Trace metal availability in soil horizons amended with various urban waste composts during 17 years – monitoring and modelling

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PHILIPPE CAMBIER et al.

Response of the Authors to Reviewers/Editor comments:

We sincerely thank the Reviewers and the Editor for these interesting comments, questions and critics. We are answering below to each reviewer on the course of his or her review. Parts of our responses concern two or more reviewers, which will be indicated each time.

Reviewer #1: Dear Editor,
Manuscript "Trace metal availability in soils of a long-term field experiment amended with various urban waste composts during 17 years - monitoring and modelling" is an prepared at an acceptable level. This study is interesting but manuscript needs a major revision or submit as new submission.

1. **Title**: Trace metal availability in soils of a long-term field experiment amended with various urban waste composts during 17 years - monitoring and modelling - why soils - there was only one soil - please correct it. Moreover, does the trace metal availability in soils model make sense without considering the plant factor - authors should explain it. The authors do not have to discuss the content of the trace elements tested, but they should take into account the plant factor in mathematical models, especially since it was a fertilization experience.

Answer: This is not a fertilisation experience. It is part of a field experiment on all agronomic and environmental effects of organic residues recycling in agriculture, **as presented in part 2.1**.

About the concepts of availability and the absence of plant data in our study, we completed the introduction and the description of Methods (Lines 76-95 of revised version with marked changes; L 204-216), to make clearer that this article goes over the assessment of soil contamination based on total contents but remains focused on soil. The revised introduction reminds more clearly that the bioavailability of contaminants involves at least two stages: the environmental availability and the interactions milieu-organisms. We think that a scientific work remaining at the first stage can present some interest. We evoked the action of plant or other organisms in the discussion (L 617-ff.).

About soil or soils: “soils” was used as a common shortcut for soil samples or soil layers; it has been changed into “soil horizons” in the title. We also adapted some sentences of the text in the same way (L 24-28 in abstract, L 134, etc.).

2. **General note** for the whole paper - what the authors mean by writing: "evolution"??? Evolution - is change in the heritable characteristics of biological populations over successive generations. Please change it!

Answer: Yes, evolution is at first used in this sense, but for example the Merriam-Webster dictionary considers this second definition: “process of change in a certain direction”, and other meanings (http://www.learnersdictionary.com/definition/evolution). There is no ambiguity in our text.

3. **Introduction:**

- L. 15 and 41 - According to the R10 method of EU waste law, the introduction of organic residues into the soil is a recovery

Answer: Terminology is important and would need enough space to explain the choice of important terms as recycling/recovery, or waste/residue. We have been influenced by the international scientific network RAMIRAN, which means "**Recycling** of Agricultural, Municipal and Industrial Residues in Agriculture Network". However, some expressions like municipal solid waste or green waste are usual and have been kept in our article. Finally, we didn't change the terms that the other reviewers seem to have accepted.

- L 47 - It should be explained why the authors suggest a problem since N and P should take into account the nutritional requirements of plants when using such materials for fertilizing purposes.

Answer: We just suggest that fertilisation is more difficult to control when using organic residues than with synthetic fertilisers. Then problems coming from poorly controlled fertilisation are well known. We cleared up the text about adjustments of nutrients to plant needs and eventual excesses of N or P (L 56-57 and 168-172).

- L 48 - It should be clarified what pollution is going on

Answer: The input of contaminants through OWP and their possible impact are a little specified in the next revised sentences (L 58-68); however, they remain focused on contaminants studied in the article.

- In the introduction of the work, the authors describe on the basis of the literature possible changes in the content of general forms of trace elements, which is evident in the repeated use of waste materials, including composts. they also inform about increasing the share of available forms. Very little attention has been paid to the reasons for changes in the availability of trace elements in soil. The role of the plant in the process of phytoextraction as well as information on the different abilities of plants to take trace elements is not taken into account. It should also be mentioned that the consequence of the accumulation of trace elements in the soil will be changes in the biomass of plants. Please consider the role of the plant in these studies (also in the introduction) and give the chemical composition of biomass.

Answer: in amended cultivated soils, various agents and processes, biotic and abiotic, induce changes of the speciation and the availability of trace elements. The main biological agents are microorganisms and plants. They are mentioned more in the discussion than in the introduction, and often implicitly through the processes of mineralisation and humification (L 615-ff.). However, we did not add new data on yields, uptake of elements, nor on microbial biomass or activity.

4. Materials and methods

- L. 117 - urban waste composts not urban compost
- L 118 - The manuscript is focused on soil analysis, so the impact on soil, not environmental
- L. 121 - what it is "maize-winter"???

Answers to the 3 previous comments: L117 corrected (L 142 of revised marked version).
L118: This sentence concerns the field experiment, not the present article, and studying environmental impacts is within the aims of the field-experiment (L 125-126, 142-144).
The crop succession is maize-"winter wheat".

- L. 123-124- The soil chemical properties should be given before the start of the experiment - especially the content of trace elements, pH and EC etc.

Answer: A new Table 1 shows the initial chemical properties of the plough horizon. The old Table 1 on OWP properties is shifted to Suppl.Info. (-> Table S1) following Reviewer 4's comment that this non-crucial part was too lengthy.

- L. 137- Please explain why the given value is not confirmed in the amounts of C entered with organic materials that the authors included in the Table 1

Answer: This field experiment is large (6 ha containing 40 plots of 450 m^2), which presents several advantages and some technical difficulties. The determination of input C needs to know the C content and the amount of OWP applied per ha. The C content is estimated before application in order to adjust the spreader, but a more representative sampling of OWP is done during spreadings. And so, the most accurate data are obtained after spreading and do not match exactly the target. Explanations have been completed (L 187-190).

- Moreover, there is lack of information about meteorological conditions, which in the case of the application of organic materials is important - the rate of mineralization - please add it.
- L 139-144- what effect was the introduction of additional N dose on the rate of mineralization of composts and at the same time on the release of trace elements???

Answer: As at the end of part 3 of this review, you raise interesting questions about the consequences of OM mineralization, influenced by climate, crop, fertilisation, and of the biogeochemical cycles, upon the release of trace elements and so on their availability. We did not add extended meteorological data to the definition of the climatic zone and to mean annual temperature and precipitation (L 144-146), but we completed the description of OWP in the new **Table S1, especially on their stability**. And we developed the interpretation of our data by considering the dynamic of soil OM, which has been addressed in other articles on the same field experiment, especially Peltre et al (2002) and Noirot-Cosson et al (2016), the latter being a new citation: L 171, 270, 640. We mentioned from this reference that the differentiation between +N and –N plots has been small with respect to the increase of soil OM in the amended plots (Lines 642-643). Concerning the evolution of available TM, we strived hard to interpret the manifest influence of OWP types (L 635--657) but not of the complementary N fertilisation.

In the introduction, the authors wrote "The main drawbacks concern the control of nutrient fluxes, especially N and P compounds which may cause environmental damages" - why, therefore, additional fertilization N???

Answer: see Answer about Line 47. We do not see any contradiction between the general idea given in the introduction (L 56-58) and the management of our experiment, now better described about this complementary fertilisation (L 167-173).

- The authors give in the Table 1 content and quantity entered C per ha. Why the value and quantity of the introduced N is not given????

Answer: Data have been added in this Table (now Table S1), on the C/N and an OM stability index, but the dynamics of OM and N in this field experiment have been treated in other articles and cannot be detailed in the present one. So now in the revised version, those articles are more used for interpreting the presented data on TM availability, as also asked by Reviewer 4: Lines 639-ff.; 817-821.

- L.152- There is no information on what composting was mixed with the soil layer - please add it.

Answer: we added more information in Lines 186-192.

- L 159 - what mean "most analysis" - please explain it
- L 163, 173 - In results there was given DOC not C total!!!
- L 168 - I can't see anywhere CEC results
- L 175-176 - Where these contents are provided - I can't see it

Answer: For OWP samples, chemical data are now presented in Tables S1, Tables 2-3, and Tables S2-S4. For soil samples, apart for the initial state (new Table 1), they are not all detailed in this paper focussed on EDTA and CaCl2-extractable metals (Fig. 2-3 and Tables S3-S5). The major soil variables (SOC, CEC, pH…) are used in correlations and regression (parts 3.7-3.8) and the discussion presents the ranges of their variations (739-755). Data on pH CaCl2 have been added in Table S5. The total contents of TM in soils are detailed and discussed in the companion paper of Michaud et al (2018), but we added here, in the revised version, the EDTA-extracted metals in % of Total (Table S3-B), as well to answer the next Questions below about L 296 and L 553.

Results and Discussion

- L 202-206 - how does this sentence have to do in line 137??? Please rewrite it.

Answer: it has to do with the words "4 Mg C.ha^{-1} per spreading" 2 lines above (now L 263); values per year and per spreading are not equal. See also answer to comment of Line 137.

- L 223- the methodology does not mention the method of Hg determination

Answer: Only total Hg has been measured in OWP and soil horizons, not "available" Hg. So, these data on total Hg have been removed from this article because they do not correspond to its topic and they were not discussed.

- L 227-233 - if the limits have been exceeded, should such materials be used?? Please explain it.

Answer: regulatory limits have been progressively imposed in France during the 2000s, whereas the experiment started in 1998. Anyway, we just want to underline that OWP applications have been intensive, over common practices (L 165-166), with inputs of a few metals close or above permitted maxima, but not unreasonably excessive. We made this clearer in the revised part 3.2, although briefly, in agreement with Reviewer 4 that this is not a crucial part of the article, and we reminded it in the conclusion (L 813-815).

- L 296- In Table S2, the share of CuEDTA in Cu total is for SGW from 7.3 to 39% for BIO 6.3 - 41% for MSW 10-45% for FYM from 12 to 52% unless they are medium, but this is too much simplification with such a distribution - please explain it.

Answer: Table S2 refers to OWP and this part of the text to topsoil. But it is right that all necessary data had not been presented to look at these %ages. We added %EDTA/Total related to soil samples in Supplementary Info: Table S3-B. This Table shows that %CuEDTA/Total do not vary too much. A more detailed answer to the related comment of L 553 is given below.

- Figure 3 - Why did the authors choose only a linear relationship to describe the presented relations? Please explain it.

Answer: We added considerations on possible non-linear relationships (L 441-444). Even interpretations of linear regressions with different slopes, slope > 1 or < 1, which have been developed in the article as asked by Reviewer 4, are attempts (L 619-656). The parameters of non-linear models fitting the data would be still harder to interpret and this has not been attempted.

- Figure 4 - there is no legend as per Figure 2

Answer: we completed the Legend of Fig.4.

General discussion

- L 519 - there was only 1 soil!!! why soils???

Answer: this has been corrected each time when the studied samples are concerned

- L 521-524 - I think that the authors should take into account not organic matter and the content of humus compounds having the ability to bind TM.

Answer: We are not sure to understand the critic; we would say that the different approaches of TM speciation in soils strive to quantify metal fractions bound to major soil constituents; it is not common to distinguish metals bound to different OM pools and this has not been done here.

- L 526 - In addition, whether the extractant's suitability for this type of assessment can be demonstrated without considering the plant. Please justify the selection of the extractant.

Answer: see previous answers about the absence of plant data. We completed the justification of the choice of extractants in Lines 203-215; and a posteriori in the Discussion: L 674-78; 695-697; 772-78.

- L 544 - Then why is Fig. 3 based solely on the linear relationship????

Answer: See previous answers about Figure 3, which presents the relationship between a balance of fluxes and the stock variation of mobilisable trace metals in soil layers, whereas Line 544 concerned sorption equations. But this part has been deeply revised.

- L 553 - It's a very simplistic approach. Authors should be based on real values and not averages

Answer: The new Table S3-B shows that CuEDTA in % of Total does not vary too much around 30%. Anyway, this simple calculation is just to enlighten that predictions by the two equations are less remote than at first sight when confounding total and mobilisable Cu. But a true validation and a comparison of the different models would need a supplementary dataset, as underlined by Reviewer 4 about Highlight 3.

- L 579- Not mentioned and CaCl2

Answer: we have not understood the question

- L 615, 620 - roughly ???

Answer: approximately. This has been changed.

- L 636-644- In fact, those elements that have not emerged are difficult to assess….

Answer: we agree.

- Table 2 - It is not clear if Input g / ha / year is calculated based on average content? The amounts introduced should be calculated based on the TOTAL content

Answer: We clarified in the caption of the Table that the input in g/ha/year has been obtained from the sum of all inputs (all spreadings) divided by the number of years

- Table 4 - Where are the actual pH values - please add it. Figure with pH H2O and pH CaCl2 is this the same???

Answer: soil pH H2O and soil pH CaCl2 are distinct (see Methods and then Lines 473-475, 532-535) but they are strongly correlated (Fig S1, better explained in the revised version). The values for pH CaCl2 have been added in the revised Table S5 related to soil CaCl2 extracts. We didn't present all soil data as explained above (last Answer about Materials and Methods). But we showed the ranges of variations of soil pH and SOC and used them to discuss the variations of soluble metals (L 740-742; 752-755).

- Please give information about salinity after so many years of application.

Answer: Obriot et al (2016) reported that soil Electrical Conductivity became higher, but not huge, in soil amended by BIO, FYM and MSW, and that it was correlated to some other soil characteristics, especially CEC. We considered in our MLR studies the possible influence of CEC on soluble TM and found no significant correlations (part 3.8). We added considerations on possible other influencing variables as Electrical Conductivity: L 564-565.

What is the point in showing the dependence shown on Fig. S1???? Really, I do not understand…

Answer: see second to last answer about Table 4

Conclusions

Should be rewritten. The inference should refer to the agro-ecological conditions in which the research was carried out

Answer: Conclusion has been deeply revised

References:

in 60th position 38 was published before 2010 in among those 38 until 17 appeared before the year 2000….Authors should update the paper and knowledge about data from the last 5 years

Answer: we added a few recent references, where they are relevant: Yoshida et al., 2018; Kumpienne et al., 2017; Iglesias et al. 2018; Noirot-Cosson et al., 2016; Sayen & Guillon, 2014; Zeng et al., 2017. We also added as supports of our answers to the Reviewers the following references: ISO 2008 upon bioavailability of contaminants in soils, Buekers et al., 2008; Manouchehri et al., 2006; Belon et al., 2012). We suppressed 2 (unnecessary) references of 2005 and 2004.

Reviewer #2: This study aimed to evaluate the evolution of trace metal availability in soils. The manuscript is below the standard to be published in STOTEN. The content presented and rational developed is not enough to justify its publication in STOTEN.

Answer: We think that the paper presents an important and original set of data collected from an uncommon field experiment. Most analyses are standard ones, but it is not common to measure CaCl2-extractable trace metals in composts and this is not technically so easy. Above all, the complementarity of the data made the dataset original and valuable.

Regarding the rationale of the study, it has been better explained in the revised version (Lines 76-95 + 135-138 of introduction in the revised version with marked changes; and further in Lines 203-216; 615 and followings).

1. Abstract is very general and it does not cover a good story of the study.

Answer: we attempted to improve it (revised abstract with marked changes, especially L 18-36; 42-43).

2. English is weak at many places. See lines 82 (conforming and not conform), line 95: few and not little. There many other examples.

Answer: these 2 examples corrected. English has been checked again, with the help of colleagues more fluent in this language in the most crucial parts.

3. Introduction - this section needs a thorough revision because the argument made by authors for developing significance of work is weak and should be discussed based on relevant and recent papers.

Answer: see our first answer about the rationale and consider the revised Lines 62-94 + 123-138 of introduction. We added in the introduction the relevant recent references Yoshida et al. (2018), Kumpiene et al (2017), Iglesias et al. (2018) and ISO-2008 which is not recent but quite relevant. Other references were added in Results or Discussion (see the last answer to Reviewer 1, and the next answer).

4. Results and discussion are confounding at many places and meaning is unclear. Discussion of results is rambling and has not been prepared using the relevant papers and their data for a critical discussion.

Answer: we better separated and attempted to clear up the presentation of Methods, Results and Discussion (Lines 235-255; 451-464; 554-578; section 4). The first submitted version already used many relevant references, although not all recent, for a critical discussion or our results. However, the discussion was not sufficient, as also noticed by other Reviewers. We added other references to support the deeply revised Discussion (L > 615): Noirot-Cosson et al (2016); Buekers et al (2008), Sayen & Guillon (2014).

5. It is claimed to be a monitoring study, but measurements were made only once.

Answer: which measurements have been made once? Yes, DOC in CaCl2 extracts of OWP has been measured once. All other variables presented in Tables and Figures have been measured between 6 and 9 times during a period of 17 years (without considering the 4 repetitions of the field experiment, the 3 samplings of each amendment).

6. It is not clear how much of this article overlaps with another one submitted by the same group (Michaud et al., 2018). The authors should have attached this paper in order for the reviewers to evaluate this aspect.
Answer: the 2 articles complement one another. But they are not ready and not submitted at the same time.

7. It is not clear to me which hypotheses the authors are testing.
Answer: added in Lines 135-138, and re-examined in the revised conclusion (793-806).

8. Unnecessary abbreviations are used (see TM for trace metals)
Answer: we think that this abbreviation eases the reading of some sentences

9. The formatting of the article is unconventional, including the use of bullet points in the text or quotations (see lines 92-93). This also includes the fact that there is a results and discussion and a general discussion section.
Answer: we made more uniform the formatting of lists in the text, using underlined subtitles included in the paragraphs and seldom just dashes. We wrote once one quotation, with the recommended quotation signs, rather than rephrasing what the authors had well expressed (L 112-113). We better separated Results and Discussion (see answer to point 4 before).

10. There is very few details on the amount and type of fertilisers. Cd can be present in some fertilizers and this seems to have been overlooked.
Answer: it was specified that fertilisers have been ammonitrate and urea, which generally show very low contents of cadmium. We made this clearer in the revised version (L 167-169).

11. Lines 190-191: This is an unnecessary clarification. If done for each data the correlation would have been artificially increased.
Answer: this clarification is not insignificant (now L 235-236). Applying linear regressions on data obtained at different times on the same 4 plots (of the 4 repetition blocks) would contradict the hypothesis of independent measurements at each time.

12. The graphical abstract is not providing any summary of the experimental aim or designs.
13. From the highlights, it is not clear what was the main finding in this article
Answer: we revised the graphical abstract and the highlights.

Overall, more work needs to be done by the authors. Hypotheses need to be presented and tested and the manuscript should read better. The broad significance of the study is not clear from the introduction.
Answer: see previous answers about the significance of the study (first answer and point 3) and about hypotheses (point 7). We worked more to deepen the discussion, as also asked by the other reviewers, and improve the readability of the article.

Reviewer #3: General comments:

This manuscript monitored and modeled the availability of trace metals in a 17-year field experiment soil amended with different organic waste products. Two fractions extractable metals were analyzed by 0.01M CaCl2 solution and 0.05M EDTA solution. Besides, the relationships between soluble and EDTA-extractable metals and other soil variables were unraveled. This paper is especially valuable in examining and predicting the evolution of metal available fractions through a long-term monitoring of field experiment, though the data analysis and the predict model were simple liner regression.

Specific comments:

1. The authors used both terms "Trace metal" and "Heavy metal" in the manuscript. Please change them consistently.

Answer: we used “heavy metal” only in Keywords, in order to facilitate database search using this keyword

2. The Graphical Abstract is not clear, modify it and enhance the resolution.

Answer: it has been modified to become clearer, with a better resolution

3. In the introduction section, the research gap related to the topic should be given and the novelty or the significance of your study should be stressed clearly.

Answer: see Answers to previous Reviewers and in the revised introduction especially the Lines 75-94, 135-138

It's better to move the part of long-term field experiment description to the section of "materials and methods".

Answer: this is not a description; Lines 123-127 just introduce QualiAgro as an essential part of our approach. The presentation is in Materials and Methods (revised; see next answer)

4. In the materials and methods section, how about the sampling methods for soil and amendments? And why you chose 0.01M CaCl2 solution and 0.05M EDTA solution to extract available metals? We have no background knowledge related to the soil pH values.

Answer: The description of sampling methods has been completed in Lines 186-190.

Some general arguments for the choice of extractants were given in Lines 86-94 of the introduction.

We added justifications in Lines 203-216 of the revised Material and Methods section, and other justifications a posteriori in Lines 675-678, 695-697, 772-778 of the Discussion.

Soil pH values now are shown in the added Table 1, and ranges of pH are used in the Discussion: L 740-743, 752-755. pH CaCl2 was added in the Table S5 showing the detailed values issued from these extractions.

5. Page 6, line 118, check the format of the reference "Houot et al., 2002; www6.inra.fr/qualiagro - eng/)"

Answer: changed into ”INRA, 2018”

6. Results and discussion part. There mainly presented the results in this part. Please put more intense discussion in "4. General discussion" part.

Answer: We revised this part in the direction of a better separation between Results and Discussion, and some points moved from Results to Materials and Methods (see Answer to Reviewer2, point 4). A few short sentences of interpretation remain in the section Results (L 444-447; 454-455; end of 3.6; end of 3.7). The General Discussion has been extended and deepened.

In the section of "Modelling relationships between soil variables and prediction of soluble TM", the introduction of the modelling method should be moved to the section of "materials and methods".
Answer: this has been done (L 235-255).

More about the parameters choice of the model and the lackless or replicability should be discussed in this paper.
Answer: The choice followed the approach summarized by Lines 579-583. We added in Table 4 the MAE (mean absolute error, or mean absolute difference between calculated and measured concentrations), in µg/L and % of Mean value, for evaluation of the fitting (L 598-600).

7. The title showed "during 17 years", but the results in figures are all from the data during 2002 to 2015, just 13 years?
Answer: The title shows “amended during 17 years”, which is right. The experiment also lasted for 17 years, but not all variables have been measured from the beginning. So monitoring the available metals in amended plots has been made during 14 years (including 2002 and 2015), less for OWP. Does this justify adding complexity to the title? But we are more precise in the revised abstract (L 23-25).

8. Some reference formats are informal, such as page 33, line 694, the "Env. Pollution", page 36, line 778, the "J. Hazard. Materials", check all references.
Answer: Done, by using CAS source index search tool

Reviewer #4: Review STOTEN-D-18-04475

General

In this manuscript a long term field trial (17 years) is described in which four different organic waste products (OWP) being compost of sewage sludge, compost of bio-waste (municipal), compost residual municipal waste and farm yard manure, were added yearly to separate plots of an agricultural field (4 replicate plots for each type and 4 control sites).

Both total metal (Cd, Cu, Zn, Ni, Pb, Cr), EDTA-extractable metal (labile or reactive metal) and 0.01 M CaCl2 extracted metal were monitored in the added products and in the top soil (plough layer 0-28 cm) of the field plots (2-yearly measurements) during the duration of the field trial. Furthermore the characteristics of both the added products and soils were monitored i.e. C and N contents, Carbonate content, CEC and pH.

The characteristics of the different OWPs are discussed including differences the extractability of metals by EDTA

The net-input of EDTA extractable metal in the top-soil was calculated from the added metal with the different OWPs, plant uptake calculated from yield and plant contents, aerial deposition and leaching as estimated from measurements in lysimeters. The measured stock of EDTA-extractable metal was then related to the calculated net input of EDTA extractable metal using linear regression. For Zn, Cu and Cr the measured stock shows a clear relation with the net input. Although the obtained slopes of the regression lines were higher than 1, close to one or smaller than 1 depending both on the metal and type of OWP. For Cd and Pb no clear relations were found in all cases. In the case of Ni negative slopes were obtained which according to the authors does not have a physical meaning. Positive slopes of more than 1 were explained by non-EDTA- extractable metal becoming available due to mineralization of organic material. No possible explanation is given for slopes smaller than 1. Evolution of the 0.01 M CaCl2-extract can not be one to one related to the EDTA extractable metal. The 0.01 M CaCl2 extracted metal resemble the soluble metal and is also depending on soil characteristics like pH and CEC.

Multiple linear regression (MLR) relations were derived between CaCl2_extractable metal and EDTA extractable together with soil properties and for the Kd (ratio EDTA/CaCl2 extractable metal and soil properties). MLR gave significant and plausable results for Cd, Cu and Zn but not for Ni and Pb is not discussed any further (why/). Regression relations for Kd compare well with relations obtained in other studies.

According to the authors it can be concluded that the followed approach is promising to predict the evolution of soil available metals at least for Cd, Cu and Zn. However as the authors conclude the slope of the relation between net inputs and stocks in soil can deviate from unity and one may expect that these slopes are highly conditional and depending on both the added OWPs and the receiving soil. So as concluded by the authors more research is needed. However research like this is very laborious and costly and takes a lot of time. So maybe the conclusion could also be the other way around and be a warning for studies on mass balances pointing that EDTA-extractable metal is not a conservative parameter for some metals.

The study is sound and well described in the paper and the work fits well into the field of STOTEN so I think it is worth publishing it. Although I found the first part of the results 3.1 - 3.3 (comparison of OWPs and metal extractability of the different OWPs) rather lengthy. I think the paper can be more attractive if the results of this part are summarized in the paper and not discussed in so much detail (maybe move that to supporting info) so you come faster to the crux of the paper. I would suggest also to summarize table 1 in the main text and just give the average numbers and present the full table in the supplementary info.

(First) Answer of authors to Reviewer 4:
Thank you for this enlightening review. We retained especially the limits of our work concerning the presentation and discussion of the regression calculations between inputs and soil stocks of EDTA-extractable metals. So we pushed further the discussion of these results in the revised version (section 4, Lines 615-658. We mitigated the affirmation of a conservative behaviour of these TM fractions in the same lines, in the conclusion (L 794-800), and in the Highlights (as asked below). About the parts 3.1 - 3.3, we simplified them a little and moved the large Table 1 to supplementary information. But we added data on the stability of the organic products in part 3.1 (L 268-272), to answer Reviewer 1's questions, and this additional information was useful for the discussion mentioned above.

Detailed comments:
Highlights:
Highlight 2: I do not agree that EDTA extractable metals is conservative. This paper shows deviations from conservative behaviour
Highlight 3: I would not use the term predicting. The regression coefficients were obtained from the data from this study. So it is rather a description than prediction
Answer: we agree that the conservative behaviour of EDTA-extractable metals was exaggerated in the first submitted version. And that the presented modelling would need more validation and probably adaptation to become predictive. So, **highlights have been modified**.

P2 L25-27 More unexpected... This sentence is difficult to understand especially when you did not read the paper yet. The abstract should be understandable without reading the paper.
Answer: the abstract has been modified to answer Reviewer 2's critic and clear up our message; it contains no more "unexpected"

P7 L143 what intensive agricultural techniques have been applied?
Answer: see Lines 173-175. This part has been completed and clarified from L 168, to answer this question and questions of Reviewers 1 and 3.

P8 L170 Please give the concentration of the EDTA, the solid to solution ratio and equilibration time (so one has not to go to the referred article for these key characteristics)
Answer: done in Lines 207-208.

P17 L332 I would specify "other vertical fluxes" i.e. uptake, deposition and leaching

Answer: done (now Line 413)

P15-19 Section 3.5

* It would be interesting to show the relative importance of the different contributions to the mass balance i.e. input by compost, aerial deposition, plant uptake and leaching

Answer: done in Lines 395-401. These contributions lead to **more uncertainties for** the balance of available metals **Ni and Cr**.

* For the case of a slope of >1 for the relation between the measured stock of EDTA extractable metal and the net input of metal **could you verify the percentage of total extractable metal in the added compost became EDTA-extractable**?
* **Please give also your thoughts on a possible explanation of a slope <1**
* **Is a negative slope really physical meaningless** or is it possible that after addition to the soil Ni from soil and added material is immobilized due to ageing as a result of changing environmental conditions including an increased pH which has been shown to induce ageing of Ni. Especially if Ni contents in the added OWPs are low compared to the soil this could be possible. Or is the change so low that it is within the error ranges. How important are the other contributions to the mass balance and how certain are these?

Answer: See the deeply revised General discussion and the conclusion: Lines > 615, L >792. Rather than percentages, we presented in kg/ha the amounts of metals apparently transferred from non-extractable to EDTA-extractable pools, or the reverse, after OWP spreadings (L >620).

For Ni, see the previous answer about the contributions of other fluxes. For instance, the estimated Ni output by leaching, assumed EDTA-extractable, is around 20% of Ni_{EDTA} input by composts but reached 86% of Ni_{EDTA} input by FYM (containing little Ni). For this reason and because amended plots do not contain more Ni_{EDTA} than the control, we consider that the negative regression found between soil stock variations of NiEDTA and corrected inputs from FYM occurred by chance.

P19 L368-370 What is meant with a roughly conservative behaviour of PbEDTA in FYM and for which other metal(s) this was also observed (i.e. to what refers the "also")?

Answer: part modified (no more “also”)

*Revised manuscript with changes marked
Click here to view linked References

Trace metal availability in soil horizons ~~of a long-term field experiment~~ amended with various urban waste composts during 17 years – monitoring and modelling

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Abstract

Recycling ~~of~~ organic residues in agrosystems presents several benefits but faces the question of contaminants, among them a few trace metals which eventually accumulate in ~~amended~~ soils following regular applications of organic waste products (OWP) and represent an ecological risk. The ~~evolution~~ increase of total trace metal contents in amended topsoils can be ~~determined at first~~predicted by a mass balance approach, but ~~predicting~~ the evolution of their available fractions is a more intricate issue. ~~This work is a contribution to this issue, based on monitoring a 17-year~~We aimed at modelling this evolution by using the dataset of a long-term field experiment of OWP applications (manure and three urban waste composts)~~to an agricultural soil, including among other variables t~~. Two operationally-defined fractions of 6 trace metals have been quantified in the OWP and amended topsoils between 2002 and 2015: the soluble and potentially available metals, extracted in 0.01M $CaCl_2$ ~~solution~~ and ~~mobilisable ones in~~ 0.05M EDTA solutions, respectively.

The ~~soil contents of EDTA-extractable~~potentially available metals have progressively increased in amended topsoils~~throughout the experiment~~, at rates depending on elements and types of OWP. ~~More unexpected was the correspondence between such increases and the balances of fluxes of estimated EDTA-extractable metals, especially zinc, and for a few other metals~~ For Zn, these increases corresponded in average to inputs of potentially available Zn from OWP. But the soil stocks of potentially available Cu increased faster than from the inputs of EDTA-extractable Cu, showing linear regression slopes between 1.4 and 2.5, depending on OWP type. The influence of OWP has been provisionally interpreted in the light of their efficiency to increase soil organic matter and their inputs of reactive oxides.

Soluble copper has ~~progressively~~ increased with repeated amendments. But soluble cadmium, nickel and zinc have generally decreased ~~with amendments~~, as they are

influenced by changing soil variables such as pH and organic matter. Statistic models were used to unravel the relationships between soluble and EDTA-extractable metals and other soil variables. ~~In the case of~~For Cu, the most satisfactory models just relate soluble and ~~mobilisable~~ potentially available Cu. ~~Combining all found models opens the way for predicting~~Developing such models could contribute to predict the long-term effects of a precise scenario of agricultural OWP recycling upon available trace metals in soils.

Keywords: Organic amendment; soil quality; heavy metal; diffuse contamination; soluble metal, long-term field experiment

1. Introduction

Recycling organic residues in agriculture presents several benefits at local and global scales: the physical, physicochemical and biological properties of the agroecosystems may be ameliorated ~~through~~ by increasing the turnover and over time the content of organic matter (OM) in soils~~, improving their physical, physicochemical and biological properties~~. Increasing the soil organic carbon (SOC) and saving fertilisers by incorporating organic residues in agricultural practices may limit the climate warming and the exhaustion of non-renewable resources.

The main drawbacks concern the ~~control of~~difficulty to adjust nutrient fluxes to plant needs, especially N and P ~~compounds~~ which may cause environmental damages when in excess, and the input of various contaminants in agroecosystems. Among contaminants, several trace metals (TM) are likely to accumulate in soils following repeated spreading of organic waste products (OWP)~~, several trace metals (TM) are especially of concern~~, even when spreadings are conform to relevant regulations. Reviews on this topic converge towards copper (Cu) and zinc (Zn) as problematic contaminants, ~~whose~~ insofar as their total contents in soils do increase after enough time of regular applications of OWP, and they present potential eco-toxicity ~~as problematic contaminants~~ (Smith, 2009; Benoit et al., 2014; Lopez-Rayo et al., 2016; Yoshida et al, 2018). These two metals are essential micronutrients, but other TM like cadmium (Cd) and lead (Pb), which are just toxic, may also accumulate in amended surface soil horizons, depending ~~of course~~ on the applied loads of OWP and on their metal contents (Benoit et al., 2014; Smith, 2009). The corroboration of the increases of total TM contents in amended soils faces technical difficulties, like spatial ~~and sample~~ heterogeneities, ~~detailed~~ lack of prolonged control of all fluxes, including lateral dilution, or changing mass of soil impacted (Berti & Jacobs, 1998; McGrath & Lane, 1989; Benoit et al., 2014; Michaud et al., 2018), but the principle~~s~~ of

predictions ~~are~~ is straightforward: the balance of fluxes through the volume of amended soil determines the variation of stock of each TM in this volume (Doelsch et al., 2016).

It is much more debated if TM inputs to soils through OWP recycling induce significant impacts on soil organisms, crops or water quality. The present work aims to contribute to this debate~~is question is here further treated only through~~ by using the concept~~s~~ of availability, and thus to go over the statement of TM accumulation in amended soils. The relationships between bioavailability, toxicity, environmental availability, and chemical extractability of contaminants in soils have been theoretically and technically discussed in several articles (e.g., Harmsen et al., 2005; Peijnenburg et al., 2007; Kumpiene et al, 2017). From such studies and the induced international standard (ISO-17402, 2008),~~. O~~ one may keep in mind ~~for the present work~~ that monitoring and predicting the extractability of TM in soils by appropriate chemical methods represent an essential ~~step~~ progress towards the assessment of potential impacts of recycling OWP in agroecosystems (Smith, 2009; Paradelo et al., 2018). On another side, at least two levels of availability of TM in soils must be distinguished (ISO-17402, 2008): the readily ~~extractable~~ available fraction, able to be dissolved in ambient conditions, most often estimated by using non-complexing neutral saline solutions, and the mobilisable, potentially available, or reactive fraction, estimated by using chelating or relatively strong acid solutions (Houba et al., 1996; Hooda et al., 1997; Harmsen, 2007; Degryse et al., 2009; Rodrigues et al., 2010; Groenenberg et al., 2012). Although the first fraction is often found better correlated with plant uptake, the second fraction appeared more meaningful in attempts of modelling soil-solution interactions (Tipping et al., 2003; Degryse et al., 2003; 2009; Groenenberg et al., 2012; 2017).

