). The distribution and partitioning of common antibiotics in water and sediment of the Pearl River Estuary, South China. *Chemosphere*, *92*(11), 1410–1416. https://doi.org/10.1016/j.chemosphere.2013.03.044

Liao, F., Yang, L., Li, Q., Li, Y. R., Yang, L. T., Anas, M., & Huang, D. L. (2018). Characteristics and inorganic N holding ability of biochar derived from the pyrolysis of agricultural and forestal residues in the southern China. *Journal of Analytical and Applied Pyrolysis*, *134*(August), 544–551. https://doi.org/10.1016/j.jaap.2018.08.001

Liao, Y., Berthion, J. M., Colet, I., Merlo, M., Nougadère, A., & Hu, R. (2018). Validation and application of analytical method for glyphosate and glufosinate in foods by liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A*, *1549*, 31–38. https://doi.org/10.1016/j.chroma.2018.03.036

Lima, I. B., Boëchat, I. G., Fernandes, M. D., Monteiro, J. A. F., Rivaroli, L., & Gücker, B. (2022). Glyphosate pollution of surface runoff, stream water, and drinking water resources in Southeast Brazil. *Environmental Science and Pollution Research*, *0123456789*. https://doi.org/10.1007/s11356-022-24167-2

Lin, J. F., Chang, F. C., & Sheen, J. F. (2022). Determination of glyphosate, aminomethylphosphonic acid, and glufosinate in river water and sediments using microwave-assisted rapid derivatization and LC–MS/MS. *Environmental Science and Pollution Research*, *29*(30), 46282–46292. https://doi.org/10.1007/s11356-022-19189-9

Liu, B., Peng, S., Liao, Y., & Wang, H. (2019). The characteristics and causes of increasingly severe saltwater intrusion in Pearl River Estuary. *Estuarine, Coastal and Shelf Science*, *220*(November 2018), 54–63. https://doi.org/10.1016/j.ecss.2019.02.041

Loganathan, P., Vigneswaran, S., Kandasamy, J., Cuprys, A. K., Maletskyi, Z., & Ratnaweera, H. (2023). Treatment Trends and Combined Methods in Removing Pharmaceuticals and Personal Care Products from Wastewater—A Review. *Membranes*, *13*(2). https://doi.org/10.3390/membranes13020158

Lolić, A., Paíga, P., Santos, L. H. M. L. M., Ramos, S., Correia, M., & Delerue-Matos, C. (2015). Assessment of non-steroidal anti-inflammatory and analgesic pharmaceuticals in seawaters of North of Portugal: Occurrence and environmental risk. *Science of the Total Environment*, *508*, 240–250. https://doi.org/10.1016/j.scitotenv.2014.11.097

Lonappan, L., Rouissi, T., Kaur Brar, S., Verma, M., & Surampalli, R. Y. (2018). An insight into the adsorption of diclofenac on different biochars: Mechanisms, surface chemistry, and thermodynamics. *Bioresource Technology*, *249*(October 2017), 386–394. https://doi.org/10.1016/j.biortech.2017.10.039

López-Vázquez, J., Pérez-Mayán, L., Fernández-Fernández, V., Cela, R., & Rodríguez, I. (2023). Direct, automated and sensitive determination of glyphosate and related anionic pesticides in environmental water samples using solid-phase extraction on-line combined with liquid chromatography tandem mass spectrometry. *Journal of Chromatography A*, *1687*. https://doi.org/10.1016/j.chroma.2022.463697

Lopez, F. J., Pitarch, E., Botero-Coy, A. M., Fabregat-Safont, D., Ibáñez, M., Marin, J. M., Peruga, A., Ontañón, N., Martínez-Morcillo, S., Olalla, A., Valcárcel, Y., Varó, I., & Hernández, F. (2022). Removal efficiency for emerging contaminants in a WWTP from Madrid (Spain) after secondary and tertiary treatment and environmental impact on the Manzanares River. *Science of the Total Environment*, *812*. https://doi.org/10.1016/j.scitotenv.2021.152567

Low, M. . J. D. (1960). Kinetics of Chemisorption of Gases on Solids. *Chemical Reviews*, *60*(3), 267–312. https://doi.org/10.1021/cr60205a003

Lu, H. P., Li, Z. A., Gascó, G., Méndez, A., Shen, Y., & Paz-Ferreiro, J. (2018). Use of magnetic biochars for the immobilization of heavy metals in a multi-contaminated soil. *Science of the Total Environment*, *622–623*, 892–899. https://doi.org/10.1016/j.scitotenv.2017.12.056

Lutri, V. F., Matteoda, E., Blarasin, M., Aparicio, V., Giacobone, D., Maldonado, L., Becher Quinodoz, F., Cabrera, A., & Giuliano Albo, J. (2020). Hydrogeological features affecting spatial distribution of glyphosate and AMPA in groundwater and surface water in an agroecosystem. Córdoba, Argentina. *Science of the Total Environment*, *711*, 134557. https://doi.org/10.1016/j.scitotenv.2019.134557

Ma, L., Liu, Y., Yang, Q., Jiang, L., & Li, G. (2022). Occurrence and distribution of Pharmaceuticals and Personal Care Products (PPCPs) in wastewater related riverbank groundwater. *Science of the Total Environment*, *821*(59), 153372. https://doi.org/10.1016/j.scitotenv.2022.153372

Mac Loughlin, T. M., Peluso, M. L., Aparicio, V. C., & Marino, D. J. G. (2020). Contribution of soluble and particulate-matter fractions to the total glyphosate and AMPA load in water bodies associated with horticulture. *Science of the Total Environment*, *703*. https://doi.org/10.1016/j.scitotenv.2019.134717

Mac Loughlin, T. M., Peluso, M. L., & Marino, D. J. G. (2022a). Evaluation of pesticide pollution in the Gualeguay Basin: An extensive agriculture area in Argentina. *Science of the Total Environment*, *851*(June). https://doi.org/10.1016/j.scitotenv.2022.158142

Mac Loughlin, T. M., Peluso, M. L., & Marino, D. J. G. (2022b). Multiple pesticides occurrence, fate, and environmental risk assessment in a small horticultural stream of Argentina. *Science of the Total Environment*, *802*, 149893. https://doi.org/10.1016/j.scitotenv.2021.149893

Macías, F., & Arbestain, M. C. (2010). Soil carbon sequestration in a changing global environment. *Mitigation and Adaptation Strategies for Global Change*, *15*(6), 511–529. https://doi.org/10.1007/s11027-010-9231-4

Madureira, T. V., Barreiro, J. C., Rocha, M. J., Rocha, E., Cass, Q. B., & Tiritan, M. E. (2010). Spatiotemporal distribution of pharmaceuticals in the Douro River estuary (Portugal). *Science of the Total Environment*, *408*(22), 5513–5520. https://doi.org/10.1016/j.scitotenv.2010.07.069

Mahler, B. J., Van Metre, P. C., Burley, T. E., Loftin, K. A., Meyer, M. T., & Nowell, L. H. (2017). Similarities and differences in occurrence and temporal fluctuations in glyphosate and atrazine in small Midwestern streams (USA) during the 2013 growing season. *Science of the Total Environment*, *579*, 149–158. https://doi.org/10.1016/j.scitotenv.2016.10.236

Maroneze, M. M., Zepka, L. Q., Vieira, J. G., Queiroz, M. I., & Jacob-Lopes, E. (2014). Assessing glyphosate concentrations in six reservoirs of Paraíba do Sul and Guandu River Basins in southeast Brazil. *Revista Ambiente e Agua*, *9*(3), 445–458. https://doi.org/10.4136/1980-993X

Marta Małysiak and Tomasz Kiljanek. (2022). Method of Glyphosate, AMPA, and Glufosinate Ammonium Determination in Beebread by Liquid Chromatography—Tandem Mass Spectrometry after Molecularly Imprinted Solid-Phase Extraction. *Molecules*, *27*(5741), 12. https://doi.org/doi.org/10.3390/molecules27175741

Martínez-lladó, X., Valderrama, C., Rovira, M., Martí, V., Giménez, J., & Pablo, J. De. (2011). Geoderma Sorption and mobility of Sb (V) in calcareous soils of Catalonia (NE Spain): Batch and column experiments. *Geoderma*, *160*(3–4), 468–476. https://doi.org/10.1016/j.geoderma.2010.10.017

Martínez, C. M., Garrido, I., Flores, P., Hellín, P., Contreras, F., & Fenoll, J. (2022). Ozonation for remediation of pesticide-contaminated soils at field scale. *Chemical Engineering Journal*, *446*(Part 3), 137182. https://doi.org/https://doi.org/10.1016/j.cej.2022.137182

Mas, L. I., Aparicio, V. C., De Gerónimo, E., & Costa, J. L. (2020). Pesticides in water sources used for human consumption in the semiarid region of Argentina. *SN Applied Sciences*, *2*(4), 1–18. https://doi.org/10.1007/s42452-020-2513-x

Masiol, M., Giannì, B., & Prete, M. (2018). Herbicides in river water across the northeastern Italy: occurrence and spatial patterns of glyphosate, aminomethylphosphonic acid, and glufosinate ammonium. *Environmental Science and Pollution Research*, *25*(24), 24368–24378. https://doi.org/10.1007/s11356-018-2511-3

Materu, S. F., Heise, S., & Urban, B. (2021). Seasonal and Spatial Detection of Pesticide

Residues Under Various Weather Conditions of Agricultural Areas of the Kilombero Valley Ramsar Site, Tanzania. *Frontiers in Environmental Science*, *9*(March). https://doi.org/10.3389/fenvs.2021.599814

Matongo, S., Birungi, G., Moodley, B., & Ndungu, P. (2015). Pharmaceutical residues in water and sediment of Msunduzi River, KwaZulu-Natal, South Africa. *Chemosphere*, *134*, 133–140. https://doi.org/10.1007/s11356-015-4217-0

McGinley, J., Healy, M. G., Ryan, P. C., Mellander, P. E., Morrison, L., O'Driscoll, J. H., & Siggins, A. (2022). Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon. *Journal of Environmental Management*, *323*(July), 116102. https://doi.org/10.1016/j.jenvman.2022.116102

Medalie, L., Baker, N. T., Shoda, M. E., Stone, W. W., Meyer, M. T., Stets, E. G., & Wilson, M. (2020). Influence of land use and region on glyphosate and aminomethylphosphonic acid in streams in the USA. *Science of the Total Environment*, *707*, 136008. https://doi.org/10.1016/j.scitotenv.2019.136008

Meftaul, I. M., Venkateswarlu, K., Dharmarajan, R., Annamalai, P., Asaduzzaman, M., Parven, A., & Megharaj, M. (2020). Controversies over human health and ecological impacts of glyphosate: Is it to be banned in modern agriculture? *Environmental Pollution*, *263*, 114372. https://doi.org/10.1016/j.envpol.2020.114372

Mehra, O. P., & Jackson, M. L. (1960). Iron oxides removed from soils and clays by a dithionite citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*, *7*, 317–327.

Mejías, C., Martín, J., Santos, J. L., Aparicio, I., & Alonso, E. (2021). Occurrence of pharmaceuticals and their metabolites in sewage sludge and soil: A review on their distribution and environmental risk assessment. *Trends in Environmental Analytical Chemistry*, *30*. https://doi.org/10.1016/j.teac.2021.e00125

Melendez-Pastor, I., Hernández, E. I., Navarro-Pedreño, J., Almendro-Candel, M. B., Lucas, I. G., & Vidal, M. M. J. (2021). Occurrence of pesticides associated with an agricultural drainage system in a mediterranean environment. *Applied Sciences (Switzerland)*, *11*(21). https://doi.org/10.3390/app112110212

Mencaroni, M., Cardinali, A., Costa, L., Morari, F., Salandin, P., Zanin, G., & Dal Ferro, N. (2022). Glyphosate and AMPA have low mobility through different soil profiles of the prosecco wine production area: A monitoring study in north-eastern Italy. *Frontiers in Environmental Science*, *10*(September), 1–18. https://doi.org/10.3389/fenvs.2022.971931

Mencaroni, M., Longo, M., Cardinali, A., Lazzaro, B., Zanin, G., Dal Ferro, N., & Morari, F. (2023). Glyphosate and AMPA dynamics during the transition towards conservation agriculture: Drivers under shallow groundwater conditions. *Soil and Tillage Research*, *229*(February), 105659. https://doi.org/10.1016/j.still.2023.105659

Mendes, R., Saldías, G. S., deCastro, M., Gómez-Gesteira, M., Vaz, N., & Dias, J. M. (2017). Seasonal and interannual variability of the Douro turbid river plume, northwestern Iberian Peninsula. *Remote Sensing of Environment*, *194*, 401–411. https://doi.org/10.1016/j.rse.2017.04.001

Mesnage, R., & Antoniou, M. N. (2017). Roundup ready! Glyphosate and the current controversy over the world's leading herbicide. In *Encyclopedia of the Anthropocene* (Vols. 1–5). Elsevier Inc. https://doi.org/10.1016/B978-0-12-809665-9.09981-X

Meyer, M. T., Loftin, K. A., Lee, E. A., Hinshaw, G. H., Dietze, J. E., & Scribner, E. A. (2009). Determination of Glyphosate, its Degradation Product Aminomethylphosphonic Acid, and Glufosinate, in Water by Isotope Dilution and Online Solid-Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. In *U.S. Geological Survey Techniques and Methods*. https://doi.org/10.3133/tm5A10

Ministério da Saúde. (2017). Portaria de Consolidação nº 5, de 28 de setembro de 2017. *Diário Oficial Da União*, 01–856. http://portalsinan.saude.gov.br/images/documentos/Legislacoes/Portaria_Consolidacao_5_28_SETEMBRO_2017.pdf

Ministerio de Agricultura Alimentación y Medio Ambiente. (2021). *Encuesta de Utilización de Productos Fitosanitarios 2019* (Ministerio de Agricultura Pesca y Alimentación Secretaría General Técnica Centro de Publicaciones (Ed.)). https://doi.org/003211161

Ministre de l'écologie du développement durable et de l'énergie. (2015). Arrêté du 27 juillet 2015 modifiant l'arrêté du 25 janvier 2010 relatif aux méthodes et critères d'évaluation de l'état écologique, de l'état chimique et du potentiel écologique des eaux de surface pris en application des articles R. 212-10, R. 212-11 et. *Journal Officiel de La République Française*, *0198*, 15032–15080. https://www.legifrance.gouv.fr/eli/arrete/2015/7/27/DEVL1513989A/jo/texte

Ministry of Health Labor and Welfare of Japan. (2003). *Tap water quality standards*. https://www.mhlw.go.jp/stf/seisakunitsuite/bunya/topics/bukyoku/kenkou/suido/kijun/index.html

Ministry of Health of China. (2006). Standards for Drinking Water Quality (GB 5749-2006). *National Standard of the People's Republic of China*, *ICS 13060*(C51), 1–18. https://www.aqsiq.net/pdf/China_GB_5749-2006_Standards_for_Drinking_Water_Quality.pdf

Minten, J., Adolfsson-Erici, M., & Alsberg, T. (2011). Extraction and analysis of pharmaceuticals in polluted sediment using liquid chromatography mass spectrometry. *International Journal of Environmental Analytical Chemistry*, *91*(6), 553–566. https://doi.org/10.1080/03067311003657983

Mohan, D., Rajput, S., Singh, V. K., Steele, P. H., & Pittman, C. U. (2011). Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. *Journal of Hazardous Materials*, *188*(1–3), 319–333. https://doi.org/10.1016/j.jhazmat.2011.01.127

Mohanty, K., Das, D., & Biswas, M. N. (2006). Preparation and characterization of activated carbons from Sterculia alata nutshell by chemical activation with zinc chloride to remove phenol from wastewater. In *Adsorption* (Vol. 12, Issue 2, pp. 119–132). https://doi.org/10.1007/s10450-006-0374-2

Mojiri, A., Zhou, J. L., Robinson, B., Ohashi, A., Ozaki, N., Kindaichi, T., Farraji, H., & Vakili, M.

(2020). Pesticides in aquatic environments and their removal by adsorption methods. *Chemosphere*, *253*, 126646. https://doi.org/10.1016/j.chemosphere.2020.126646

Mole, R. A., & Brooks, B. W. (2019). Global scanning of selective serotonin reuptake inhibitors: occurrence, wastewater treatment and hazards in aquatic systems. *Environmental Pollution*, *250*, 1019–1031. https://doi.org/10.1016/j.envpol.2019.04.118

Montagner, C. C., Sodré, F. F., Acayaba, R. D., Vidal, C., Campestrini, I., Locatelli, M. A., Pescara, I. C., Albuquerque, A. F., Umbuzeiro, G. A., & Jardim, W. F. (2019). Ten years-snapshot of the occurrence of emerging contaminants in drinking, surface and ground waters and wastewaters from São Paulo State, Brazil. *Journal of the Brazilian Chemical Society*, *30*(3), 614–632. https://doi.org/10.21577/0103-5053.20180232

Montiel-León, J. M., Munoz, G., Vo Duy, S., Do, D. T., Vaudreuil, M. A., Goeury, K., Guillemette, F., Amyot, M., & Sauvé, S. (2019). Widespread occurrence and spatial distribution of glyphosate, atrazine, and neonicotinoids pesticides in the St. Lawrence and tributary rivers. *Environmental Pollution*, *250*, 29–39. https://doi.org/10.1016/j.envpol.2019.03.125

Moreira, M. M., Barroso, M. F., Boeykens, A., Withouck, H., Morais, S., & Delerue-Matos, C. (2017). Valorization of apple tree wood residues by polyphenols extraction: Comparison between conventional and microwave-assisted extraction. *Industrial Crops and Products*, *104*(February), 210–220. https://doi.org/10.1016/j.indcrop.2017.04.038

Moreira, M. M., Barroso, M. F., Porto, J. V., Ramalhosa, M. J., Švarc-Gajić, J., Estevinho, L., Morais, S., & Delerue-Matos, C. (2018). Potential of Portuguese vine shoot wastes as natural resources of bioactive compounds. *Science of the Total Environment*, *634*, 831–842. https://doi.org/10.1016/j.scitotenv.2018.04.035

Morone, A., Mulay, P., & Kamble, S. P. (2019). Removal of pharmaceutical and personal care products from wastewater using advanced materials. In *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology* (pp. 173–212). Elsevier Inc. https://doi.org/10.1016/B978-0-12-816189-0.00008-1

Mukhopadhyay, A., Duttagupta, S., & Mukherjee, A. (2022). Emerging organic contaminants in global community drinking water sources and supply: A review of occurrence, processes and remediation. *Journal of Environmental Chemical Engineering*, *10*(3), 107560. https://doi.org/10.1016/j.jece.2022.107560

Müller, B. P., Zumdick, A., Schuphan, I., & Schmidt, B. (2001). Metabolism of the herbicide glufosinate-ammonium in plant cell cultures of transgenic (rhizomania-resistant) and non-transgenic sugarbeet (Beta vulgaris), carrot (Daucus carota), purple foxglove (Digitalis purpurea) and thorn apple (Datura stramonium). *Pest Management Science*, *57*(1), 46–56. https://doi.org/10.1002/1526-4998(200101)57:1<46::AID-PS256>3.3.CO;2-T

Munari, M., Marin, M. G., & Matozzo, V. (2014). Effects of the antidepressant fluoxetine on the immune parameters and acetylcholinesterase activity of the clam Venerupis philippinarum. *Marine Environmental Research*, *94*, 32–37. https://doi.org/10.1016/j.marenvres.2013.11.007

Muñoz, J. P., Bleak, T. C., & Calaf, G. M. (2021). Glyphosate and the key characteristics of an endocrine disruptor: A review. *Chemosphere*, *270*, 128619. https://doi.org/10.1016/J.CHEMOSPHERE.2020.128619

Muralikrishna, I. V., & Manickam, V. (2017). Introduction. *Environmental Management*, 1–4. https://doi.org/10.1016/B978-0-12-811989-1.00001-4

Mussa, S. A. Ben, Elferjani, H. S., Haroun, F. A., & Abdelnabi, F. F. (2009). Determination of Available Nitrate , Phosphate and Sulfate in Soil Samples. *International Journal of PharmTech Research*, *1*(3), 598–604.

Nannou, C., Ofrydopoulou, A., Heath, D., Heath, E., & Lambropoulou, D. (2019). QuEChERS—A Green Alternative Approach for the Determination of Pharmaceuticals and Personal Care Products in Environmental and Food Samples. In J. Płotka-Wasylka, J., Namieśnik (Ed.), *Green Chemistry and Sustainable Technology* (pp. 395–430). Springer Singapore. https://doi.org/10.1007/978-981-13-9105-7_14

Napoletano, P., Colombo, C., Di Iorio, E., Memoli, V., Panico, S. C., Ruggiero, A. G., Santorufo, L., Maisto, G., & De Marco, A. (2021). Integrated approach for quality assessment of technosols in experimental mesocosms. *Sustainability (Switzerland)*, *13*(16), 1–20. https://doi.org/10.3390/su13169101

Narimani, M., & Silva, G. da. (2020). Thermal decomposition kinetics of glyphosate (GP) and its metabolite aminomethylphosphonic acid (AMPA). *Environmental Science: Processes and Impacts*, *22*(1), 152–160. https://doi.org/10.1039/c9em00422j

National Center for Biotechnology Information. (2023a). *PubChem Annotation Record for GLUFOSINATE-AMMONIUM, Source: Hazardous Substances Data Bank (HSDB)*. https://pubchem.ncbi.nlm.nih.gov.

National Center for Biotechnology Information. (2023b). *PubChem Compound Summary for CID 3386, Fluoxetine*. PubChem. https://pubchem.ncbi.nlm.nih.gov/compound/Fluoxetine

National Center for Biotechnology Information. (2023c). *PubChem Compound Summary for CID 3496, Glyphosate*. PubChem. https://pubchem.ncbi.nlm.nih.gov/compound/Glyphosate

National Center for Biotechnology Information. (2023d). *PubChem Compound Summary for CID 4794, Glufosinate*. PubChem. https://pubchem.ncbi.nlm.nih.gov/compound/Glufosinate

NHMRC, & NRMMC. (2011). *Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy, Version 3.8 updated September 2022*. National Health and Medical Research Council, National Resource Management Ministerial Council.

Nikolaou, A., Meric, S., & Fatta, D. (2007). Occurrence patterns of pharmaceuticals in water and wastewater environments. *Analytical and Bioanalytical Chemistry*, *387*(4), 1225–1234. https://doi.org/10.1007/s00216-006-1035-8

Nourouzi, M. M., Chuah, T. G., & Choong, T. S. Y. (2012). Adsorption of glyphosate onto activated carbon derived from waste newspaper. *Desalination and Water Treatment*, *24*(2010), 321–326. https://doi.org/10.5004/dwt.2010.1461

Nova, P., Calheiros, C. S. C., & Silva, M. (2020). Glyphosate in Portuguese Adults – A Pilot Study. *Environmental Toxicology and Pharmacology*, *80*(August), 103462. https://doi.org/10.1016/j.etap.2020.103462

Novotny, E. (2022). Glyphosate, Roundup and the Failures of Regulatory Assessment. *Toxics*, *10*(6). https://doi.org/10.3390/toxics10060321

OECD.Stat. (2022). *Pharmaceutical Market: Pharmaceutical consumption*. https://stats.oecd.org/Index.aspx?ThemeTreeId=9#

Ojelade, B. S., Durowoju, O. S., Adesoye, P. O., Gibb, S. W., & Ekosse, G. I. (2022). Review of Glyphosate-Based Herbicide and Aminomethylphosphonic Acid (AMPA): Environmental and Health Impacts. *Applied Sciences (Switzerland)*, *12*(17). https://doi.org/10.3390/app12178789

Okada, E., Allinson, M., Barral, M. P., Clarke, B., & Allinson, G. (2020). Glyphosate and aminomethylphosphonic acid (AMPA) are commonly found in urban streams and wetlands of Melbourne, Australia. *Water Research*, *168*, 115139. https://doi.org/10.1016/j.watres.2019.115139

Okada, E., Costa, J. L., & Bedmar, F. (2016). Adsorption and mobility of glyphosate in different soils under no-till and conventional tillage. *Geoderma*, *263*, 78–85. https://doi.org/10.1016/j.geoderma.2015.09.009

Okada, E., Pérez, D., De Gerónimo, E., Aparicio, V., Massone, H., & Costa, J. L. (2018). Non-point source pollution of glyphosate and AMPA in a rural basin from the southeast Pampas, Argentina. *Environmental Science and Pollution Research*, *25*(15), 15120–15132. https://doi.org/10.1007/s11356-018-1734-7

Olaitan, J. O., Anyakora, C., Adetifa, I. O., & Adepoju-bello, A. A. (2017). A Screening for Selected Human Pharmaceuticals in Water Using SPE-HPLC , Ogun State , Nigeria. *African Journal of Pharmaceutical Sciences and Pharmacy*, *5*(1), 1–14.

Oliveira, F. R., Patel, A. K., Jaisi, D. P., Adhikari, S., Lu, H., & Khanal, S. K. (2017). Environmental application of biochar: Current status and perspectives. *Bioresource Technology*, *246*(July), 110–122. https://doi.org/10.1016/j.biortech.2017.08.122

Oliveira, G., Calisto, V., Santos, S. M., Otero, M., & Esteves, V. I. (2018). Paper pulp-based adsorbents for the removal of pharmaceuticals from wastewater: A novel approach towards diversification. *Science of the Total Environment*, *631–632*, 1018–1028. https://doi.org/10.1016/j.scitotenv.2018.03.072

Oliveira Pereira, E. A., Freitas Melo, V., Abate, G., & Masini, J. C. (2019). Determination of glyphosate and aminomethylphosphonic acid by sequential-injection reversed-phase chromatography: method improvements and application in adsorption studies. *Analytical and Bioanalytical Chemistry*, *411*(11), 2317–2326. https://doi.org/10.1007/s00216-019-01672-x

Olsen, S., Cole, C., Watanabe, C., & Dean, L. (1954). Estimation of available phosphorus in soils by extraction with sodiumbicarbonate. *USDA Circular No. 939*.

Ortega-Calvo, J. J., Tejeda-Agredano, M. C., Jimenez-Sanchez, C., Congiu, E., Sungthong, R., Niqui-Arroyo, J. L., & Cantos, M. (2013). Is it possible to increase bioavailability but not environmental risk of PAHs in bioremediation? *Journal of Hazardous Materials*, *261*, 733–745. https://doi.org/10.1016/j.jhazmat.2013.03.042

Ortiz de García, S., Pinto Pinto, G., García Encina, P., & Irusta Mata, R. (2013). Consumption and occurrence of pharmaceutical and personal care products in the aquatic environment in Spain. *Science of the Total Environment*, *444*, 451–465. https://doi.org/10.1016/j.scitotenv.2012.11.057

Ospina, M., Schütze, A., Morales-Agudelo, P., Vidal, M., Wong, L.-Y., & Calafat, A. M. (2022). Exposure to glyphosate in the United States: Data from the 2013–2014 National Health and Nutrition Examination Survey. *Environment International*, *170*(November), 107620. https://doi.org/10.1016/j.envint.2022.107620

Othman, N. H., Alias, N. H., Fuzil, N. S., Marpani, F., Shahruddin, M. Z., Chew, C. M., Ng, K. M. D., Lau, W. J., & Ismail, A. F. (2022). A review on the use of membrane technology systems in developing countries. *Membranes*, *12*(1). https://doi.org/10.3390/membranes12010030

Özçimen, D., & Ersoy-Meriçboyu, A. (2009). Removal of copper from aqueous solutions by adsorption onto chestnut shell and grapeseed activated carbons. *Journal of Hazardous Materials*, *168*, 1118–1125. https://doi.org/10.1016/j.jhazmat.2009.02.148

Padilla, J. T., & Selim, H. M. (2019). Time-Dependent Sorption and Desorption of Glyphosate in Soils: Multi-reaction Modeling. *Vadose Zone Journal*, *18*(1), 1–10. https://doi.org/10.2136/vzj2018.12.0214

Padilla, J. T., & Selim, H. M. (2020). Environmental behavior of glyphosate in soils. In *Advances in Agronomy* (1st ed., Vol. 159). Elsevier Inc. https://doi.org/10.1016/bs.agron.2019.07.005

Paíga, P., Santos, L. H. M. L. M., & Delerue-Matos, C. (2017). Development of a multi-residue method for the determination of human and veterinary pharmaceuticals and some of their metabolites in aqueous environmental matrices by SPE-UHPLC–MS/MS. *Journal of Pharmaceutical and Biomedical Analysis*, *135*, 75–86. https://doi.org/10.1016/j.jpba.2016.12.013

Paíga, Paula, Correia, M., Fernandes, M. J., Silva, A., Carvalho, M., Vieira, J., Jorge, S., Silva, J. G., Freire, C., & Delerue-Matos, C. (2019). Assessment of 83 pharmaceuticals in WWTP influent and effluent samples by UHPLC-MS/MS: Hourly variation. *Science of the Total Environment*, *648*(648), 582 – 600. https://doi.org/10.1016/j.scitotenv.2018.08.129

Paíga, Paula, Santos, L. H. M. L. M., Ramos, S., Jorge, S., Silva, J. G., & Delerue-Matos, C. (2016). Presence of pharmaceuticals in the Lis river (Portugal): Sources, fate and seasonal variation. *Science of the Total Environment*, *573*, 164–177. https://doi.org/10.1016/j.scitotenv.2016.08.089

Pan, C., Zhu, F., Wu, M., Jiang, L., Zhao, X., & Yang, M. (2022). Degradation and toxicity of the antidepressant fluoxetine in an aqueous system by UV irradiation. *Chemosphere*, *287*, 132434. https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.132434

Papageorgiou, M., Kosma, C., & Lambropoulou, D. (2016). Seasonal occurrence, removal, mass loading and environmental risk assessment of 55 pharmaceuticals and personal care products in a municipal wastewater treatment plant in Central Greece. *Science of the Total Environment*, *543*, 547–569. https://doi.org/10.1016/j.scitotenv.2015.11.047

Patel, M., Kumar, R., Kishor, K., Mlsna, T., Pittman, C. U., & Mohan, D. (2019). Pharmaceuticals of emerging concern in aquatic systems: Chemistry, occurrence, effects, and removal methods. *Chemical Reviews*, *119*(6), 3510–3673. https://doi.org/10.1021/acs.chemrev.8b00299

Pathak, V. M., Verma, V. K., Rawat, B. S., Kaur, B., Babu, N., Sharma, A., Dewali, S., Yadav, M., Kumari, R., Singh, S., Mohapatra, A., Pandey, V., Rana, N., & Cunill, J. M. (2022). Current status of pesticide effects on environment, human health and it's eco-friendly management as bioremediation: A comprehensive review. *Frontiers in Microbiology*, *13*(August), 1–29. https://doi.org/10.3389/fmicb.2022.962619

Pavlovic, D. M., Pinušić, T., Periša, M., & Babić, S. (2012). Optimization of matrix solid-phase dispersion for liquid chromatography tandem mass spectrometry analysis of 12 pharmaceuticals in sediments. *Journal of Chromatography A*, *1258*, 1–15. https://doi.org/10.1016/j.chroma.2012.08.025

Pazikowska-Sapota, G., Galer-Tatarowicz, K., Dembska, G., Wojtkiewicz, M., Duljas, E., Pietrzak, S., & Dzierzbicka-Glowacka, L. A. (2020). The impact of pesticides used at the agricultural land of the Puck commune on the environment of the Puck Bay. *PeerJ*, *2020*(3), 1–21. https://doi.org/10.7717/peerj.8789

Pazzagli, L., Reutfors, J., Lucian, E., Zerial, G., Perulli, A., & Castelpietra, G. (2022). Increased antidepressant use during the COVID-19 pandemic: Findings from the Friuli Venezia Giulia region, Italy, 2015–2020. *Psychiatry Research*, *315*(June), 114704. https://doi.org/10.1016/j.psychres.2022.114704

Pereira, E., Melo, V. F., Abate, G., & Masini, J. C. (2019). Adsorption of glyphosate on Brazilian subtropical soils rich in iron and aluminum oxides. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, *54*(11), 906–914. https://doi.org/10.1080/03601234.2019.1644947