~~Using this point of view, s~~Several studies tended to show that available TM in soils amended by OWP increase more rapidly than their total contents. For instance~~; e.g.~~, Madrid

et al. (2007) found that repeated applications of composted municipal solid waste (CMSW), conforming to Spanish regulations, led to an increase ofd total contents of Zn, Pb, Cu and Ni in the cultivated horizon of a sandy soil, and to a larger increases of DTPA extractable fractions of the same metals. Hargreaves et al. (2008) in their review on CMSW reported several cases of increased DTPA, EDTA or other available fractions of particularly Pb, Cu, Mn, and Zn in amended soils, and a few cases of decreasing availability attributed to an alkaline pH of CMSW (above all for Mn) or to interactions with organic constituents (for Cu). Iglesias et al. (2018) analysed 13 trace elements in soil after 15 years of mineral fertilization or moderate sewage sludge applications and found a positive effect of sewage sludge on total and DTPA-extractable contents for several elements; however, only Zn and As showed significantly higher percentages of DTPA versus total contents. Thiele & Leinweber (2001) compareding TM contents of 30 soils receiving manure to geochemical background values, and found higher ratios while considering metals extracted in NH_4EDTA solution than for pseudo-total contents, especially for Zn. Baldantoni et al. (2010) concluded from their field experiments on two types of soils that "compost amendment affects more the available than the total metal concentrations". Such studies confirm general ideas that anthropogenic metal contaminants, in particular compost-born metals, are more available than lithogenic TMones. Nevertheless, little few publications attempted to relate the evolutions of available TM in amended soils to the inputs of available TM present in applied amendments.

So, the general topic of our study is the availability of trace metals in cultivated soil horizons receiving OWP. After considering total contents of TM in amendments and in amended soils (Michaud et al., 2018), we focus here on monitoring other chemically defined TM fractions, on interpretation and possible prediction of their evolution in amended soils.

~~Our study~~It is based on ~~the same~~ a long-term field experiment, Qualiagro, ~~than Michaud et al.'s (2018). This field experiment~~which started in 1998 in the frame of an INRA-Veolia collaborative research program~~, being~~ devoted to the evaluation of all agronomic and environmental impacts of using urban waste composts on arable crops~~, and~~. This field experiment has been conducted ~~according to~~with the same procedure until 2013.

By using its extensive dataset, our specific objectives are the followings:

- comparison between inputs of EDTA-extractable metals from organic amendments and variations of EDTA-extractable metals in amended soil layers;
- interpretation of the evolution of soluble, i.e., $CaCl_2$-extractable trace metals in amended horizons, from relevant characteristics of OWP and soil~~s~~;
- prediction of variations of these two fractions~~compartments~~ of TM in amended soil layers.

The underlying hypotheses are that reactive trace metals evaluated by EDTA extractions from OWP are added to EDTA-extractable metals present in amended soil horizons and that the soluble metals in these horizons can be predicted by sorption models based on their reactive fractions and other soil variables.

2. Material and methods

2.1. Field experiment QualiAgro

The long-term field experiment QualiAgro has been initiated in 1998 by INRA and Veolia Recherche & Innovation with the aim of studying the agronomic value of urban waste composts and their environmental impacts (Houot et al., 2002; INRA, 2018~~www6.inra.fr/qualiagro_eng/~~). It is located 35 km west of Paris, under a moderate oceanic climate (mean annual temperature 11°C and mean annual rainfall 650 mm over the studied period). The crop succession has been maize - winter wheat without intermediate plant cover since 1998, except for the year 2007 when barley was inserted because of a

regional infestation by *Diabrotica virgifera*, a harsh pest of maize. The soil is a silt loam Luvisol, according to IUSS-FAO classification and USDA texture triangle, developed on aeolian loess. Table 1 presents the physicochemical characteristics of its initial plough horizon, including total contents of 7 trace metals which are close to median values found for comparable soil materials (Houot et al., 2009).

Within a 6 ha parcel divided in 4 replication blocks, 40 plots of 450 m^2 have been differentiated by 5 treatments related to OWP and 2 levels of complementary mineral N fertilisation (Figure 1). The 5 treatments correspond to applications of 4 types of OWP or none amendment:

- composts of sewage sludge with green waste and wood chips (SGW);
- composts of biowastes (mostly fermentable fraction of municipal waste) with green waste (BIO);
- composts of residual municipal waste (after separate collection of packaging, paper, glass, etc.) (MSW);
- farmyard manure of dairy cows on straw (FYM);
- the control plots without organic amendment (CTR).

OWP have been applied every two years on wheat stubble, and in 2007 on barley stubble, in early September, at doses equivalent to 4 Mg C ha^{-1}, i.e., about 2-times the mass flux commonly applied by farmers in similar conditions.

The two levels of complementary fertilisation, using ammo-nitrate and urea, are “N optimal” or +N, to get maximal yields, and “N minimal” or –N. No other fertilisers were applied. Indeed, ~~in the second modality after a few years, only CTR received nitrogen. T~~the N fertilisation has been adjusted~~, mainly during wheat years,~~ by measuring mineral N stocks at 3 depths down to 90 cm, 3 times a year (Noirot-Cosson et al, 2016) and it has been null the years of maize on amended plots –N. Except for fertilisers and amendments, intensive

agricultural techniques have been applied on the whole field: ploughing and other mechanical tillage, phytosanitary control of weeds every year and other pesticides when necessary.

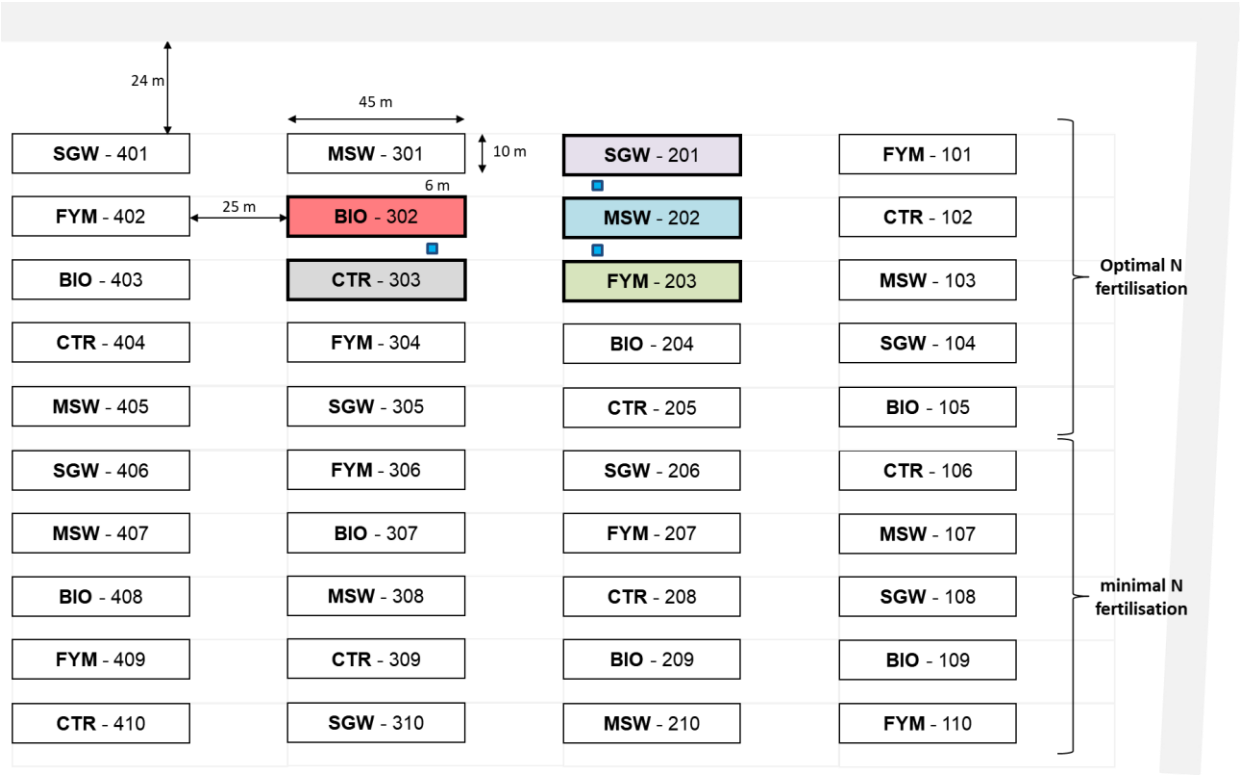


Figure 1. Plan of the QualiAgro field experiment *(thick coloured rectangles show plots equipped for hydrodynamic monitoring and leachate samplings).* ***SGW****: compost of sewage sludge with green waste and wood chips;* ***BIO****: compost of biowaste and green waste;* ***MSW****: compost of organic fraction of municipal solid waste;* ***FYM****: farmyard manure of dairy cows on straw;* ***CTR****: control soil without amendments*

Every year before mechanical harvest, yield measurement and sampling of grain and aerial part have been performed by using a pattern 10 times in each plot. The plough layer (0-28 cm) of each plot has been sampled every two years just before spreading amendments, so that data sets for the present study include soil analyses until 2015 and OWP analyses until 2013. Soil sampling was performed manually, 40 composite samples being prepared from 10 spadesful across each plot. From preliminary estimations of OM, spreaders were

adjusted on side areas of the field by using lines of rugs and trays and portable scales. OWP were carefully sampled during spreading ~~day~~s, ~~with~~ providing three composite samples of each applied OWP for analyse~~d~~s and stor~~ageed~~. ~~Spreaders were adjusted on side areas of the field by using lines of trays and scales.~~Applied OWP were rapidly incorporated by surface stubble ploughing and later, in October, more deeply by ploughing at 28 cm.

2.2. Methods of analysis

Most analyses of soils and amendments were performed by the LAS (Laboratoire d'Analyses des Sols, INRA, Arras, France), which is accredited according to NF ISO/CEI 17025 for soil analyses. The LAS applied the same Quality Controls and validation methods for OWP and soils (NF T 90-210).

Soil samples were prepared according to norm ISO 11464. Total C and N were determined by catalysed combustion-oxidation (ISO 10694). Total carbonate expressed as $CaCO_3$ was measured by a volumetric method (ISO 10693). Other total analyses were performed by ICP-AES or ICP-MS after heating at 450 °C and complete digestion in HF-$HClO_4$ (NF X 31-147). pH was measured on a 10 g aliquot dispersed in pure water (ISO 10390). Cation exchange capacity (CEC) was measured by the Cobaltihexamine method (ISO 23470). The potentially available fraction ~~EDTA extractable~~of trace metals ~~were determined o~~in soil and composts has been evaluated by~~according to~~ the ''BCR'' method (Quevauviller, 1998). Beyond EU standardisation attempts, EDTA at moderate concentration has been often recommended to extract sorbed TM (Degryse et al.'s review, 2009). We retained the concentration 0.05 mol.L^{-1} and the soil:solution ratio 1:10 of the BCR method in order to avoid a possible lack of chelating agent in case of abundant calcium carbonate (Manouchehri et al., 2006), which was the case of some studied OWP. The readily available or s~~S~~oluble metals were extracted in 0.01 M $CaCl_2$ solution (ratio 1:10, shaking 2 h, norm NEN 5704 in NL; Houba et al., 1990; Lebourg et al., 1996). ~~m~~Many studies ~~have~~

~~related such~~correlated this fraction, for certain trace metals, ~~to~~with their concentrations in soil pore water (Degryse et al., 2003), their effects on organisms (Beaumelle et al., 2014) or their uptake by plant ~~(Degryse et al., 2003;~~ (e.g., Nolan et al., 2005)~~; Beaumelle et al., 2014).~~

OWP samples were freeze-dried, ground and sieved at 5 mm. Total C was analysed like for soils. The carbonate content was also analysed and, when significant, inorganic C was subtracted from total C to get the organic C. Total metal contents were obtained after the same digestion method than soil samples, and then by ICP-AES (ISO 2203).

All chemical contents were expressed per dry weight (DW) at 105°C, according to norms ISO 11465 and NF U 44-171 for soils and amendments, respectively.

2.3. Data treatments

Variations of extracted TM according to OWP types were interpreted by ANOVA and Newman-Keuls comparisons (α = 5%) applied on all data (6 years), after testing the normality of residues and equality of variances by Shapiro and Levenne tests. In cases far from these conditions, Kruskal-Wallis and Dunn tests were applied. For results on topsoils, the same procedure was applied to compare plots submitted to the 5 modalities, on data gathered per year of sampling. More precisely, topsoil was sampled and analysed every two years in the 8 plots per modality, ~~in the whole field,~~ but between 2009 and 2013, TM have been analysed only in the 4 plots of the half-part +N.

Simple linear regressions were calculated between selected TM fluxes and stocks of mobilisable TM in topsoils. The detailed calculations are explained in part 3.5. Multiple linear regression studies were performed between soluble metals and other soil properties. For these calculations, means from the 4 blocks were used rather than all soil data to improve the accuracy of studied variables and avoid factor interactions. Another choice~~, in our context of limited variations of total contents, and in accordance to arguments of~~

~~Degryse et al. (2003),~~ has been to select EDTA-extractable metals rather than total metals as possible explicative variables. EDTA-extractable metals may represent the "labile" (Degryse et al., 2009) or reactive (Groenenberg et al., 2017) fraction in equilibrium with solubilised metals in 0.01 M $CaCl_2$. Then, logarithms of variables were preferred to untransformed variables (pH being already considered as the log of a variable), for statistical and mechanistic reasons~~. L~~: linear log-relationships correspond to ratios between metal concentrations and soil reactive constituents, which may be related to chemical equilibrium equations (McBride et al., 1997). Preliminary statistical treatments, including calculations of 3rd and 4th order moments, showed some discrepancies with hypotheses of normal distributions but much less for log-transformed variables than for untransformed ones. Finally, two MLR approaches have been followed, likely to lead to different predicting equations:~~.~~

(i) explaining variations of log(soluble TM)~~$_{CaCl2}$~~ by variations of log(M_{EDTA}), pH, ~~CEC,~~ etc.,

(ii) forcing a proportionality between $CaCl_2$-extracted and EDTA-extracted TM_{CaCl2} ~~and M_{EDTA}~~ through the calculation of distribution coefficients Kds and explaining log(Kd) by major soil variables (Sauvé et al., 2000; Groenenberg et al., 2010).

More precisely, Kd coefficients were calculated as ratios of mobilisable on soluble TM, expressed respectively in $mg.kg^{-1}$ of soil and $mg.L^{-1}$ of extracting solution.

3. Results ~~and discussion~~

3.1. Major characteristics of spread composts and manure

Results related to major components likely to interact with the fate of trace metals (TM) are ~~summarized~~ presented in Table S1 (Supplementary Material), ~~completing~~ taking over~~data of~~ previous articles on the same site (e.g., Obriot et al., 2016). FYM and MSW were

generally richer in organic C than SGW and BIO. Consequently, with the target of 4 Mg C.ha^{-1} per spreading, applied loads have been lower with FYM and MSW. The resulting average inputs of organic Carbon ~~are calculated over the period 1998-2015, i.e., 17 years. They~~ stand between 2.0 and 2.3 Mg.ha^{-1}.year^{-1} for MSW and SGW composts respectively, and at 2.1 Mg.ha^{-1}.year^{-1} for BIO composts and FYM.

On another side, organic matter of OWP can be characterised by its ratio C/N and the index of residual organic C (I_{ROC}) expressing its stability after incorporation to soil. They show the following orders (Noirot-Cosson et al, 2016):

C/N: BIO ≈ SGW < FYM < MSW

I_{ROC}: BIO ≈ SGW > FYM > MSW.

With respect to other major constituents, BIO and MSW composts are richer in carbonate than FYM and SGW. SGW contains two to three times more P than the other amendments. SGW and BIO contain about twice more Fe than MSW and FYM.

3.2. Total contents in OWP and inputs of trace metals

TM contents with respect to regulations: All applied SGW composts presented TM contents lower than thresholds enforced in France since 2002 for sewage sludge composts, defined in norm NF U 44-095. Applied MSW composts overpassed the limits imposed since 2006 to other types of composts (NF U 44-051), several times before 2006 and once in 2013, precisely for Zn in MSW (Table S1-B).

~~Regarding evolution with~~Over the years, an overall decrease of concentrations of most TM was observed in the different products, except for SGW composts. ~~One consequence is that variation coefficients over the 9 spreadings were relatively large for BIO, MSW and FYM, exceeding 100% for some elements, while they stood around 30% in SGW.~~ Therefore, in order to assess amendments with respect to potential accumulation of TM in soil~~s~~,

comparing ~~cumulated~~ average annual inputs appeared more adequate than total contents which have varied. We can see that:

- Cd inputs have been similar with all amendments;
- Pb inputs have been similar through spreadings of BIO, MSW or FYM, and lower via SGW applications;
- but SGW have carried more Cu~~, Hg~~ and Zn than the other products;
- MSW, besides Pb already mentioned, also input a relatively high amount of Cr;
- BIO, besides Pb, carried more Ni and Mn than the other products during the studied period.

Comparison between average inputs of TM and regulatory limits: spreading of SGW composts overpassed the limits for Cu and Zn, with respectively 1501 and 3500 $g.ha^{-1}.year^{-1}$, higher than the respective maxima of 1000 and 3000 $g.ha^{-1}.year^{-1}$ (~~expressed as averages~~10 000 and 30 000 over 10 years: Table S1-B). BIO and MSW composts brought slightly too much Pb, just above the regulatory limit of 900 $g.ha^{-1}.year^{-1}$. In summary, the intensive applications of OWP have induced~~average~~ inputs of TM ~~have been~~ lower or close to the regulatory limits ~~imposed during the 2000s~~, except for Cu brought by SGW composts which exceeded the limit by 50%.

3.3. EDTA-extractable metals in composts and manure, and induced inputs to soil~~s~~

From 2004 to 2013, we applied EDTA and $CaCl_2$ extractions to OWP, using the same triplicate samples as those used for major and trace element analyses. The six trace metals analysed after EDTA extractions have always been above quantification limits and the repeatability was generally satisfactory (124/144 data with CV < 25%, MSW being the matrix with the highest dispersion).

Among amendments, SGW generally showed the highest contents of Cd_{EDTA}, Cu_{EDTA} and Zn_{EDTA}, ~~although not significantly in all cases,~~ and induced the highest inputs to soil~~s~~

(Table 2). MSW showed relatively high contents of Cr_{EDTA} and Ni_{EDTA} and induced the highest inputs of these metals. Pb_{EDTA} was similar in the four products, standing in average between 24 $mg.kg^{-1}$ (in BIO) and 35 $mg.kg^{-1}$ (in FYM) and induced inputs between 180 and 260 $g.ha^{-1}.year^{-1}$ (from FYM). So, except for Pb_{EDTA} in FYM, the amendments BIO and FYM presented the lowest average contents and induced the lowest inputs of EDTA-extractable metals.

Now among EDTA-extractable metals, the following sequence was observed, similar to the order of total contents: Zn > Cu ≥ Pb > Ni > Cr > Cd (Table 2). Zn, Cu and Pb have been also noticed as the trace elements mostly extracted by chelating agents in composts by Paradelo et al. (2011b).

Some strong correlations exist between EDTA-extractable metals, especially between Cr_{EDTA} and Ni_{EDTA} on one side, Cd_{EDTA} and Zn_{EDTA} on another side, what reminds correlations often observed between TM total contents in soils (Baize et al., 2007). Temporal variations occurred along the period 2004-2013, but without the clear decreasing trend found for total metal contents of OWP. ~~Indeed, the lowest values of EDTA-extractable metals were often recorded in 2004 (Table 2).~~

EDTA extractabilities, in % of total contents, followed a distinct sequence, almost constant through years and for the four types of amendments (Table S2):

Cd ≥ Zn ≥ Pb ≥ Cu > Ni > Cr ~~(Table S2)~~.

~~Amir et al. (2005) found a somehow different order from studying varying sludge composts, with a higher EDTA extractability of Zn and Ni compared to Cu and Pb.~~

3.4. Evolution of EDTA-extractable metals in topsoil and effect of treatments

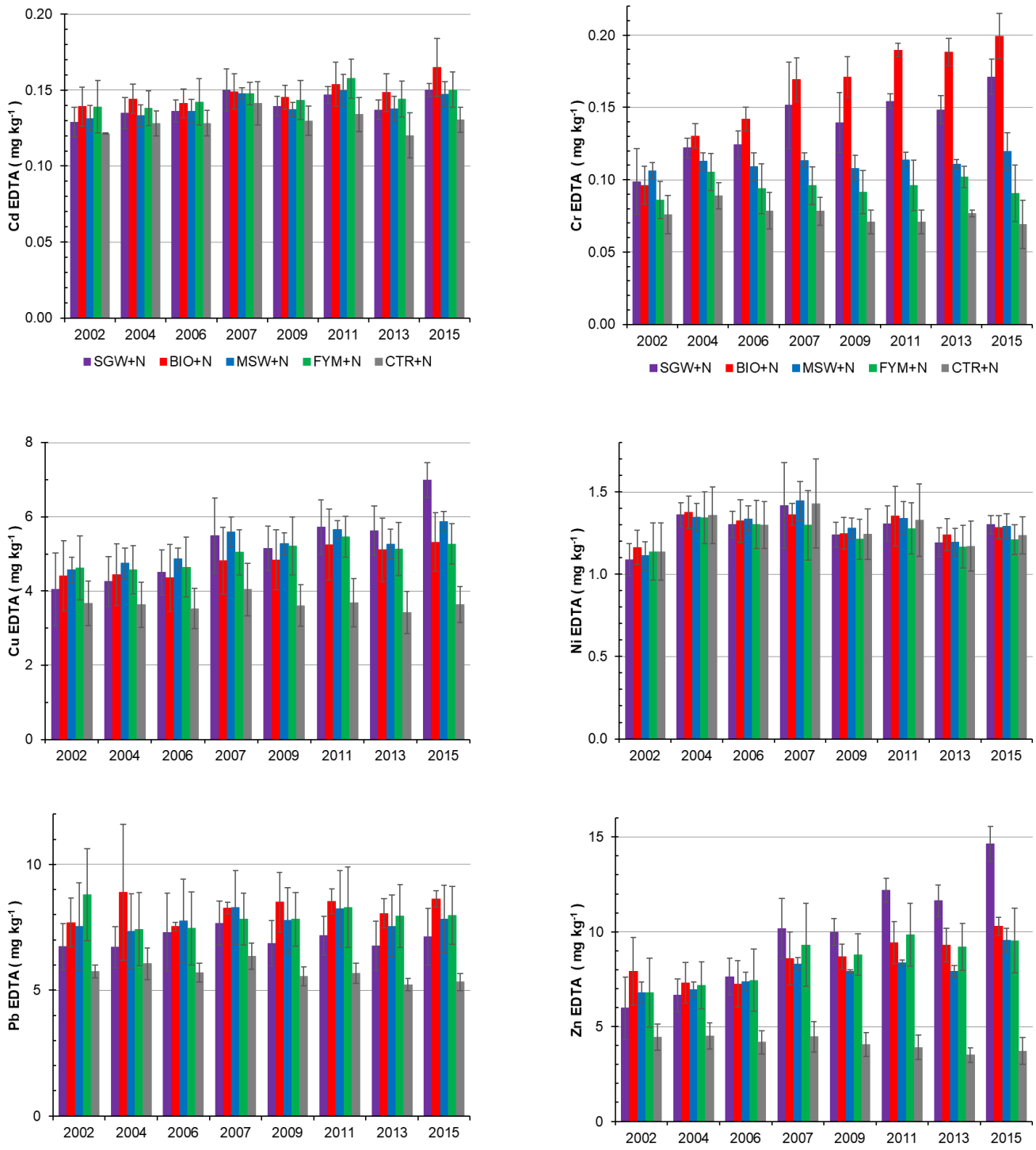
Figure 2 shows the absolute concentrations of EDTA-extractable metals ($mg.kg^{-1}$ dry soil) for the plots "N optimal" (n=4), whereas Table S3-A includes the results of statistical

comparisons between treatments for all available data. The effects of treatments differ between TM:

Cd_{EDTA}: there was a trend of higher values in amended plots with respect to the control, but significant differences appeared only with BIO in 2004 and 2006, in 2013 with BIO and FYM, and for all amended plots in 2015.

Cr_{EDTA}**:** data often presented dispersion and deviations from hypotheses supporting parametric comparisons. Nevertheless, a positive influence of amendments, especially of BIO and SGW, can be deduced from non-parametric tests and Fig. 2.

Cu_{EDTA}**:** a significant d~~D~~ifference~~s were not significant in 2002 but did~~ appeared in 2004 between MSW and the control plots. From 2006, Cu_{EDTA} has been significantly higher in all amended plots compared to CTR, without differences between amended plots until 2015. This last year, more differentiations occurred, with SGW at the highest level.



349 **Figure 2. EDTA-extractable metals in the plough layers (plots +N) versus sampling year and treatment**
350 – vertical bars present standard deviations between blocks (n=4) – Legend of treatments in 1st row (+N = in
351 the half-part with optimal N fertilisation; SGW: compost of sewage sludge with green waste and wood chips;
352 BIO: compost of biowaste and green waste; MSW: compost of organic fraction of municipal solid waste;
353 FYM: farmyard manure of dairy cows on straw)
354

Ni_{EDTA} never appeared influenced by treatments, except at last in 2015, when considering the whole data giving mean values of 1.33 and 1.21 $mg.kg^{-1}$respectively for SGW and FYM (Table S3-A).

Pb_{EDTA}: as for Cd but more often, we observed higher values in plots treated with BIO and FYM, and less often with MSW, compared to the control, and finally in 2015 all amended plots above CTR.

Zn_{EDTA} followed the same trends as Cu but with larger amplitude, becoming in amended soils twice or three times higher compared to CTR (Fig. 2). Indeed, Zn_{EDTA} slightly decreased with time in CTR+N plots, and differences between some amended plots and CTR became non-significant some years after 2009, according to non-parametric statistics. In 2015, Zn_{EDTA} in SGW plots became significantly above other amended plots.

Overall, EDTA-extractable fractions represented about 60% of total Cd in topsoil, 30% of total Pb or Cu, 10-20% of total Zn, less than 10% of total Ni, and around 0.2% of total Cr (Table S3-B). ~~Concerning Cu, t~~The differences between treatments appeared attenuated when expressed in %: only MSW plots from 2006~~(3 years)~~ and ~~FYM and BIO in~~the other amended plots from 2013 showed higher $\%Cu_{EDTA}$ than CTR. Zn extractability seemed also less influenced by treatments than Zn_{EDTA} absolute values, but it appeared clearly higher in amended plots than in CTR from 2004, and significantly higher in SGW compared to the other treatments from 2009. ~~Cr extractabilities remained < 0.4%, with variations quite parallel to Cr_{EDTA} in $mg.kg^{-1}$.~~ Pb showed a significantly higher extractability in BIO plots for ~~5~~6 sampling years and in FYM plots ~~in 2011-2013~~for 3 years, compared to control. Cd extractability~~ies~~ showed ~~some parallel variations versus time, but~~ no significant differences between treatments. Ni extractability~~ies~~, as Ni_{EDTA} contents, ~~did not~~hardly appeared influenced by amendments.

3.5. Relationships between EDTA-extractable metals in the amended soil layers and their inputs from amendments

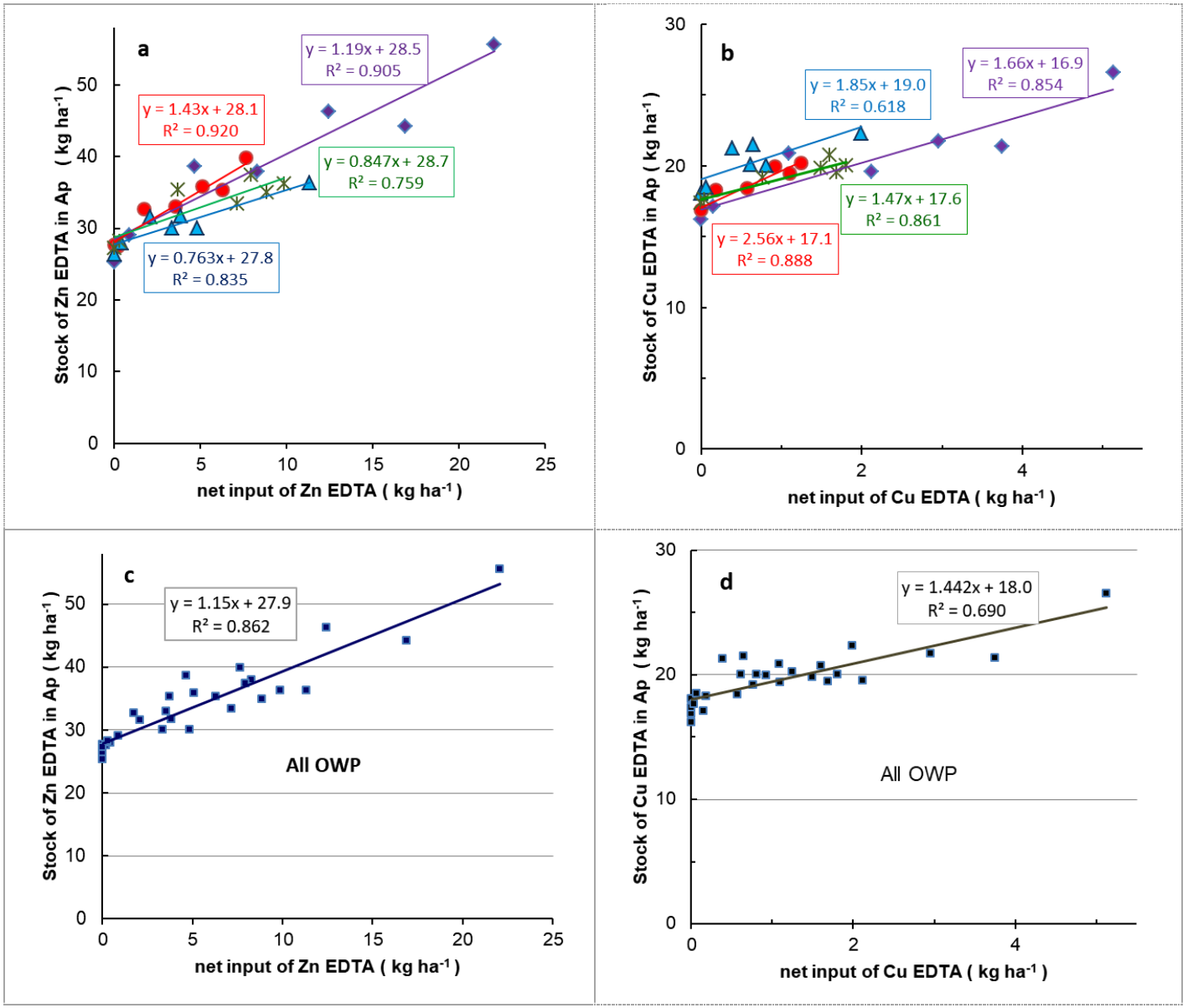
Stocks of EDTA-extractable TM contained in plough layers were calculated from mean metal contents per treatment and an average mass of 3800~~28~~ $Mg.ha^{-1}$ (Michaud et al., 2018). The variations of these stocks along 2004-2015 were at first compared to cumulated inputs of EDTA-extractable TM from each OWP (~~§~~part 3.3). Significant correlations were found (not shown) but a finer study was pursued by correcting these inputs according to a few rational hypotheses and estimations:

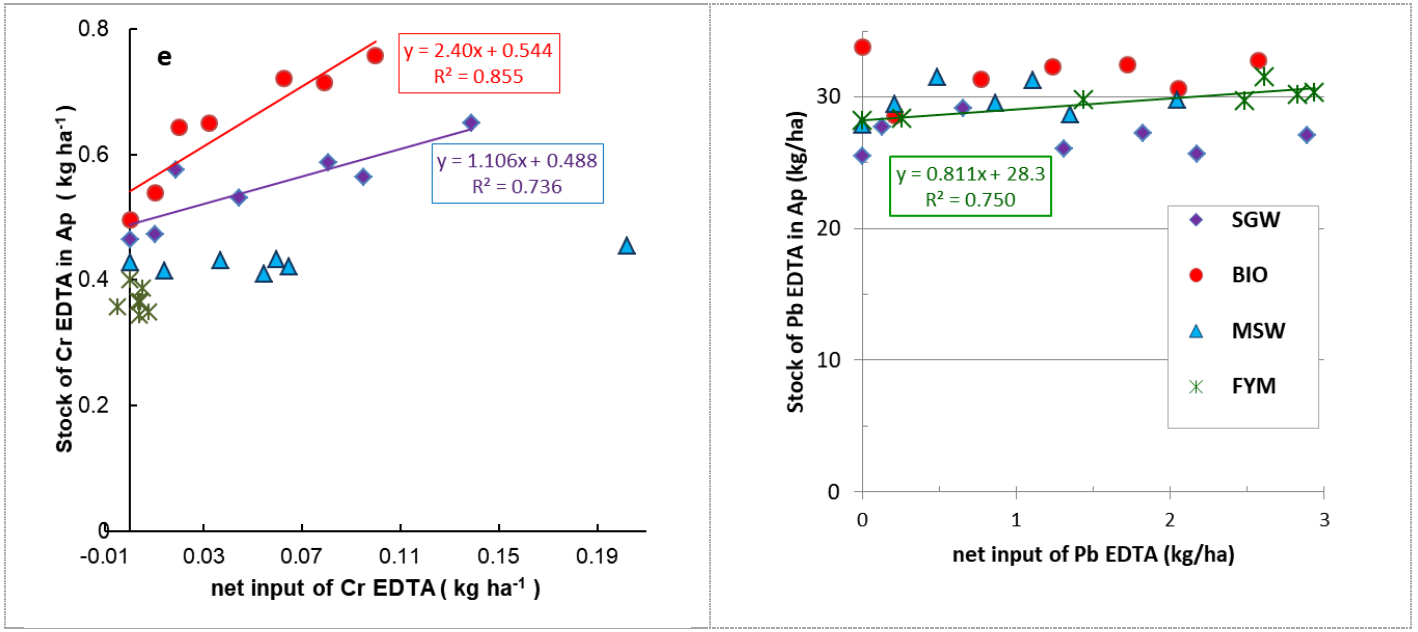
- crop uptake of TM, determined by yield and plant organ contents, were assumed to be removed from EDTA-extractable pools of the plough layers;
- a second output from these pools, due to leaching, was estimated from monitoring waters collected by 10 lysimeters (two per equipped plot; Fig. 1) during the period 2012-2015 (Cambier et al., 2014);
- minor inputs due to atmospheric diffuse deposits were also assumed EDTA-extractable and estimated from relevant references (Belon et al. 2012~~as in;~~ Michaud et al., 2018).