Pereira, H. A., Hernandes, P. R. T., Netto, M. S., Reske, G. D., Vieceli, V., Oliveira, L. F. S., & Dotto, G. L. (2021). Adsorbents for glyphosate removal in contaminated waters: a review. *Environmental Chemistry Letters*, *19*(2), 1525–1543. https://doi.org/10.1007/s10311-020-01108-4

Perelo, L. W. (2010). Review: In situ and bioremediation of organic pollutants in aquatic sediments. *Journal of Hazardous Materials*, *177*(1–3), 81–89. https://doi.org/10.1016/j.jhazmat.2009.12.090

Pérez-Fernández, V., Mainero Rocca, L., Tomai, P., Fanali, S., & Gentili, A. (2017). Recent advancements and future trends in environmental analysis: Sample preparation, liquid chromatography and mass spectrometry. *Analytica Chimica Acta*, *983*, 9–41. https://doi.org/10.1016/j.aca.2017.06.029

Pérez-Parada, A., Goyenola, G., Mello, F. T. De, & Heinzen, H. (2018). Recent advances and open questions around pesticide dynamics and effects on freshwater fishes. *Current Opinion in Environmental Science & Health*, *4*, 38–44. https://doi.org/10.1016/j.coesh.2018.08.004

Pérez, A. L., Tibaldo, G., Sánchez, G. H., Siano, G. G., Marsili, N. R., & Schenone, A. V. (2019). A novel fluorimetric method for glyphosate and AMPA determination with NBD-Cl and MCR-ALS. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, *214*, 119–128. https://doi.org/10.1016/j.saa.2019.01.078

Pérez, D. J., Iturburu, F. G., Calderon, G., Oyesqui, L. A. E., De Gerónimo, E., & Aparicio, V. C. (2021). Ecological risk assessment of current-use pesticides and biocides in soils, sediments and surface water of a mixed land-use basin of the Pampas region, Argentina. *Chemosphere*, *263*. https://doi.org/10.1016/j.chemosphere.2020.128061

Piccirillo, C., Moreira, I. S., Novais, R. M., Fernandes, A. J. S., Pullar, R. C., & Castro, P. M. L. (2017). Biphasic apatite-carbon materials derived from pyrolysed fish bones for effective adsorption of persistent pollutants and heavy metals. *Journal of Environmental Chemical Engineering*, *5*(5), 4884–4894. https://doi.org/10.1016/j.jece.2017.09.010

Pinto, E., Soares, A. G., & Ferreira, I. M. P. L. V. O. (2018). Quantitative analysis of glyphosate, glufosinate and AMPA in irrigation water by: In situ derivatization-dispersive liquid-liquid microextraction combined with UPLC-MS/MS. *Analytical Methods*, *10*(5), 554–561. https://doi.org/10.1039/c7ay02722b

Pires, N. L., de Araújo, E. P., Oliveira-Filho, E. C., & Caldas, E. D. (2023). An ultrasensitive LC-MS/MS method for the determination of glyphosate, AMPA and glufosinate in water – analysis of surface and groundwater from a hydrographic basin in the Midwestern region of Brazil. *Science of The Total Environment*, *875*(December 2022), 162499. https://doi.org/10.1016/j.scitotenv.2023.162499

Pires, N. L., Passos, C. J. S., Morgado, M. G. A., Mello, D. C., Infante, C. M. C., & Caldas, E. D. (2020). Determination of glyphosate, AMPA and glufosinate by high performance liquid chromatography with fluorescence detection in waters of the Santarém Plateau, Brazilian Amazon. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, *55*(9), 794–802. https://doi.org/10.1080/03601234.2020.1784668

Poiger, T., Buerge, I. J., Bächli, A., Müller, M. D., & Balmer, M. E. (2017). Occurrence of the herbicide glyphosate and its metabolite AMPA in surface waters in Switzerland determined with on-line solid phase extraction LC-MS/MS. *Environmental Science and Pollution Research*, *24*(2), 1588–1596. https://doi.org/10.1007/s11356-016-7835-2

Pokharel, A., Acharya, B., & Farooque, A. (2020). Biochar-Assisted Wastewater Treatment and waste Valorization. In A. Abdelhafez & M. Abbas (Eds.), *Applications of Biochar for Environmental Safety* (p. 19). IntechOpen. https://doi.org/http://dx.doi.org/10.5772/intechopen.92288

Portail Substaces Chimiques. (2020). *Normes de Qualité Environnementale et Valeurs Guides Environnementales*. https://substances.ineris.fr/fr/substance/cas/1066-51-9/3

Portier, C. J. (2020). A comprehensive analysis of the animal carcinogenicity data for glyphosate from chronic exposure rodent carcinogenicity studies. *Environmental Health: A Global Access Science Source*, *19*(1), 1–18. https://doi.org/10.1186/s12940-020-00574-1

Postigo, C., Ginebreda, A., Barbieri, M. V., Barceló, D., Martín-Alonso, J., de la Cal, A., Boleda, M. R., Otero, N., Carrey, R., Solà, V., Queralt, E., Isla, E., Casanovas, A., Frances, G., & López de Alda, M. (2021). Investigative monitoring of pesticide and nitrogen pollution sources in a complex multi-stressed catchment: The lower Llobregat River basin case study (Barcelona, Spain). *Science of the Total Environment*, *755*, 142377. https://doi.org/10.1016/j.scitotenv.2020.142377

Pradhan, B., Chand, S., Chand, S., Rout, P. R., & Naik, S. K. (2023). Emerging groundwater contaminants: A comprehensive review on their health hazards and remediation technologies. *Groundwater for Sustainable Development*, *20*(July 2022), 100868. https://doi.org/10.1016/j.gsd.2022.100868

Primost, J. E., Marino, D. J. G., Aparicio, V. C., Costa, J. L., & Carriquiriborde, P. (2017). Glyphosate and AMPA, “pseudo-persistent” pollutants under real-world agricultural management practices in the Mesopotamic Pampas agroecosystem, Argentina. *Environmental Pollution*, *229*, 771–779. https://doi.org/10.1016/j.envpol.2017.06.006

Programa Nacional para a Saúde Mental. (2017). *Programa Nacional para a Saúde Mental*.

Puri, M., Gandhi, K., & Kumar, M. S. (2023). Emerging environmental contaminants: A global perspective on policies and regulations. *Journal of Environmental Management*, *332*(November 2022), 117344. https://doi.org/10.1016/j.jenvman.2023.117344

Qian, K., Kumar, A., Patil, K., Bellmer, D., Wang, D., Yuan, W., & Huhnke, R. L. (2013). Effects of biomass feedstocks and gasification conditions on the physiochemical properties of char. *Energies*, *6*(8), 3972–3986. https://doi.org/10.3390/en6083972

Raby, M., Lissemore, L., Kaltenecker, G., Beaton, D., & Prosser, R. S. (2022). Characterizing the exposure of streams in southern Ontario to agricultural pesticides. *Chemosphere*, *294*(November 2021), 133769. https://doi.org/10.1016/j.chemosphere.2022.133769

Rahman, F., Ismail, A., Yusof, S., Mazlan, N., & Engku-Ahmad-Khairi, E. A. (2019). Evaluation of glyphosate levels in sediments of milky stork foraging areas in Kuala Gula Bird Sanctuary, Perak, Malaysia. *Pertanika Journal of Tropical Agricultural Science*, *42*(3), 995–1007.

Raina-Fulton, R. (2014). A review of methods for the analysis of orphan and difficult pesticides: Glyphosate, glufosinate, quaternary ammonium and phenoxy acid herbicides, and dithiocarbamate and phthalimide fungicides. *Journal of AOAC International*, *97*(4), 965–977. https://doi.org/10.5740/jaoacint.SGERaina-Fulton

Raj, A., Dubey, A., Ahmad, M., & Kumar, A. (2023). Pesticide pestilence : Global scenario and recent advances in detection and degradation methods. *Journal of Environmental Management*, *338*(April), 117680. https://doi.org/10.1016/j.jenvman.2023.117680

Rajapaksha, A. U., Vithanage, M., Lim, J. E., Ahmed, M. B. M., Zhang, M., Lee, S. S., & Ok, Y. S. (2014). Invasive plant-derived biochar inhibits sulfamethazine uptake by lettuce in soil. *Chemosphere*, *111*, 500–504. https://doi.org/10.1016/J.CHEMOSPHERE.2014.04.040

Ramirez-Haberkon, N. B., Aimar, S. B., Aparicio, V. C., Buschiazzo, D. E., De Gerónimo, E., Costa, J. L., & Mendez, M. J. (2021). Management effects on glyphosate and AMPA concentrations in the PM10 emitted by soils of the central semi-arid region of Argentina. *Aeolian Research*, *49*(December 2020). https://doi.org/10.1016/j.aeolia.2020.100658

Ramirez-Haberkon, N. B., Aparicio, V. C., & Mendez, M. J. (2021). First evidence of glyphosate and aminomethylphosphonic acid (AMPA) in the respirable dust (PM10) emitted from unpaved rural roads of Argentina. *Science of The Total Environment*, *773*, 145055. https://doi.org/10.1016/j.scitotenv.2021.145055

Ramirez, C. E., Bellmund, S., & Gardinali, P. R. (2014). A simple method for routine monitoring of glyphosate and its main metabolite in surface waters using lyophilization and LC-FLD + MS/MS. Case study: Canals with influence on Biscayne National Park. *Science of the Total Environment*, *496*, 389–401. https://doi.org/10.1016/j.scitotenv.2014.06.118

Redshaw, C. H., Cooke, M. P., Talbot, H. M., McGrath, S., & Rowland, S. J. (2008). Low biodegradability of fluoxetine HCl, diazepam and their human metabolites in sewage sludge-amended soil. *Journal of Soils and Sediments*, *8*(4), 217–230. https://doi.org/10.1007/s11368-008-0024-2

Reid, B. J., Jones, K. C., & Semple, K. T. (2000). Bioavailability of persistent organic pollutants in soils and sediments - A perspective on mechanisms, consequences and assessment. *Environmental Pollution*, *108*(1), 103–112. https://doi.org/10.1016/S0269-7491(99)00206-7

Reynoso, E. C., Peña, R. D., Reyes, D., Chavarin-Pineda, Y., Palchetti, I., & Torres, E. (2020). Determination of glyphosate in water from a rural locality in méxico and its implications for the population based on water consumption and use habits. *International Journal of Environmental Research and Public Health*, *17*(19), 1–16. https://doi.org/10.3390/ijerph17197102

Rezaei Kalantary, R., Barzegar, G., & Jorfi, S. (2022). Monitoring of pesticides in surface water, pesticides removal efficiency in drinking water treatment plant and potential health risk to consumers using Monte Carlo simulation in Behbahan City, Iran. *Chemosphere*, *286*(P1), 131667. https://doi.org/10.1016/j.chemosphere.2021.131667

Richards, B. K., Pacenka, S., Meyer, M. T., Dietze, J. E., Schatz, A. L., Teuffer, K., Aristilde, L., & Steenhuis, T. S. (2018). Antecedent and Post-Application Rain Events Trigger Glyphosate Transport from Runoff-Prone Soils. *Environmental Science and Technology Letters*, *5*(5), 249–254. https://doi.org/10.1021/acs.estlett.8b00085

Rissouli, L., Benicha, M., Chafik, T., & Chabbi, M. (2017). *Decontamination of water polluted with pesticide using biopolymers : Adsorption of glyphosate by chitin and chitosan*. *8*(12), 4544–4549.

Rivas-Garcia, T., Espinosa-Calderón, A., Hernández-Vázquez, B., & Schwentesius-Rindermann, R. (2022). Overview of Environmental and Health Effects Related to Glyphosate Usage. *Sustainability (Switzerland)*, *14*(11), 1–14. https://doi.org/10.3390/su14116868

Rivera-Utrilla, J., Bautista-Toledo, I., Ferro-Garca, M. A., & Moreno-Castilla, C. (2001). Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption. *Journal of Chemical Technology and Biotechnology*, *76*(12), 1209–1215. https://doi.org/10.1002/jctb.506

Rocío-Bautista, P., Moreno-González, D., Martínez-Piernas, A. B., García-Reyes, J. F., & Molina-Díaz, A. (2022). Novel liquid chromatography/mass spectrometry-based approaches for the determination of glyphosate and related compounds: A review. *Trends in Environmental Analytical Chemistry*, *36*(e00186), 1–11. https://doi.org/10.1016/j.teac.2022.e00186

Rodrigues, M. do R., Lebre, A. I., Alves, A., Félix, A. M., Tavares, D., Noriega, E., Neves, I., Valente, M., Silva, M. G., Faria, M. J., Pereira, N., & Pacheco, P. (2018). *Infeções e Resistências aos Antimicrobianos - Relatório Anual do Programa Prioritário 2018*.

Rodríguez-Bolaña, C., Pérez-Parada, A., Tesitore, G., Goyenola, G., Kröger, A., Pacheco, M., Gérez, N., Berton, A., Zinola, G., Gil, G., Mangarelli, A., Pequeño, F., Besil, N., Niell, S., Heinzen, H., & Teixeira de Mello, F. (2023). Multicompartmental monitoring of legacy and currently used pesticides in a subtropical lake used as a drinking water source (Laguna del Cisne, Uruguay). *Science of the Total Environment*, *874*(February). https://doi.org/10.1016/j.scitotenv.2023.162310

Rodriguez-Mozaz, S., Ricart, M., Köck-Schulmeyer, M., Guasch, H., Bonnineau, C., Proia, L., de Alda, M. L., Sabater, S., & Barceló, D. (2015). Pharmaceuticals and pesticides in reclaimed water: Efficiency assessment of a microfiltration-reverse osmosis (MF-RO) pilot plant. *Journal of Hazardous Materials*, *282*, 165–173. https://doi.org/10.1016/j.jhazmat.2014.09.015

Rosales, E., Meijide, J., Pazos, M., & Sanromán, M. A. (2017). Challenges and recent advances in biochar as low-cost biosorbent: From batch assays to continuous-flow systems. *Bioresource Technology*, *246*, 176–192. https://doi.org/10.1016/j.biortech.2017.06.084

Rubio, R. S. (2018). *Contribution to waste valorisation by producing biochars for different environmental purposes* [Universidade de Santiago de Compostela]. https://dialnet.unirioja.es/servlet/tesis?codigo=171691

Ruiz, F., Cherubin, M. R., & Ferreira, T. O. (2020). Soil quality assessment of constructed Technosols: Towards the validation of a promising strategy for land reclamation, waste management and the recovery of soil functions. *Journal of Environmental Management*, *276*(August). https://doi.org/10.1016/j.jenvman.2020.111344

S.K. Lagergren. (1898). About the Theory of So-called Adsorption of Soluble Substances. *Sven. Vetenskapsakad. Handingarl*, *24*, 1–39. https://cir.nii.ac.jp/crid/1570009750361875328.bib?lang=en

Saiz-Rubio, R., Balseiro-Romero, M., Antelo, J., Díez, E., Fiol, S., & Macías, F. (2019). Biochar as low-cost sorbent of volatile fuel organic compounds: potential application to water remediation. *Environmental Science and Pollution Research*, *26*(12), 11605–11617. https://doi.org/10.1007/s11356-018-3798-9

Sakari, M., Hsia, B. S., Tahir, R., Rafiq, S., Nahavandi, R., Shah, M. D., Annammala, K. V., Soon, Z. Y., & Yi, A. L. J. (2014). Estuary and Sea - associated Wetlands as Final Sink for Organic Pollutants : A Case Study in Sabah , Malaysia. *International Journal of Environment and*

Bioenergy, *9*(1), 1–16. https://doi.org/10.1111/jocn.13970

Samal, K., Mahapatra, S., & Hibzur Ali, M. (2022). Pharmaceutical wastewater as Emerging Contaminants (EC): Treatment technologies, impact on environment and human health. *Energy Nexus*, *6*(February), 100076. https://doi.org/10.1016/j.nexus.2022.100076

Samson-Brais, É., Lucotte, M., Moingt, M., Tremblay, G., & Paquet, S. (2022). Glyphosate and aminomethylphosphonic acid contents in field crops soils under various weed management practices. *Agrosystems, Geosciences and Environment*, *5*(3), 1–15. https://doi.org/10.1002/agg2.20273

Santos, E., Abreu, M. M., Macías, F., Anjos, C., Magalhães, M. C., & de Varennes, A. (2010). Efeito de correctivos orgânicos e inorgânicos na recuperação de escombreiras ricas em sulfuretos. In D. Flores & M. Marques (Eds.), *X Congresso de Geoquímica dos Países de Língua Portuguesa - XVI Semana Geoquímica* (pp. 1059–1065).