The two last fluxes are only estimated but each one represents less than 11% of inputs by OWP for Cd, Cu, Pb and Zn and they are opposite. About crop uptakes, their ranges in % of OWP inputs are 3-5% for Cd, 5-19% for Cu, 9-23% for Zn; 0.4-0.6% for Pb, 6-25% for Ni, 10-56% for Cr. So, these calculations present uncertainties, especially for Cr and Ni in the case of FYM low in these metals. But they provide net inputs of potentially available metals more relevant for comparisons with variations of EDTA-extractable metals in soil than the raw inputs from OWP.

~~At the end,~~ Figure 3 presents ~~correlations obtained~~the relationships obtained between the field stocks of EDTA-extractable TM and the ~~cumulated balances of TM fluxes~~net inputs

404 explained above. It has to be taken into account that soil sampling always occurred just
405 before spreadings, so that for example spreading of 2004 have impacted the soil stocks
406 determined in 2006, and soil samples analysed in 2015 have been impacted by spreadings
407 until 2013. The graphs comply with this shifted correspondence. They call for the following
408 comments:
409


a
y = 1.19x + 28.5
R² = 0.905
y = 1.43x + 28.1
R² = 0.920
y = 0.847x + 28.7
R² = 0.759
y = 0.763x + 27.8
R² = 0.835
Stock of Zn EDTA in Ap (kg ha-1)
net input of Zn EDTA (kg ha-1)
b
y = 1.66x + 16.9
R² = 0.854
y = 1.85x + 19.0
R² = 0.618
y = 1.47x + 17.6
R² = 0.861
y = 2.56x + 17.1
R² = 0.888
Stock of Cu EDTA in Ap (kg ha-1)
net input of Cu EDTA (kg ha-1)
c
y = 1.15x + 27.9
R² = 0.862
All OWP
Stock of Zn EDTA in Ap (kg ha-1)
net input of Zn EDTA (kg ha-1)
d
y = 1.442x + 18.0
R² = 0.690
All OWP
Stock of Cu EDTA in Ap (kg ha-1)
net input of Cu EDTA (kg ha-1)



411

412 **Figure 3**. Relationships between the stocks of EDTA-extractable TM in plough layers and inputs of EDTA-extractable TM carried by OWP corrected

413 by other vertical fluxes (crop uptake, leaching, atmospheric deposits) – Legends of treatments in last graph (SGW, BIO; MSW; FYM explained in

414 Legend of Fig. 2)

415

Zn_{EDTA}: the correlations between the cumulated balances and soil stock variations appear significant or highly significant for each treatment separately (the critical value for the two-tailed test on the Pearson coefficient, for n=7 and p = 0.05, is 0.75, hence R_{critic}^2 = 0.569; and R_{critic}^2 = 0.904 for p = 0.001). Another important result concerns the slope of the linear regression, which stands between 0.76 and 1.43 (Fig. 3a). Fig. 3c shows the highly significant correlation obtained from all data together (n = 28, R^2= 0.86), with a regression slope equal to 1.15.

Cu_{EDTA}: similar correlations were found (R^2 > 0.62), but the regression slopes are higher than for Zn_{EDTA}, i.e., between 1.473 and 2.562. When all data corresponding to the four OWP are gathered, the correlation is highly significant with R^2 = 0.6970 (n=28) and a slope 1.44 (Fig. 3d). This later dataset and other apparently curved relationships have been also tested using a 2nd order polynomial regression, which hardly increased R^2.

Cr_{EDTA}: only two significant correlations appeared (~~in~~ Fig. 3e), with SGW compost applications, inducing variations of stocks in the plough layers ~~roughly~~ approximately equal to the cumulated balance of fluxes (R^2 = 0.74; slope 1.11), and with BIO compost applications, increasing Cr_{EDTA} stocks faster than the cumulated balance of fluxes (slope 2.43). ~~No significant correlations were observed in the cases of MSW and FYM, in consistency with Fig.2 that showed no variations.~~

Other TM studied: a few significant correlations were found between soil stocks of EDTA-extractable metals and cumulated flux balances, for Cd_{EDTA} in the case of BIO composts (R^2 = 0.68; regression slope 2.5; ~~Fig. 3f~~not shown), and for Pb_{EDTA} in the case of FYM (R^2 = 0.875; slope 0.813). Ni_{EDTA} showed ~~in one treatment~~ a significant correlation only in the case of FYM, with an unexpected negative slope~~, which assumed physically meaningless~~.

~~Therefore, for some elements, EDTA-extractable fractions showed a conservative behaviour, as if they represented stable physical compartments in OWP and in amended~~

soils. INon-linear regressions have been attempted, which fitted better the data in a few cases, e.g., a 2nd order polynomial for Cr_{EDTA} in BIO treatment, but most often they hardly increased R^2 and always appeared difficult to interpret. By contrast, linear regressions with a slope close to 1 indicate a conservative behaviour: inputs of, e.g., especially Zn_{EDTA} of compost in a cultivated soil would be added to the soil Zn_{EDTA} pool without much loss by leaching or plant uptake, nor much transfer from or to the non-extractable fraction quantifiable by the difference $Zn_{TOT} - Zn_{EDTA}$. Of course, soluble fractions exist in composts and in soils, *a priori* highly reactive during and after amendment incorporation, but due to their low weight, they would not hinder the relationships illustrated by Fig. 3a and 3c.

Cu_{EDTA} generally showed higher regression slopes compared to Zn_{EDTA} (Fig. 3a-d). This could be due to a part of non EDTA-extractable Cu, contained in biodegradable particles of OWP, becoming extractable in soils after amendment as their mineralization proceeds. This process would be less important for Zn which is proportionally less associated to organic phases compared to Cu (Ashworth and Alloway, 2004; Paradelo et al., 2017a; 20187b). A roughly conservative behaviour was also observed for Pb_{EDTA} in FYM amended plots and with Cr_{EDTA} in SGW plots (Fig. 3). The conservation of Cr_{EDTA} was not expected, considering the low extractability of this element and specific redox transformations which could intervene on such a minor fraction. Finally, it is noteworthy that for Zn, Cu and Cr, EDTA-extractable metals carried through BIO composts seem to induce higher increases of EDTA-extractable metals in soils, compared to other amendments (Fig. 3a-b, 3e). The regression slope for Cd_{EDTA} related to BIO treatment is also relatively high, *c.* 2.5 (Fig. 3f), but comparisons with other treatments cannot be done with other treatments due towhich showed non-significant correlations.

3.6. Results of $CaCl_2$ extractions on OWP

The application of these mild extractions to OWP led to relatively precise and meaningful data for the six analysed TM, coming across only 7 values < QL (for Cr or Pb in SGW composts). Variation coefficients were lower than 20% 116 times out of 144 determinations. The absolute values of $CaCl_2$-extractable, say soluble metals, followed a slightly different sequence compared to total and EDTA-extractable contents: Zn ≈ Cu > Ni > Cr ≈ Pb > Cd (Table 3). On another side, $CaCl_2$ extractability (% of total metal) was much lower than in EDTA (Tables S4 and S2), and followed another sequence: Ni ≥ Cu ≥ Cd ≥ Zn > Cr ≥ Pb, with especially a high extractability of Ni and Cu in MSW and FYM.

Among OWP, MSW composts showed the highest soluble fractions (in $\mu g.kg^{-1}$ DW), followed by FYM which presented noteworthy high soluble Pb and Cd contents. Based on $CaCl_2$ extractability (% of total), MSW composts and FYM were also above BIO and SGW composts. In order to understand these differences, one must consider the variable pH, ~~an important factor of trace metal solubility,~~ measured in water (Table S1-A) and in the $CaCl_2$ extracts (Table 3), as well as dissolved organic carbon (DOC) which has been analysed once, in 2013. FYM generally presented the highest pH and SGW the lowest. So, differences of pH between OWP cannot explain the observed differences for $CaCl_2$ extractable metals. On the contrary, DOC in $CaCl_2$ extracts ranked SGW and BIO in low DOC producers, FYM and even more MSW in high producers. Thus, DOC could play a role in the differentiation between the soluble TM of these two groups of OWP.

3.7. Results of $CaCl_2$ extractions in soil~~s~~

The results on $CaCl_2$-extractable or soluble TM in soil~~s~~, further written, e.g., Zn_{CaCl2}, were different from those obtained with EDTA on several aspects. First of all, extractability was very low, under 1%, except for Cd_{CaCl2} which reached 8% of total Cd.

The least soluble metals were Cr and Pb, known as seldom mobile in arable soils, with $CaCl_2$ extractability ~~around 0.01~~<0.03%. ~~More specifically~~Indeed, Cr_{CaCl2} was ~~practically~~ always under quantification limits, so that eventual effects of organic amendment or evolution with time cannot be ascertained.~~:~~ Pb_{CaCl2} was also often < QL but its partial quantification showed a trend of higher mobility of Pb in CTR, followed by SGW and FYM (Table S5). The lower mobility of Pb in amended plots with respect to unamended ones can likely be due to higher SOC contents~~, as pointed out in the literature~~ (~~Brown et al., 2004;~~ Smith, 2009; Paradelo et al., 2011a).

Concerning Cd and Ni, this trend of higher soluble TM in CTR plots appeared more clearly, although progressively (Fig. 4; Table S5): ~~differences remained uncertain after a few spreadings, but between 2006 and 2009,~~ soluble Ni and Cd have become significantly higher in control than in amended plots between 2006 and 2009. Ni_{CaCl2} has been often <QL in the first years but never in CTR plots from 2006 (Fig. 4). Other differences between treatments concern BIO plots which provided less soluble Ni and Cd than the other treatments, and SGW which often stood above the other amended plots.

Concerning soluble Zn, despite non-monotonous variations, it gradually decreased with BIO and MSW treatments, but remained high in SGW and CTR plots (Table S5; Fig. 4). Zn_{CaCl2} was significantly higher in SGW than in all other modalities in 2002; then from 2006, it became higher in both SGW and CTR than in BIO and MSW, and also above FYM later on, suggesting the following overall order, almost opposite to pH measured in $CaCl_2$ extracts (Table S5):

$$BIO < MSW < FYM < CTR \leq SGW$$

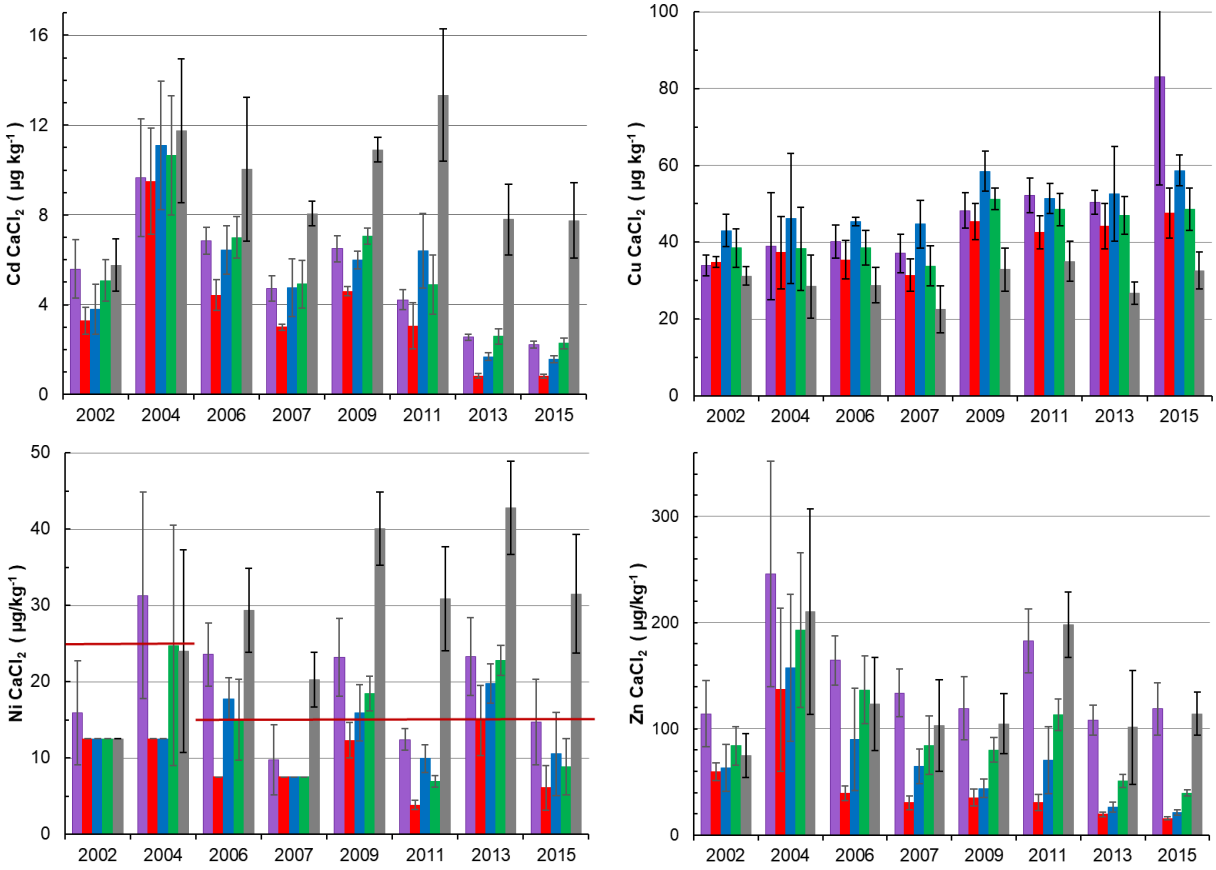
In brief, soluble Cd, Ni and Zn always appeared lower in amended plots than in control ones, except for Zn in SGW plots.

513 Soluble Cu presented a completely distinct behaviour, MSW plots appearing significantly
514 above CTR as soon as 2002 (but not in 2004), and all amended plots above CTR from 2006.
515 Other less systematic differences between treatments occurred, leading to the following
516 trend for soluble Cu (Fig. 4):

517 $$CTR \leq BIO \leq FYM \leq SGW = MSW$$

518

519



520

521

522 **Figure 4: $CaCl_2$ extractable Cd, Cu, Ni and Zn in topsoil of plots +N: SGW, BIO, MSW, FYM,**

523 **CTR from left to right every sampling year** (means from the 4 blocks; vertical bars show Standard-

524 Deviations; horizontal red segments show QL of soluble Ni; some values <QL arbitrarily set at QL/2) –

525 +N, SGW, BIO; MSW; FYM, CTR explained in Legend of Fig. 2

~~All these results make obvious that v~~Variations of soluble fractions in soil~~s~~ cannot be interpreted like for EDTA fractions from inputs of $CaCl_2$-extractable metals present in composts and manure. These minor and mobile fractions react fast with all solid phases, and their variations look like an attenuation by amendments, at least for Cd, Ni, Zn and Pb. So they must be related to changes of pH and other retention factors, themselves linked to the input of OWP components.

Concerning pH, measurements have been conducted as standard analyses of soil pH in H_2O (pH_{H2O}) and, from 2004, on $CaCl_2$-extracts, from the same soil samples representative of the plough layer of each plot. The results appear strongly correlated (R^2 = 0.96, slope 0.98; Fig. S1) and show the same trend between treatments, i.e., BIO ≥ MSW ≥ FYM ≥ SGW ≥ CTR. This order did not match exactly the order of pH of OWP, but rather their carbonate contents (Table S1-A). ~~Anyway~~For soil samples, highly significant negative correlations were found between pH_{H2O} or pH_{CaCl2} on one side, and soluble Cd, Ni or Zn on another side, for plots + N or for all plots.

Concerning soil organic C (SOC), it was positively correlated with Cu_{CaCl2} (R=0.66, n = 40 pairs of mean values related to plots +N, or n = 65 for all treatments), and negatively correlated with soluble Cd or Ni. Cd_{CaCl2}, Ni_{CaCl2}, as well as Zn_{CaCl2}, were also negatively correlated with CEC, whereas Cu_{CaCl2} was positively correlated to CEC. These correlations suggest a contrasting effect of organic matter on metal mobility, driven by the different fractions of OM involved and the solubility of organometallic complexes: an increase of mobility in the case of Cu, related to the formation of soluble complexes with dissolved OM, and a reduction in the other cases, due to a low solubility of the complexes formed or a preference of Cd, Ni and Zn for insoluble OM fractions.

549 *3.8. Modelling relationships between soil variables and ~~prediction of~~ soluble TM*

550 For further interpretation and possible prediction of TM mobility in these amended soil
551 horizons, and taking into account the numerous studies on this topic (Sauvé et al., 2000;
552 Groenenberg et al., 2010; Tipping et al., 2003; Degryse et al., 2009; Rodrigues et al., 2010),
553 we attempted multilinear regressions (MLR) between each quantified soluble metal and
554 selected soil ~~parameters~~ variables, as described in part 2.3 of Materials and methods. ~~More~~
555 ~~precisely, we always used means, obtained from the 4 repetition blocks, rather than all data,~~
556 ~~to improve the accuracy of studied variables and avoid factor interactions. Another choice,~~
557 ~~in our context of limited variations of total contents, and in accordance to arguments of~~
558 ~~Degryse et al. (2003), has been to select EDTA extractable metals rather than total metals~~
559 ~~as possible explicative variables. EDTA extractable metals may represent the "labile"~~
560 ~~(Degryse et al., 2009) or reactive (Groenenberg et al., 2017) fraction in equilibrium with~~
561 ~~solubilised metals in 0.01 M $CaCl_2$.~~ ~~Concerning major soil variables, w~~. We always tested
562 one of the two pH values among explicative variables, but not the two together, SOC,~~and~~
563 CEC, but not clay content since it is unlikely that texture has been influenced by treatments.
564 Many other soil variables like N or P contents, electrical conductivity, etc., which are
565 influenced by treatments and are partly correlated (Obriot et al., 2016) have not been used.
566 ~~Then, logarithms of variables were preferred to untransformed variables (pH being already~~
567 ~~considered as the log of a variable), for statistical and mechanistic reasons. Linear log-~~
568 ~~relationships correspond to ratios between metal concentrations and soil reactive~~
569 ~~constituents, which may be related to chemical equilibrium equations (McBride et al.,~~
570 ~~1997). Preliminary statistical treatments, including calculations of 3rd and 4th order~~
571 ~~moments, showed some discrepancies with hypotheses of normal distributions but much~~
572 ~~less for log transformed variables than for untransformed ones.~~

~~Finally, two MLR approaches have been followed, likely to lead to different predicting equations:~~

(iii) ~~explaining variations of M_{CaCl2} by variations of M_{EDTA}, pH, CEC, etc.,~~

(iv) ~~forcing a proportionality between M_{CaCl2} and M_{EDTA} through the calculation of distribution coefficients Kds and explaining log(Kd) by major soil variables (Sauvé et al., 2000; Groenenberg et al., 2010).~~

MLR equations were selected ~~(Table 4)~~ through a step by step approach, starting from models with all ~~relevant~~ explicative variables, and suppressing terms without statistically significant influence. ~~However, intending an assessment of the effect of accumulating TM on their soluble fraction, log (M_{EDTA}) was kept in models of log (M_{CaCl2}) as far as possible.~~ For modelling log (Kd), only pH, log of SOC and CEC were considered.

Cadmium: using pH_{CaCl2} led to exclude Cd_{EDTA} from variables explaining Cd_{CaCl2}~~, limiting the interest of such models~~. Using pH_{H2O} led to the first equation reported in Table 4, expressing the highly significant influence of SOC and pH on Cd_{CaCl2}, and excluding CEC. Such formula can be transformed into a Freundlich equation, whose the exponent here equals about 0.41 (Cd_{EDTA} would increase as $Cd_{CaCl2}^{0.41}$). To get a linear model for predicting Cd_{CaCl2}, we should consider the first Kd model of Table 4, which still shows the influence of pH and SOC, and explain 65% of the variations of log(Kd):

$$\log (Kd_{Cd}) = -2.85 + 0.323 \times pH_{H2O} + 2.71 \times \log(SOC) \quad (8)$$

Copper: a simple equation has been obtained for all data, without significant influence of soil ~~parameters~~major variables. Reminding the units of fractions in Table 4, it can be transformed into:

$$Cu_{solution}\ (\mu g/L) = 0.617 \times Cu_{EDTA}\ (mg/kg)^{1.21} \quad (9)$$

This is not far from a linear model, which was confirmed when looking for a Kd model: no significant influence of pH, SOC or CEC was found. The mean or median Kd value can

598 serve as well as a simple model (Table 5). Both models represent the measured Cu_{CaCl2} with
599 reasonable accuracy, with a MAE (mean absolute error) around 10% of the mean value
600 (Table 4). For the other metals, regression models induce MAE around 30% of mean values.
601 Nickel: log(Ni_{CaCl2}) was found with an inconsistently negative influence of Ni_{EDTA}. A more
602 consistent and statistically acceptable model included log(SOC) and pH_{CaCl2} as independent
603 variables, without Ni_{EDTA}. The Kd approach forcing the linear dependency between
604 extracted Ni fractions led to functions of pH or of SOC and pH (Table 4) explaining 56% or
605 58% of Kd variations. Remind us that no significant influence of treatments was found
606 upon Ni fractions, and that part of Ni_{CaCl2} values were < QL.
607 Zinc: MLR applied on log(Zn_{CaCl2}) led to interesting models based on independent
608 variables log(Zn_{EDTA}), pH_{H2O} and log (SOC), with R^2 = 68%, and an exponent of Zn_{EDTA}
609 equal to 1.30. While looking for a linear model, the best equation was obtained by using
610 pH_{H2O} and log (SOC), with R^2 = 81%:

611 $$\log(Kd_{Zn}) = -4.98 + 0.741 \times pH_{H2O} + 2.36 \times \log(SOC) \quad (10)$$

612 **4. General discussion**

613 ~~Monitoring and predicting the fate of available trace metals in amended soils have been~~
614 ~~attempted by combining the understanding of involved processes and the formulation of~~
615 ~~empirical relationships.~~ Considering the EDTA, or potentially available fractions of TM in
616 OWP, they are susceptible to be transformed in soil during days or years, due to
617 mineralization-humification of OM, rhizosphere interactions, dissolution-precipitation or
618 ageing of components such as carbonates and poorly-ordered oxides. We noticed that
619 Cu_{EDTA} increased more in soil than the estimated input of Cu_{EDTA} and by comparison to
620 Zn_{EDTA}. For instance, the regression slope 1.66 obtained for Cu in the case of SGW which
621 introduced 5.4 kg/ha of Cu_{EDTA} after corrections from minor fluxes (Fig. 3b), suggests that
622 3.56 kg/ha (0.66 × 5.4) of unavailable Cu has become EDTA-extractable in amended soil

layers between 2004 and 2015. One may relate this amount to the total Cu input via SGW, i.e., 19.4 kg/ha (Table S1): from these 19.4 kg/ha of total Cu, about 5.4 kg/ha were initially EDTA-extractable and 3.6 kg/ha became progressively extractable in soil. Doing the same type of calculations with Zn in BIO plots (slope 1.43; Fig. 3a), we estimate that 22.4 kg/ha of total Zn have been input, including 8.7 kg/ha of Zn_{EDTA}, plus 3.7 kg/ha that became EDTA-extractable in soil. On the contrary in MSW plots (slope 0.76), 28.7 kg/ha of total Zn have been input, including 12.4 kg/ha of Zn_{EDTA} minus 3.0 becoming non-extractable. Of course, we cannot assert that transformations of unavailable to EDTA-extractable metals concern only those input through OWP; they may partly affect soil TM. But anyway, such transformations appeared lower with Zn than with Cu, and even could go in the opposite direction with Zn. This could be due at first to the stronger and larger association of Cu within organic particles, protecting this metal from extraction in OWP but then partly mineralised in soil. Such interpretation must be examined through the influence of treatment, since especially BIO stands out from the others by high regression slopes obtained for Cu, Zn, Cr and Cd. For Cd and Cr, possible comparisons between amendments are limited, and the reasoning is pushed further only for Cu and Zn.

Studying the dynamics of C and N in the same field experiment, Noirot-Cosson et al. (2016) underlined the opposition between the stable BIO and SGW composts and the more easily mineralised FYM and MSW, in the field like in the lab. For example, the storage of C in soil followed the order of I_{ROC}, the OM stability index reminded in Table S1-A, with little influence of the mineral N fertilisation except for the control plots. Yet, BIO and SGW induced the highest regression slopes for soil Cu_{EDTA} and Zn_{EDTA} versus inputs of corresponding available metals. So, even if OM mineralisation has been lower with BIO and SGW treatments, the increase of soil OM and the transfers between TM pools finally led to higher EDTA-extractable metals in plots BIO and SGW compared to FYM and

MSW. The possible role of ageing processes between Zn and reactive oxides, well established between this metal and reactive oxides (Buekers et al., 2008; Sayen & Guillon 2014) can be interpreted in the same way. The higher contents of Fe and Mn in BIO composts (Table S1) and the higher increase of soil pH by BIO amendments should enhance these processes of ageing and reduce the solubility of especially Zn (Buekers et al., 2008). However, they do not generate more unavailable, inert Zn, but rather more EDTA-extractable Zn. So, the results obtained from this long-term field experiment suggest that organic and inorganic phases carrying potentially available TM have been developed more by BIO and SGW than by the two other amendments. More investigation by speciation studies on selected samples from the field or from comparable systems driven in the lab would be necessary for a better understanding of involved components and processes.

~~The assessment of a~~Considering the soil soluble TM fraction ~~in soils~~quantified by ~~single~~ 0.01 M $CaCl_2$ extractions ~~is of particular interest since many studies have related such fraction, for certain metals, to their concentrations in soil pore water, their effects on organisms or their uptake by plant (Degryse et al., 2003; Nolan et al., 2005; Beaumelle et al., 2014). O~~, our results ~~clearly~~ showed that variations of this fraction cannot be interpreted, nor predicted, without monitoring other variables in amended soils. At least, soil organic matter (SOM) and soil pH are influential factors of soluble Cd, Ni and Zn. And SOM and pH did vary versus the type and the number of amendments (Houot et al., 2009; Peltre et al., 2010; Obriot et al., 2016). ~~So, in addition to specific interests in these variables, studying and modelling the evolution of SOM and pH are necessary for predicting the behaviour of OWP-originated trace metals in soils. EDTA extractions quantify another fraction, bringing complementary information, although it is certainly not homogeneous. It includes cations complexed with different strengths by different components, and metals in relatively soluble minerals as carbonates. But the studied soils do not contain carbonates, even after~~

673 ~~many applications of alkaline OWP. And~~Besides, ~~for Cu and Zn, TM which have increased~~
674 ~~the most in repeatedly amended soils,~~ we found a strong positive influence of the EDTA
675 fraction on the soluble fraction for Cu and Zn, TM which have increased the most with
676 repeated amendments. This strengthens the hypothesis of sorption-desorption reactions
677 between these two compartments~~, as illustrated by~~ (Degryse et al., ~~(~~2009), and the search of
678 possible equilibrium equations.
679 More discussion of the modelling results ~~is conducted below for each metal of interest~~,
680 including from the ~~simplest~~ Kd approach~~,~~ of restricted applicability but suitable for
681 comparisons of published values, is conducted below for each metal.
682 Copper: the nearly constant Kd of 1200 L/kg obtained for our samples is in the range of
683 published values. ~~Published sorption equations are often not linear, which makes~~
684 ~~comparisons less easy than between Kd models.~~ Discrepancies may come obviously from
685 sample sets, but also from the experimental approach of soil:solution equilibrium, i.e., from
686 the definition of the two phases. For example, two noticeable works on Cu sorption by soils
687 concluded with simple models similar to equation (9) written above:

688 $Cu_{solution} = 0.427 \times (Cu_{TOT})^{1.16}$ Gray & McLaren (2006) (n=74)

689 $Cu_{solution} = 0.891 \times (Cu_{TOT})^{0.76}$ McBride et al. (1997) (n=31, "GVD series")

690 A crucial difference between these equations and our equation (9) lies in the choice of total
691 soil Cu to express the adsorbed metal fraction in equilibrium with soluble Cu. Reminding
692 that Cu_{EDTA} represents about 30% of total Cu in our samples (~~§ 3.4~~Table S3-B), a
693 substitution of Cu_{EDTA} by $0.3 \times Cu_{TOT}$ in equation (9) shows that its predictions are a little
694 lower than the predictions of McBride et al.'s equation, below 60 $mg.kg^{-1}$. So, ~~this last~~
695 ~~simple model and~~these two equations converge ~~(9) are close~~, but our equation based on
696 Cu_{EDTA} could be more relevant in case of low contamination, ~~i.e.,~~ when non-extractable Cu
697 is relatively high.

McBride et al. (1997) fitted another MLR equation from a second larger data set, involving the variables soil OM and pH. Other authors like McGrath et al. (1988), Fotovat et al., (1997), Römkens & Salomons (1998) noticed that the influence of pH upon the retention of Cu by soils is relatively small when compared to the influence of SOM, or when Cu is compared to Zn or Cd. On another side, the mobilising effect of OWP amendments on Cu has been also highlighted, linked to the increase of complexing DOM (Zhou & Wong, 2001; Planquart et al., 1999) and~~.~~ Temminghoff et al. (1994) supported that the distribution of Cu in liquid and solid phases is mainly determined by the distribution of OM, with ratios Cu/OM similar in the two phases. ~~But the distribution of OM itself is actually influenced by pH, texture, etc.~~ Here, from monitoring two extractable fractions in repeatedly amended soil horizons, we conclude that increased solubility of Cu is directly determined by the increase of a reactive sorbed EDTA-extractable pool.

~~In this way, our work incites to assess not only the total content and input of Cu from OWP but also its EDTA-extractable fraction. We have seen that this fraction in soils can increase faster than cumulated inputs of Cu_{EDTA} by OWP (Figure 3): slopes between 1.6 and 2.2 were obtained, for FYM and BIO respectively. Such differences between OWP could be related to their composition, FYM and BIO being contrasted with respect to their organic and inorganic fractions (§ 3.1). The relative abundance of carbonate and Fe in BIO composts could reduce the efficiency of EDTA for extracting TM due to competition with major cations, and this disturbance of the TM extraction could disappear after dilution and transformation of OWP in soils. More investigation would be necessary for a better understanding of involved components and processes.~~

Cadmium: sorption-desorption of Cd on soils has been widely studied. Values of Kd(Cd) summarized in Table 5 are of the same order, although often lower, than Kd(Cd) obtained by Anderson & Christensen (1988), Welp & Brümmer (1999)~~,~~ or Andersen et al. (2002)~~,~~

with soil samples not too far from our amended silt loam horizons. With respect to experimental conditions, these authors measured soluble Cd in equilibrium solutions or in aqueous extracts of low ionic strength, not in 0.01 M $CaCl_2$. Indeed, Degryse et al. (2003) estimated that Kd deduced from 0.01 M $CaCl_2$ extraction should be multiplied by a factor about 2, related to the importance of chloride complexes in the extracts, for better predicting Cd concentration in soil pore water. This may explain the relatively low coefficients found for Kd(Cd). Again, the varying definitions of adsorbed Cd, EDTA-extractable or pseudo-total, can also intervene, but less than for Cu since Cd_{EDTA} represents around 60% of total Cd (~~§~~part 3.4).

When considering the pH dependency of log(Kd(Cd)) or log(Cd_{CaCl2}), the coefficients 0.35 or 0.32 (equation 8; Table 4) ~~is relatively low compared to~~stand among the low values of corresponding coefficients found by other authors: ~~for example,~~ Anderson & Christensen (1988), Lee et al. (1996), Streck & Richter (1997), Ingwersen et al. (2000), Sauvé et al. (2000), Römkens & Salomons (1998) and Tipping et al. (2003) found values of 0.6, 0.5, 0.4, 0.4, 0.5, 0.34 and 0.20, respectively~~. In turn, Römkens & Salomons (1998) and Tipping et al. (2003) found coefficients 0.34 and 0.20, which are closer to ours~~.

The dependency of Cd_{CaCl2} or Kd with SOC appeared higher than with pH~~. This is not only a matter of coefficients but also of~~ when considering the ranges of variations w~~. W~~ithin our data set, i.e.,~~pH and SOC stand in ranges~~ [6.6, 7.8] and [9, 16] for pH and SOC respectively. Everything else fixed, a pH increase from 6.6 to 7.8 would multiply Kd(Cd) by a factor 2.4, and a SOC increase from 9 to 16 $g.kg^{-1}$ multiplies Kd(Cd) by a factor 4.8 (equation 8). So, the influence of SOC on the mobility of cadmium in the plough horizons of the field experiment is major, the influence of pH of second importance, and Cd_{EDTA} hardly varied with treatments (Fig. 2). Thus the main process involved in Cd mobility in this field

747 experiment is the building up of soil organic matter in amended plots, increasing their
748 capacity to fix this metal on solid phases by comparison to unamended plots (Fig. 4).
749 Zinc: Contrarily to Cd, Zn_{EDTA} showed large variations following repeated amendments
750 (Fig. 2). Soluble Zn was closely correlated to Zn_{EDTA} through a close to linear or a Kd
751 model (Table 4). Choosing the Kd model for easier comparisons, we noticed that the
752 coefficients of SOC are close for log(Kd_{Cd}) and log(Kd_{Zn}) (equations 8 and 10); SOC
753 variations between extrema of our dataset multiply log(Kd_{Zn}) by a factor close to 4 as for
754 log(Kd_{Cd}). But the higher coefficient of pH in equation 10 induces an increase by a factor
755 7.8 when pH increases from 6.6 to 7.8.
756 So, although Zn_{EDTA} ~~roughly~~ approximately doubled with repeated amendments during 15
757 years and that this would increase as well Zn_{CaCl2}, ~~since both fractions are roughly~~
758 ~~proportional but~~ this impact ~~on Zn_{CaCl2}~~ was more than compensated, i.e., Zn_{CaCl2} became
759 lower in amended soil~~s~~ than in CTR, due to increasing SOC and pH with ~~applications of~~
760 FYM, MSW or BIO composts (Fig. 2). In case of SGW applications, which increased SOC
761 but not pH, the increase of Zn_{EDTA} was ~~roughly~~ approximately compensated by increasing
762 SOC, with respect to Zn_{CaCl2} variations. As for Cd, the respective roles of SOC, pH, and
763 Zn_{EDTA} on the mobility of Zn are quantitatively unravelled through using equation 10 or
764 other equations of Table 4.
765 When comparing this equation to published models fitted to other data set, the dependency
766 of Kd on pH was found a little lower by Degryse et al. (2003), and a little higher by
767 Anderson & Christensen (1988). The former authors attributed to soil pH more influence on
768 Zn sorption than to SOC, while the latter ranged at first pH and then CEC. Freundlich-type
769 equations of Koopmans et al. (2007), Luo et al. (2006) and McBride et al. (1997) selected
770 only pH among influencing soil variables; whereas soil organic matter was also included by
771 Sauvé et al. (2000) and by Tipping et al. (2003), and CEC by Thiele & Leinweber (2001).

So, many distinct functions between soil variables and soluble Zn can be found in the scientific literature, but ~~many of them have~~most of them did not distinguish~~ed~~ the solid sorbed fraction from total Zn, although geogenic Zn is often major and variable in soils. Here the EDTA fractions of Zn ~~have~~ varied from less than 10% of total Zn in CTR ~~soils~~ up to 21% in amended soil layers, i.e., much more widely than total Zn, and ~~with~~ interesting relationships between soil Zn_{EDTA} and inputs of Zn_{EDTA} from OWP have been found (Fig. 3).

Other TM: Considering Pb, we noticed that its EDTA fraction, as for Zn, was more significantly affected by OWP applications than its total content. We also found that Kd(Pb) defined from its EDTA and $CaCl_2$ fractions, beyond uncertainties linked to analytical limits for the latter, showed the highest variations among the five metals of Table 5. Nevertheless, we found no satisfactory MLR models for Kd(Pb) or for soluble Pb. ~~Therefore, little prediction appears feasible for this metal.~~ In case of Ni, MLR equations were obtained, but with relatively low R^2~~. Since our~~, and from a data set which presents very little variations of Ni fractions, without influence of the treatments~~,~~. So, we expect a narrow applicability of these equations~~models~~.

5. Conclusion and perspectives of prediction of available trace metals

We have studied the availability of several trace metals in a long-term field experiment, designed for assessment of organic waste product applications to cultivated soils, by monitoring their mobilisable and soluble fractions~~,~~ operationally defined by EDTA and $CaCl_2$ extractions. ~~This approach is promising in order to predict the evolution of soil available metals,~~ We hypothesise that mobilisable metals brought via OWP could be added to EDTA-extractable pools of soil amended horizons. This was approximately confirmed for Zn, in average with the 4 types of OWP, and for Pb in one case of significant increase of Pb_{EDTA} in soil. ~~at least for Cu, Zn and Cd. Evaluations of EDTA-extractable metal inputs~~

~~from known organic amendments to soils facilitate this goal, especially for Zn and Cu.~~ ~~However~~But for Cu, the regression slope between net inputs and stock variations in soil~~s~~ was far from unity and varied with OWP types. The influence of OWP on the same regression slopes for Zn was also noticeable. Therefore, in order to predict the evolution of available metals in amended horizons, such relationships need further understanding, calling on inspired laboratory studies and/or complementary analyses of TM speciation in chosen samples of the field experiment ~~using other types of OWP and soils~~.

Our second hypothesis was that soluble metals can be predicted by sorption models based on their mobilisable fractions and other soil variables. It has been supported to some extent and at least~~Concerning the key soluble Zn, Cu, and Cd, as in other studies~~, such models help to unravel and quantify the influence of the different soil variables. For example soluble Cu appeared determined only by Cu_{EDTA}, which regularly increased with all types of organic amendments, whereas soluble Cd decreased in soil with amendments, which can be attributed mainly to increasing organic matter. Of course, these trends depend on the studied system and collected dataset. Our field experiment considered 4 distinct important types of organic residues, and one type of soil-crop system representative of NW Europe agriculture in the 2000s. But OWP applications have been over common practices and inputs of a few trace metals got close to regulatory thresholds~~they appear mainly determined by sorbed metal pools, here EDTA-extractable pools, and important soil variables such as pH and soil organic matter~~. Actually, in this context of agricultural OWP recycling, more and more field studies and modelling improve the predictions of soil organic matter (e.g., ~~Lopez-Rayo et al., 2016;~~ Peltre et al., 2010). There are also possibilities to predict the effect of organic amendments on soil pH and the accumulation of persistent contaminants through balance approaches (Zeng et al., 2017; Michaud et al., 2018). So that the relationships and the modelling presented in our work can complete the

tools for~~should finally contribute in~~ assessing and predicting the effects of regular applications of ~~OWP~~ organic residues on available trace metals~~TM~~ in soils.

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Competing interests

The authors declare no competing interests.

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~~**Table 1: Major characteristics of Organic Waste Products…**~~ ***This Table 1 on OWP characteristics (of the first submitted version) has been completed by data on OM stability, to answer Reviewer 1's comments, and has been moved to Supplementary Information according to Reviewer 4's suggestion (=> now Table S1-A in the revised version)***

Table 1. Chemical characteristics (total contents unless specified) of the initial soil plough horizon, sampled in 1998 in all sub-plots: means (standard deviations; n = 40)

	Texture ($g.kg^{-1}$)			pH H_2O	CEC	C organic	N total	P_2O_5 Olsen
	Clay	Silt	Sand		$cmol^+.kg^{-1}$		$g.kg^{-1}$	
	149 (9)	783 (8)	68 (4)	6.90 (0.23)	9.55 (0.65)	10.50 (0.66)	1.11 (0.05)	0.082 (0.016)
Trace Metals	($mg.kg^{-1}$)	Cd	Cr	Cu	Hg	Ni	Pb	Zn
		0.236 (0.013)	45.8 (2.8)	11.78 (0.96)	0.095 (0.015)	15.1 (0.8)	25.0 (3.5)	49.7 (3.4)
Referential*	"	0.30	44	12	0.05	19	26	55

* Surface layers of agricultural soils developed on loess of the Paris Basin: median values from 700 samples with < 21% clay (Baize et al., 2007)

Table 2: EDTA-extractable metals in spread OWP ~~spread every year~~ (Mean ± standard-deviation from 3 samplings; SGW: compost of sewage sludge with green waste and wood chips; BIO: compost of biowaste and green waste; MSW: compost of organic fraction of municipal solid waste; FYM: farmyard manure of dairy cows on straw~~, BIO, MSW, FYM: see Table 1~~), **average EDTA-extractable contents over 2004-2013** (small letters indicate significant differences between OWP types)**, average inputs per year** (cumulated inputs divided by 11 years)

Trace Metal extracted by EDTA	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
			mg.kg^{-1} DW			
~~1998-2002~~	~~NA~~	~~NA~~	~~NA~~	~~NA~~	~~NA~~	~~NA~~
2004 SGW	0.172 ± 0.006	0.713 ± 0.073	12.2 ± 0.1	1.50 ± 0.01	6.76 ± 0.17	63.7 ± 2.5
2006 SGW	0.553 ± 0.012	0.756 ± 0.082	56.2 ± 2.8	2.15 ± 0.09	29.5 ± 1.18	227 ± 6
2007 SGW	0.634 ± 0.012	1.79 ± 0.12	69.7 ± 2.3	4.03 ± 0.25	40.6 ± 2.7	249 ± 13
2009 SGW	0.509 ± 0.064	2.21 ± 0.11	51.8 ± 1.3	4.51 ± 0.37	29.2 ± 0.3	255 ± 7
2011 SGW	0.638 ± 0.057	1.09 ± 0.14	61.1 ± 3.6	3.00 ± 0.17	23.8 ± 1.5	338 ± 14
2013 SGW	0.693 ± 0.015	2.40 ± 0.06	82.1 ± 2.1	3.06 ± 0.05	40.1 ± 1.8	316 ± 6
Average content (SD) n=6	**0.53 (0.19) (a)**	**1.49 (0.74) (a)**	**55.5 (23.8) (a)**	**3.04 (1.12) (a)**	**28.3 (12.5) (a)**	**242 (97) (a)**
Average i~~I~~nput g/ha/year	**4.78**	**13.5**	**498**	**27.3**	**256**	**2153**
2004 BIO	0.082 ± 0	0.720 ± 0.034	2.74 ± 0.17	0.371 ± 0.028	10.1 ± 0.3	22.6 ± 1
2006 BIO	0.266 ± 0.006	0.747 ± 0.026	12.8 ± 0.5	2.03 ± 0.823	28.6 ± 0.7	87.7 ± 1.9
2007 BIO	0.315 ± 0.019	1.10 ± 0.07	28.3 ± 1.4	1.42 ± 0.37	27.6 ± 0.7	127 ± 2
2009 BIO	0.261 ± 0.04	1.81 ± 0.11	23.5 ± 0.4	1.74 ± 0.18	26.2 ± 1.7	102 ± 2
2011 BIO	0.308 ± 0.031	1.49 ± 0.04	20.9 ± 1.3	1.86 ± 0.03	26.0 ± 1.2	126 ± 5

2013 BIO	0.268 ± 0.005	1.01 ± 0.06	9.89 ± 0.57	1.22 ± 0.11	25.5 ± 1.2	84.3 ± 2.7
Average content	**0.25 (0.09) (b)**	**1.15 (0.43) (a)**	**16.4 (9.5) (b)**	**1.44 (0.6) (b)**	**24.0 (6.9) (a)**	**91.5 (38) (b)**
Input g/ha/year	**2.34**	**10.7**	**150**	**13.5**	**228**	**844**
2004 MSW	0.221 ± 0.16	1.41 ± 0.15	9.32 ± 0.62	1.50 ± 0.37	13.6 ± 2.9	46.4 ± 12.5
2006 MSW	0.443 ± 0.1	2.96 ± 1.16	39.4 ± 9.96	8.06 ± 2.02	27.4 ± 9	188 ± 38
2007 MSW	0.394 ± 0.171	2.20 ± 1.02	29.9 ± 13.2	6.81 ± 2.81	34.5 ± 15.2	146 ± 55
2009 MSW	0.239 ± 0.029	0.950 ± 0.041	11.7 ± 0.6	1.77 ± 0.06	24.6 ± 2.1	82.9 ± 2.6
2011 MSW	0.340 ± 0.016	0.759 ± 0.085	17.97 ± 1.14	1.40 ± 0.17	17.5 ± 0.8	101 ± 4
2013 MSW	1.50 ± 0.05	10.4 ± 0.3	92.6 ± 3.75	15.2 ± 3.4	50.6 ± 0.7	505 ± 18
Average content (SD) n=6	**0.52 (0.49) (ab)**	**3.11 (3.65) (a)**	**33.5 (31.1) (b)**	**5.79 (5.46) (a)**	**28.0 (13.3) (a)**	**178 (168) (ab)**
Input g/ha/year	**3.52**	**21.0**	**221**	**37.6**	**180**	**1180**
2004 FYM	0.156 ± 0.027	0.448 ± 0.079	9.91 ± 1.57	0.372 ± 0.122	18.3 ± 6.4	46.2 ± 5.3
2006 FYM	0.914 ± 0.175	0.977 ± 0.117	52.1 ± 8.1	1.83 ± 0.08	78.9 ± 22.3	240 ± 58
2007 FYM	0.798 ± 0.09	1.08 ± 0.03	61.4 ± 18.4	1.70 ± 0.087	77.6 ± 4.9	281 ± 202
2009 FYM	0.282 ± 0.132	0.323 ± 0.047	19.7 ± 1.6	0.911 ± 0.328	12.7 ± 1.8	119 ± 8
2011 FYM	0.258 ± 0.016	0.526 ± 0.124	11.8 ± 0.5	1.50 ± 0.18	13.9 ± 1.2	85.0 ± 1.5
2013 FYM	0.267 ± 0.021	0.218 ± 0.047	18.5 ± 0.6	0.658 ± 0.172	10.1 ± 0.4	131 ± 4
Average content	**0.45 (0.32) (ab)**	**0.59 (0.35) (b)**	**28.9 (22.1) (b)**	**1.16 (0.6) (b)**	**35.2 (33.4) (a)**	**150 (91) (ab)**
Input g/ha/year	**3.21**	**4.34**	**205**	**8.33**	**261**	**1050**

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Table 3: Results of CaCl2 extractions on OWP spread every year (mean ± SD, n=3; a few isolated values < QL were replaced by QL/2), then **average values over 2004-2013**

CaCl2 extractable metals	**Cadmium µg.kg^{-1} DW**	**Chrome**	**Copper**	**Nickel**	**Lead**	**Zinc**	**pH**	**DOC, g.kg^{-1}**
2004 SGW	5.22 ± 0.15	103 ± 7	895 ± 63	266 ± 17	11 ± 0.8	962 ± 37	6.96 ± 0.07	
2006 SGW	7.02 ± 0.43	60 ± 1	1180 ± 17	241 ± 13	70.8 ± 14.2	1423 ± 96	7.08 ± 0.07	
2007 SGW	6.09 ± 0.22	< 10.3 (QL)	585 ± 26	67 ± 6	16.5 ± 1.7	468 ± 5	7.18 ± 0.12	
2009 SGW	9.25 ± 0.17	41.7 ± 5.5	819 ± 14	192 ± 9	12.8 ± 0.8	841 ± 33	6.68 ± 0.06	
2011 SGW	2.06 ± 0.11	27.5 ± 1.8	1107 ± 6	196 ± 5	< 3.3 (QL)	1130 ± 46	6.60 ± 0.06	
2013 SGW	3.74 ± 0.27	65.5 ± 6.9	1577 ± 76	238 ± 21	2.52 ± 1.27	1330 ± 46	7.20 ± 0.02	9.54± 0.31
Average values ± SD (n=6)	**5.56 ± 2.52**	**50.6 ± 33.9**	**1027 ± 343**	**200 ± 71**	**19.1 ± 26.1**	**1026 ± 349**	**6.95 ± 0.26**	
input mg.ha^{-1}.y^{-1}	**51.1**	**470**	**9329**	**1826**	**180**	**9333**		
2004 BIO	2.45 ± 0.07	69.7 ± 7.5	314 ± 17	116 ± 6	36.2 ± 3.4	522 ± 19	8.10 ± 0.08	
2006 BIO	5.09 ± 0.35	51.6 ± 7.2	577 ± 25	266 ± 80	79.9 ± 5.3	835 ± 66	7.97 ± 0.03	
2007 BIO	3.32 ± 1.22	24.3 ± 2.5	502 ± 73	142 ± 17	25 ± 1.8	494 ± 69	7.42 ± 0.04	
2009 BIO	8.42 ± 0.1	69.7 ± 6.6	636 ± 28	242 ± 19	34 ± 0.7	743 ± 31	7.17 ± 0.10	
2011 BIO	1.8 ± 0.18	65.2 ± 1.8	518 ± 27	159 ± 7	27.8 ± 0.8	1227 ± 6	6.94 ± 0.03	
2013 BIO	2.5 ± 0.1	58.6 ± 1.6	370 ± 13	185 ± 23	13.9 ± 4	629 ± 21	7.14 ± 0.02	8.86± 0.38

Average values	**3.93 ± 2.48**	**56.5 ± 17.3**	**486 ± 123**	**185 ± 58**	**36.1 ± 22.8**	**742 ± 271**	**7.46 ± 0.48**	
input mg.ha^{-1}.y^{-1}	**38.8**	**546**	**4626**	**1801**	**355**	**6876**		
2004 MSW	37.5 ± 19.2	927 ± 33	9870 ± 1933	3583 ± 116	772 ± 44	14133 ± 416	6.99 ± 0.02	
2006 MSW	40.6 ± 3.9	1720 ± 36	18067 ± 603	6810 ± 197	745 ± 64	19700 ± 1082	7.42 ± 0.2	
2007 MSW	19.1 ± 8.8	444 ± 313	8193 ± 5495	3857 ± 2638	203 ± 125	6777 ± 4095	6.88 ± 0.28	
2009 MSW	3.98 ± 0.23	100 ± 4	870 ± 41	379 ± 8	36 ± 1	1087 ± 15	7.51 ± 0.07	
2011 MSW	2.58 ± 0.12	27.6 ± 1.6	847 ± 51	198 ± 14	12.4 ± 1.3	642 ± 31	7.44 ± 0.07	
2013 MSW	57.7 ± 1.5	2397 ± 55	20100 ± 700	7113 ± 443	379 ± 34	38467 ± 1097	7.87 ± 0.0	28.8± 0.10
Average values	**26.9 ± 22**	**936 ± 950**	**9658 ± 8207**	**3657 ± 2988**	**358 ± 337**	**13468 ± 14330**	**7.35 ± 0.36**	
input mg.ha^{-1}.y^{-1}	**181.9**	**6262**	**63639**	**23874**	**2404**	**91791**		
2004 FYM	42.1 ± 3.4	189 ± 14	4165 ± 115	530 ± 86	1440 ± 165	12367 ± 1704	9.00 ± 0.05	
2006 FYM	31.6 ± 3.3	138 ± 32	4237 ± 869	627 ± 124	644 ± 172	4720 ± 701	8.26 ± 0.32	
2007 FYM	13.7 ± 2.4	69 ± 12	3643 ± 717	292 ± 61	356 ± 30	2217 ± 284	8.59 ± 0.12	
2009 FYM	27.2 ± 3.7	125 ± 15	4633 ± 581	344 ± 43	191 ± 41	4717 ± 410	8.88 ± 0.09	
2011 FYM	13.6 ± 0.9	66.2 ± 2.3	1477 ± 71	342 ± 12	83.9 ± 7.3	1537 ± 208	8.80 ± 0.04	
2013 FYM	22.1 ± 0.6	132 ± 7	3350 ± 161	487 ± 27	142 ± 14	3290 ± 131	8.19 ± 0.03	17.2± 0.27
Average values	**25.0 ± 11.0**	**120 ± 46**	**3584 ± 1128**	**437 ± 131**	**476 ± 513**	**4808 ± 3921**	**8.62 ± 0.33**	
input mg.ha^{-1}.y^{-1}	**171.8**	**814**	**24096**	**3029**	**3493**	**33345**		

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Table 4: Selected results of Multiple Linear Regression studies – Units: M_{EDTA} in mg/kg dry soil; M_{CaCl2} in mg/L of $CaCl_2$ extracts, corresponding Kd in L/kg; SOC in g/kg – n = 65 mean values from the 4 repetition blocks, or n = 55 when explicative variables include pH_{CaCl2} not measured in 2002 – MAE = Mean Absolute Error, calculated for M_{CaCl2} in $\mu g.L^{-1}$ (and in % of Mean Concentration)

MLR for	R^2_{adj}	Equation *(P-value between brackets for each variable)*	MAE
Log(Cd_{CaCl2})	60% n=65	= 4.80 + 2.45×log(Cd_{EDTA}) (*P = 0.11*) - 0.351×pH_{H2O} (*P = 0.00*) - 3.18×log(SOC) (*P = 0.00*)	0.19 (31%)
Log(Cu_{CaCl2})	69% n=65	= -3.21 + 1.21×log(Cu_{EDTA}) (*P = 0.00*)	0.39 (10%)
Log(Ni_{CaCl2})		All MLR rejected (coefficient of log(Ni_{EDTA}) always < 0)	
Log(Zn_{CaCl2})	68% n=65	= 5.56+ 1.305×log(Zn_{EDTA}) (*P = 0.00*) - 0.753×pH_{H2O} (*P = 0.00*) - 3.04×log(SOC) (*P = 0.00*)	2.97 (30%)
MLR for	R^2_{adj}	Equation *(P-value for each variable)*	
Log(Kd_{Cd})	65% n=65	= -2.85 + 0.323×pH_{H2O} *(P=0.00)* + 2.71×log(SOC) *(P=0.00)*	0.19 (32%)
Log(Kd_{Cu})		All MLR rejected. So, best model = mean	0.42 (11%)
Log(Kd_{Ni})	58% n=65	= -1.35 + 0.492×pH_{H2O} *(P=0.00)* +0.704×log(SOC) *(P=0.05)*	0.45 (26%)
Log(Kd_{Ni})	56% n=65	= -1.106 + 0.564×pH_{H2O} *(P=0.00)*	
Log(Kd_{Zn})	81% n=65	= -4.98+ 0.741×pH_{H2O} *(P=0.00)* + 2.36×log(SOC) *(P=0.00)*	3.00 (31%)
Log(Kd_{Zn})	74% n=55	= -4.48 + 0.646×pH_{CaCl2} *(P=0.00)* + 2.88×log(SOC) *(P=0.00)*	

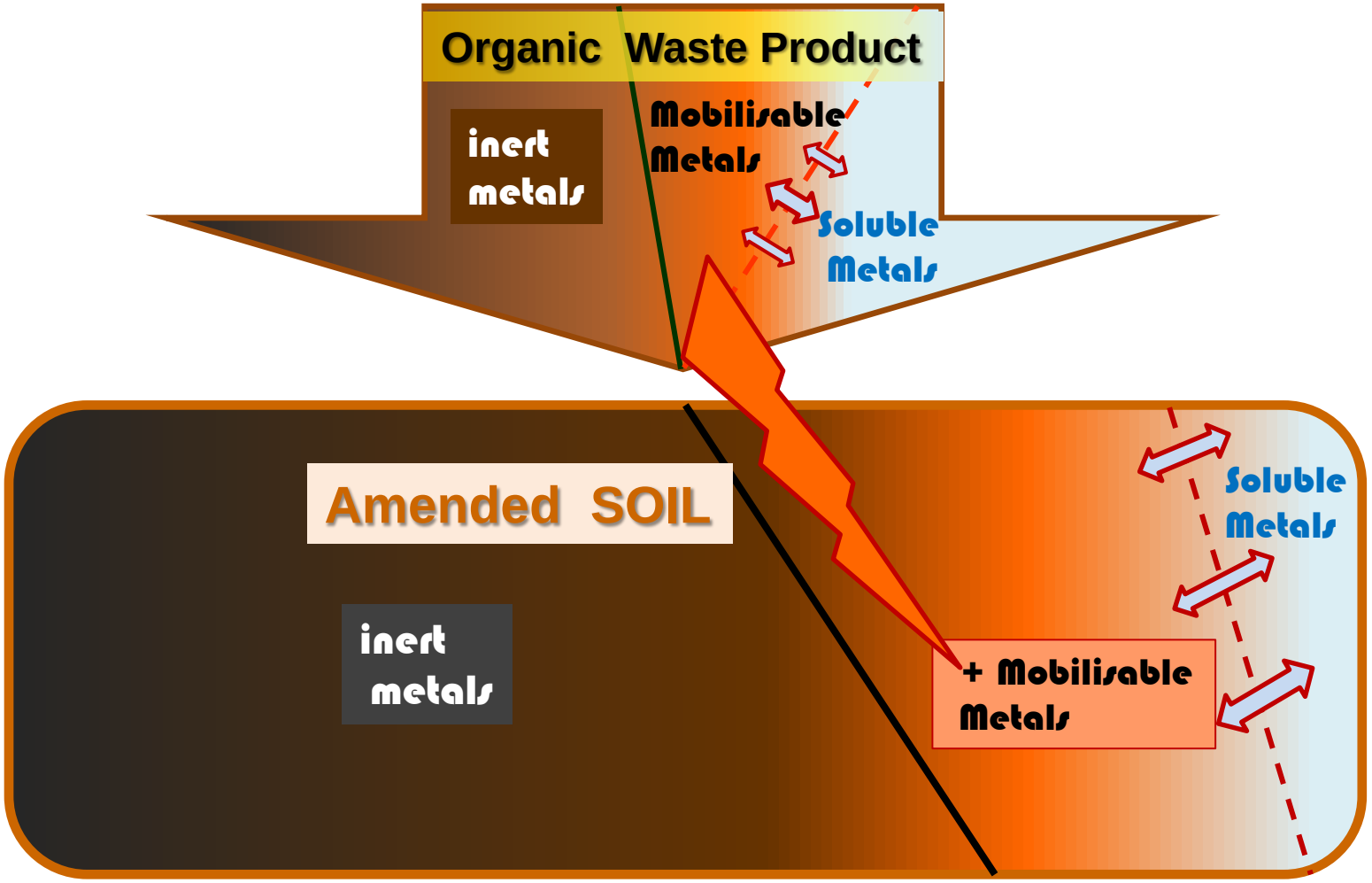
Table 5: Descriptive statistics of Kd and log(Kd) – Means, medians, Coefficients of Variation

L/kg	Mean	Median	CV%		Mean	Median	CV%
Kd(Cd)	368	230	106%	$\log(Kd_{Cd})$	2.430	2.361	13%
Kd(Cu)	1195	1164	16%	$\log(Kd_{Cu})$	3.072	3.066	2%
Kd(Ni)*	1036	890	59%	$\log(Kd_{Ni})$	2.945	2.949	8%
Kd(Pb)*	621634	44498	187%	$\log(Kd_{Pb})$	4.855	4.648	18%
Kd(Zn)	1236	749	106%	$\log(Kd_{Zn})$	2.908	2.875	13%

* Part of values for Ni_{CaCl2} and Pb_{CaCl2}, under quantification limits, have been replaced by QL/2, or by analytical indications < QL when available, for these calculations.

*Graphical Abstract Revised

STOTEN_ Cambier et al: Trace metal availability in soil horizons amended with various urban waste composts during 17 years - monitoring and modelling



Trace metal availability in soil horizons amended with various urban waste composts during 17 years – monitoring and modelling

Authors: Philippe Cambier, Aurélia Michaud, Remigio Paradelo, Myriam Germain, Vincent Mercier, Annie Guérin-Lebourg, Agathe Revallier, Sabine Houot

Highlights

- long-term monitoring the EDTA and $CaCl_2$ extractable metals in composts and topsoil
- EDTA-extractable Zn conservative in systems composts – amended cultivated soil
- Modelling the evolution of available metal fractions in regularly amended soil

*Revised manuscript with no changes marked
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Trace metal availability in soil horizons amended with various urban waste composts during 17 years – monitoring and modelling

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Abstract

Recycling organic residues in agrosystems presents several benefits but faces the question of contaminants, among them a few trace metals which eventually accumulate in soils following regular applications of organic waste products (OWP) and represent an ecological risk. The increase of total trace metal contents in amended topsoils can be predicted by a mass balance approach, but the evolution of their available fractions is a more intricate issue. We aimed at modelling this evolution by using the dataset of a long-term field experiment of OWP applications (manure and three urban waste composts). Two operationally-defined fractions of 6 trace metals have been quantified in the OWP and amended topsoils between 2002 and 2015: the soluble and potentially available metals, extracted in 0.01M $CaCl_2$ and 0.05M EDTA solutions, respectively.

The potentially available metals have progressively increased in amended topsoils, at rates depending on elements and types of OWP. For Zn, these increases corresponded in average to inputs of potentially available Zn from OWP. But the soil stocks of potentially available Cu increased faster than from the inputs of EDTA-extractable Cu, showing linear regression slopes between 1.4 and 2.5, depending on OWP type. The influence of OWP has been provisionally interpreted in the light of their efficiency to increase soil organic matter and their inputs of reactive oxides.

Soluble copper has increased with repeated amendments. But soluble cadmium, nickel and zinc have generally decreased, as they are influenced by changing soil variables such as pH and organic matter. Statistic models were used to unravel the relationships between soluble and EDTA-extractable metals and other soil variables. For Cu, the most satisfactory models just relate soluble and potentially available Cu. Developing such models could contribute to predict the long-term effects of a precise scenario of agricultural OWP recycling upon available trace metals in soils.

Keywords: Organic amendment; soil quality; heavy metal; diffuse contamination; soluble metal, long-term field experiment

1. Introduction

Recycling organic residues in agriculture presents several benefits at local and global scales: the physical, physicochemical and biological properties of the agroecosystems may be ameliorated by increasing the turnover and over time the content of organic matter (OM) in soils. Increasing the soil organic carbon (SOC) and saving fertilisers by incorporating organic residues in agricultural practices may limit the climate warming and the exhaustion of non-renewable resources.

The main drawbacks concern the difficulty to adjust nutrient fluxes to plant needs, especially N and P which may cause environmental damages when in excess, and the input of various contaminants in agroecosystems. Among contaminants, several trace metals (TM) are likely to accumulate in soils following repeated spreading of organic waste products (OWP), even when spreadings are conform to relevant regulations. Reviews on this topic converge towards copper (Cu) and zinc (Zn) as problematic contaminants, insofar as their total contents in soils do increase after enough time of regular applications of OWP, and they present potential eco-toxicity (Smith, 2009; Benoit et al., 2014; Lopez-Rayo et al., 2016; Yoshida et al, 2018). These two metals are essential micronutrients, but other TM like cadmium (Cd) and lead (Pb), which are just toxic, may also accumulate in amended surface soil horizons, depending on the applied loads of OWP and on their metal contents (Benoit et al., 2014; Smith, 2009). The corroboration of the increases of total TM contents in amended soils faces technical difficulties, like spatial heterogeneities, lack of prolonged control of all fluxes, including lateral dilution, or changing mass of soil impacted (Berti & Jacobs, 1998; McGrath & Lane, 1989; Benoit et al., 2014; Michaud et al., 2018), but the principle of predictions is straightforward: the balance of fluxes through the volume of amended soil determines the variation of stock of each TM in this volume (Doelsch et al., 2016).

It is much more debated if TM inputs to soils through OWP recycling induce significant impacts on soil organisms, crops or water quality. The present work aims to contribute to this debate by using the concept of availability, and thus to go over the statement of TM accumulation in amended soils. The relationships between bioavailability, toxicity, environmental availability, and chemical extractability of contaminants in soils have been theoretically and technically discussed in several articles (e.g., Harmsen et al., 2005; Peijnenburg et al., 2007; Kumpiene et al, 2017). From such studies and the induced international standard (ISO-17402, 2008), one may keep in mind that monitoring and predicting the extractability of TM in soils by appropriate chemical methods represent an essential progress towards the assessment of potential impacts of recycling OWP in agroecosystems (Smith, 2009; Paradelo et al., 2018). On another side, at least two levels of availability of TM in soils must be distinguished (ISO-17402, 2008): the readily available fraction, able to be dissolved in ambient conditions, most often estimated by using non-complexing neutral saline solutions, and the mobilisable, potentially available, or reactive fraction, estimated by using chelating or relatively strong acid solutions (Houba et al., 1996; Hooda et al., 1997; Harmsen, 2007; Degryse et al., 2009; Rodrigues et al., 2010; Groenenberg et al., 2012). Although the first fraction is often found better correlated with plant uptake, the second fraction appeared more meaningful in attempts of modelling soil-solution interactions (Tipping et al., 2003; Degryse et al., 2003; 2009; Groenenberg et al., 2012; 2017).

Several studies tended to show that available TM in soils amended by OWP increase more rapidly than their total contents. For instance, Madrid et al. (2007) found that repeated applications of composted municipal solid waste (CMSW), conforming to Spanish regulations, led to an increase of total contents of Zn, Pb, Cu and Ni in the cultivated horizon of a sandy soil, and to a larger increase of DTPA extractable fractions of the same

92 metals. Hargreaves et al. (2008) in their review on CMSW reported several cases of
93 increased DTPA, EDTA or other available fractions of particularly Pb, Cu, Mn, and Zn in
94 amended soils, and a few cases of decreasing availability attributed to an alkaline pH of
95 CMSW (above all for Mn) or to interactions with organic constituents (for Cu). Iglesias et
96 al. (2018) analysed 13 trace elements in soil after 15 years of mineral fertilization or
97 moderate sewage sludge applications and found a positive effect of sewage sludge on total
98 and DTPA-extractable contents for several elements; however, only Zn and As showed
99 significantly higher percentages of DTPA versus total contents. Thiele & Leinweber (2001)
100 compared TM contents of 30 soils receiving manure to geochemical background values and
101 found higher ratios while considering metals extracted in NH_4EDTA solution than for
102 pseudo-total contents, especially for Zn. Baldantoni et al. (2010) concluded from their field
103 experiments on two types of soils that "compost amendment affects more the available than
104 the total metal concentrations". Such studies confirm general ideas that anthropogenic
105 metal contaminants, in particular compost-born metals, are more available than lithogenic
106 ones. Nevertheless, few publications attempted to relate the evolutions of available TM in
107 amended soils to the inputs of available TM present in applied amendments.
108 So, the general topic of our study is the availability of trace metals in cultivated soil
109 horizons receiving OWP. It is based on a long-term field experiment, Qualiagro, which
110 started in 1998 in the frame of an INRA-Veolia collaborative research program devoted to
111 the evaluation of all agronomic and environmental impacts of using urban waste composts
112 on arable crops. This field experiment has been conducted with the same procedure until
113 2013.
114 By using its extensive dataset, our specific objectives are the followings:
115 - comparison between inputs of EDTA-extractable metals from organic amendments
116 and variations of EDTA-extractable metals in amended soil layers;

- interpretation of the evolution of soluble, i.e., $CaCl_2$-extractable trace metals in amended horizons, from relevant characteristics of OWP and soil;
- prediction of variations of these two fractions of TM in amended soil layers.