Santos, E. S., Abreu, M. M., & Macías, F. (2019). Rehabilitation of mining areas through integrated biotechnological approach: Technosols derived from organic/inorganic wastes and autochthonous plant development. *Chemosphere*, *224*, 765–775. https://doi.org/10.1016/j.chemosphere.2019.02.172

Santos, E. S., Abreu, M. M., Macías, F., & Magalhães, M. C. F. (2017). Potential environmental impact of technosols composed of gossan and sulfide-rich wastes from São Domingos mine: assay of simulated leaching. *Journal of Soils and Sediments*, *17*(5), 1369–1383. https://doi.org/10.1007/s11368-016-1518-y

Santos, J. L., Martín, J., Mejías, C., Aparicio, I., & Alonso, E. (2022). Pharmaceuticals and Their Metabolites in Sewage Sludge and Soils: Distribution and Environmental Risk Assessment. In A. Núñez-Delgado & M. Arias-Estévez (Eds.), *Emerging Pollutants in Sewage Sludge and Soils. The Handbook of Environmental Chemistry, vol. 114* (pp. 19–36). Springer International Publishing. https://doi.org/10.1007/698_2022_847

Santos, L. H. M. L. M., Ramalhosa, M. J., Ferreira, M., & Delerue-Matos, C. (2016). Development of a modified acetonitrile-based extraction procedure followed by ultra-high performance liquid chromatography-tandem mass spectrometry for the analysis of psychiatric drugs in sediments. *Journal of Chromatography A*, *1437*, 37–48. https://doi.org/10.1016/j.chroma.2016.01.079

Sardella, F., Gimenez, M., Navas, C., Morandi, C., Deiana, C., & Sapag, K. (2015). Conversion of viticultural industry wastes into activated carbons for removal of lead and cadmium. *Journal of Environmental Chemical Engineering*, *3*(1), 253–260. https://doi.org/10.1016/j.jece.2014.06.026

Sarıkaya, M., Ulusoy, H. I., Morgul, U., Ulusoy, S., Tartaglia, A., Yılmaz, E., Soylak, M., Locatelli, M., & Kabir, A. (2021). Sensitive determination of Fluoxetine and Citalopram antidepressants in urine and wastewater samples by liquid chromatography coupled with photodiode array detector. *Journal of Chromatography A*, *1648*, 462215. https://doi.org/https://doi.org/10.1016/j.chroma.2021.462215

Sasal, M. C., Wilson, M. G., Sione, S. M., Beghetto, S. M., Gabioud, E. A., Oszust, J. D., Paravani, E. V., Demonte, L., Repetti, M. R., Bedendo, D. J., Medero, S. L., Goette, J. J., Pautasso, N.,

& Schulz, G. A. (2017). Monitoreo de glifosato en agua superficial en Entre Ríos. La investigación acción participativa como metodología de abordaje. *Revista de Investigaciones Agropecuarias*, *43*(2), 195–205.

Sayğılı, H., Güzel, F., & Önal, Y. (2015). Conversion of grape industrial processing waste to activated carbon sorbent and its performance in cationic and anionic dyes adsorption. *Journal of Cleaner Production*, *93*, 84–93. https://doi.org/10.1016/j.jclepro.2015.01.009

Schleiffer, M., & Speiser, B. (2022). Presence of pesticides in the environment, transition into organic food, and implications for quality assurance along the European organic food chain – A review. *Environmental Pollution*, *313*(August), 120116. https://doi.org/10.1016/j.envpol.2022.120116

Schütze, A., Morales-Agudelo, P., Vidal, M., Calafat, A. M., & Ospina, M. (2021). Quantification of glyphosate and other organophosphorus compounds in human urine via ion chromatography isotope dilution tandem mass spectrometry. *Chemosphere*, *274*, 129427. https://doi.org/10.1016/j.chemosphere.2020.129427

Seesen, M., & Sapbamrer, R. (2020). A systematic review of association between pesticide exposure and respiratory outcomes among farmers and farmworkers. *Malaysian Journal of Medicine and Health Sciences*, *16*(1), 312–324.

Séralini, G. E., Clair, E., Mesnage, R., Gress, S., Defarge, N., Malatesta, M., Hennequin, D., & de Vendômois, J. S. (2014). Republished study: long-term toxicity of a Roundup herbicide and a Roundup-tolerant genetically modified maize. *Environmental Sciences Europe*, *26*(1), 1–17. https://doi.org/10.1186/s12302-014-0014-5

Sharma, A. D., & Lai, D. (2019). Sorption of radiolabelled glyphosate on biochar aged in contrasting soils. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, *54*(1), 49–53. https://doi.org/10.1080/03601234.2018.1531658

Sharma, Akanksha, Shukla, A., Attri, K., Kumar, M., Kumar, P., Suttee, A., Singh, G., Barnwal, R. P., & Singla, N. (2020). Global trends in pesticides: A looming threat and viable alternatives. *Ecotoxicology and Environmental Safety*, *201*(110812), 1–15. https://doi.org/10.1016/j.ecoenv.2020.110812

Sharma, Anket, Kumar, V., Shahzad, B., Tanveer, M., Sidhu, G. P. S., Handa, N., Kohli, S. K., Yadav, P., Bali, A. S., Parihar, R. D., Dar, O. I., Singh, K., Jasrotia, S., Bakshi, P., Ramakrishnan, M., Kumar, S., Bhardwaj, R., & Thukral, A. K. (2019). Worldwide pesticide usage and its impacts on ecosystem. *SN Applied Sciences*, *1*(11), 1–16. https://doi.org/10.1007/s42452-019-1485-1

Sharma, B. M., Bečanová, J., Scheringer, M., Sharma, A., Bharat, G. K., Whitehead, P. G., Klánová, J., & Nizzetto, L. (2019). Health and ecological risk assessment of emerging contaminants (pharmaceuticals, personal care products, and artificial sweeteners) in surface and groundwater (drinking water) in the Ganges River Basin, India. *Science of the Total Environment*, *646*, 1459–1467. https://doi.org/10.1016/j.scitotenv.2018.07.235

Sharma, J., Joshi, M., Bhatnagar, A., Chaurasia, A. K., & Nigam, S. (2022). Pharmaceutical residues: One of the significant problems in achieving 'clean water for all' and its solution.

Environmental Research, *215*(P1), 114219. https://doi.org/10.1016/j.envres.2022.114219

Sidoli, P., Baran, N., & Angulo-Jaramillo, R. (2016). Glyphosate and AMPA adsorption in soils: laboratory experiments and pedotransfer rules. *Environmental Science and Pollution Research*, *23*(6), 5733–5742. https://doi.org/10.1007/s11356-015-5796-5

Silori, R., Shrivastava, V., Singh, A., Sharma, P., Aouad, M., Mahlknecht, J., & Kumar, M. (2022). Global groundwater vulnerability for Pharmaceutical and Personal care products (PPCPs): The scenario of second decade of 21st century. *Journal of Environmental Management*, *320*(115703), 1–18. https://doi.org/10.1016/j.jenvman.2022.115703

Silva-Madera, R. J., Salazar-Flores, J., Peregrina-Lucano, A. A., Mendoza-Michel, J., Ceja-Gálvez, H. R., Rojas-Bravo, D., Reyna-Villela, M. Z., & Torres-Sánchez, E. D. (2021). Pesticide Contamination in Drinking and Surface Water in the Cienega, Jalisco, Mexico. *Water, Air, and Soil Pollution*, *232*(2). https://doi.org/10.1007/s11270-021-04990-y

Silva, Andreia, Fernandes, D. F., Figueiredo, S. A., Freitas, O. M., & Delerue-Matos, C. (2022). Fluoxetine and Nutrients Removal from Aqueous Solutions by Phycoremediation. *International Journal of Environmental Research and Public Health*, *19*(10). https://doi.org/10.3390/ijerph19106081

Silva, Andreia, Martinho, S., Stawiński, W., Węgrzyn, A., Figueiredo, S., Santos, L. H. M. L. M., & Freitas, O. (2018). Application of vermiculite-derived sustainable adsorbents for removal of venlafaxine. *Environmental Science and Pollution Research*, *25*(17), 17066–17076. https://doi.org/10.1007/s11356-018-1869-6

Silva, Andreia, Stawiński, W., Romacho, J., Santos, L. H. M. L. M., Figueiredo, S. A., Freitas, O. M., & Delerue-Matos, C. (2019). Adsorption of Fluoxetine and Venlafaxine onto the Marine Seaweed Bifurcaria bifurcata. *Environmental Engineering Science*, *36*(5), 573–582. https://doi.org/10.1089/ees.2018.0332

Silva, Aurora, Santos, L. H. M. L. M., Delerue-Matos, C., & Figueiredo, S. A. (2014). Impact of excipients in the chronic toxicity of fluoxetine on the alga Chlorella vulgaris. *Environmental Technology (United Kingdom)*, *35*(24), 3124–3129. https://doi.org/10.1080/09593330.2014.932438

Silva, V., Mol, H. G. J., Zomer, P., Tienstra, M., Ritsema, C. J., & Geissen, V. (2019). Pesticide residues in European agricultural soils – A hidden reality unfolded. *Science of the Total Environment*, *653*, 1532–1545. https://doi.org/10.1016/j.scitotenv.2018.10.441

Silva, V., Montanarella, L., Jones, A., Fernández-Ugalde, O., Mol, H. G. J. J., Ritsema, C. J., & Geissen, V. (2018). Distribution of glyphosate and aminomethylphosphonic acid (AMPA) in agricultural topsoils of the European Union. *Science of the Total Environment*, *621*, 1352–1359. https://doi.org/10.1016/j.scitotenv.2017.10.093

Singh, S., Kumar, V., Gill, J. P. K., Datta, S., Singh, S., Dhaka, V., Kapoor, D., Wani, A. B., Dhanjal, D. S., Kumar, M., Harikumar, S. L., & Singh, J. (2020). Herbicide glyphosate: Toxicity and microbial degradation. *International Journal of Environmental Research and Public Health*, *17*(20), 1–18. https://doi.org/10.3390/ijerph17207519

Skark, C., Zullei-Seibert, N., Schöttler, U., & Schlett, C. (1998). The occurrence of glyphosate in surface water. *International Journal of Environmental Analytical Chemistry*, *70*(1–4), 93–104. https://doi.org/10.1080/03067319808032607

Skeff, W., Recknagel, C., Düwel, Y., & Schulz-Bull, D. E. (2018). Adsorption behaviors of glyphosate, glufosinate, aminomethylphosphonic acid, and 2-aminoethylphosphonic acid on three typical Baltic Sea sediments. *Marine Chemistry*, *198*(June 2017), 1–9. https://doi.org/10.1016/j.marchem.2017.11.008

Smith, N. J., Martin, R. C., & St. Croix, R. G. (1996). Levels of the herbicide glyphosate in well water. *Bulletin of Environmental Contamination and Toxicology*, *57*(5), 759–765. https://doi.org/10.1007/s001289900254

Soares, S., Rosado, T., Barroso, M., & Gallardo, E. (2021). New method for the monitoring of antidepressants in oral fluid using dried spot sampling. *Pharmaceuticals*, *14*(12), 1–20. https://doi.org/10.3390/ph14121284

Sohel, A. J., Shutter, M. C., & Molla, M. (2023). Fluoxetine. In *StatPearls [Internet]*.

Solomon, K. R. (2020). Estimated exposure to glyphosate in humans via environmental, occupational, and dietary pathways: an updated review of the scientific literature. *Pest Management Science*, *76*(9), 2878–2885. https://doi.org/10.1002/ps.5717

Sousa, J. C. G., Ribeiro, A. R., Barbosa, M. O., Pereira, M. F. R., & Silva, A. M. T. (2018). A review on environmental monitoring of water organic pollutants identified by EU guidelines. *Journal of Hazardous Materials*, *344*, 146–162. https://doi.org/10.1016/j.jhazmat.2017.09.058

Souza, F. L., Saéz, C., Llanos, J., Lanza, M. R. V., Cañizares, P., & Rodrigo, M. A. (2016). Solar-powered electrokinetic remediation for the treatment of soil polluted with the herbicide 2,4-D. *Electrochimica Acta*, *190*, 371–377. https://doi.org/10.1016/j.electacta.2015.12.134

Spengler, S. R., Heskett, M. D., & Spengler, S. C. (2021). Occurrence and Persistence of the Herbicide Glyphosate in a suburban tropical watershed. *International Journal of Environmental Impacts: Management, Mitigation and Recovery*, *4*(2), 141–156. https://doi.org/10.2495/ei-v4-n2-141-156

Suárez, R. P., Goijman, A. P., Cappelletti, S., Solari, L. M., Cristos, D., Rojas, D., Krug, P., Babbitt, K. J., & Gavier-Pizarro, G. I. (2021). Combined effects of agrochemical contamination and forest loss on anuran diversity in agroecosystems of east-central Argentina. *Science of the Total Environment*, *759*, 143435. https://doi.org/10.1016/j.scitotenv.2020.143435

Subsecretaria de Recursos Hídricos de la Nación. (2003). Desarrollos de niveles guia nacionales de calidad de agua ambiente correspondientes a difenilos policlorados. *Niveles Guía Nacionales de Calidad de Agua Ambiente*.

Suciu, N., Russo, E., Calliera, M., Luciani, G. P., Trevisan, M., & Capri, E. (2023). Glyphosate, glufosinate ammonium, and AMPA occurrences and sources in groundwater of hilly vineyards. *Science of the Total Environment*, *866*(161171), 1–9. https://doi.org/10.1016/j.scitotenv.2022.161171

Sun, M., Li, H., & Jaisi, D. P. (2019). Degradation of glyphosate and bioavailability of phosphorus derived from glyphosate in a soil-water system. *Water Research*, *163*, 114840. https://doi.org/10.1016/j.watres.2019.07.007

Syafrudin, M., Kristanti, R. A., Yuniarto, A., Hadibarata, T., & Rhee, J. (2021). *Pesticides in Drinking Water — A Review*.

Takano, H. K., & Dayan, F. E. (2020). Glufosinate-ammonium: a review of the current state of knowledge. *Pest Management Science*, *76*(12), 3911–3925. https://doi.org/10.1002/ps.5965

Taleghani, A. S., Ebrahimnejad, P., Heydarinasab, A., & Akbarzadeh, A. (2020). Adsorption and controlled release of iron-chelating drug from the amino-terminated PAMAM/ordered mesoporous silica hybrid materials. *Journal of Drug Delivery Science and Technology*, *56*(January), 101579. https://doi.org/10.1016/j.jddst.2020.101579

Tauchnitz, N., Kurzius, F., Rupp, H., Schmidt, G., Hauser, B., Schrödter, M., & Meissner, R. (2020). Assessment of pesticide inputs into surface waters by agricultural and urban sources - A case study in the Querne/Weida catchment, central Germany. *Environmental Pollution*, *267*. https://doi.org/10.1016/j.envpol.2020.115186

Tee, G. T., Gok, X. Y., & Yong, W. F. (2022). Adsorption of pollutants in wastewater via biosorbents, nanoparticles and magnetic biosorbents: A review. *Environmental Research*, *212*, 113248. https://doi.org/10.1016/j.envres.2022.113248

Terpenning, M., & Öberg, G. (2017). Grappling with contaminants of emerging concern (CECs) in sewage. In *UNESCO project: Emerging Pollutants in Wastewater Reuse in Developing Countries: Case Studies on Emerging Pollutants in Water and Wastewater*. UNESCO.

Thomas, H. C. (1944). Heterogeneous Ion Exchange in a Flowing System. *Journal of the American Chemical Society*, *66*(10), 1664–1666. https://doi.org/10.1021/ja01238a017

Tittlemier, S. A., Drul, D., Lake, B., Zirdum, T., Hammond, E., Sobering, D., Lin, W. J., Tran, M., & Roscoe, M. (2017). Evaluation of a commercially available enzyme-linked immunosorbent assay and a liquid chromatography-tande mmass spectrometric method for the analysis of glyphosate in wheat, oats, barley, malt, and lentils. *Cereal Chemistry*, *94*(6), 1028–1036. https://doi.org/10.1094/CCHEM-01-17-0021-R

Tongo, I., Onokpasa, A., Emerure, F., Balogun, P. T., Enuneku, A. A., Erhunmwunse, N., Asemota, O., Ogbomida, E., Ogbeide, O., & Ezemonye, L. (2022). Levels, bioaccumulation and biomagnification of pesticide residues in a tropical freshwater food web. *International Journal of Environmental Science and Technology*, *19*(3), 1467–1482. https://doi.org/10.1007/s13762-021-03212-6

Tóth, G., Háhn, J., Szoboszlay, S., Harkai, P., Farkas, M., Radó, J., Göbölös, B., Kaszab, E., Szabó, I., Urbányi, B., & Kriszt, B. (2022). Spatiotemporal analysis of multi-pesticide residues in the largest Central European shallow lake, Lake Balaton, and its sub-catchment area. *Environmental Sciences Europe*, *34*(1). https://doi.org/10.1186/s12302-022-00630-2

Tran, H. N., You, S. J., Hosseini-Bandegharaei, A., & Chao, H. P. (2017). Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. *Water Research*, *120*, 88–116. https://doi.org/10.1016/j.watres.2017.04.014

Trass, M. (2014). *Glyphosate Analysis by LC/MS/MS using FMOC Derivatization and Gemini ® 3 µm NX-C18*. https://www.phenomenex.com/Application/Detail/22749?returnURL=/Application/Search&fsr=1

Tripathi, M., Sahu, J. N., & Ganesan, P. (2016). Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review. *Renewable and Sustainable Energy Reviews*, *55*, 467–481. https://doi.org/10.1016/j.rser.2015.10.122

Turk Sekulić, M., Pap, S., Stojanović, Z., Bošković, N., Radonić, J., & Šolević Knudsen, T. (2018). Efficient removal of priority, hazardous priority and emerging pollutants with Prunus armeniaca functionalized biochar from aqueous wastes: Experimental optimization and modeling. *Science of the Total Environment*, *613–614*, 736–750. https://doi.org/10.1016/j.scitotenv.2017.09.082

U.S. EPA. (2007). *Method 3051A (SW-846): Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils: Vol. Revision 1* (Issue February).

Ulrich, J. C., & Ferguson, P. L. (2021). Development of a sensitive direct injection LC-MS/MS method for the detection of glyphosate and aminomethylphosphonic acid (AMPA) in hard waters. *Anal Bioanal Chem*, *413*(14), 3763–3774. https://doi.org/10.1007/s00216-021-03324-5

Valle, A. L., Mello, F. C. C., Alves-Balvedi, R. P., Rodrigues, L. P., & Goulart, L. R. (2019). Glyphosate detection: methods, needs and challenges. *Environmental Chemistry Letters*, *17*(1), 291–317. https://doi.org/10.1007/s10311-018-0789-5

Van Bruggen, A. H. C., He, M. M., Shin, K., Mai, V., Jeong, K. C., Finckh, M. R., & Morris, J. G. (2018). Environmental and health effects of the herbicide glyphosate. *Science of the Total Environment*, *616–617*, 255–268. https://doi.org/10.1016/j.scitotenv.2017.10.309

Van Opstal, Natalia Veronica, Gabioud, E. A., Seehaus, M. S., Pighini, R. J., Repetti, M. R., Wilson, M. G., Wingeyer, A. B., Cuatrin, A. L., Regaldo, L. M., Gagneten, A. M., & Sasal, M. C. (2023). Spatial distribution of pesticides in surface water of the Estacas stream (Argentine Espinal region) associated with crop production. *Environmental Science and Pollution Research*, *0123456789*. https://doi.org/10.1007/s11356-023-25373-2

Van Opstal, Natalia Verónica, Seehaus, M. S., Gabioud, E. A., Wilson, M. G., Galizzi, F. J., Pighini, R. J., Repetti, M. R., Regaldo, L. M., Gagneten, A. M., & Sasal, M. C. (2022). Quality of the surface water of a basin affected by the expansion of the agricultural frontier over the native forest in the Argentine Espinal region. *Environmental Science and Pollution Research*, *29*(38), 57395–57411. https://doi.org/10.1007/s11356-022-19760-4

Vasiljević, B. N., Obradović, M., Bajuk-Bogdanović, D., Milojević-Rakić, M., Jovanović, Z., Gavrilov, N., & Holclajtner-Antunović, I. (2019). In situ synthesis of potassium tungstophosphate supported on BEA zeolite and perspective application for pesticide removal. *Journal of Environmental Sciences*, *81*, 136–147. https://doi.org/10.1016/j.jes.2019.01.018

Veiga, A., Sousa, A. C., Sousa, C., Oliveira, M., & Neto, B. (2023). End-of-life management strategies of pharmaceuticals in Portuguese households. *Waste Management and*

Research, *41*(1), 235–247. https://doi.org/10.1177/0734242X221105416

Vera-Candioti, J., Araujo, P. I., Huerga, I. R., Rojas, D. E., Cristos, D. S., & Malmantile, A. D. (2021). Pesticides detected in surface and groundwater from agroecosystems in the Pampas region of Argentina: occurrence and ecological risk assessment. *Environmental Monitoring and Assessment*, *193*(10). https://doi.org/10.1007/s10661-021-09462-8

von Mérey, G., Manson, P. S., Mehrsheikh, A., Sutton, P., & Levine, S. L. (2016). Glyphosate and aminomethylphosphonic acid chronic risk assessment for soil biota. *Environmental Toxicology and Chemistry*, *35*(11), 2742–2752. https://doi.org/10.1002/etc.3438

Vu, C. T., Le, P. T., Chu, D. B., Bui, V. H., Phung, T. L. A., Nguyen Le, H. Y., Labanowski, J., Mondamert, L., Herrmann, M., & Behra, P. (2021). One-step purification/extraction method to access glyphosate, glufosinate, and their metabolites in natural waters. *Journal of Chromatography A*, *1649*, 462188. https://doi.org/10.1016/j.chroma.2021.462188

Wang, J., & Guo, X. (2020a). Adsorption isotherm models: Classification, physical meaning, application and solving method. *Chemosphere*, *258*, 127279. https://doi.org/10.1016/j.chemosphere.2020.127279

Wang, J., & Guo, X. (2020b). Adsorption kinetic models: Physical meanings, applications, and solving methods. In *Journal of Hazardous Materials* (Vol. 390). https://doi.org/10.1016/j.jhazmat.2020.122156

Weber, K., & Quicker, P. (2018). Properties of biochar. *Fuel*, *217*(December 2017), 240–261. https://doi.org/10.1016/j.fuel.2017.12.054

Weber, W., & Morris, J. (1963). Kinetics of Adsorption on Carbon from Solution. *American Society of Civil Engineers*, *89*, 31–60. https://doi.org/https://doi.org/10.1061/JSEDAI.0000430

Welch, E. M., Dulai, H., El-Kadi, A., & Shuler, C. K. (2019). Submarine Groundwater Discharge and Stream Baseflow Sustain Pesticide and Nutrient Fluxes in Faga'alu Bay, American Samoa. *Frontiers in Environmental Science*, *7*(October). https://doi.org/10.3389/fenvs.2019.00162

WHO/UNICEF. (2021). *Progress on household drinking water, sanitation and hygiene 2000-2020: five years into the SDGs*. Licence: CC BY-NC-SA 3.0 IGO. http://apps.who.int/bookorders.

Wimmer, B., Neidhardt, H., Schwientek, M., Haderlein, S. B., & Huhn, C. (2022). Phosphate addition enhances alkaline extraction of glyphosate from highly sorptive soils and aquatic sediments. *Pest Management Science*, *78*(6), 2550–2559. https://doi.org/10.1002/ps.6883

Wirth, M. A., Schulz-Bull, D. E., & Kanwischer, M. (2021). The challenge of detecting the herbicide glyphosate and its metabolite AMPA in seawater – Method development and application in the Baltic Sea. *Chemosphere*, *262*, 128327. https://doi.org/10.1016/j.chemosphere.2020.128327

World Health Organization, & United Nations Children's Fund (Eds.). (2020). *State of the* *world's sanitation An urgent call to transform sanitation for better health, environments, economies and societies*. UNICEF and WHO Programme Division/WASH. https://www.who.int/publications/i/item/9789240014473

Xiang, L., Harindintwali, J. D., Wang, F., Redmile-Gordon, M., Chang, S. X., Fu, Y., He, C., Muhoza, B., Brahushi, F., Bolan, N., Jiang, X., Ok, Y. S., Rinklebe, J., Schaeffer, A., Zhu, Y. G., Tiedje, J. M., & Xing, B. (2022). Integrating Biochar, Bacteria, and Plants for Sustainable Remediation of Soils Contaminated with Organic Pollutants. *Environmental Science and Technology*, *56*(23), 16546–16566. https://doi.org/10.1021/acs.est.2c02976

Xiang, Y., Wu, H., Li, L., Ren, M., Qie, H., & Lin, A. (2021). A review of distribution and risk of pharmaceuticals and personal care products in the aquatic environment in China. *Ecotoxicology and Environmental Safety*, *213*. https://doi.org/10.1016/j.ecoenv.2021.112044

Xiong, G., Deng, Y., Li, J., Cao, Z., Liao, X., Liu, Y., & Lu, H. (2019). Immunotoxicity and transcriptome analysis of zebrafish embryos in response to glufosinate-ammonium exposure. *Chemosphere*, *236*, 124423. https://doi.org/10.1016/j.chemosphere.2019.124423

Xu, J., Smith, S., Smith, G., Wang, W., & Li, Y. (2019). Glyphosate contamination in grains and foods: An overview. *Food Control*, *106*(June). https://doi.org/10.1016/j.foodcont.2019.106710

Xu, L., Granger, C., Dong, H., Mao, Y., Duan, S., Li, J., & Qiang, Z. (2020). Occurrences of 29 pesticides in the Huangpu River, China: Highest ecological risk identified in Shanghai metropolitan area. *Chemosphere*, *251*, 126411. https://doi.org/10.1016/j.chemosphere.2020.126411

Yan, B., Lei, L., Chen, X., Men, J., Sun, Y., Guo, Y., Yang, L., Wang, Q., Han, J., & Zhou, B. (2022). Glyphosate and glufosinate-ammonium in aquaculture ponds and aquatic products: Occurrence and health risk assessment. *Environmental Pollution*, *296*(November 2021), 118742. https://doi.org/10.1016/j.envpol.2021.118742

Yan, G., & Viraraghavan, T. (2001). *Heavy metal removal in a biosorption column by immobilized M . rouxii biomass*. *78*, 243–249.

Yan, G., Viraraghavan, T., & Chen, M. (2001). A New Model for Heavy Metal Removal in a Biosorption Column. *Adsorption Science & Technology*, *19*(1), 25–43.

Yang, X., Wang, F., Bento, C. P. M., Meng, L., van Dam, R., Mol, H., Liu, G., Ritsema, C. J., & Geissen, V. (2015). Decay characteristics and erosion-related transport of glyphosate in Chinese loess soil under field conditions. *Science of the Total Environment*, *530–531*, 87–95. https://doi.org/10.1016/j.scitotenv.2015.05.082

Yin, L., Ma, R., Wang, B., Yuan, H., & Yu, G. (2017). The degradation and persistence of five pharmaceuticals in an artificial climate incubator during a one year period. *RSC Advances*, *7*(14), 8280–8287. https://doi.org/10.1039/c6ra28351a

Yoon, Y. H., & Nelson, J. H. (1984). Application of gas adsorption kinetics. I. A theoretical model for respirator cartridge service life. *American Industrial Hygiene Association Journal*, *45*(8), 509–516. https://doi.org/10.1080/15298668491400197

Yu, H., Zou, W., Chen, J., Chen, H., Yu, Z., Huang, J., Tang, H., Wei, X., & Gao, B. (2019). Biochar amendment improves crop production in problem soils: A review. *Journal of Environmental Management*, *232*(September 2018), 8–21. https://doi.org/10.1016/J.JENVMAN.2018.10.117

Zabaloy, M. C., Allegrini, M., Hernandez Guijarro, K., Behrends Kraemer, F., Morrás, H., & Erijman, L. (2022). Microbiomes and glyphosate biodegradation in edaphic and aquatic environments: recent issues and trends. *World Journal of Microbiology and Biotechnology*, *38*(6), 1–29. https://doi.org/10.1007/s11274-022-03281-w

Zhan, H., Feng, Y., Fan, X., & Chen, S. (2018). Recent advances in glyphosate biodegradation. *Applied Microbiology and Biotechnology*, *102*(12), 5033–5043. https://doi.org/10.1007/s00253-018-9035-0

Zhang, P., Zhou, H., Li, K., Zhao, X., Liu, Q., Li, D., & Zhao, G. (2017). Occurrence of pharmaceuticals and personal care products, and their associated environmental risks in a large shallow lake in north China. *Environmental Geochemistry and Health*, *40*(4), 1525–1539. https://doi.org/10.1007/s10653-018-0069-0

Zhang, R., Zhang, G., Zheng, Q., Tang, J., Chen, Y., Xu, W., Zou, Y., & Chen, X. (2012). Occurrence and risks of antibiotics in the Laizhou Bay, China: Impacts of river discharge. *Ecotoxicology and Environmental Safety*, *80*, 208–215. https://doi.org/10.1016/j.ecoenv.2012.03.002

Zhao, J., Pacenka, S., Wu, J., Richards, B. K., Steenhuis, T., Simpson, K., & Hay, A. G. (2018). Detection of glyphosate residues in companion animal feeds. *Environmental Pollution*, *243*, 1113–1118. https://doi.org/10.1016/j.envpol.2018.08.100

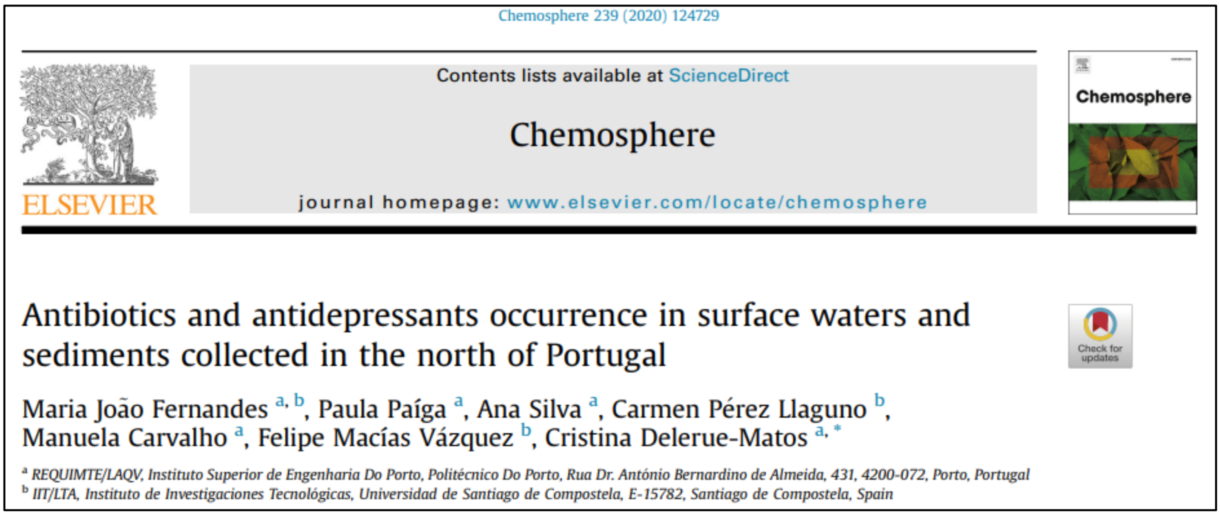
Zhelezova, A., Cederlund, H., & Stenström, J. (2017). Effect of Biochar Amendment and Ageing on Adsorption and Degradation of Two Herbicides. *Water, Air, and Soil Pollution*, *228*(6). https://doi.org/10.1007/s11270-017-3392-7

Zhou, C., Luo, X., Chen, N., Zhang, L., & Gao, J. (2020). C-P Natural Products as Next-Generation Herbicides: Chemistry and Biology of Glufosinate. *ACS Applied Materials and Interfaces*. https://doi.org/10.1021/acs.jafc.0c00052

Zhou, L. J., Ying, G. G., Zhao, J. L., Yang, J. F., Wang, L., Yang, B., & Liu, S. (2011). Trends in the occurrence of human and veterinary antibiotics in the sediments of the Yellow River, Hai River and Liao River in northern China. *Environmental Pollution*, *159*(7), 1877–1885. https://doi.org/10.1016/j.envpol.2011.03.034

LIST OF PUBLICATIONS

Published articles used in this Thesis: rights, contributions and quality indicators



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Antibiotics and antidepressants occurrence in surface waters and sediments collected in the north of Portugal

Maria João Fernandes [a, b], Paula Paíga [a], Ana Silva [a], Carmen Pérez Llaguno [b], Manuela Carvalho [a], Felipe Macías Vázquez [b], Cristina Delerue-Matos [a, *]

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Specific contribution to the publication

Maria João Fernandes contributes with sample collection and pre-treatment, experimental work, namely: extraction and analysis, data statistical analysis and to the writing of the original article draft.