The underlying hypotheses are that reactive trace metals evaluated by EDTA extractions from OWP are added to EDTA-extractable metals present in amended soil horizons and that the soluble metals in these horizons can be predicted by sorption models based on their reactive fractions and other soil variables.

2. Material and methods

2.1. Field experiment QualiAgro

The long-term field experiment QualiAgro has been initiated in 1998 by INRA and Veolia Recherche & Innovation with the aim of studying the agronomic value of urban waste composts and their environmental impacts (Houot et al., 2002; INRA, 2018). It is located 35 km west of Paris, under a moderate oceanic climate (mean annual temperature 11°C and mean annual rainfall 650 mm over the studied period). The crop succession has been maize - winter wheat without intermediate plant cover since 1998, except for the year 2007 when barley was inserted because of a regional infestation by *Diabrotica virgifera*, a harsh pest of maize. The soil is a silt loam Luvisol, according to IUSS-FAO classification and USDA texture triangle, developed on aeolian loess. Table 1 presents the physicochemical characteristics of its initial plough horizon, including total contents of 7 trace metals which are close to median values found for comparable soil materials (Houot et al., 2009).

Within a 6 ha parcel divided in 4 replication blocks, 40 plots of 450 m^2 have been differentiated by 5 treatments related to OWP and 2 levels of complementary mineral N fertilisation (Figure 1). The 5 treatments correspond to applications of 4 types of OWP or none amendment:

- composts of sewage sludge with green waste and wood chips (SGW);

- composts of biowastes (mostly fermentable fraction of municipal waste) with green waste (BIO);
- composts of residual municipal waste (after separate collection of packaging, paper, glass, etc.) (MSW);
- farmyard manure of dairy cows on straw (FYM);
- the control plots without organic amendment (CTR).

OWP have been applied every two years on wheat stubble, and in 2007 on barley stubble, in early September, at doses equivalent to 4 Mg C ha^{-1}, i.e., about 2-times the mass flux commonly applied by farmers in similar conditions.

The two levels of complementary fertilisation, using ammo-nitrate and urea, are “N optimal” or +N, to get maximal yields, and “N minimal” or –N. No other fertilisers were applied. Indeed, the N fertilisation has been adjusted by measuring mineral N stocks at 3 depths down to 90 cm, 3 times a year (Noirot-Cosson et al, 2016) and it has been null the years of maize on amended plots –N. Except for fertilisers and amendments, intensive agricultural techniques have been applied on the whole field: ploughing and other mechanical tillage, phytosanitary control of weeds every year and other pesticides when necessary.

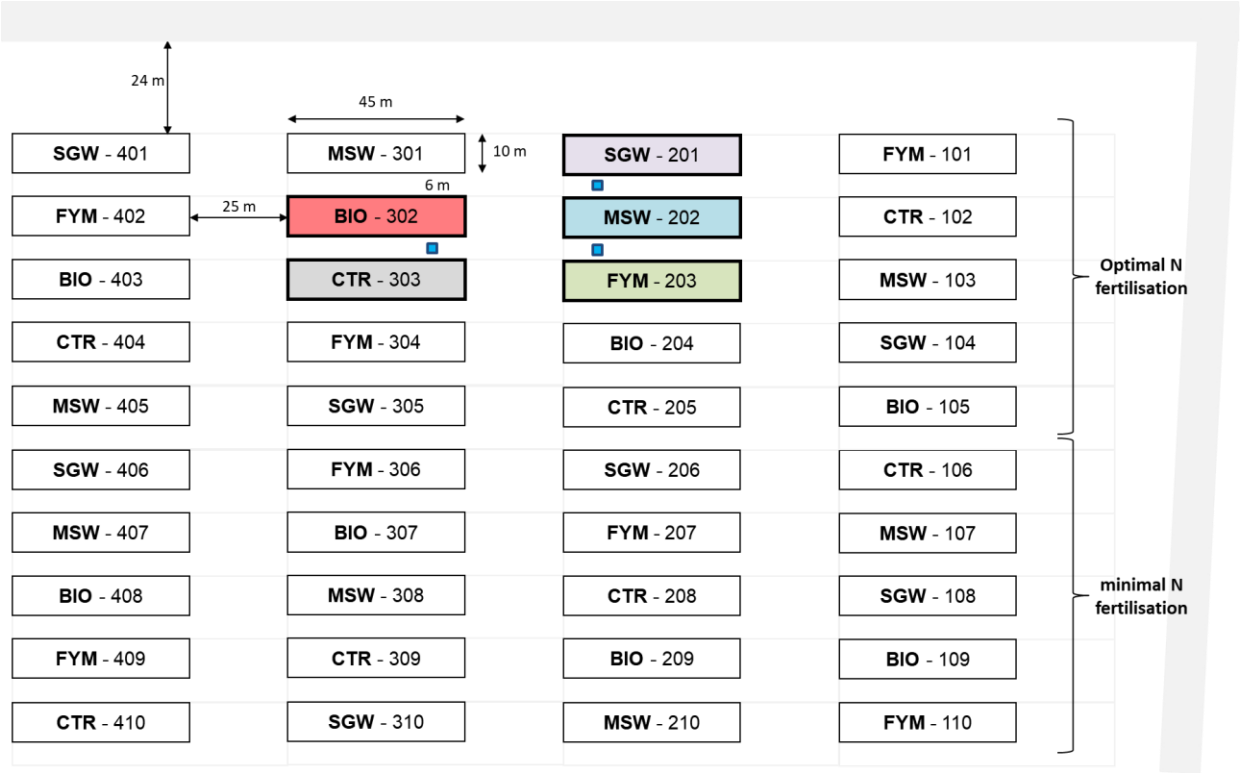


Figure 1. Plan of the QualiAgro field experiment *(thick coloured rectangles show plots equipped for hydrodynamic monitoring and leachate samplings).* ***SGW****: compost of sewage sludge with green waste and wood chips;* ***BIO****: compost of biowaste and green waste;* ***MSW****: compost of organic fraction of municipal solid waste;* ***FYM****: farmyard manure of dairy cows on straw;* ***CTR****: control soil without amendments*

Every year before mechanical harvest, yield measurement and sampling of grain and aerial part have been performed by using a pattern 10 times in each plot. The plough layer (0-28 cm) of each plot has been sampled every two years just before spreading amendments, so that data sets for the present study include soil analyses until 2015 and OWP analyses until 2013. Soil sampling was performed manually, 40 composite samples being prepared from 10 spadesful across each plot. From preliminary estimations of OM, spreaders were adjusted on side areas of the field by using lines of rugs and trays and portable scales. OWP were carefully sampled during spreadings, providing three composite samples of each

applied OWP for analyses and storage. Applied OWP were rapidly incorporated by surface stubble ploughing and later, in October, more deeply by ploughing at 28 cm.

2.2. Methods of analysis

Most analyses of soils and amendments were performed by the LAS (Laboratoire d'Analyses des Sols, INRA, Arras, France), which is accredited according to NF ISO/CEI 17025 for soil analyses. The LAS applied the same Quality Controls and validation methods for OWP and soils (NF T 90-210).

Soil samples were prepared according to norm ISO 11464. Total C and N were determined by catalysed combustion-oxidation (ISO 10694). Total carbonate expressed as $CaCO_3$ was measured by a volumetric method (ISO 10693). Other total analyses were performed by ICP-AES or ICP-MS after heating at 450 °C and complete digestion in HF-$HClO_4$ (NF X 31-147). pH was measured on a 10 g aliquot dispersed in pure water (ISO 10390). Cation exchange capacity (CEC) was measured by the Cobaltihexamine method (ISO 23470). The potentially available fraction of trace metals in soil and composts has been evaluated by the ''BCR'' method (Quevauviller, 1998). Beyond EU standardisation attempts, EDTA at moderate concentration has been often recommended to extract sorbed TM (Degryse et al.'s review, 2009). We retained the concentration 0.05 $mol.L^{-1}$ and the soil:solution ratio 1:10 of the BCR method in order to avoid a possible lack of chelating agent in case of abundant calcium carbonate (Manouchehri et al., 2006), which was the case of some studied OWP. The readily available or soluble metals were extracted in 0.01 M $CaCl_2$ solution (ratio 1:10, shaking 2 h, norm NEN 5704 in NL; Houba et al., 1990; Lebourg et al., 1996). Many studies correlated this fraction, for certain trace metals, with their concentrations in soil pore water (Degryse et al., 2003), their effects on organisms (Beaumelle et al., 2014) or their uptake by plant (e.g., Nolan et al., 2005).

196 OWP samples were freeze-dried, ground and sieved at 5 mm. Total C was analysed like for
197 soils. The carbonate content was also analysed and, when significant, inorganic C was
198 subtracted from total C to get the organic C. Total metal contents were obtained after the
199 same digestion method than soil samples, and then by ICP-AES (ISO 2203).
200 All chemical contents were expressed per dry weight (DW) at 105°C, according to norms
201 ISO 11465 and NF U 44-171 for soils and amendments, respectively.
202 *2.3. Data treatments*
203 Variations of extracted TM according to OWP types were interpreted by ANOVA and
204 Newman-Keuls comparisons (α = 5%) applied on all data (6 years), after testing the
205 normality of residues and equality of variances by Shapiro and Levenne tests. In cases far
206 from these conditions, Kruskal-Wallis and Dunn tests were applied. For results on topsoils,
207 the same procedure was applied to compare plots submitted to the 5 modalities, on data
208 gathered per year of sampling. More precisely, topsoil was sampled and analysed every two
209 years in the 8 plots per modality, but between 2009 and 2013, TM have been analysed only
210 in the 4 plots of the half-part +N.
211 Simple linear regressions were calculated between selected TM fluxes and stocks of
212 mobilisable TM in topsoils. The detailed calculations are explained in part 3.5. Multiple
213 linear regression studies were performed between soluble metals and other soil properties.
214 For these calculations, means from the 4 blocks were used rather than all soil data to
215 improve the accuracy of studied variables and avoid factor interactions. Another choice has
216 been to select EDTA-extractable metals rather than total metals as possible explicative
217 variables. EDTA-extractable metals may represent the “labile” (Degryse et al., 2009) or
218 reactive (Groenenberg et al., 2017) fraction in equilibrium with solubilised metals in 0.01
219 M $CaCl_2$. Then, logarithms of variables were preferred to untransformed variables (pH
220 being already considered as the log of a variable), for statistical and mechanistic reasons:

linear log-relationships correspond to ratios between metal concentrations and soil reactive constituents, which may be related to chemical equilibrium equations (McBride et al., 1997). Preliminary statistical treatments, including calculations of 3^{rd} and 4^{th} order moments, showed some discrepancies with hypotheses of normal distributions but much less for log-transformed variables than for untransformed ones. Finally, two MLR approaches have been followed, likely to lead to different predicting equations:

(i) explaining variations of log(soluble TM) by variations of log(M_{EDTA}), pH, etc.,

(ii) forcing a proportionality between $CaCl_2$-extracted and EDTA-extracted TM through the calculation of distribution coefficients Kds and explaining log(Kd) by major soil variables (Sauvé et al., 2000; Groenenberg et al., 2010).

More precisely, Kd coefficients were calculated as ratios of mobilisable on soluble TM, expressed respectively in $mg.kg^{-1}$ of soil and $mg.L^{-1}$ of extracting solution.

3. Results

3.1. Major characteristics of spread composts and manure

Results related to major components likely to interact with the fate of trace metals (TM) are presented in Table S1 (Supplementary Material), taking over previous articles on the same site (e.g., Obriot et al., 2016). FYM and MSW were generally richer in organic C than SGW and BIO. Consequently, with the target of 4 Mg $C.ha^{-1}$ per spreading, applied loads have been lower with FYM and MSW. The resulting average inputs of organic Carbon stand between 2.0 and 2.3 $Mg.ha^{-1}.year^{-1}$ for MSW and SGW composts respectively, and at 2.1 $Mg.ha^{-1}.year^{-1}$ for BIO composts and FYM.

On another side, organic matter of OWP can be characterised by its ratio C/N and the index of residual organic C (I_{ROC}) expressing its stability after incorporation to soil. They show the following orders (Noirot-Cosson et al, 2016):

C/N: BIO ≈ SGW < FYM < MSW

246 I_{ROC}: BIO ≈ SGW > FYM > MSW.

247 With respect to other major constituents, BIO and MSW composts are richer in carbonate
248 than FYM and SGW. SGW contains two to three times more P than the other amendments.
249 SGW and BIO contain about twice more Fe than MSW and FYM.

250 *3.2. Total contents in OWP and inputs of trace metals*

251 TM contents with respect to regulations: All applied SGW composts presented TM
252 contents lower than thresholds enforced in France since 2002 for sewage sludge composts,
253 defined in norm NF U 44-095. Applied MSW composts overpassed the limits imposed
254 since 2006 to other types of composts (NF U 44-051), several times before 2006 and once
255 in 2013, precisely for Zn in MSW (Table S1-B). Over the years, an overall decrease of
256 concentrations of most TM was observed in the different products, except for SGW
257 composts. Therefore, in order to assess amendments with respect to potential accumulation
258 of TM in soil, comparing average annual inputs appeared more adequate than total contents
259 which have varied. We can see that:

260 - Cd inputs have been similar with all amendments;
261 - Pb inputs have been similar through spreadings of BIO, MSW or FYM, and lower
262 via SGW applications;
263 - but SGW have carried more Cu and Zn than the other products;
264 - MSW, besides Pb already mentioned, also input a relatively high amount of Cr;
265 - BIO, besides Pb, carried more Ni and Mn than the other products during the studied
266 period.

267 Comparison between average inputs of TM and regulatory limits: spreading of SGW
268 composts overpassed the limits for Cu and Zn, with respectively 1501 and 3500 $g.ha^{-1}.year^{-1}$
269, higher than the respective maxima of 1000 and 3000 $g.ha^{-1}.year^{-1}$ (10 000 and 30 000
270 over 10 years: Table S1-B). BIO and MSW composts brought slightly too much Pb, just

above the regulatory limit of 900 $g.ha^{-1}.year^{-1}$. In summary, the intensive applications of OWP have induced inputs of TM lower or close to the regulatory limits, except for Cu brought by SGW composts which exceeded the limit by 50%.

3.3. EDTA-extractable metals in composts and manure, and induced inputs to soil

From 2004 to 2013, we applied EDTA and $CaCl_2$ extractions to OWP, using the same triplicate samples as those used for major and trace element analyses. The six trace metals analysed after EDTA extractions have always been above quantification limits and the repeatability was generally satisfactory (124/144 data with CV < 25%, MSW being the matrix with the highest dispersion).

Among amendments, SGW generally showed the highest contents of Cd_{EDTA}, Cu_{EDTA} and Zn_{EDTA}, and induced the highest inputs to soil (Table 2). MSW showed relatively high contents of Cr_{EDTA} and Ni_{EDTA} and induced the highest inputs of these metals. Pb_{EDTA} was similar in the four products, standing in average between 24 $mg.kg^{-1}$ (in BIO) and 35 $mg.kg^{-1}$ (in FYM) and induced inputs between 180 and 260 $g.ha^{-1}.year^{-1}$ (from FYM). So, except for Pb_{EDTA} in FYM, the amendments BIO and FYM presented the lowest average contents and induced the lowest inputs of EDTA-extractable metals.

Now among EDTA-extractable metals, the following sequence was observed, similar to the order of total contents: Zn > Cu ≥ Pb > Ni > Cr > Cd (Table 2). Zn, Cu and Pb have been also noticed as the trace elements mostly extracted by chelating agents in composts by Paradelo et al. (2011b). Some strong correlations exist between EDTA-extractable metals, especially between Cr_{EDTA} and Ni_{EDTA} on one side, Cd_{EDTA} and Zn_{EDTA} on another side, what reminds correlations often observed between TM total contents in soils (Baize et al., 2007). Temporal variations occurred along the period 2004-2013, but without the clear decreasing trend found for total metal contents of OWP.

295 EDTA extractabilities, in % of total contents, followed a distinct sequence, almost constant
296 through years and for the four types of amendments (Table S2):

297 $Cd \geq Zn \geq Pb \geq Cu > Ni > Cr$.

298 *3.4. Evolution of EDTA-extractable metals in topsoil and effect of treatments*

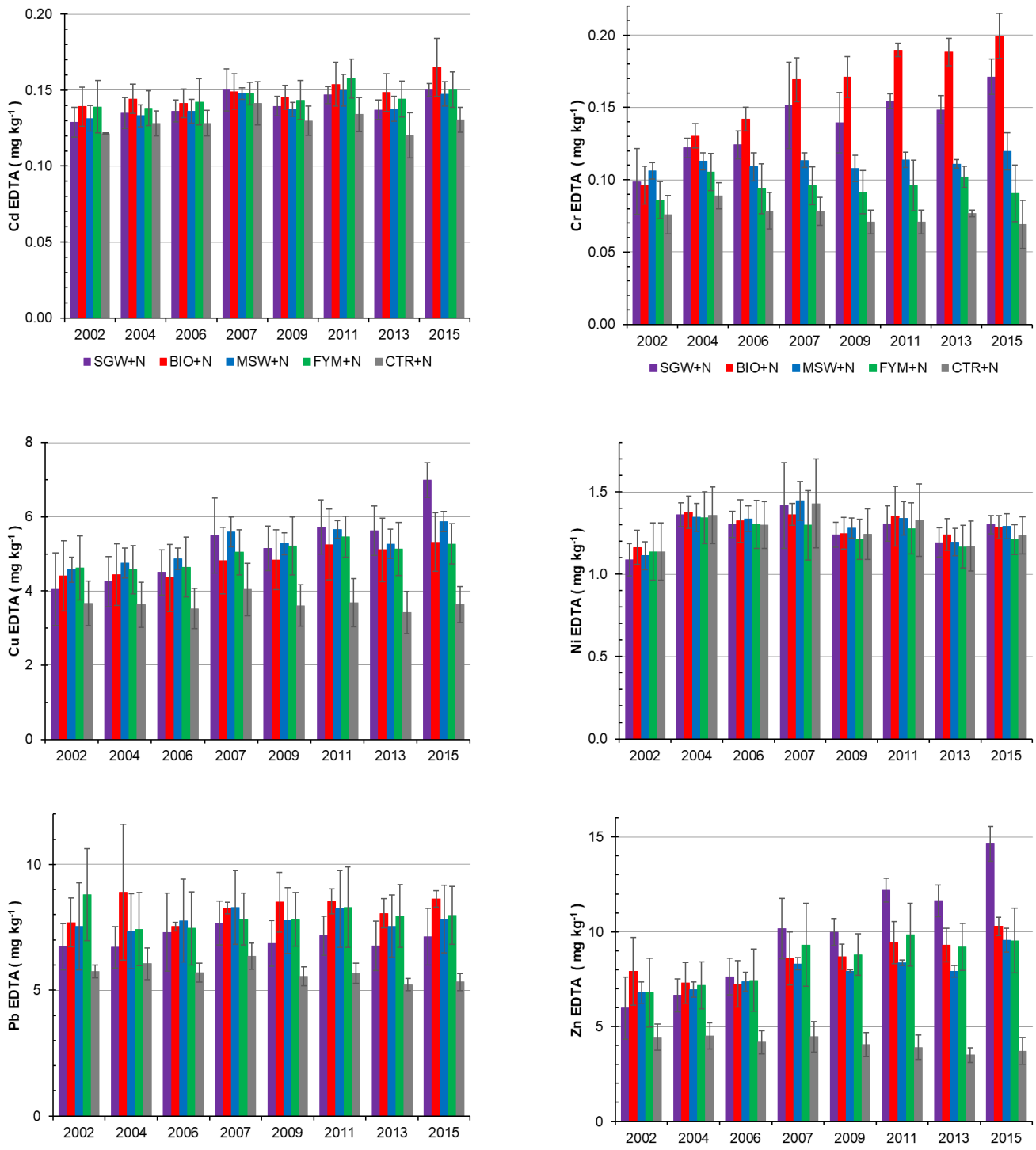
299 Figure 2 shows the absolute concentrations of EDTA-extractable metals ($mg.kg^{-1}$ dry soil)
300 for the plots "N optimal" (n=4), whereas Table S3-A includes the results of statistical
301 comparisons between treatments for all available data. The effects of treatments differ
302 between TM:

303 Cd_{EDTA}: there was a trend of higher values in amended plots with respect to the control, but
304 significant differences appeared only with BIO in 2004 and 2006, in 2013 with BIO and
305 FYM, and for all amended plots in 2015.

306 Cr_{EDTA}**:** data often presented dispersion and deviations from hypotheses supporting
307 parametric comparisons. Nevertheless, a positive influence of amendments, especially of
308 BIO and SGW, can be deduced from non-parametric tests and Fig. 2.

309 Cu_{EDTA}**:** a significant difference appeared in 2004 between MSW and the control plots.
310 From 2006, Cu_{EDTA} has been significantly higher in all amended plots compared to CTR,
311 without differences between amended plots until 2015. This last year, more differentiations
312 occurred, with SGW at the highest level.

313



314 **Figure 2. EDTA-extractable metals in the plough layers (plots +N) versus sampling year and treatment**
315 – vertical bars present standard deviations between blocks (n=4) – Legend of treatments in 1st row (+N = in
316 the half-part with optimal N fertilisation; SGW: compost of sewage sludge with green waste and wood chips;
317 BIO: compost of biowaste and green waste; MSW: compost of organic fraction of municipal solid waste;
318 FYM: farmyard manure of dairy cows on straw)
319

320 Ni_{EDTA} never appeared influenced by treatments, except at last in 2015, when considering
321 the whole data giving mean values of 1.33 and 1.21 $mg.kg^{-1}$respectively for SGW and FYM
322 (Table S3-A).
323 Pb_{EDTA}: as for Cd but more often, we observed higher values in plots treated with BIO and
324 FYM, and less often with MSW, compared to the control, and finally in 2015 all amended
325 plots above CTR.
326 Zn_{EDTA} followed the same trends as Cu but with larger amplitude, becoming in amended
327 soil twice or three times higher compared to CTR (Fig. 2). Indeed, Zn_{EDTA} slightly
328 decreased with time in CTR+N plots, and differences between some amended plots and
329 CTR became non-significant some years after 2009, according to non-parametric statistics.
330 In 2015, Zn_{EDTA} in SGW plots became significantly above other amended plots.
331 Overall, EDTA-extractable fractions represented about 60% of total Cd in topsoil, 30% of
332 total Pb or Cu, 10-20% of total Zn, less than 10% of total Ni, and around 0.2% of total Cr
333 (Table S3-B). The differences between treatments appeared attenuated when expressed
334 in %: only MSW plots from 2006 and the other amended plots from 2013 showed
335 higher $\%Cu_{EDTA}$ than CTR. Zn extractability seemed also less influenced by treatments
336 than Zn_{EDTA} absolute values, but it appeared clearly higher in amended plots than in CTR
337 from 2004, and significantly higher in SGW compared to the other treatments from 2009.
338 Pb showed a significantly higher extractability in BIO plots for 6 sampling years and in
339 FYM plots for 3 years, compared to control. Cd extractability showed no significant
340 differences between treatments. Ni extractability, as Ni_{EDTA} contents, hardly appeared
341 influenced by amendments.
342 *3.5. Relationships between EDTA-extractable metals in the amended soil layers and their*
343 *inputs from amendments*

Stocks of EDTA-extractable TM contained in plough layers were calculated from mean metal contents per treatment and an average mass of 3800 $Mg.ha^{-1}$ (Michaud et al., 2018). The variations of these stocks along 2004-2015 were at first compared to cumulated inputs of EDTA-extractable TM from each OWP (part 3.3). Significant correlations were found (not shown) but a finer study was pursued by correcting these inputs according to a few rational hypotheses and estimations:

- crop uptake of TM, determined by yield and plant organ contents, were assumed to be removed from EDTA-extractable pools of the plough layers;
- a second output from these pools, due to leaching, was estimated from monitoring waters collected by 10 lysimeters (two per equipped plot; Fig. 1) during the period 2012-2015 (Cambier et al., 2014);
- minor inputs due to atmospheric diffuse deposits were also assumed EDTA-extractable and estimated from relevant references (Belon et al. 2012; Michaud et al., 2018).

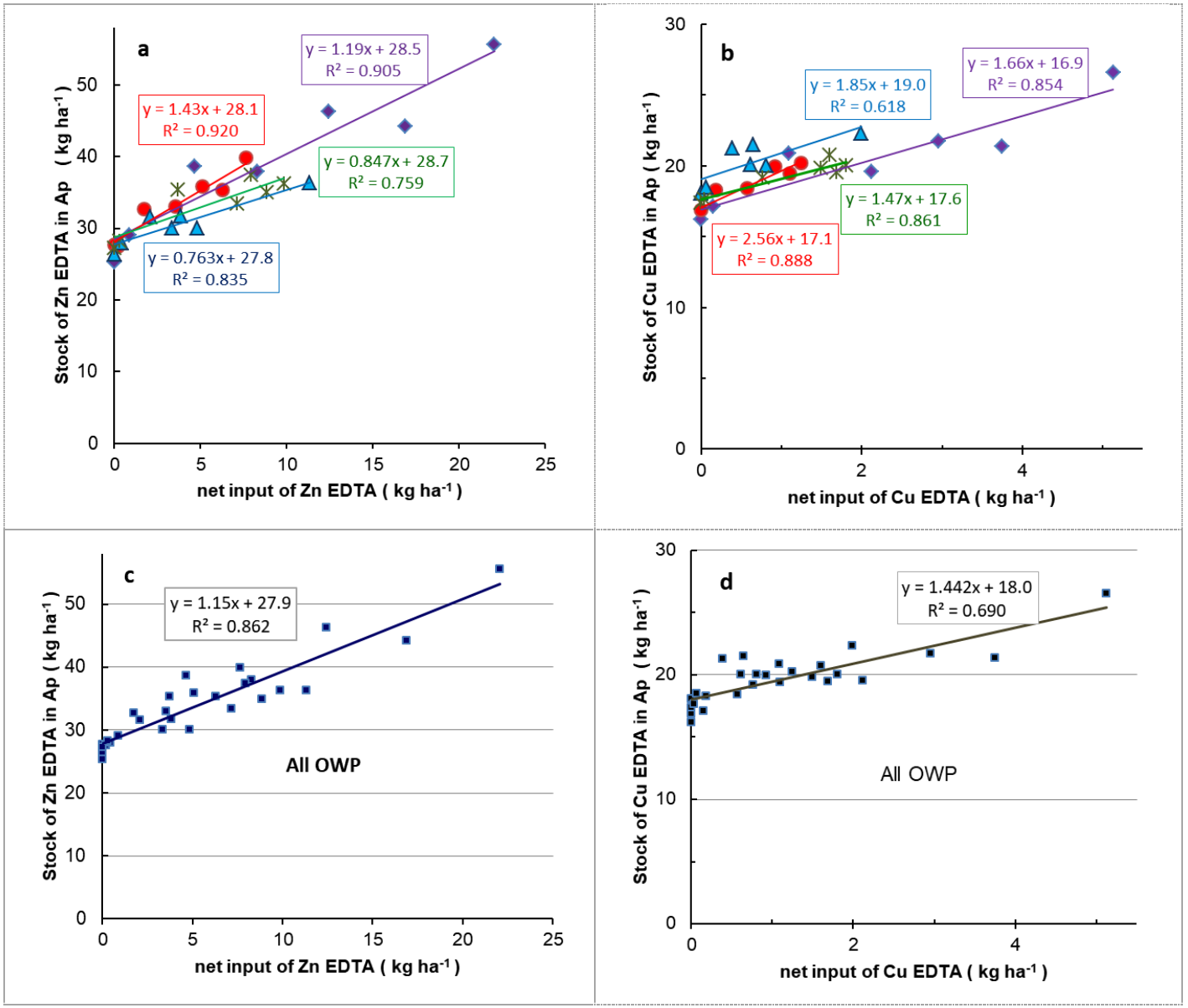
The two last fluxes are only estimated but each one represents less than 11% of inputs by OWP for Cd, Cu, Pb and Zn and they are opposite. About crop uptakes, their ranges in % of OWP inputs are 3-5% for Cd, 5-19% for Cu, 9-23% for Zn; 0.4-0.6% for Pb, 6-25% for Ni, 10-56% for Cr. So, these calculations present uncertainties, especially for Cr and Ni in the case of FYM low in these metals. But they provide net inputs of potentially available metals more relevant for comparisons with variations of EDTA-extractable metals in soil than the raw inputs from OWP.

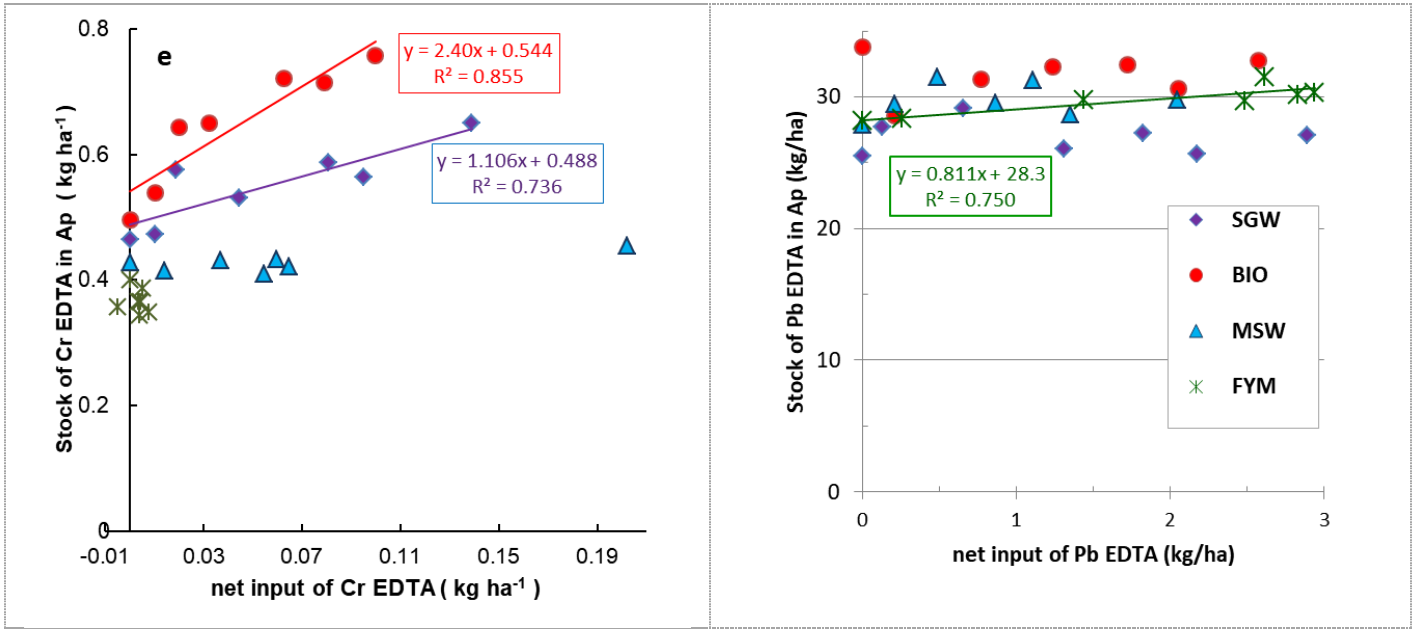
Figure 3 presents the relationships obtained between the field stocks of EDTA-extractable TM and the net inputs explained above. It has to be taken into account that soil sampling always occurred just before spreadings, so that for example spreading of 2004 have impacted the soil stocks determined in 2006, and soil samples analysed in 2015 have been

369 impacted by spreadings until 2013. The graphs comply with this shifted correspondence.

370 They call for the following comments:

371


a
y = 1.19x + 28.5
R² = 0.905
y = 1.43x + 28.1
R² = 0.920
y = 0.847x + 28.7
R² = 0.759
y = 0.763x + 27.8
R² = 0.835
Stock of Zn EDTA in Ap (kg ha-1)
net input of Zn EDTA (kg ha-1)
b
y = 1.66x + 16.9
R² = 0.854
y = 1.85x + 19.0
R² = 0.618
y = 1.47x + 17.6
R² = 0.861
y = 2.56x + 17.1
R² = 0.888
Stock of Cu EDTA in Ap (kg ha-1)
net input of Cu EDTA (kg ha-1)
c
y = 1.15x + 27.9
R² = 0.862
All OWP
Stock of Zn EDTA in Ap (kg ha-1)
net input of Zn EDTA (kg ha-1)
d
y = 1.442x + 18.0
R² = 0.690
All OWP
Stock of Cu EDTA in Ap (kg ha-1)
net input of Cu EDTA (kg ha-1)



373

374 **Figure 3**. Relationships between the stocks of EDTA-extractable TM in plough layers and inputs of EDTA-extractable TM carried by OWP corrected
375 by other vertical fluxes (crop uptake, leaching, atmospheric deposits) – Legends of treatments in last graph (SGW, BIO; MSW; FYM explained in
376 Legend of Fig. 2)

377

$\underline{Zn_{EDTA}}$: the correlations between the cumulated balances and soil stock variations appear significant or highly significant for each treatment separately (the critical value for the two-tailed test on the Pearson coefficient, for n=7 and p = 0.05, is 0.75, hence $R_{critic}^2 = 0.569$; and $R_{critic}^2 = 0.904$ for p = 0.001). Another important result concerns the slope of the linear regression, which stands between 0.76 and 1.43 (Fig. 3a). Fig. 3c shows the highly significant correlation obtained from all data together (n = 28, R^2= 0.86), with a regression slope equal to 1.15.

$\underline{Cu_{EDTA}}$: similar correlations were found ($R^2 > 0.62$), but the regression slopes are higher than for Zn_{EDTA}, i.e., between 1.47 and 2.56. When all data corresponding to the four OWP are gathered, the correlation is highly significant with $R^2 = 0.69$ (n=28) and a slope 1.44 (Fig. 3d). This later dataset and other apparently curved relationships have been also tested using a 2nd order polynomial regression, which hardly increased R^2.