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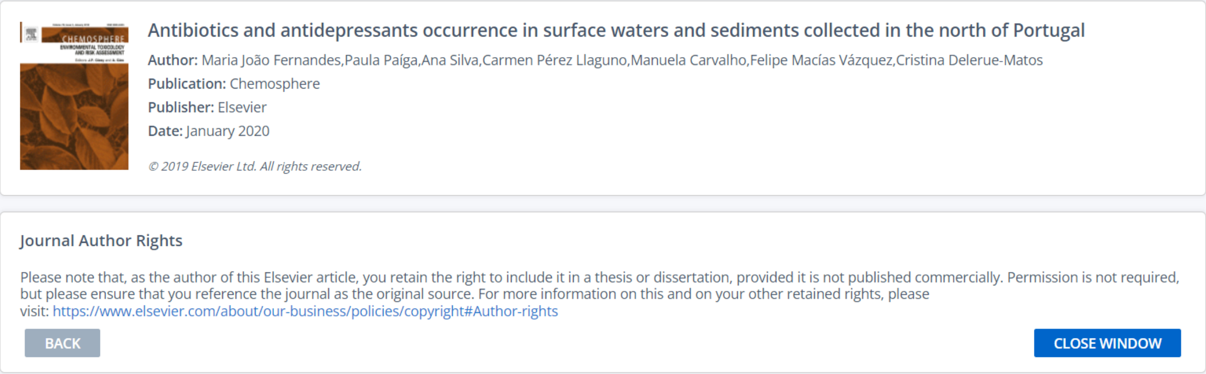

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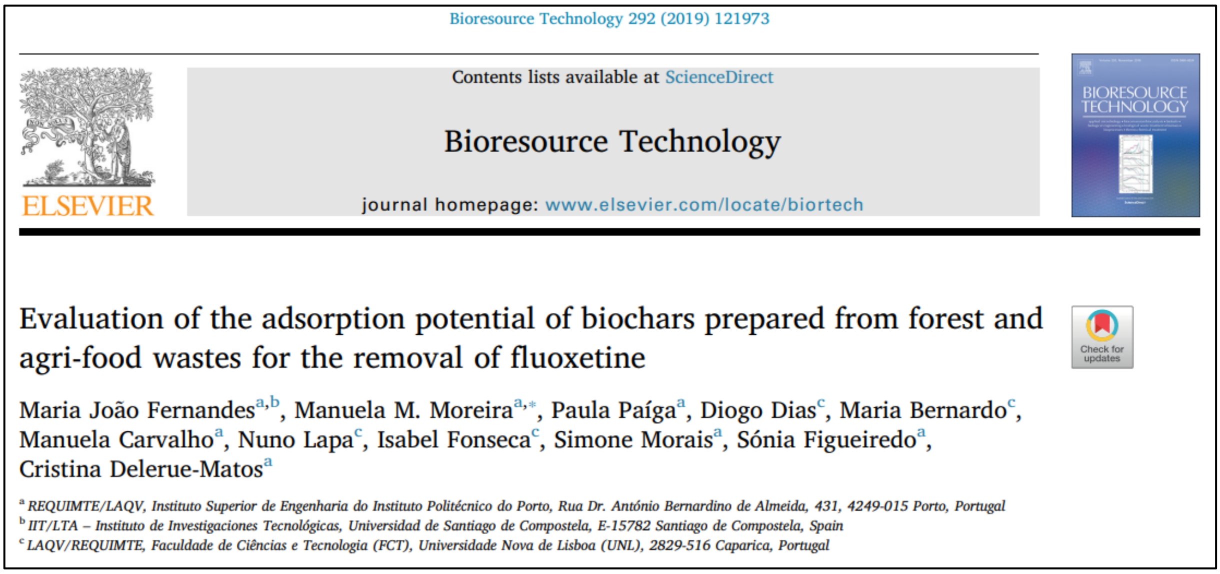

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Maria João Fernandes[a,b], Manuela M. Moreira[a,*], Paula Paíga[a], Diogo Dias[c], Maria Bernardo[c], Manuela Carvalho[a], Nuno Lapa[c], Isabel Fonseca[c], Simone Morais[a], Sónia Figueiredo[a], Cristina Delerue-Matos[a]

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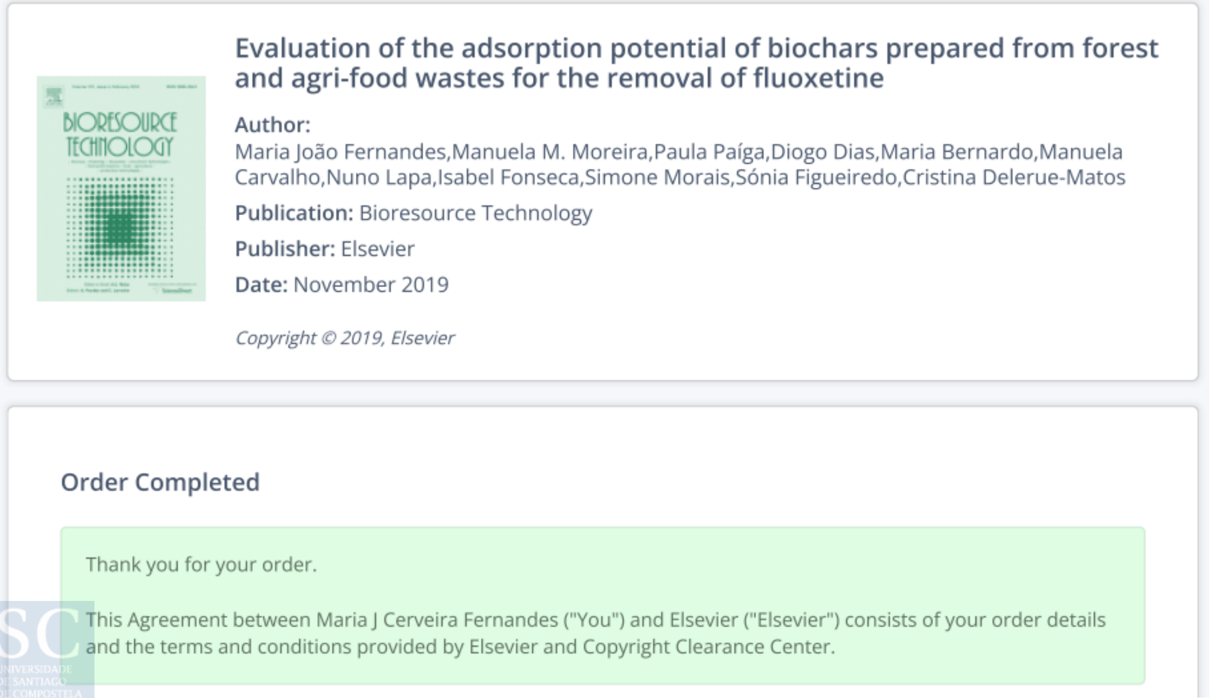

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Congress Proceedings

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Maria J. Fernandes, Paula Paíga, Sónia Figueiredo, Felipe Macías & Cristina Delerue-Matos. "Glyphosate and Aminomethylphosphonic acid adsorption in soils". Presented in Congreso Internacional XXVI Encontro Galego Portugês de Química, 2022

Maria J. Fernandes, Felipe Macías & Cristina Delerue-Matos. "Tecnosolos a la carte: Um método inovador, abrangente e sustentável de remedição de contaminações de solos e águas". Presented in GEO em FOCO, 2019

Poster contributions

Maria João Fernandes; Paula Paíga; Ana Silva; Carmen Llaguno; Manuela Carvalho; Felipe Macías Vázquez; Cristina Delerue-Matos. "Assessment of antibiotics and psychiatric drugs in sediments from Douro and Leça Rivers (Portugal)". Presented in 4GEO|resources, materials, technologies & environment| 1st Conference 2019, 2019.

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Maria João Fernandes; Manuela Moreira; Diogo Dias; Maria Bernardo; Manuela Carvalho; Nuno Lapa; Isabel Fonseca; *et al*. "Micropollutant Removal From Water Through Biochar Adsorbents". Presented in 1st International Conference on Advanced Production and Processing (ICAPP), poster NP-P.52, Novi Sad, Sérvia, Novi Sad, 2019.

Maria João Fernandes; Manuela M. Moreira; Paula Paíga; Silvia Capelas; Manuela Carvalho; Sónia Figueiredo; Simone Morais; Cristina Delerue-Matos. "Evaluation of the adsorption potential of biochars prepared from agro-food wastes for the removal of fluoxetine". Presented in XXIV Encontro Luso-Galego de Química, 2018.

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Silva, A.; Maria João Fernandes; Paula Paíga; Carvalho, M. M.; Llaguno, C.; Vázquez, F. Macías; Delerue-Matos, C.. "Development of a QuEChERS Sample Preparation Method for Fluoxetine Determination in Sediments". Presented in 40th International Conference on Environmental & Food Monitoring, 2018.

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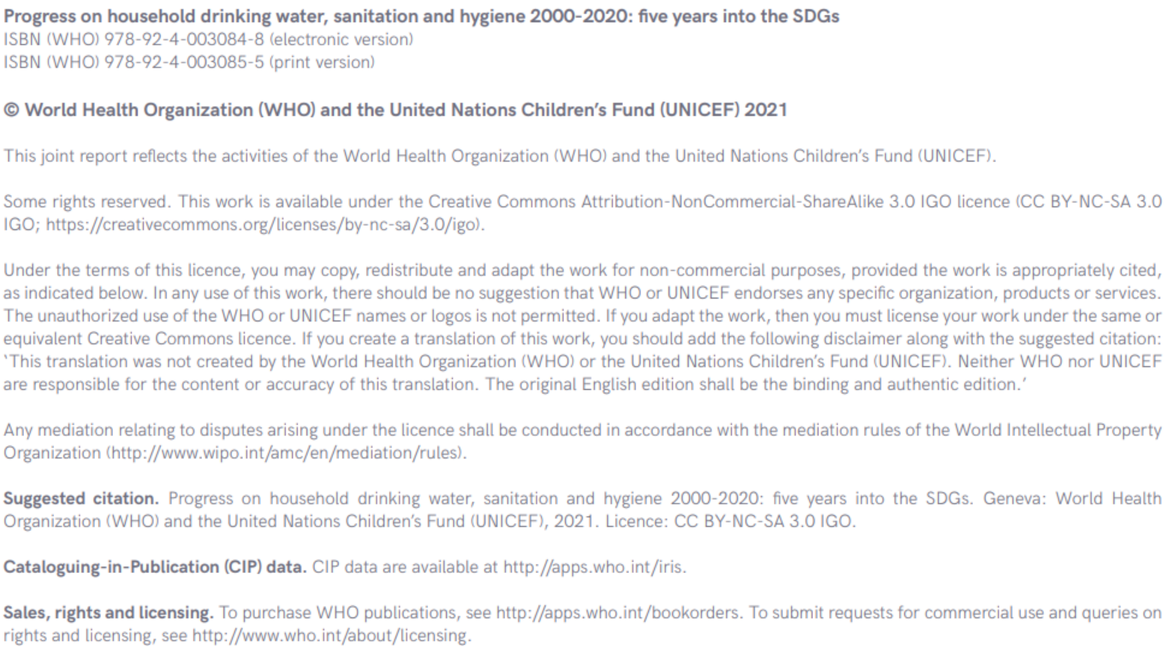

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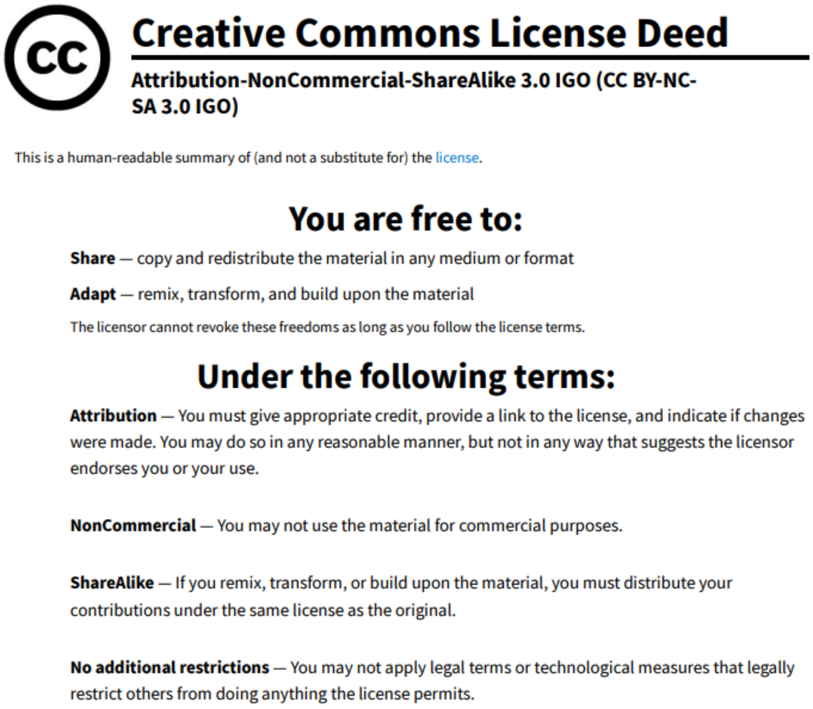

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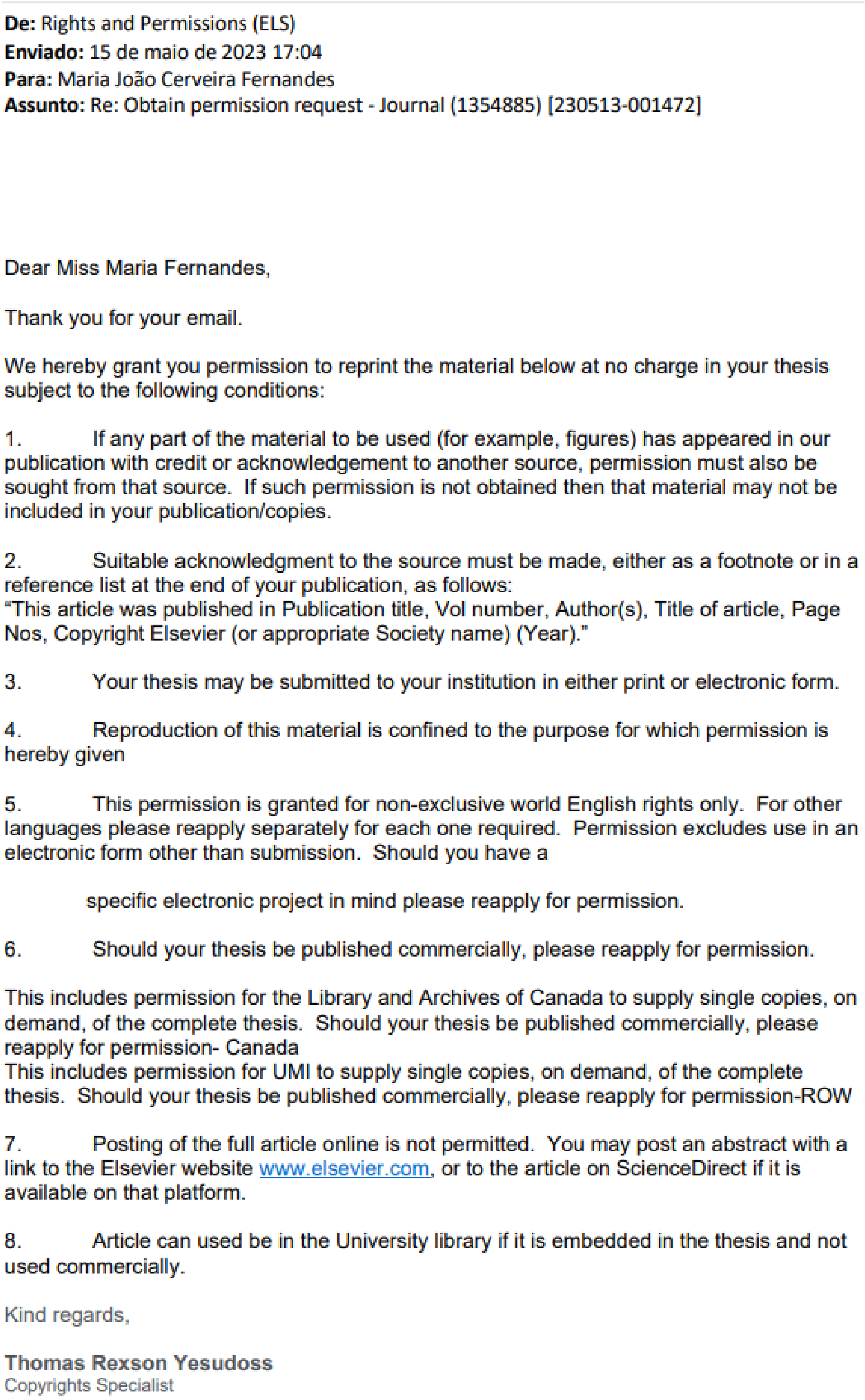