$\underline{Cr_{EDTA}}$: only two significant correlations appeared (Fig. 3e), with SGW compost applications, inducing variations of stocks in the plough layers approximately equal to the cumulated balance of fluxes ($R^2 = 0.74$; slope 1.11), and with BIO compost applications, increasing Cr_{EDTA} stocks faster than the cumulated balance of fluxes (slope 2.4).

Other TM studied: a few significant correlations were found between soil stocks of EDTA-extractable metals and cumulated flux balances, for Cd_{EDTA} in the case of BIO composts ($R^2 = 0.68$; regression slope 2.5; not shown), and for Pb_{EDTA} in the case of FYM ($R^2 = 0.75$; slope 0.81). Ni_{EDTA} showed a significant correlation only in the case of FYM, with an unexpected negative slope.

Non-linear regressions have been attempted, which fitted better the data in a few cases, e.g., a 2nd order polynomial for Cr_{EDTA} in BIO treatment, but most often they hardly increased R^2 and always appeared difficult to interpret. By contrast, linear regressions with a slope close to 1 indicate a conservative behaviour: inputs of especially Zn_{EDTA} of compost in a

cultivated soil would be added to the soil Zn_{EDTA} pool without much transfer from or to the non-extractable fraction quantifiable by the difference $Zn_{TOT} - Zn_{EDTA}$. Of course, soluble fractions exist in composts and in soils, *a priori* highly reactive during and after amendment incorporation, but due to their low weight, they would not hinder the relationships illustrated by Fig. 3a and 3c.

Cu_{EDTA} showed higher regression slopes compared to Zn_{EDTA} (Fig. 3a-d). This could be due to a part of non EDTA-extractable Cu, contained in biodegradable particles of OWP, becoming extractable in soil after amendment as their mineralization proceeds. This process would be less important for Zn which is proportionally less associated to organic phases compared to Cu (Ashworth and Alloway, 2004; Paradelo et al., 2017; 2018). Finally, it is noteworthy that for Zn, Cu and Cr, EDTA-extractable metals carried through BIO composts seem to induce higher increases of EDTA-extractable metals in soil, compared to other amendments. The regression slope for Cd_{EDTA} related to BIO treatment is also relatively high, *c.* 2.5, but comparisons cannot be done with other treatments which showed non-significant correlations.

3.6. Results of $CaCl_2$ extractions on OWP

The application of these mild extractions to OWP led to relatively precise and meaningful data for the six analysed TM, coming across only 7 values < QL (for Cr or Pb in SGW composts). Variation coefficients were lower than 20% 116 times out of 144 determinations. The absolute values of $CaCl_2$-extractable, say soluble metals, followed a slightly different sequence compared to total and EDTA-extractable contents: Zn ≈ Cu > Ni > Cr ≈ Pb > Cd (Table 3). On another side, $CaCl_2$ extractability (% of total metal) was much lower than in EDTA (Tables S4 and S2), and followed another sequence: Ni ≥ Cu ≥ Cd ≥ Zn > Cr ≥ Pb, with especially a high extractability of Ni and Cu in MSW and FYM.

Among OWP, MSW composts showed the highest soluble fractions (in µg.kg^{-1} DW), followed by FYM which presented noteworthy high soluble Pb and Cd contents. Based on $CaCl_2$ extractability (% of total), MSW composts and FYM were also above BIO and SGW composts. In order to understand these differences, one must consider the variable pH, measured in water (Table S1-A) and in the $CaCl_2$ extracts (Table 3), as well as dissolved organic carbon (DOC) which has been analysed once, in 2013. FYM generally presented the highest pH and SGW the lowest. So, differences of pH between OWP cannot explain the observed differences for $CaCl_2$ extractable metals. On the contrary, DOC in $CaCl_2$ extracts ranked SGW and BIO in low DOC producers, FYM and even more MSW in high producers. Thus, DOC could play a role in the differentiation between the soluble TM of these two groups of OWP.

3.7. Results of $CaCl_2$ extractions in soil

The results on $CaCl_2$-extractable or soluble TM in soil, further written, e.g., Zn_{CaCl2}, were different from those obtained with EDTA on several aspects. First of all, extractability was very low, under 1%, except for Cd_{CaCl2} which reached 8% of total Cd.

The least soluble metals were Cr and Pb, known as seldom mobile in arable soils, with $CaCl_2$ extractability <0.03%. Indeed, Cr_{CaCl2} was always under quantification limits, so that eventual effects of organic amendment or evolution with time cannot be ascertained. Pb_{CaCl2} was also often < QL but its partial quantification showed a trend of higher mobility of Pb in CTR, followed by SGW and FYM (Table S5). The lower mobility of Pb in amended plots with respect to unamended ones can likely be due to higher SOC contents (Smith, 2009; Paradelo et al., 2011a).

Concerning Cd and Ni, this trend of higher soluble TM in CTR plots appeared more clearly, although progressively (Fig. 4; Table S5): soluble Ni and Cd have become significantly higher in control than in amended plots between 2006 and 2009. Ni_{CaCl2} has been often

<QL in the first years but never in CTR plots from 2006 (Fig. 4). Other differences between treatments concern BIO plots which provided less soluble Ni and Cd than the other treatments, and SGW which often stood above the other amended plots.

Concerning soluble Zn, despite non-monotonous variations, it gradually decreased with BIO and MSW treatments, but remained high in SGW and CTR plots (Table S5; Fig. 4). Zn_{CaCl2} was significantly higher in SGW than in all other modalities in 2002; then from 2006, it became higher in both SGW and CTR than in BIO and MSW, and also above FYM later on, suggesting the following overall order, almost opposite to pH measured in $CaCl_2$ extracts (Table S5):

BIO < MSW < FYM < CTR ≤ SGW

In brief, soluble Cd, Ni and Zn always appeared lower in amended plots than in control ones, except for Zn in SGW plots.

Soluble Cu presented a completely distinct behaviour, MSW plots appearing significantly above CTR as soon as 2002 (but not in 2004), and all amended plots above CTR from 2006. Other less systematic differences between treatments occurred, leading to the following trend for soluble Cu (Fig. 4):

CTR ≤ BIO ≤ FYM ≤ SGW = MSW

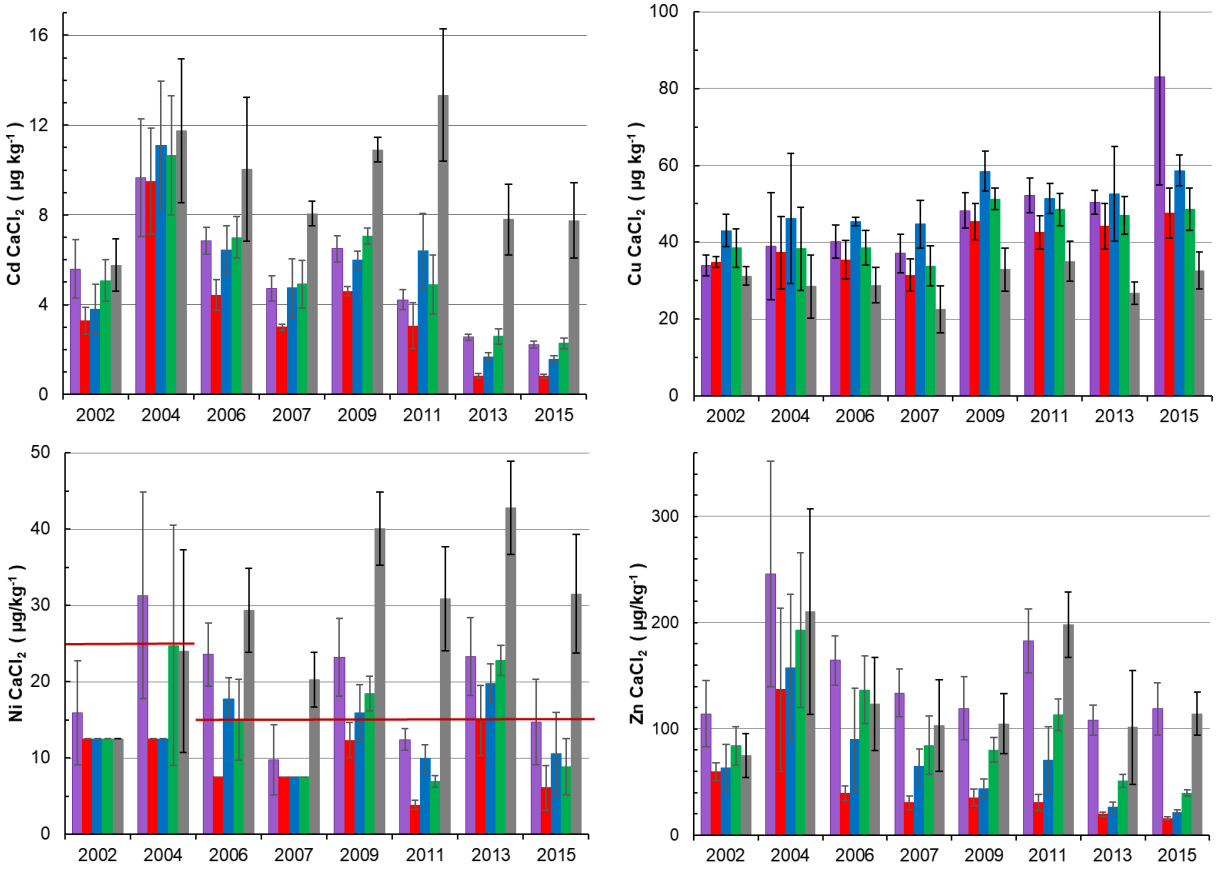


Figure 4: $CaCl_2$ extractable Cd, Cu, Ni and Zn in topsoil of plots +N: SGW, BIO, MSW, FYM, CTR from left to right every sampling year (means from the 4 blocks; vertical bars show Standard-Deviations; horizontal red segments show QL of soluble Ni; some values <QL arbitrarily set at QL/2) – +N, SGW, BIO; MSW; FYM, CTR explained in Legend of Fig. 2

Variations of soluble fractions in soil cannot be interpreted like for EDTA fractions from inputs of $CaCl_2$-extractable metals present in composts and manure. These minor and mobile fractions react fast with all solid phases, and their variations look like an attenuation by amendments, at least for Cd, Ni, Zn and Pb. So they must be related to changes of pH and other retention factors, themselves linked to the input of OWP components.

Concerning pH, measurements have been conducted as standard analyses of soil pH in H_2O (pH_{H2O}) and, from 2004, on $CaCl_2$-extracts, from the same soil samples representative of the plough layer of each plot. The results appear strongly correlated ($R^2 = 0.96$, slope 0.98; Fig. S1) and show the same trend between treatments, i.e., BIO ≥ MSW ≥ FYM ≥ SGW ≥ CTR. This order did not match exactly the order of pH of OWP, but rather their carbonate contents (Table S1-A). For soil samples, highly significant negative correlations were found between pH_{H2O} or pH_{CaCl2} on one side, and soluble Cd, Ni or Zn on another side, for plots + N or for all plots.

Concerning soil organic C (SOC), it was positively correlated with Cu_{CaCl2} (R=0.66, n = 40 pairs of mean values related to plots +N, or n = 65 for all treatments), and negatively correlated with soluble Cd or Ni. Cd_{CaCl2}, Ni_{CaCl2}, as well as Zn_{CaCl2}, were also negatively correlated with CEC, whereas Cu_{CaCl2} was positively correlated to CEC. These correlations suggest a contrasting effect of organic matter on metal mobility, driven by the different fractions of OM involved and the solubility of organometallic complexes: an increase of mobility in the case of Cu, related to the formation of soluble complexes with dissolved OM, and a reduction in the other cases, due to a low solubility of the complexes formed or a preference of Cd, Ni and Zn for insoluble OM fractions.

3.8. Modelling relationships between soil variables and soluble TM

For further interpretation and possible prediction of TM mobility in these amended soil horizons, and taking into account the numerous studies on this topic (Sauvé et al., 2000;

Groenenberg et al., 2010; Tipping et al., 2003; Degryse et al., 2009; Rodrigues et al., 2010), we attempted multilinear regressions (MLR) between each quantified soluble metal and selected soil variables, as described in part 2.3 of Materials and methods. . We always tested one of the two pH values among explicative variables, but not the two together, SOC, CEC, but not clay content since it is unlikely that texture has been influenced by treatments. Many other soil variables like N or P contents, electrical conductivity, etc., which are influenced by treatments and are partly correlated (Obriot et al., 2016) have not been used.

MLR equations were selected through a step by step approach, starting from models with all explicative variables, and suppressing terms without statistically significant influence. For modelling log (Kd), only pH, log of SOC and CEC were considered.

Cadmium: using pH_{CaCl2} led to exclude Cd_{EDTA} from variables explaining Cd_{CaCl2}. Using pH_{H2O} led to the first equation reported in Table 4, expressing the highly significant influence of SOC and pH on Cd_{CaCl2}, and excluding CEC. Such formula can be transformed into a Freundlich equation, whose the exponent here equals about 0.41 (Cd_{EDTA} would increase as $Cd_{CaCl2}^{0.41}$). To get a linear model for predicting Cd_{CaCl2}, we should consider the first Kd model of Table 4, which still shows the influence of pH and SOC, and explain 65% of the variations of log(Kd):

$$\log (Kd_{Cd}) = -2.85 + 0.323 \times pH_{H2O} + 2.71 \times \log(SOC) \quad (8)$$

Copper: a simple equation has been obtained for all data, without significant influence of soil major variables. Reminding the units of fractions in Table 4, it can be transformed into:

$$Cu_{solution}\ (\mu g/L) = 0.617 \times Cu_{EDTA}\ (mg/kg)^{1.21} \quad (9)$$

This is not far from a linear model, which was confirmed when looking for a Kd model: no significant influence of pH, SOC or CEC was found. The mean or median Kd value can serve as well as a simple model (Table 5). Both models represent the measured Cu_{CaCl2} with

reasonable accuracy, with a MAE (mean absolute error) around 10% of the mean value (Table 4). For the other metals, regression models induce MAE around 30% of mean values.

Nickel: $\log(Ni_{CaCl2})$ was found with an inconsistently negative influence of Ni_{EDTA}. A more consistent and statistically acceptable model included log(SOC) and pH_{CaCl2} as independent variables, without Ni_{EDTA}. The Kd approach forcing the linear dependency between extracted Ni fractions led to functions of pH or of SOC and pH (Table 4) explaining 56% or 58% of Kd variations. Remind us that no significant influence of treatments was found upon Ni fractions, and that part of Ni_{CaCl2} values were < QL.

Zinc: MLR applied on $\log(Zn_{CaCl2})$ led to interesting models based on independent variables $\log(Zn_{EDTA})$, pH_{H2O} and log (SOC), with R^2 = 68%, and an exponent of Zn_{EDTA} equal to 1.30. While looking for a linear model, the best equation was obtained by using pH_{H2O} and log (SOC), with R^2 = 81%:

$$\log(Kd_{Zn}) = -4.98 + 0.741 \times pH_{H2O} + 2.36 \times \log(SOC) \quad (10)$$

4. General discussion

Considering the EDTA, or potentially available fractions of TM in OWP, they are susceptible to be transformed in soil during days or years, due to mineralization-humification of OM, rhizosphere interactions, dissolution-precipitation or ageing of components such as carbonates and poorly-ordered oxides. We noticed that Cu_{EDTA} increased more in soil than the estimated input of Cu_{EDTA} and by comparison to Zn_{EDTA}. For instance, the regression slope 1.66 obtained for Cu in the case of SGW which introduced 5.4 kg/ha of Cu_{EDTA} after corrections from minor fluxes (Fig. 3b), suggests that 3.56 kg/ha (0.66×5.4) of unavailable Cu has become EDTA-extractable in amended soil layers between 2004 and 2015. One may relate this amount to the total Cu input via SGW, i.e., 19.4 kg/ha (Table S1): from these 19.4 kg/ha of total Cu, about 5.4 kg/ha were initially EDTA-extractable and 3.6 kg/ha became progressively extractable in soil. Doing the same

type of calculations with Zn in BIO plots (slope 1.43; Fig. 3a), we estimate that 22.4 kg/ha of total Zn have been input, including 8.7 kg/ha of Zn_{EDTA}, plus 3.7 kg/ha that became EDTA-extractable in soil. On the contrary in MSW plots (slope 0.76), 28.7 kg/ha of total Zn have been input, including 12.4 kg/ha of Zn_{EDTA} minus 3.0 becoming non-extractable. Of course, we cannot assert that transformations of unavailable to EDTA-extractable metals concern only those input through OWP; they may partly affect soil TM. But anyway, such transformations appeared lower with Zn than with Cu, and even could go in the opposite direction with Zn. This could be due at first to the stronger and larger association of Cu within organic particles, protecting this metal from extraction in OWP but then partly mineralised in soil. Such interpretation must be examined through the influence of treatment, since especially BIO stands out from the others by high regression slopes obtained for Cu, Zn, Cr and Cd. For Cd and Cr, possible comparisons between amendments are limited, and the reasoning is pushed further only for Cu and Zn.

Studying the dynamics of C and N in the same field experiment, Noirot-Cosson et al. (2016) underlined the opposition between the stable BIO and SGW composts and the more easily mineralised FYM and MSW, in the field like in the lab. For example, the storage of C in soil followed the order of I_{ROC}, the OM stability index reminded in Table S1-A, with little influence of the mineral N fertilisation except for the control plots. Yet, BIO and SGW induced the highest regression slopes for soil Cu_{EDTA} and Zn_{EDTA} versus inputs of corresponding available metals. So, even if OM mineralisation has been lower with BIO and SGW treatments, the increase of soil OM and the transfers between TM pools finally led to higher EDTA-extractable metals in plots BIO and SGW compared to FYM and MSW. The possible role of ageing processes between Zn and reactive oxides, well established between this metal and reactive oxides (Buekers et al., 2008; Sayen & Guillon 2014) can be interpreted in the same way. The higher contents of Fe and Mn in BIO

composts (Table S1) and the higher increase of soil pH by BIO amendments should enhance these processes of ageing and reduce the solubility of especially Zn (Buekers et al., 2008). However, they do not generate more unavailable, inert Zn, but rather more EDTA-extractable Zn. So, the results obtained from this long-term field experiment suggest that organic and inorganic phases carrying potentially available TM have been developed more by BIO and SGW than by the two other amendments. More investigation by speciation studies on selected samples from the field or from comparable systems driven in the lab would be necessary for a better understanding of involved components and processes.

Considering the soil soluble TM fraction quantified by 0.01 M $CaCl_2$ extractions, our results showed that variations of this fraction cannot be interpreted, nor predicted, without monitoring other variables in amended soils. At least, soil organic matter (SOM) and soil pH are influential factors of soluble Cd, Ni and Zn. And SOM and pH did vary versus the type and the number of amendments (Houot et al., 2009; Peltre et al., 2010; Obriot et al., 2016). Besides, we found a strong positive influence of the EDTA fraction on the soluble fraction for Cu and Zn, TM which have increased the most with repeated amendments. This strengthens the hypothesis of sorption-desorption reactions between these two compartments (Degryse et al., 2009), and the search of possible equilibrium equations.

More discussion of the modelling results, including from the Kd approach of restricted applicability but suitable for comparisons of published values, is conducted below for each metal.

Copper: the nearly constant Kd of 1200 L/kg obtained for our samples is in the range of published values. Discrepancies may come obviously from sample sets, but also from the experimental approach of soil:solution equilibrium, i.e., from the definition of the two phases. For example, two noticeable works on Cu sorption by soils concluded with simple models similar to equation (9) written above:

601 $Cu_{solution} = 0.427 \times (Cu_{TOT})^{1.16}$ Gray & McLaren (2006) (n=74)

602 $Cu_{solution} = 0.891 \times (Cu_{TOT})^{0.76}$ McBride et al. (1997) (n=31, "GVD series")

603 A crucial difference between these equations and our equation (9) lies in the choice of total
604 soil Cu to express the adsorbed metal fraction in equilibrium with soluble Cu. Reminding
605 that Cu_{EDTA} represents about 30% of total Cu in our samples (Table S3-B), a substitution of
606 Cu_{EDTA} by $0.3 \times Cu_{TOT}$ in equation (9) shows that its predictions are a little lower than the
607 predictions of McBride et al.'s equation, below 60 $mg.kg^{-1}$. So, these two equations
608 converge, but our equation based on Cu_{EDTA} could be more relevant in case of low
609 contamination, when non-extractable Cu is relatively high.

610 McBride et al. (1997) fitted another MLR equation from a second larger data set, involving
611 the variables soil OM and pH. Other authors like McGrath et al. (1988), Fotovat et al.,
612 (1997), Römkens & Salomons (1998) noticed that the influence of pH upon the retention of
613 Cu by soils is relatively small when compared to the influence of SOM, or when Cu is
614 compared to Zn or Cd. On another side, the mobilising effect of OWP amendments on Cu
615 has been also highlighted, linked to the increase of complexing DOM (Zhou & Wong,
616 2001; Planquart et al., 1999) and Temminghoff et al. (1994) supported that the distribution
617 of Cu in liquid and solid phases is mainly determined by the distribution of OM, with ratios
618 Cu/OM similar in the two phases. Here, from monitoring two extractable fractions in
619 repeatedly amended soil horizons, we conclude that increased solubility of Cu is directly
620 determined by the increase of a reactive sorbed EDTA-extractable pool.

621 Cadmium: sorption-desorption of Cd on soils has been widely studied. Values of Kd(Cd)
622 summarized in Table 5 are of the same order, although often lower, than Kd(Cd) obtained
623 by Anderson & Christensen (1988), Welp & Brümmer (1999) or Andersen et al. (2002)
624 with soil samples not too far from our amended silt loam horizons. With respect to
625 experimental conditions, these authors measured soluble Cd in equilibrium solutions or in

626 aqueous extracts of low ionic strength, not in 0.01 M $CaCl_2$. Indeed, Degryse et al. (2003)
627 estimated that Kd deduced from 0.01 M $CaCl_2$ extraction should be multiplied by a factor
628 about 2, related to the importance of chloride complexes in the extracts, for better
629 predicting Cd concentration in soil pore water. This may explain the relatively low
630 coefficients found for Kd(Cd). Again, the varying definitions of adsorbed Cd, EDTA-
631 extractable or pseudo-total, can also intervene, but less than for Cu since Cd_{EDTA} represents
632 around 60% of total Cd (part 3.4).
633 When considering the pH dependency of log(Kd(Cd)) or log(Cd_{CaCl2}), the coefficients 0.35
634 or 0.32 (equation 8; Table 4) stand among the low values of corresponding coefficients
635 found by other authors: Anderson & Christensen (1988), Lee et al. (1996), Streck & Richter
636 (1997), Ingwersen et al. (2000), Sauvé et al. (2000), Römkens & Salomons (1998) and
637 Tipping et al. (2003) found values of 0.6, 0.5, 0.4, 0.4, 0.5, 0.34 and 0.20, respectively.
638 The dependency of Cd_{CaCl2} or Kd with SOC appeared higher than with pH when
639 considering the ranges of variations within our data set, i.e., [6.6, 7.8] and [9, 16] for pH
640 and SOC respectively. Everything else fixed, a pH increase from 6.6 to 7.8 would multiply
641 Kd(Cd) by a factor 2.4, and a SOC increase from 9 to 16 $g.kg^{-1}$ multiplies Kd(Cd) by a
642 factor 4.8 (equation 8). So, the influence of SOC on the mobility of cadmium in the plough
643 horizons of the field experiment is major, the influence of pH of second importance, and
644 Cd_{EDTA} hardly varied with treatments (Fig. 2). Thus the main process involved in Cd
645 mobility in this field experiment is the building up of soil organic matter in amended plots,
646 increasing their capacity to fix this metal on solid phases by comparison to unamended
647 plots (Fig. 4).
648 Zinc: Contrarily to Cd, Zn_{EDTA} showed large variations following repeated amendments
649 (Fig. 2). Soluble Zn was closely correlated to Zn_{EDTA} through a close to linear or a Kd
650 model (Table 4). Choosing the Kd model for easier comparisons, we noticed that the

651 coefficients of SOC are close for log(Kd_{Cd}) and log(Kd_{Zn}) (equations 8 and 10); SOC
652 variations between extrema of our dataset multiply log(Kd_{Zn}) by a factor close to 4 as for
653 log(Kd_{Cd}). But the higher coefficient of pH in equation 10 induces an increase by a factor
654 7.8 when pH increases from 6.6 to 7.8.
655 So, although Zn_{EDTA} approximately doubled with repeated amendments during 15 years and
656 that this would increase as well Zn_{CaCl2}, this impact was more than compensated, i.e.,
657 Zn_{CaCl2} became lower in amended soil than in CTR, due to increasing SOC and pH with
658 FYM, MSW or BIO composts (Fig. 2). In case of SGW applications, which increased SOC
659 but not pH, the increase of Zn_{EDTA} was approximately compensated by increasing SOC,
660 with respect to Zn_{CaCl2} variations. As for Cd, the respective roles of SOC, pH, and Zn_{EDTA}
661 on the mobility of Zn are quantitatively unravelled through using equation 10 or other
662 equations of Table 4.
663 When comparing this equation to published models fitted to other data set, the dependency
664 of Kd on pH was found a little lower by Degryse et al. (2003), and a little higher by
665 Anderson & Christensen (1988). The former authors attributed to soil pH more influence on
666 Zn sorption than to SOC, while the latter ranged at first pH and then CEC. Freundlich-type
667 equations of Koopmans et al. (2007), Luo et al. (2006) and McBride et al. (1997) selected
668 only pH among influencing soil variables; whereas soil organic matter was also included by
669 Sauvé et al. (2000) and by Tipping et al. (2003), and CEC by Thiele & Leinweber (2001).
670 So, many distinct functions between soil variables and soluble Zn can be found in the
671 scientific literature, but most of them did not distinguish the solid sorbed fraction from total
672 Zn, although geogenic Zn is often major and variable in soils. Here the EDTA fractions of
673 Zn varied from less than 10% of total Zn in CTR up to 21% in amended soil layers, i.e.,
674 much more widely than total Zn, and interesting relationships between soil Zn_{EDTA} and
675 inputs of Zn_{EDTA} from OWP have been found (Fig. 3).

Other TM: Considering Pb, we noticed that its EDTA fraction, as for Zn, was more significantly affected by OWP applications than its total content. We also found that Kd(Pb) defined from its EDTA and $CaCl_2$ fractions, beyond uncertainties linked to analytical limits for the latter, showed the highest variations among the five metals of Table 5. Nevertheless, we found no satisfactory MLR models for Kd(Pb) or for soluble Pb. In case of Ni, MLR equations were obtained, but with relatively low R^2, and from a data set which presents very little variations of Ni fractions, without influence of the treatments. So, we expect a narrow applicability of these equations.

5. Conclusion and perspectives of prediction of available trace metals

We have studied the availability of several trace metals in a long-term field experiment, designed for assessment of organic waste product applications to cultivated soils, by monitoring their mobilisable and soluble fractions operationally defined by EDTA and $CaCl_2$ extractions. We hypothesise that mobilisable metals brought via OWP could be added to EDTA-extractable pools of soil amended horizons. This was approximately confirmed for Zn, in average with the 4 types of OWP, and for Pb in one case of significant increase of Pb_{EDTA} in soil. But for Cu, the regression slope between net inputs and stock variations in soil was far from unity and varied with OWP types. The influence of OWP on the same regression slopes for Zn was also noticeable. Therefore, in order to predict the evolution of available metals in amended horizons, such relationships need further understanding, calling on inspired laboratory studies and/or complementary analyses of TM speciation in chosen samples of the field experiment.

Our second hypothesis was that soluble metals can be predicted by sorption models based on their mobilisable fractions and other soil variables. It has been supported to some extent and at least, such models help to unravel and quantify the influence of the different soil variables. For example soluble Cu appeared determined only by Cu_{EDTA}, which regularly

increased with all types of organic amendments, whereas soluble Cd decreased in soil with amendments, which can be attributed mainly to increasing organic matter. Of course, these trends depend on the studied system and collected dataset. Our field experiment considered 4 distinct important types of organic residues, and one type of soil-crop system representative of NW Europe agriculture in the 2000s. But OWP applications have been over common practices and inputs of a few trace metals got close to regulatory thresholds. Actually, in this context of agricultural OWP recycling, more and more field studies and modelling improve the predictions of soil organic matter (e.g., Peltre et al., 2010). There are also possibilities to predict the effect of organic amendments on soil pH and the accumulation of persistent contaminants through balance approaches (Zeng et al., 2017; Michaud et al., 2018). So that the relationships and the modelling presented in our work can complete the tools for assessing and predicting the effects of regular applications of organic residues on available trace metals in soils.

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Competing interests

The authors declare no competing interests.

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935 **Table 1. Chemical characteristics (total contents unless specified) of the initial soil plough horizon, sampled in 1998 in all sub-plots: means (standard**

936 **deviations; n = 40)**

		Texture ($g.kg^{-1}$)		pH H_2O	CEC	C organic	N total	P_2O_5 Olsen
	Clay	Silt	Sand		$cmol^{+}.kg^{-1}$		$g.kg^{-1}$	
	149 (9)	783 (8)	68 (4)	6.90 (0.23)	9.55 (0.65)	10.50 (0.66)	1.11 (0.05)	0.082 (0.016)
Trace Metals	($mg.kg^{-1}$)	Cd	Cr	Cu	Hg	Ni	Pb	Zn
		0.236 (0.013)	45.8 (2.8)	11.78 (0.96)	0.095 (0.015)	15.1 (0.8)	25.0 (3.5)	49.7 (3.4)
Referential*	"	0.30	44	12	0.05	19	26	55

937 * Surface layers of agricultural soils developed on loess of the Paris Basin: median values from 700 samples with < 21% clay (Baize et al., 2007)

938

939 **Table 2: EDTA-extractable metals in spread OWP** (Mean ± standard-deviation from 3 samplings; SGW: compost of sewage sludge with green waste and
940 wood chips; BIO: compost of biowaste and green waste; MSW: compost of organic fraction of municipal solid waste; FYM: farmyard manure of dairy cows
941 on straw), **average EDTA-extractable contents over 2004-2013** (small letters indicate significant differences between OWP types)**, average inputs per year**
942 (cumulated inputs divided by 11 years)

Trace Metal extracted by EDTA	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
			mg.kg^{-1} DW			
2004 SGW	0.172 ± 0.006	0.713 ± 0.073	12.2 ± 0.1	1.50 ± 0.01	6.76 ± 0.17	63.7 ± 2.5
2006 SGW	0.553 ± 0.012	0.756 ± 0.082	56.2 ± 2.8	2.15 ± 0.09	29.5 ± 1.18	227 ± 6
2007 SGW	0.634 ± 0.012	1.79 ± 0.12	69.7 ± 2.3	4.03 ± 0.25	40.6 ± 2.7	249 ± 13
2009 SGW	0.509 ± 0.064	2.21 ± 0.11	51.8 ± 1.3	4.51 ± 0.37	29.2 ± 0.3	255 ± 7
2011 SGW	0.638 ± 0.057	1.09 ± 0.14	61.1 ± 3.6	3.00 ± 0.17	23.8 ± 1.5	338 ± 14
2013 SGW	0.693 ± 0.015	2.40 ± 0.06	82.1 ± 2.1	3.06 ± 0.05	40.1 ± 1.8	316 ± 6
Average content (SD) n=6	**0.53 (0.19) (a)**	**1.49 (0.74) (a)**	**55.5 (23.8) (a)**	**3.04 (1.12) (a)**	**28.3 (12.5) (a)**	**242 (97) (a)**
Average input g/ha/year	**4.78**	**13.5**	**498**	**27.3**	**256**	**2153**
2004 BIO	0.082 ± 0	0.720 ± 0.034	2.74 ± 0.17	0.371 ± 0.028	10.1 ± 0.3	22.6 ± 1
2006 BIO	0.266 ± 0.006	0.747 ± 0.026	12.8 ± 0.5	2.03 ± 0.823	28.6 ± 0.7	87.7 ± 1.9
2007 BIO	0.315 ± 0.019	1.10 ± 0.07	28.3 ± 1.4	1.42 ± 0.37	27.6 ± 0.7	127 ± 2
2009 BIO	0.261 ± 0.04	1.81 ± 0.11	23.5 ± 0.4	1.74 ± 0.18	26.2 ± 1.7	102 ± 2
2011 BIO	0.308 ± 0.031	1.49 ± 0.04	20.9 ± 1.3	1.86 ± 0.03	26.0 ± 1.2	126 ± 5
2013 BIO	0.268 ± 0.005	1.01 ± 0.06	9.89 ± 0.57	1.22 ± 0.11	25.5 ± 1.2	84.3 ± 2.7