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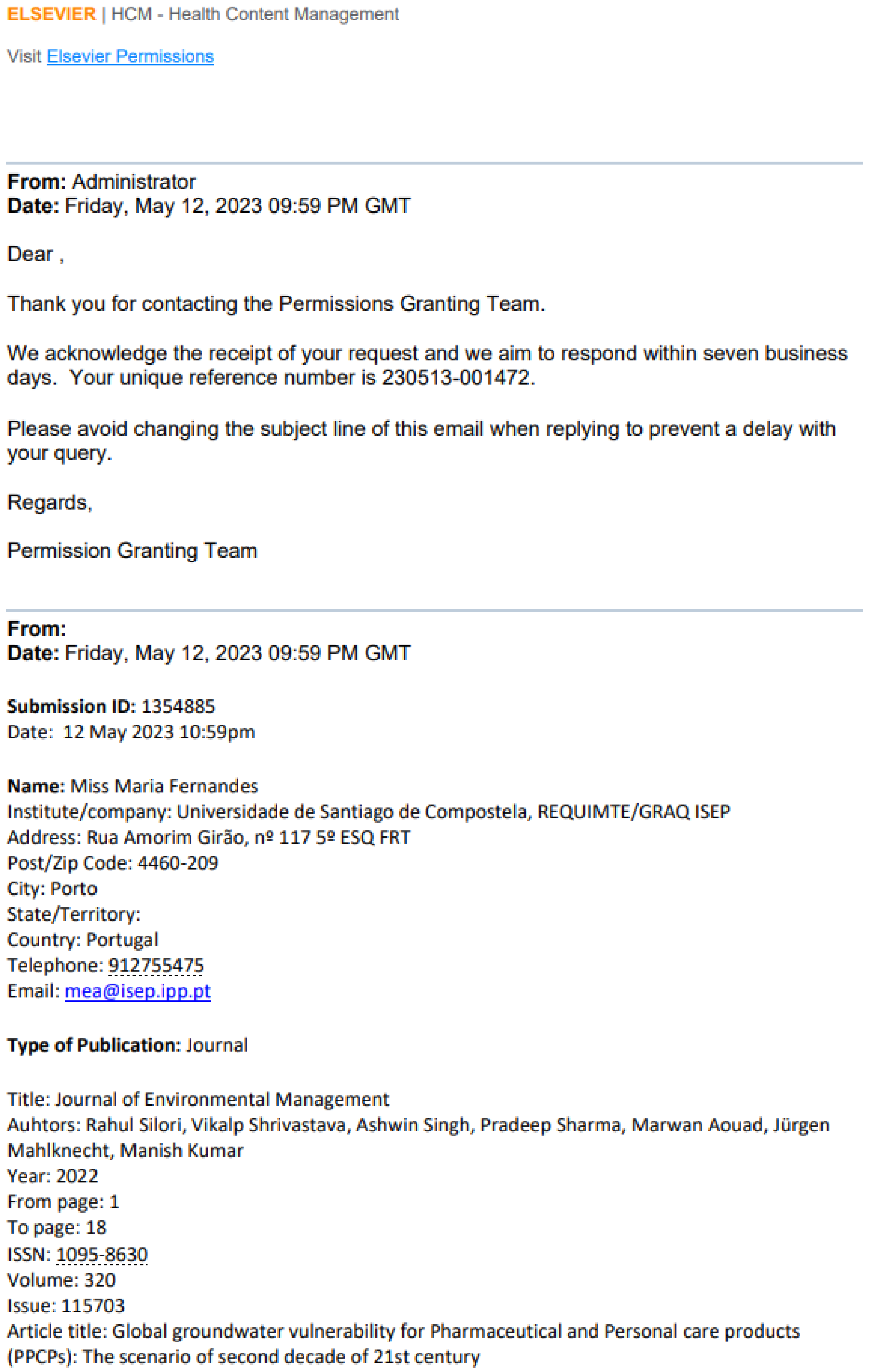

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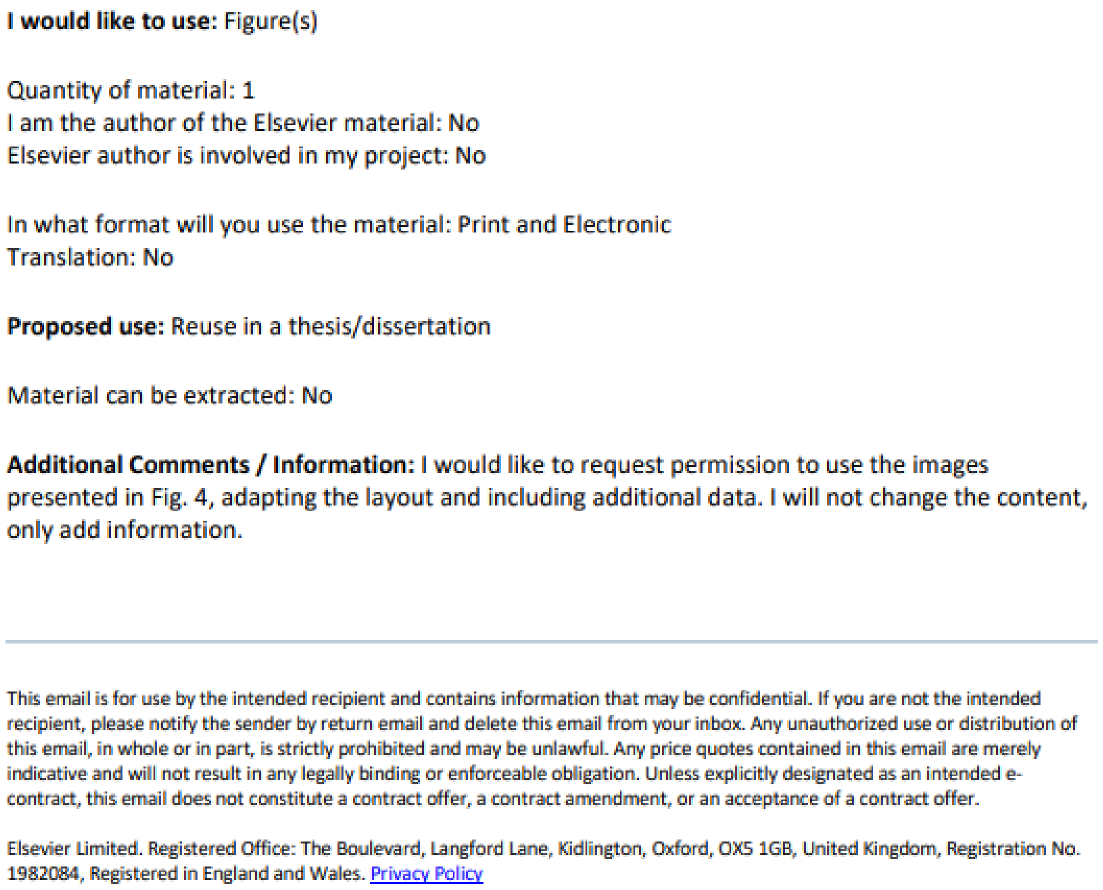

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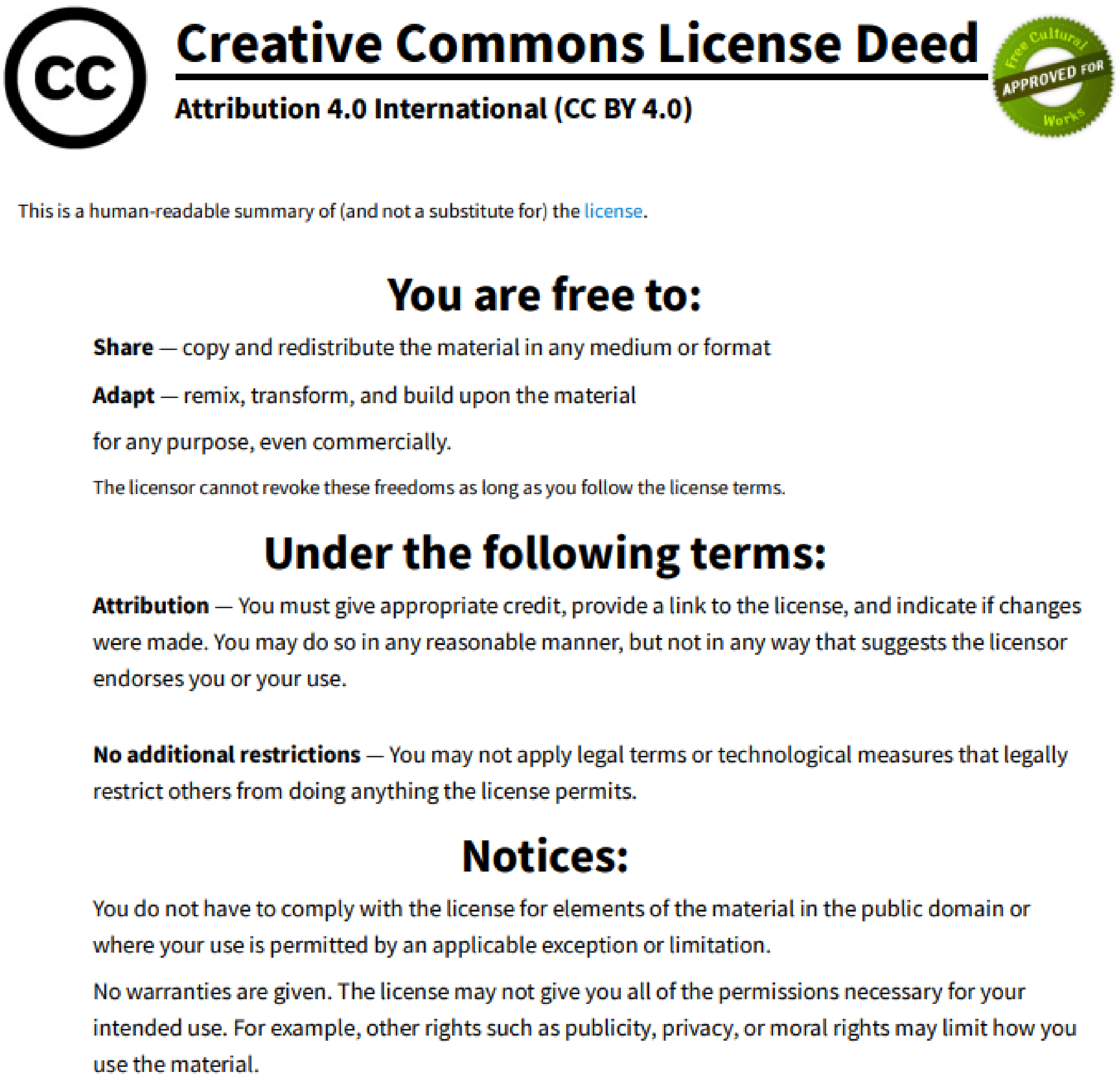

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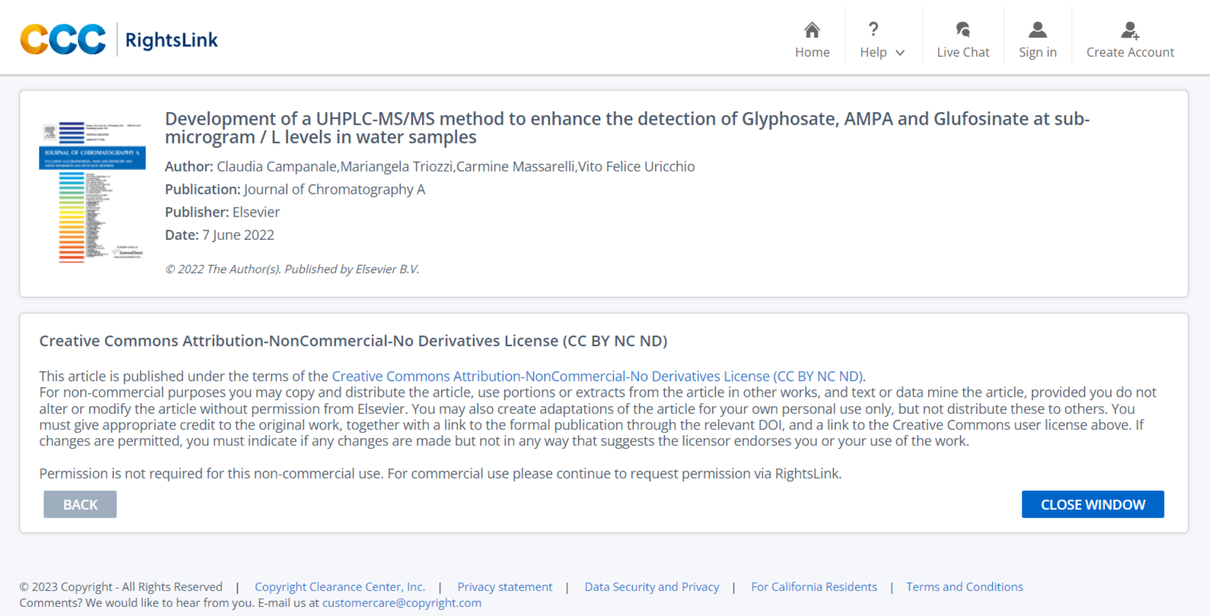

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Publication: Journal of Chromatography A

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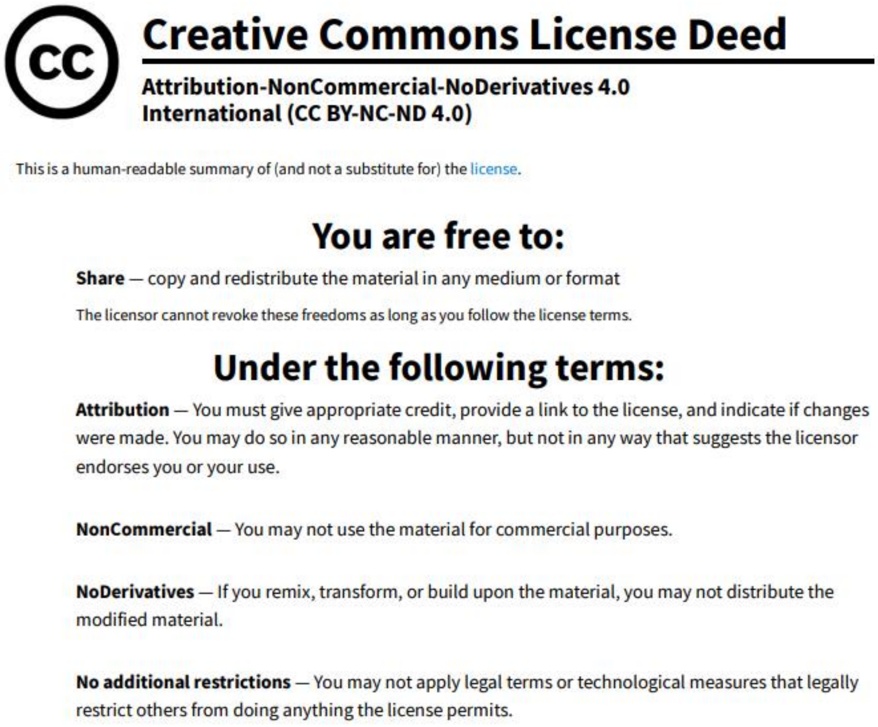

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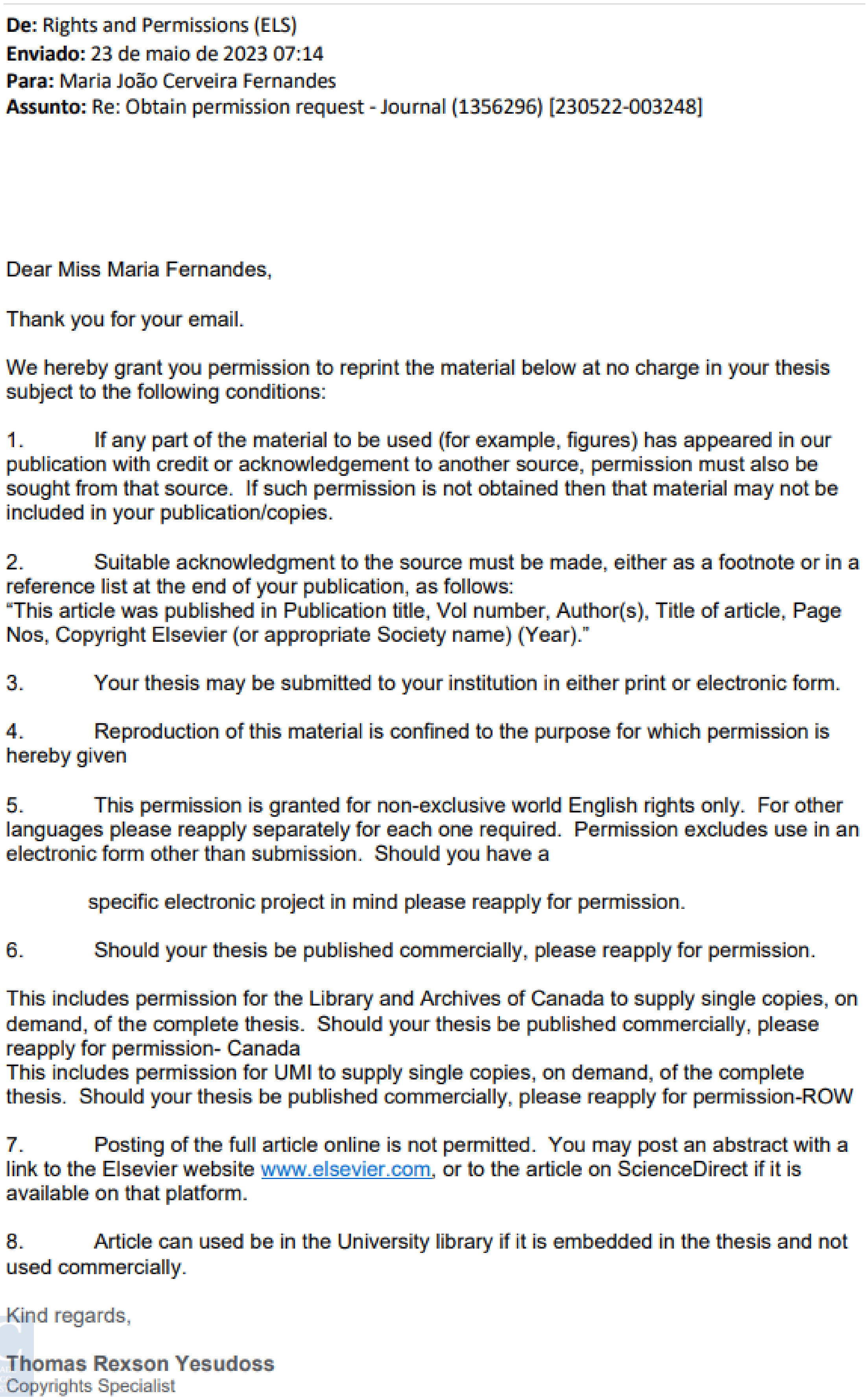

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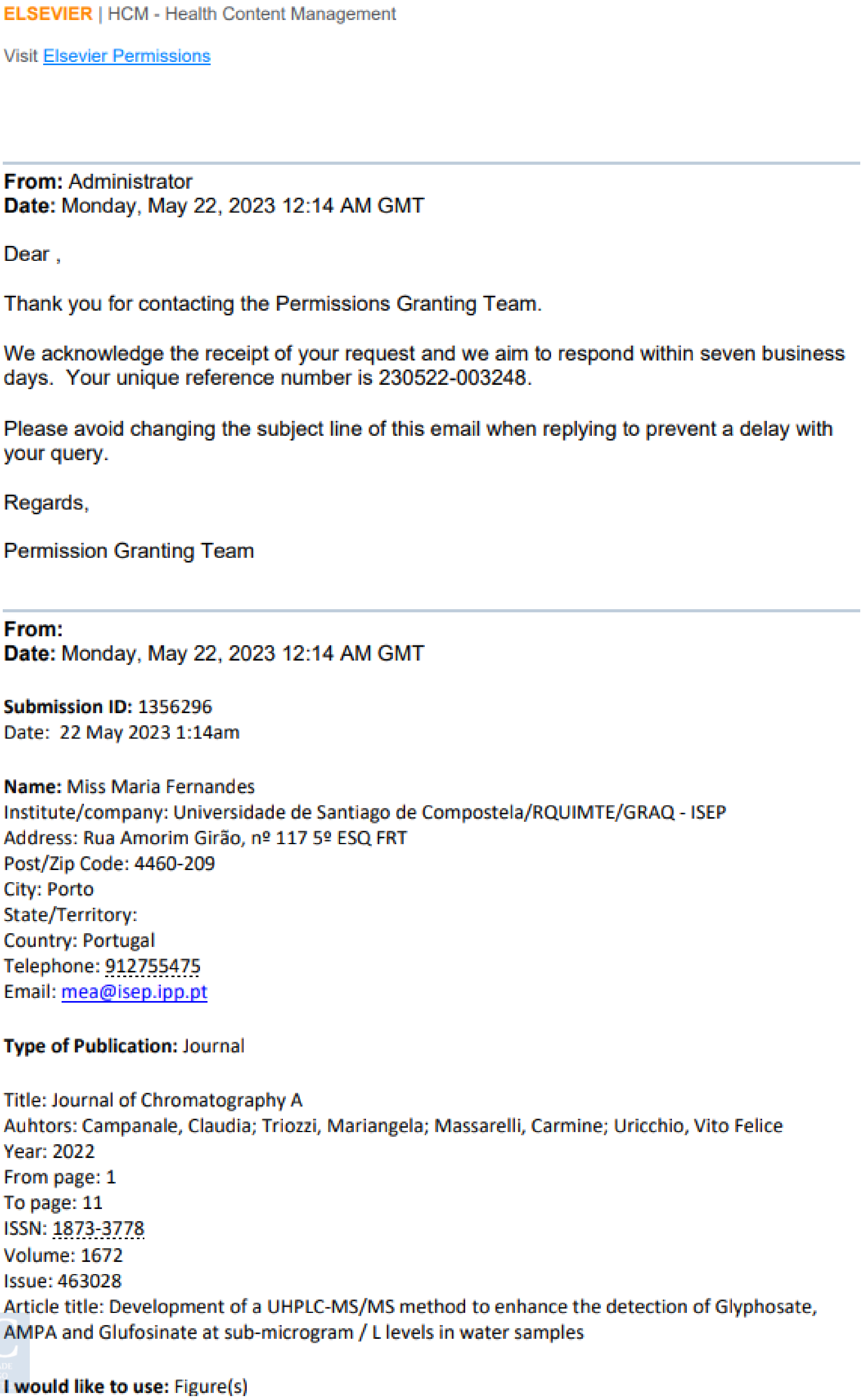

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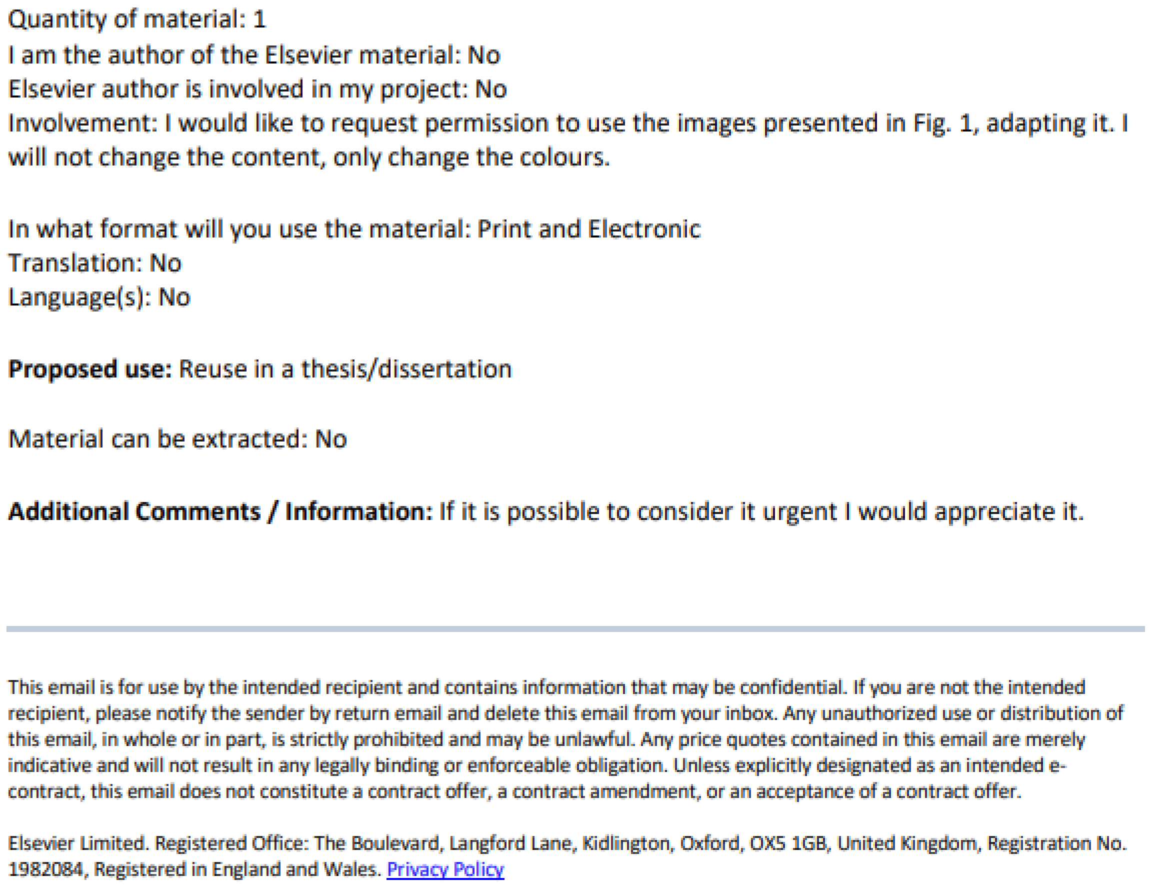

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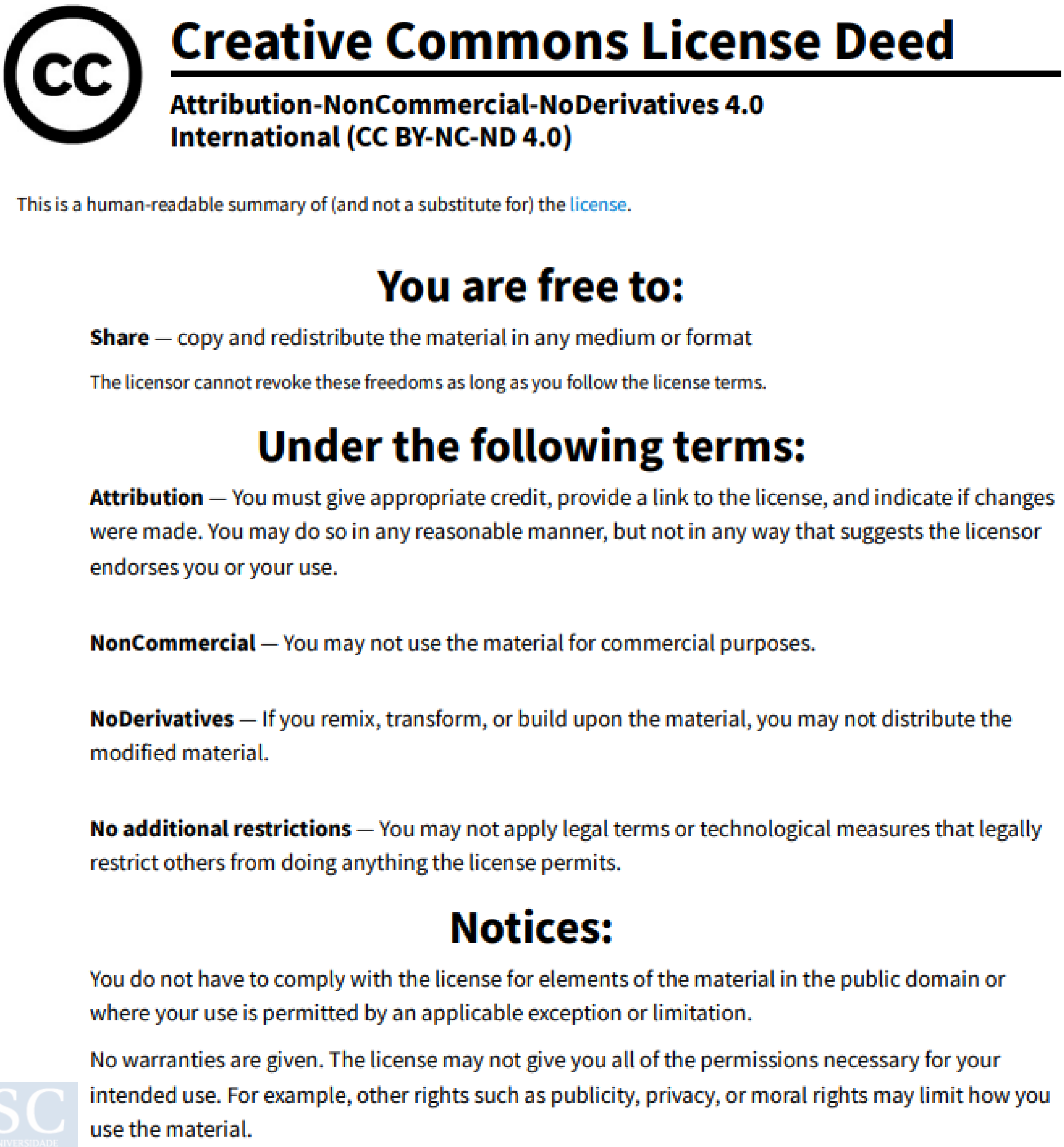

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The substantial population growth and consequent alterations in consumption patterns of pharmaceuticals and pesticides are increasingly acknowledged. Environmental contamination by the anti-depressant fluoxetine, the herbicides glyphosate and glufosinate, and AMPA, glyphosate’s primary metabolite, require the development of remediation techniques for the rehabilitation of the affected areas. Monitoring antibiotics and anti-depressants in water and sediments and a literature review of glyphosate, AMPA, and glufosinate water and sediment contamination worldwide were performed to evaluate their mobility. The use of adsorption as remediation technology, applying new, low-cost, and sustainable materials such as biochar and tailor-made technosols was, also, proposed and investigated in this work.