Average content	**0.25 (0.09) (b)**	**1.15 (0.43) (a)**	**16.4 (9.5) (b)**	**1.44 (0.6) (b)**	**24.0 (6.9) (a)**	**91.5 (38) (b)**
Input g/ha/year	**2.34**	**10.7**	**150**	**13.5**	**228**	**844**
2004 MSW	0.221 ± 0.16	1.41 ± 0.15	9.32 ± 0.62	1.50 ± 0.37	13.6 ± 2.9	46.4 ± 12.5
2006 MSW	0.443 ± 0.1	2.96 ± 1.16	39.4 ± 9.96	8.06 ± 2.02	27.4 ± 9	188 ± 38
2007 MSW	0.394 ± 0.171	2.20 ± 1.02	29.9 ± 13.2	6.81 ± 2.81	34.5 ± 15.2	146 ± 55
2009 MSW	0.239 ± 0.029	0.950 ± 0.041	11.7 ± 0.6	1.77 ± 0.06	24.6 ± 2.1	82.9 ± 2.6
2011 MSW	0.340 ± 0.016	0.759 ± 0.085	17.97 ± 1.14	1.40 ± 0.17	17.5 ± 0.8	101 ± 4
2013 MSW	1.50 ± 0.05	10.4 ± 0.3	92.6 ± 3.75	15.2 ± 3.4	50.6 ± 0.7	505 ± 18
Average content (SD) n=6	**0.52 (0.49) (ab)**	**3.11 (3.65) (a)**	**33.5 (31.1) (b)**	**5.79 (5.46) (a)**	**28.0 (13.3) (a)**	**178 (168) (ab)**
Input g/ha/year	**3.52**	**21.0**	**221**	**37.6**	**180**	**1180**
2004 FYM	0.156 ± 0.027	0.448 ± 0.079	9.91 ± 1.57	0.372 ± 0.122	18.3 ± 6.4	46.2 ± 5.3
2006 FYM	0.914 ± 0.175	0.977 ± 0.117	52.1 ± 8.1	1.83 ± 0.08	78.9 ± 22.3	240 ± 58
2007 FYM	0.798 ± 0.09	1.08 ± 0.03	61.4 ± 18.4	1.70 ± 0.087	77.6 ± 4.9	281 ± 202
2009 FYM	0.282 ± 0.132	0.323 ± 0.047	19.7 ± 1.6	0.911 ± 0.328	12.7 ± 1.8	119 ± 8
2011 FYM	0.258 ± 0.016	0.526 ± 0.124	11.8 ± 0.5	1.50 ± 0.18	13.9 ± 1.2	85.0 ± 1.5
2013 FYM	0.267 ± 0.021	0.218 ± 0.047	18.5 ± 0.6	0.658 ± 0.172	10.1 ± 0.4	131 ± 4
Average content	**0.45 (0.32) (ab)**	**0.59 (0.35) (b)**	**28.9 (22.1) (b)**	**1.16 (0.6) (b)**	**35.2 (33.4) (a)**	**150 (91) (ab)**
Input g/ha/year	**3.21**	**4.34**	**205**	**8.33**	**261**	**1050**

943

944 **Table 3: Results of CaCl2 extractions on OWP spread every year** (mean ± SD, n=3; a few isolated values < QL were replaced by QL/2), then **average**

945 **values over 2004-2013**

CaCl2 extractable metals	**Cadmium µg.kg^{-1} DW**	**Chrome**	**Copper**	**Nickel**	**Lead**	**Zinc**	**pH**	**DOC, g.kg^{-1}**
2004 SGW	5.22 ± 0.15	103 ± 7	895 ± 63	266 ± 17	11 ± 0.8	962 ± 37	6.96 ± 0.07	
2006 SGW	7.02 ± 0.43	60 ± 1	1180 ± 17	241 ± 13	70.8 ± 14.2	1423 ± 96	7.08 ± 0.07	
2007 SGW	6.09 ± 0.22	< 10.3 (QL)	585 ± 26	67 ± 6	16.5 ± 1.7	468 ± 5	7.18 ± 0.12	
2009 SGW	9.25 ± 0.17	41.7 ± 5.5	819 ± 14	192 ± 9	12.8 ± 0.8	841 ± 33	6.68 ± 0.06	
2011 SGW	2.06 ± 0.11	27.5 ± 1.8	1107 ± 6	196 ± 5	< 3.3 (QL)	1130 ± 46	6.60 ± 0.06	
2013 SGW	3.74 ± 0.27	65.5 ± 6.9	1577 ± 76	238 ± 21	2.52 ± 1.27	1330 ± 46	7.20 ± 0.02	9.54± 0.31
Average values ± SD (n=6)	**5.56 ± 2.52**	**50.6 ± 33.9**	**1027 ± 343**	**200 ± 71**	**19.1 ± 26.1**	**1026 ± 349**	**6.95 ± 0.26**	
input mg.ha^{-1}.y^{-1}	**51.1**	**470**	**9329**	**1826**	**180**	**9333**		
2004 BIO	2.45 ± 0.07	69.7 ± 7.5	314 ± 17	116 ± 6	36.2 ± 3.4	522 ± 19	8.10 ± 0.08	
2006 BIO	5.09 ± 0.35	51.6 ± 7.2	577 ± 25	266 ± 80	79.9 ± 5.3	835 ± 66	7.97 ± 0.03	
2007 BIO	3.32 ± 1.22	24.3 ± 2.5	502 ± 73	142 ± 17	25 ± 1.8	494 ± 69	7.42 ± 0.04	
2009 BIO	8.42 ± 0.1	69.7 ± 6.6	636 ± 28	242 ± 19	34 ± 0.7	743 ± 31	7.17 ± 0.10	
2011 BIO	1.8 ± 0.18	65.2 ± 1.8	518 ± 27	159 ± 7	27.8 ± 0.8	1227 ± 6	6.94 ± 0.03	
2013 BIO	2.5 ± 0.1	58.6 ± 1.6	370 ± 13	185 ± 23	13.9 ± 4	629 ± 21	7.14 ± 0.02	8.86± 0.38

Average values	**3.93 ± 2.48**	**56.5 ± 17.3**	**486 ± 123**	**185 ± 58**	**36.1 ± 22.8**	**742 ± 271**	**7.46 ± 0.48**	
input mg.ha^{-1}.y^{-1}	**38.8**	**546**	**4626**	**1801**	**355**	**6876**		
2004 MSW	37.5 ± 19.2	927 ± 33	9870 ± 1933	3583 ± 116	772 ± 44	14133 ± 416	6.99 ± 0.02	
2006 MSW	40.6 ± 3.9	1720 ± 36	18067 ± 603	6810 ± 197	745 ± 64	19700 ± 1082	7.42 ± 0.2	
2007 MSW	19.1 ± 8.8	444 ± 313	8193 ± 5495	3857 ± 2638	203 ± 125	6777 ± 4095	6.88 ± 0.28	
2009 MSW	3.98 ± 0.23	100 ± 4	870 ± 41	379 ± 8	36 ± 1	1087 ± 15	7.51 ± 0.07	
2011 MSW	2.58 ± 0.12	27.6 ± 1.6	847 ± 51	198 ± 14	12.4 ± 1.3	642 ± 31	7.44 ± 0.07	
2013 MSW	57.7 ± 1.5	2397 ± 55	20100 ± 700	7113 ± 443	379 ± 34	38467 ± 1097	7.87 ± 0.0	28.8± 0.10
Average values	**26.9 ± 22**	**936 ± 950**	**9658 ± 8207**	**3657 ± 2988**	**358 ± 337**	**13468 ± 14330**	**7.35 ± 0.36**	
input mg.ha^{-1}.y^{-1}	**181.9**	**6262**	**63639**	**23874**	**2404**	**91791**		
2004 FYM	42.1 ± 3.4	189 ± 14	4165 ± 115	530 ± 86	1440 ± 165	12367 ± 1704	9.00 ± 0.05	
2006 FYM	31.6 ± 3.3	138 ± 32	4237 ± 869	627 ± 124	644 ± 172	4720 ± 701	8.26 ± 0.32	
2007 FYM	13.7 ± 2.4	69 ± 12	3643 ± 717	292 ± 61	356 ± 30	2217 ± 284	8.59 ± 0.12	
2009 FYM	27.2 ± 3.7	125 ± 15	4633 ± 581	344 ± 43	191 ± 41	4717 ± 410	8.88 ± 0.09	
2011 FYM	13.6 ± 0.9	66.2 ± 2.3	1477 ± 71	342 ± 12	83.9 ± 7.3	1537 ± 208	8.80 ± 0.04	
2013 FYM	22.1 ± 0.6	132 ± 7	3350 ± 161	487 ± 27	142 ± 14	3290 ± 131	8.19 ± 0.03	17.2± 0.27
Average values	**25.0 ± 11.0**	**120 ± 46**	**3584 ± 1128**	**437 ± 131**	**476 ± 513**	**4808 ± 3921**	**8.62 ± 0.33**	
input mg.ha^{-1}.y^{-1}	**171.8**	**814**	**24096**	**3029**	**3493**	**33345**		

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948 **Table 4: Selected results of Multiple Linear Regression studies –** Units: M_{EDTA} in mg/kg dry soil;

949 M_{CaCl2} in mg/L of $CaCl_2$ extracts, corresponding Kd in L/kg; SOC in g/kg – n = 65 mean values from the 4

950 repetition blocks, or n = 55 when explicative variables include pH_{CaCl2} not measured in 2002 – MAE =

951 Mean Absolute Error, calculated for M_{CaCl2} in $\mu g.L^{-1}$ (and in % of Mean Concentration)

MLR for	R^2_{adj}	Equation *(P-value between brackets for each variable)*	MAE
Log(Cd_{CaCl2})	60% n=65	= 4.80 + 2.45×log(Cd_{EDTA}) (*P = 0.11*) - 0.351×pH_{H2O} (*P = 0.00*) - 3.18×log(SOC) (*P = 0.00*)	0.19 (31%)
Log(Cu_{CaCl2})	69% n=65	= -3.21 + 1.21×log(Cu_{EDTA}) (*P = 0.00*)	0.39 (10%)
Log(Ni_{CaCl2})		All MLR rejected (coefficient of log(Ni_{EDTA}) always < 0)	
Log(Zn_{CaCl2})	68% n=65	= 5.56+ 1.305×log(Zn_{EDTA}) (*P = 0.00*) - 0.753×pH_{H2O} (*P = 0.00*) - 3.04×log(SOC) (*P = 0.00*)	2.97 (30%)
MLR for	R^2_{adj}	Equation *(P-value for each variable)*	
Log(Kd_{Cd})	65% n=65	= -2.85 + 0.323×pH_{H2O} *(P=0.00)* + 2.71×log(SOC) *(P=0.00)*	0.19 (32%)
Log(Kd_{Cu})		All MLR rejected. So, best model = mean	0.42 (11%)
Log(Kd_{Ni})	58% n=65	= -1.35 + 0.492×pH_{H2O} *(P=0.00)* +0.704×log(SOC) *(P=0.05)*	0.45 (26%)
Log(Kd_{Ni})	56% n=65	= -1.106 + 0.564×pH_{H2O} *(P=0.00)*	
Log(Kd_{Zn})	81% n=65	= -4.98+ 0.741×pH_{H2O} *(P=0.00)* + 2.36×log(SOC) *(P=0.00)*	3.00 (31%)
Log(Kd_{Zn})	74% n=55	= -4.48 + 0.646×pH_{CaCl2} *(P=0.00)* + 2.88×log(SOC) *(P=0.00)*	

952

953

954 **Table 5: Descriptive statistics of Kd and log(Kd) – Means, medians, Coefficients of Variation**

L/kg	Mean	Median	CV%		Mean	Median	CV%
Kd(Cd)	368	230	106%	$\log(Kd_{Cd})$	2.430	2.361	13%
Kd(Cu)	1195	1164	16%	$\log(Kd_{Cu})$	3.072	3.066	2%
Kd(Ni)*	1036	890	59%	$\log(Kd_{Ni})$	2.945	2.949	8%
Kd(Pb)*	621634	44498	187%	$\log(Kd_{Pb})$	4.855	4.648	18%
Kd(Zn)	1236	749	106%	$\log(Kd_{Zn})$	2.908	2.875	13%

955 * Part of values for Ni_{CaCl2} and Pb_{CaCl2}, under quantification limits, have been replaced by QL/2, or by
956 analytical indications < QL when available, for these calculations.

957

Figure (graphs separated, color and Black/grey)
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Cambier etal STOTEN – FIGURES (separated, larger, Coloured versions, then in Black

Figure 1 colored

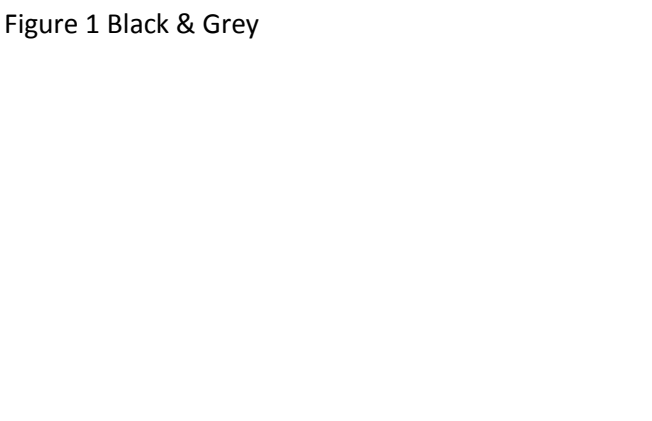
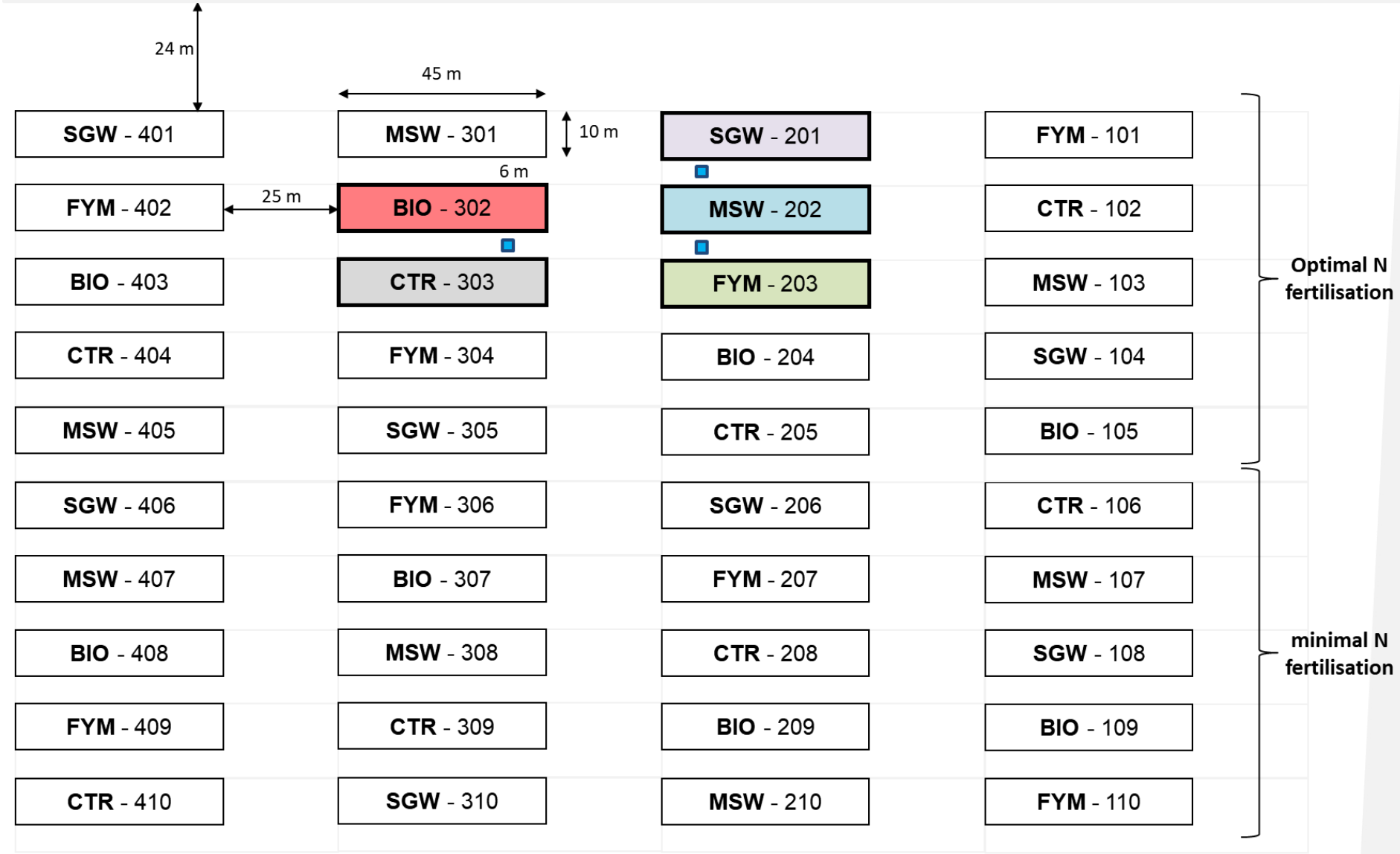


Figure 1 Black & Grey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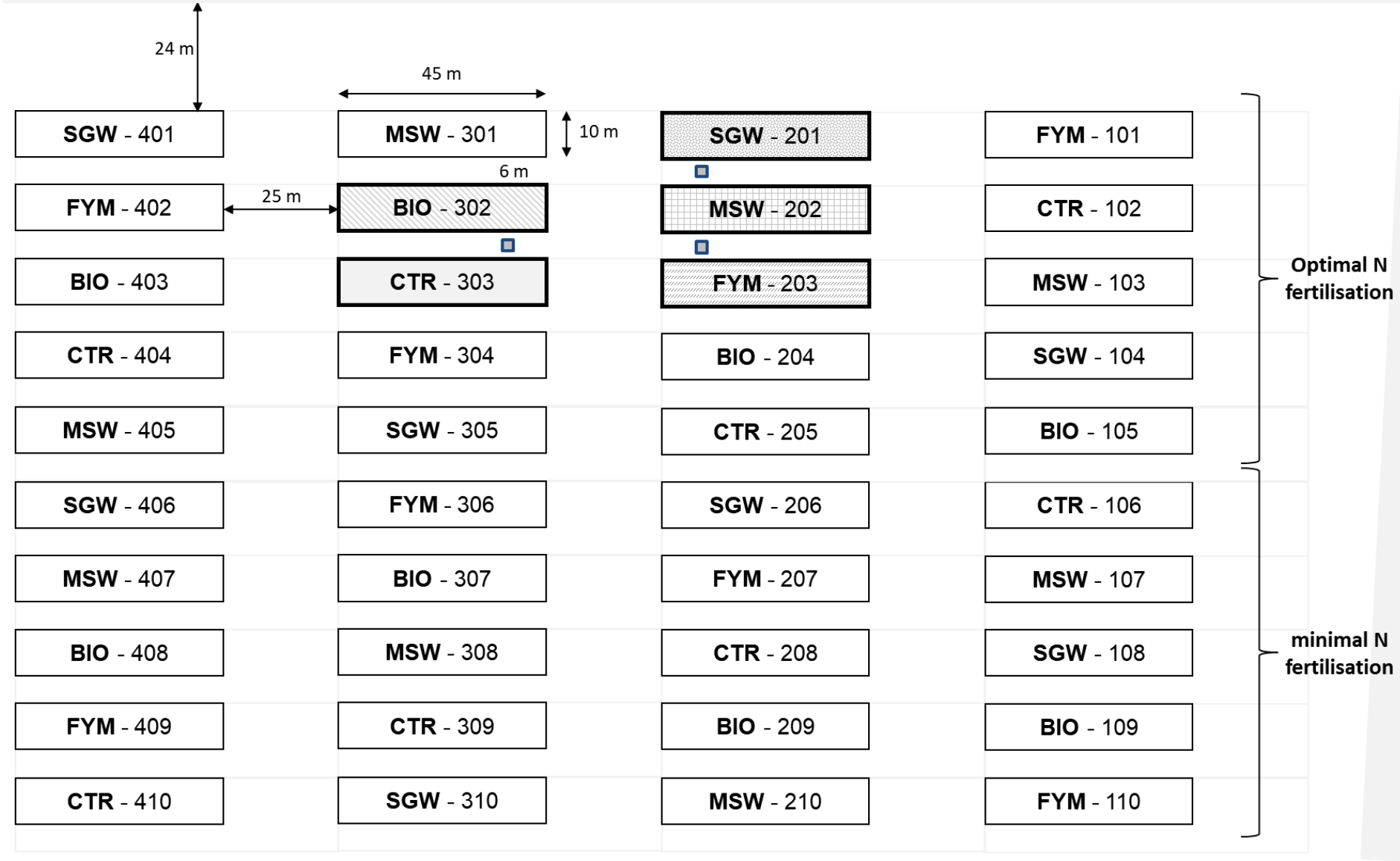
45 m
10 m
6 m
25 m
SGW - 401
MSW - 301
SGW - 201
FYM - 101
FYM - 402
BIO - 302
MSW - 202
CTR - 102
BIO - 403
CTR - 303
FYM - 203
MSW - 103
CTR - 404
FYM - 304
BIO - 204
SGW - 104
MSW - 405
SGW - 305
CTR - 205
BIO - 105
SGW - 406
FYM - 306
SGW - 206
CTR - 106
MSW - 407
BIO - 307
FYM - 207
MSW - 107
BIO - 408
MSW - 308
CTR - 208
SGW - 108
FYM - 409
CTR - 309
BIO - 209
BIO - 109
CTR - 410
SGW - 310
MSW - 210
FYM - 110
Optimal N fertilisation
minimal N fertilisation


24 m
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MSW - 301
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FYM - 101
FYM - 402
BIO - 302
MSW - 202
CTR - 102
BIO - 403
CTR - 303
FYM - 203
MSW - 103
CTR - 404
FYM - 304
BIO - 204
SGW - 104
MSW - 405
SGW - 305
CTR - 205
BIO - 105
SGW - 406
FYM - 306
SGW - 206
CTR - 106
MSW - 407
BIO - 307
FYM - 207
MSW - 107
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MSW - 308
CTR - 208
SGW - 108
FYM - 409
CTR - 309
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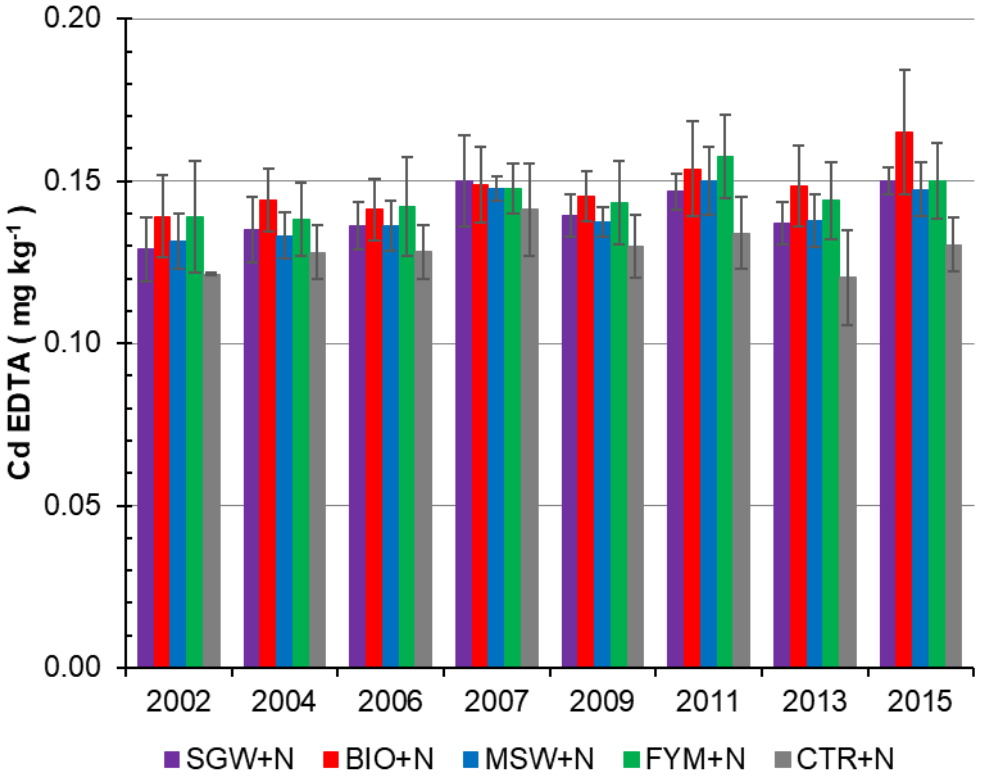
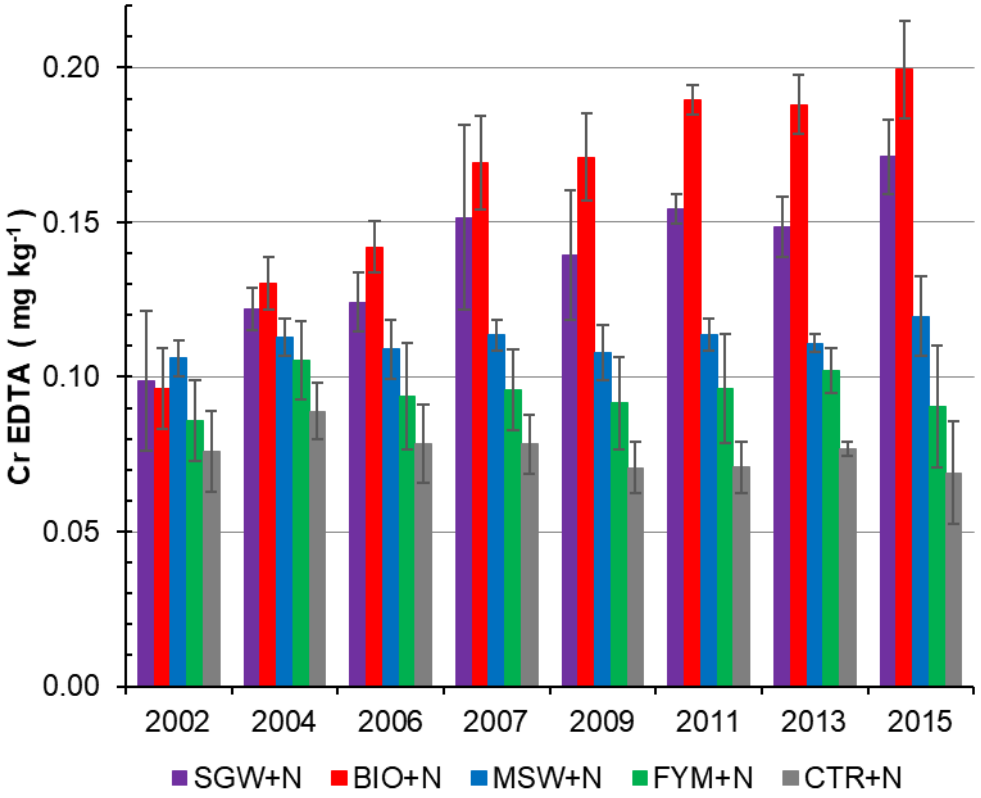
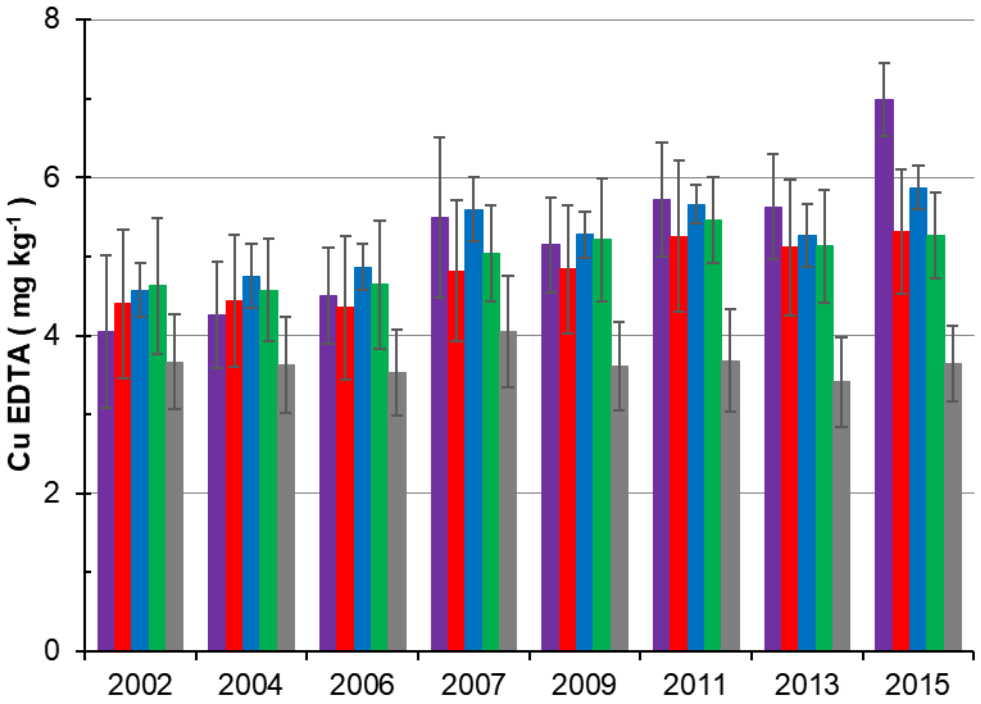
CTR - 410
SGW - 310
MSW - 210
FYM - 110
Optimal N fertilisation
minimal N fertilisation

FIGURE 2 (6 graphs)






Cu EDTA (mg kg-1)
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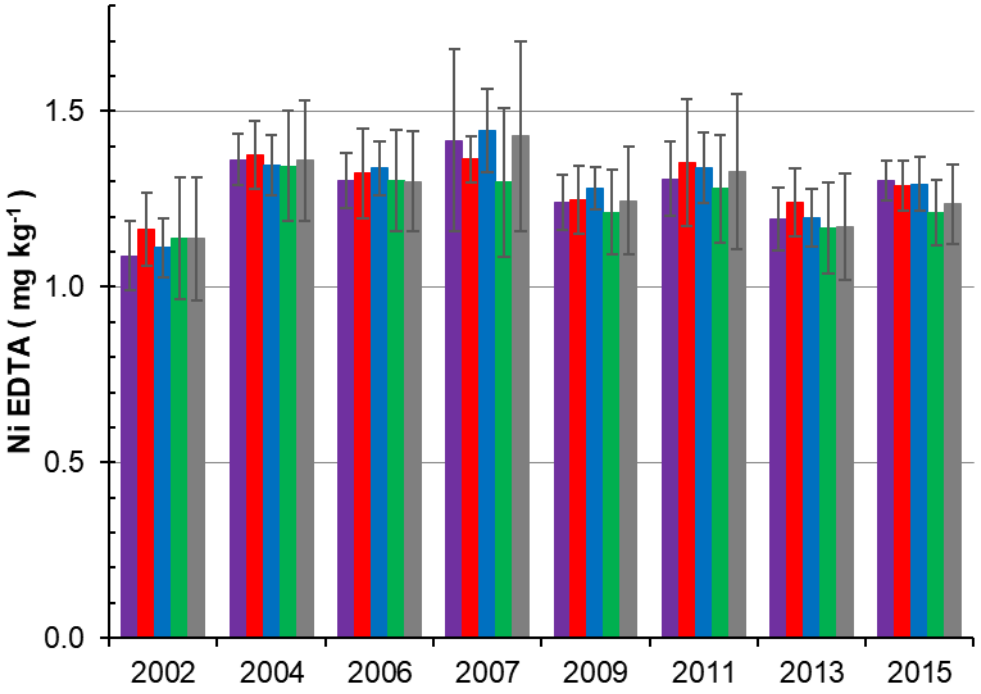
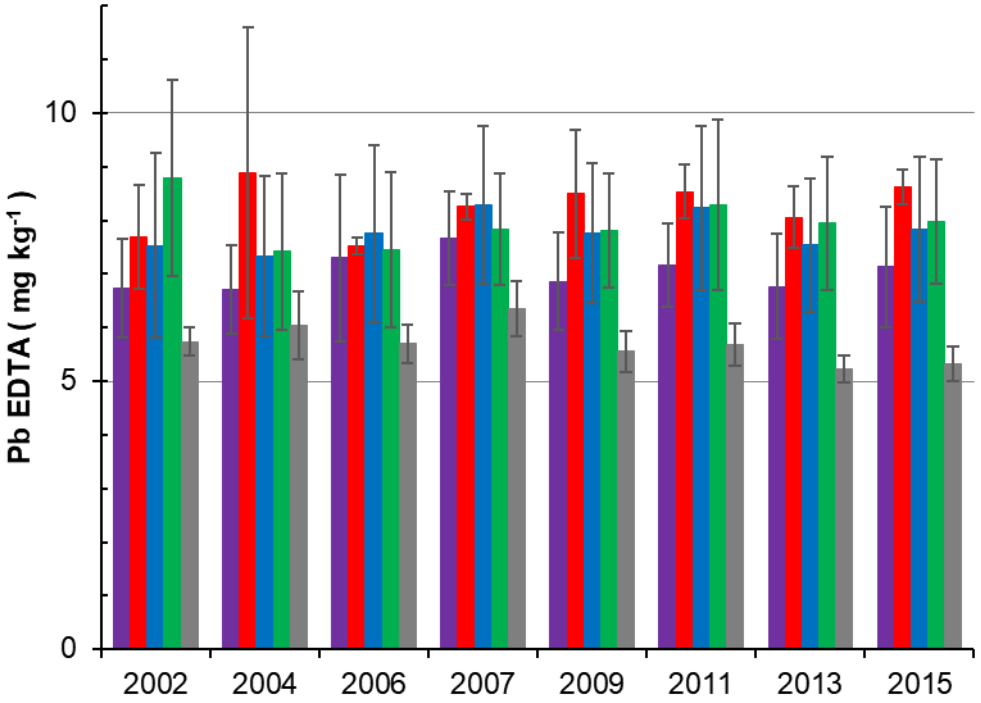
6
4
2
0
2002
2004
2006
2007
2009
2011
2013
2015


Ni EDTA (mg kg-1)
1.5
1.0
0.5
0.0
2002
2004
2006
2007
2009
2011
2013
2015


Pb EDTA (mg kg-1)
10
5
0
2002
2004
2006
2007
2009
2011
2013
2015

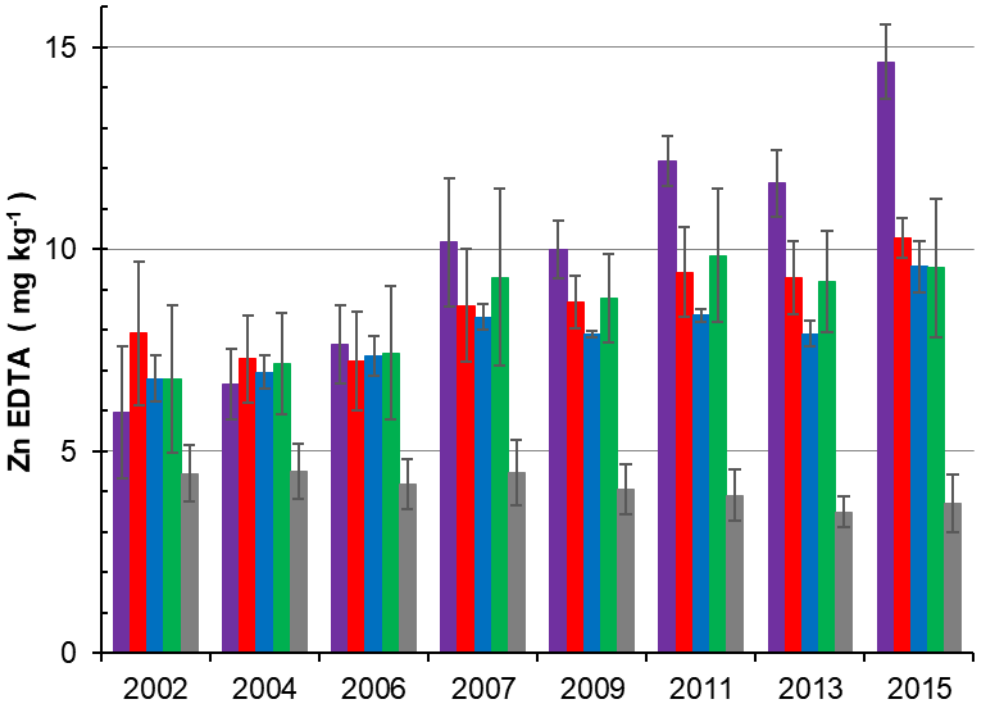
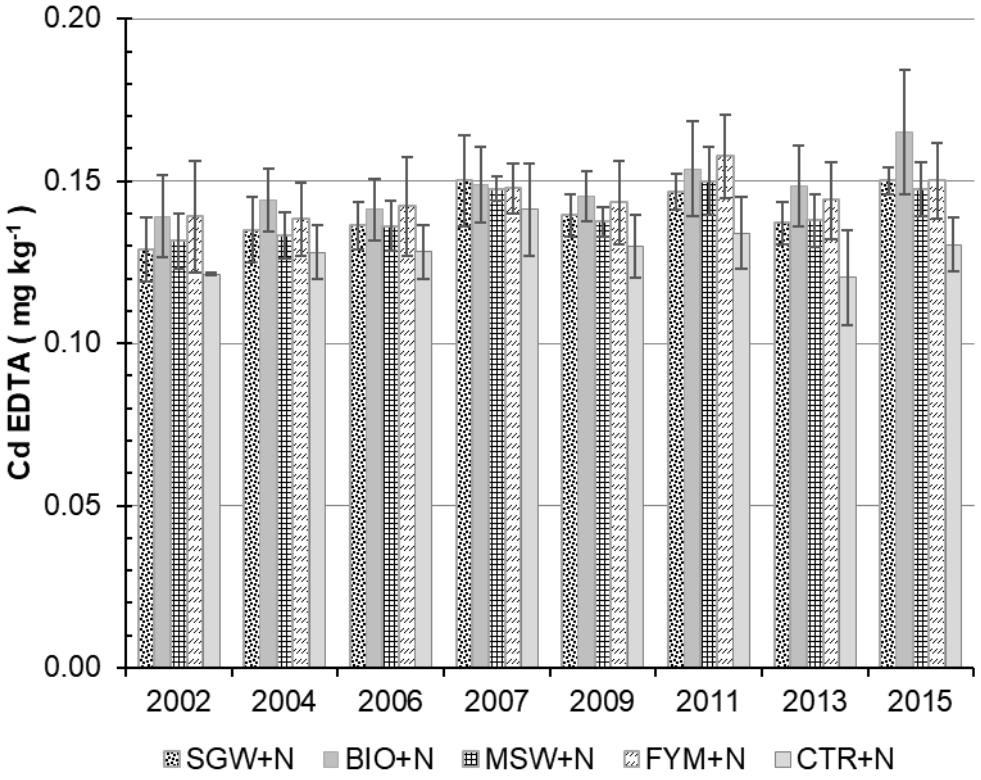
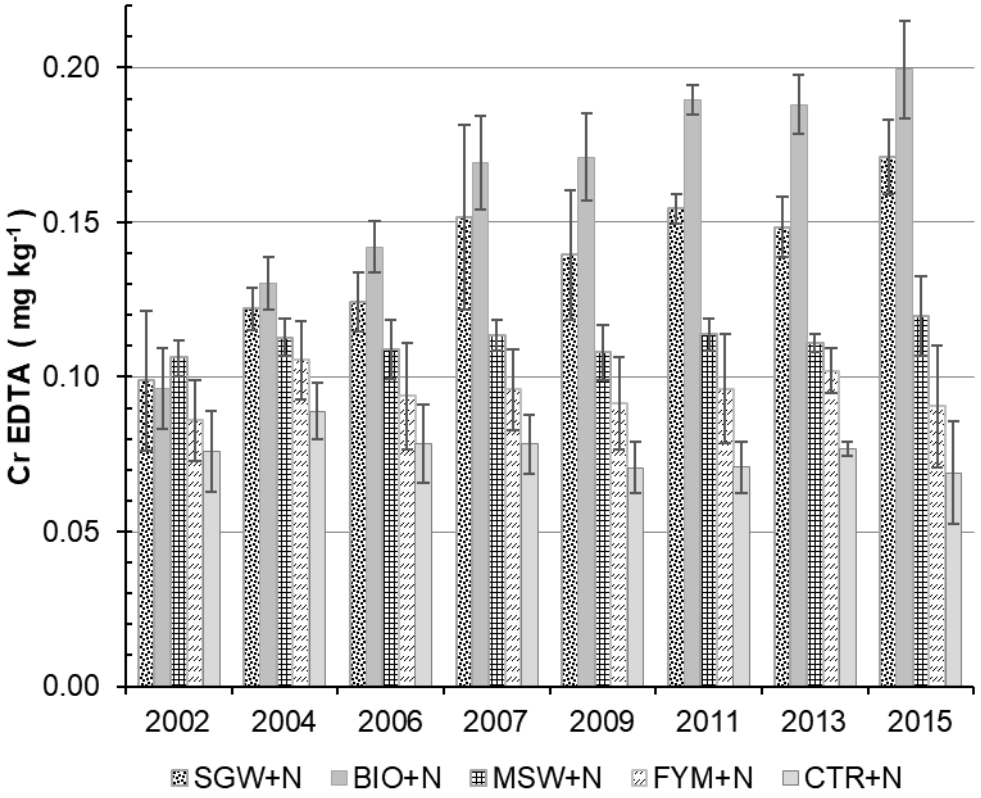
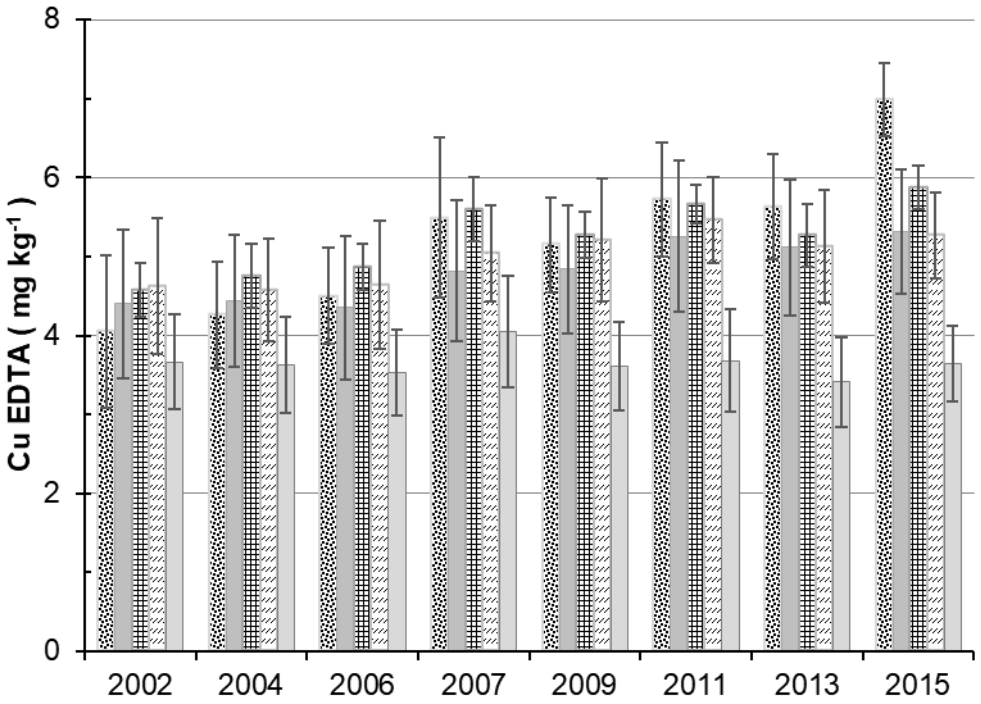
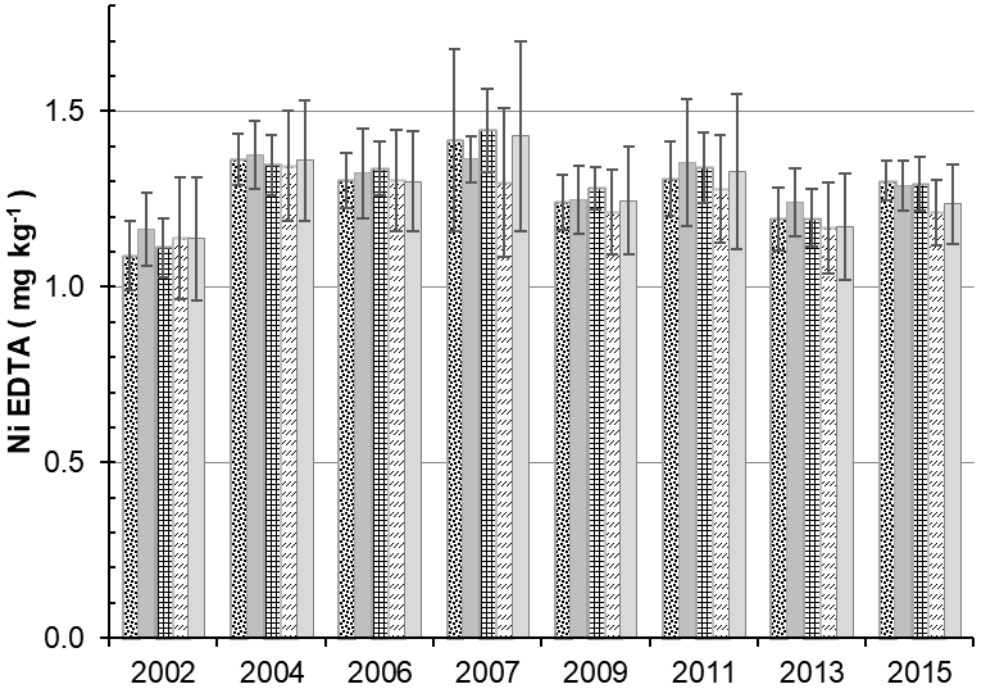

Zn EDTA (mg kg-1)
15
10
5
0
2002
2004
2006
2007
2009
2011
2013
2015

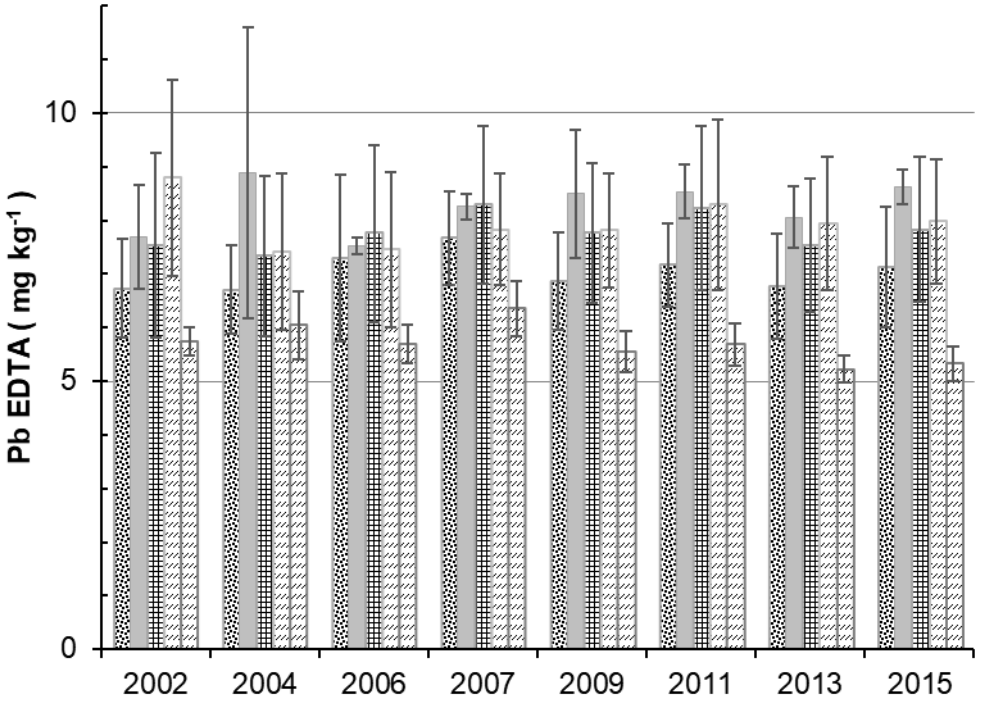
FIGURE 2 Black & Grey






Cu EDTA (mg kg-1)
8
6
4
2
0
2002
2004
2006
2007
2009
2011
2013
2015


Ni EDTA (mg kg-1)
1.5
1.0
0.5
0.0
2002
2004
2006
2007
2009
2011
2013
2015


Pb EDTA (mg kg-1)
10
5
0
2002
2004
2006
2007
2009
2011
2013
2015

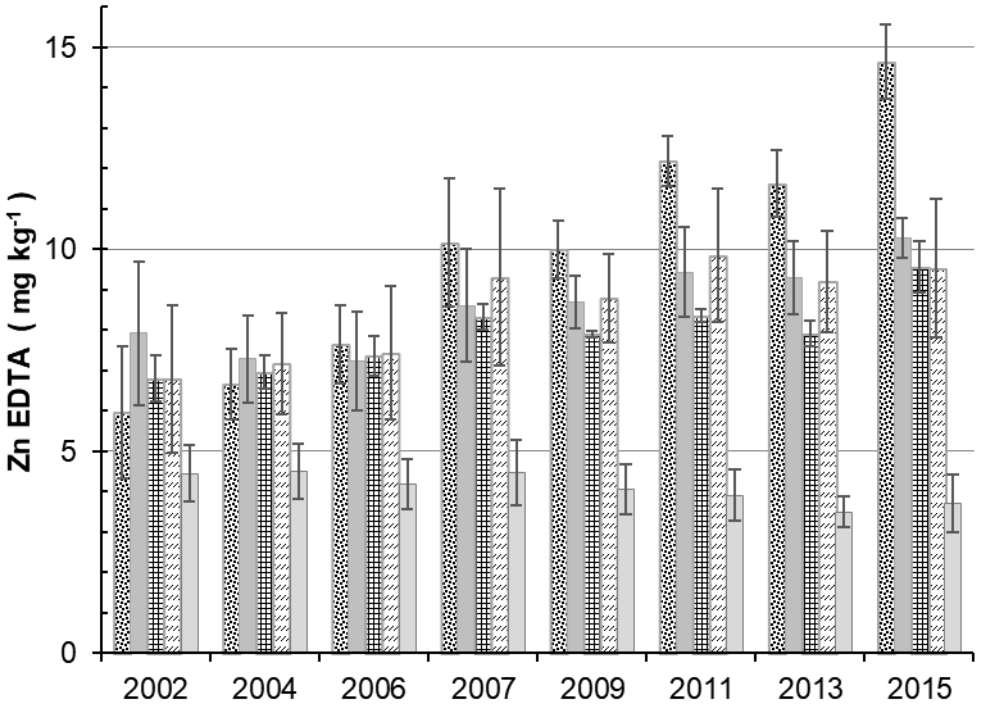
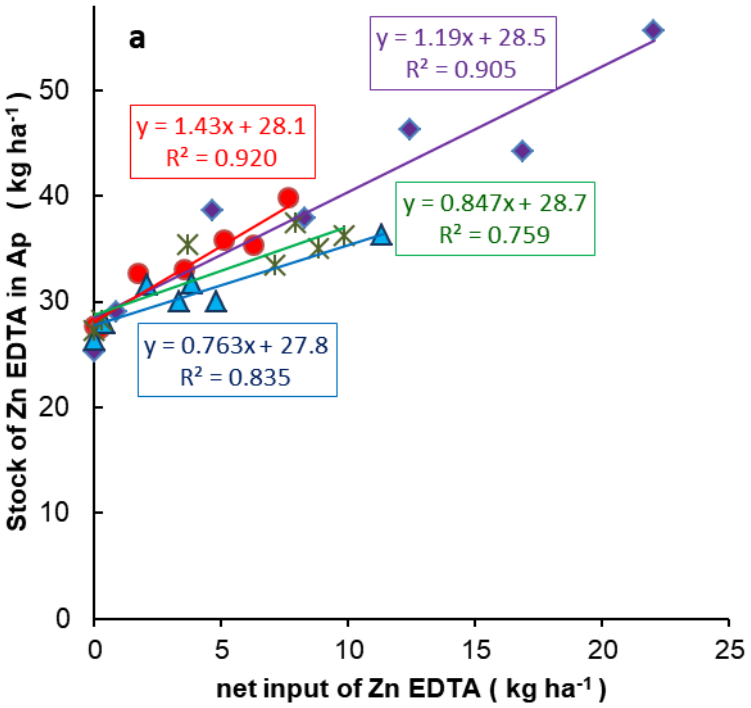
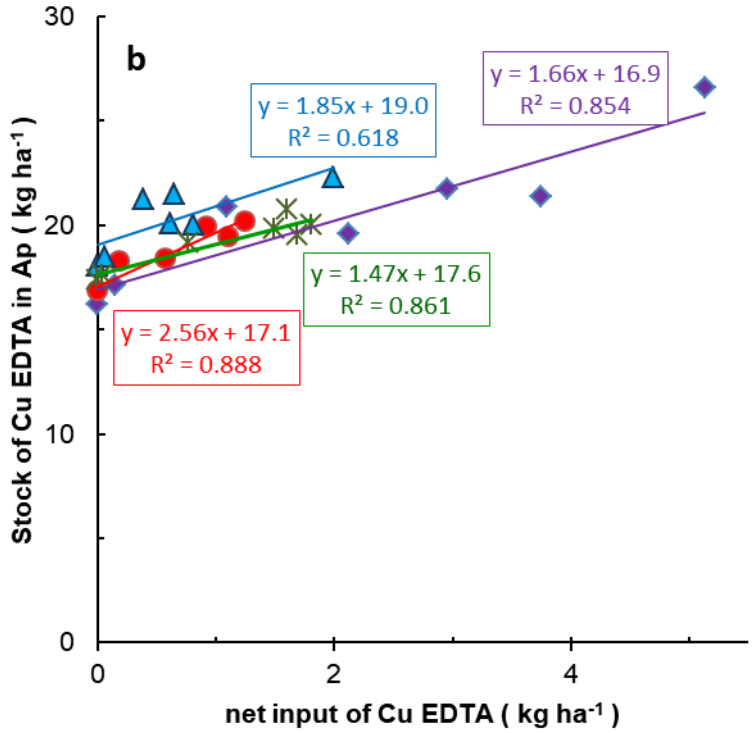
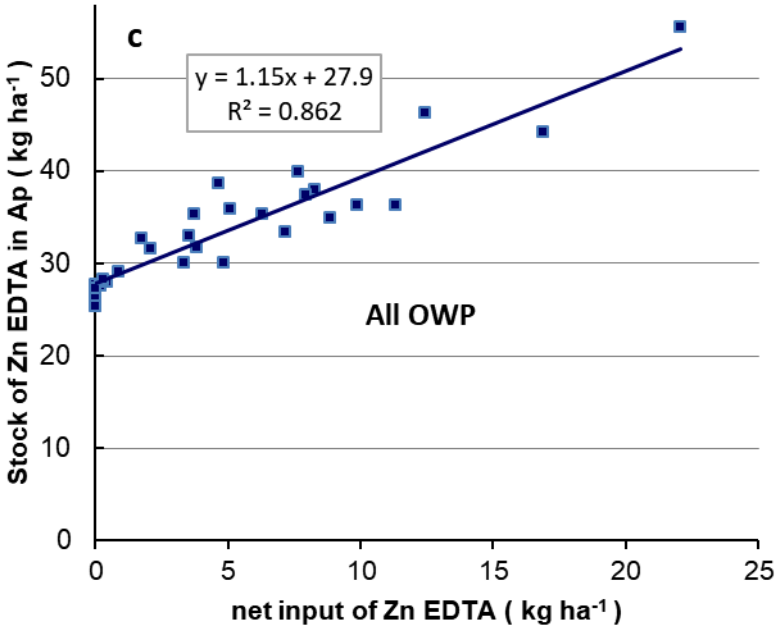
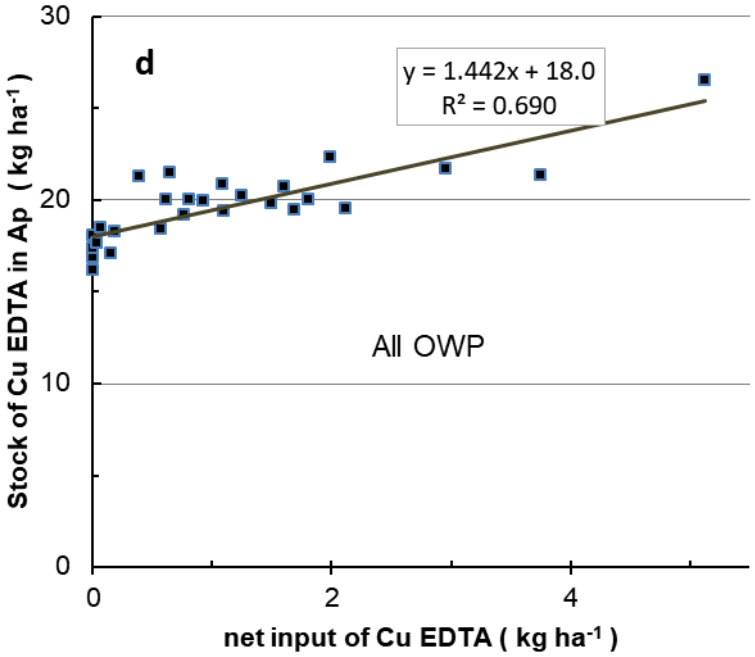

Zn EDTA (mg kg-1)
15
10
5
0
2002
2004
2006
2007
2009
2011
2013
2015

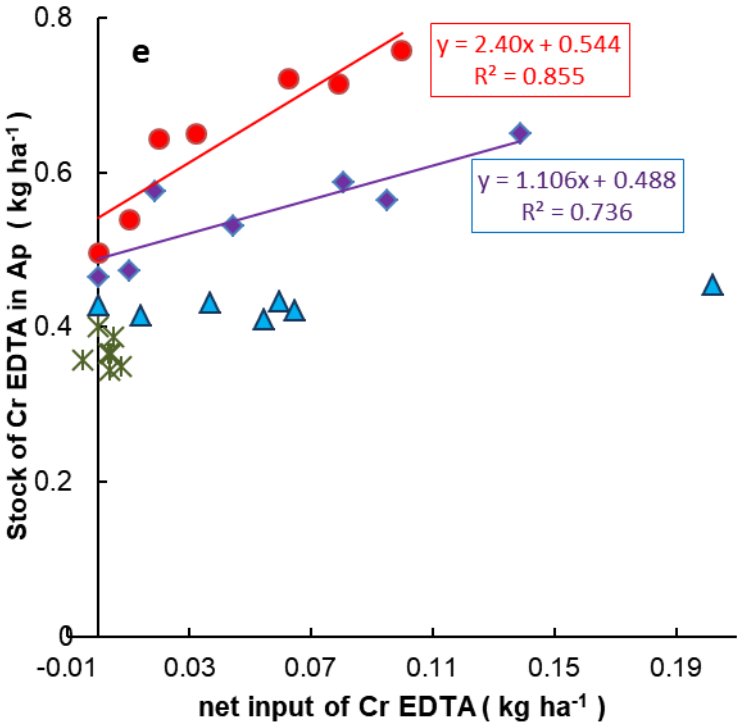
Figure 3 (a b c d e f), coloured






c
y = 1.15x + 27.9
R² = 0.862
All OWP
Stock of Zn EDTA in Ap (kg ha-1)
net input of Zn EDTA (kg ha-1)
0
10
20
30
40
50
0
5
10
15
20
25


d
y = 1.442x + 18.0
R² = 0.690
All OWP
Stock of Cu EDTA in Ap (kg ha-1)
net input of Cu EDTA (kg ha-1)
0
10
20
30
0
2
4



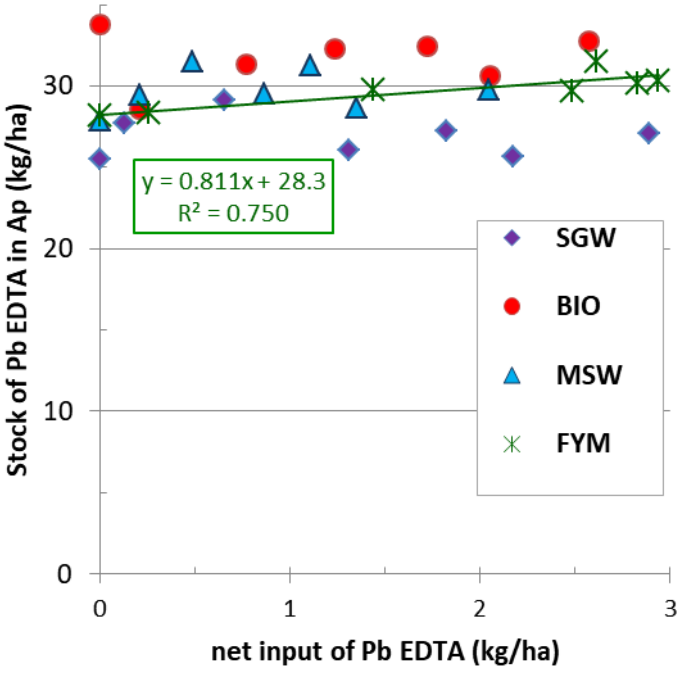
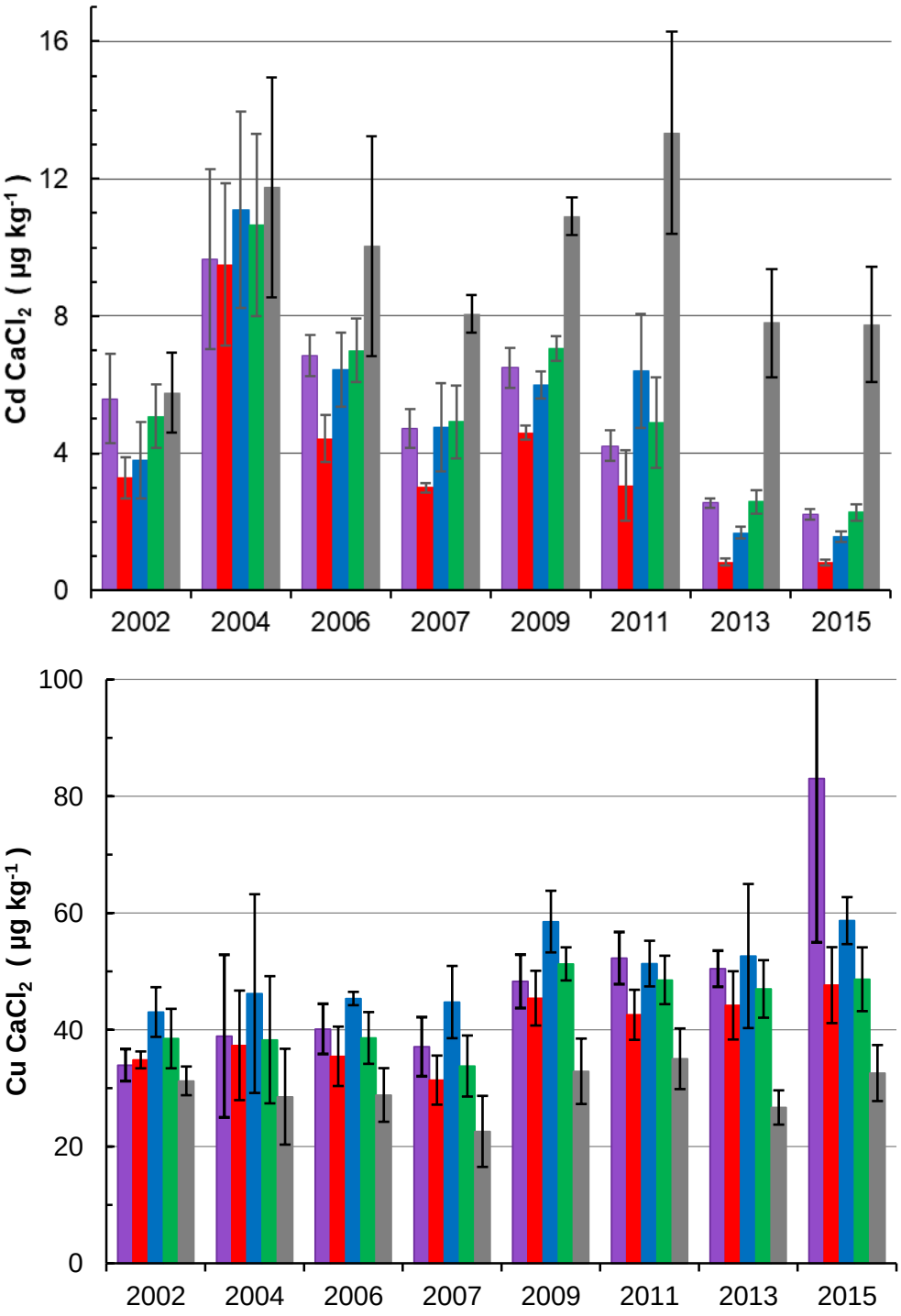


FIGURE 3 black & Grey

Figure 4, coloured



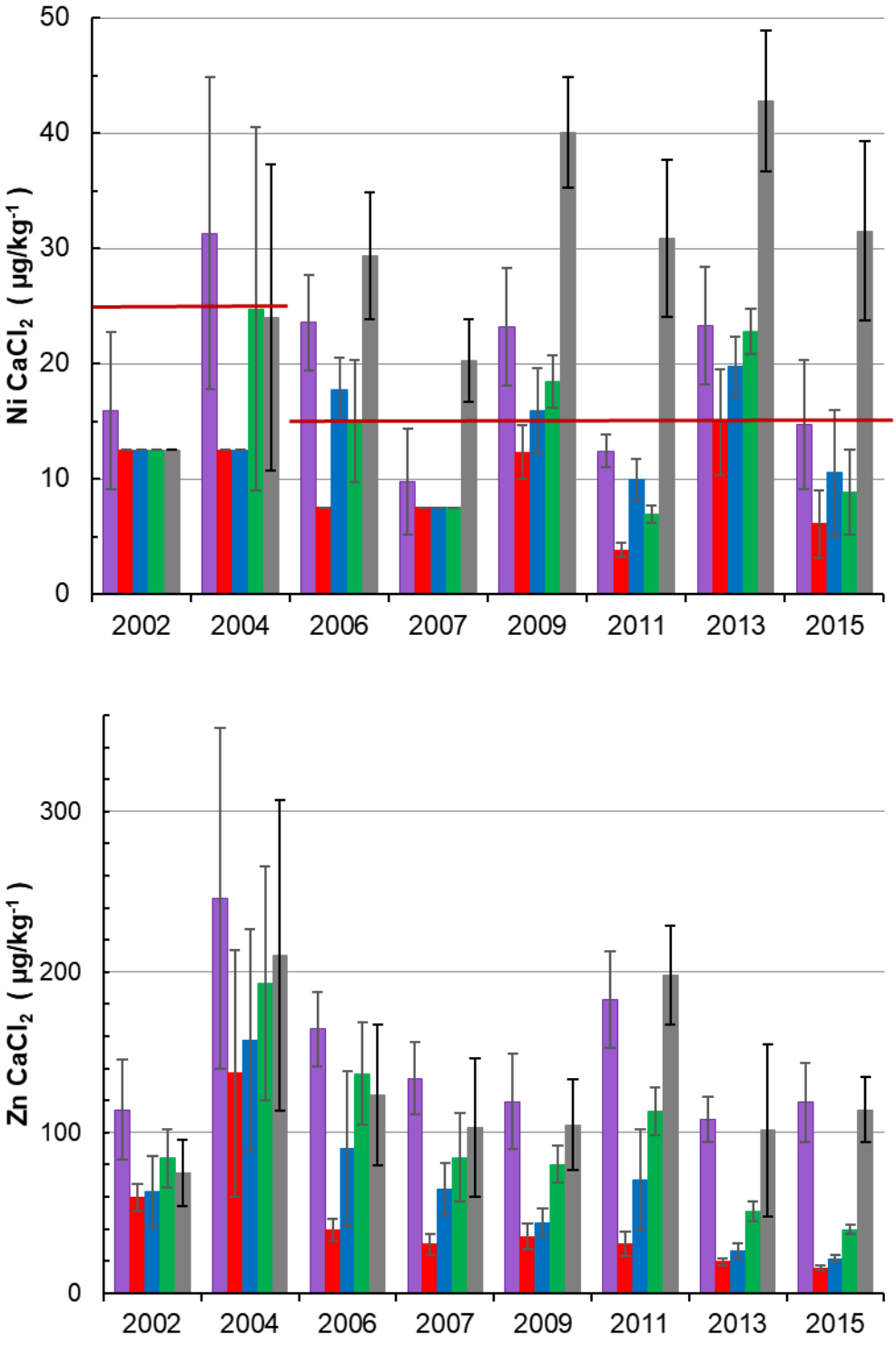
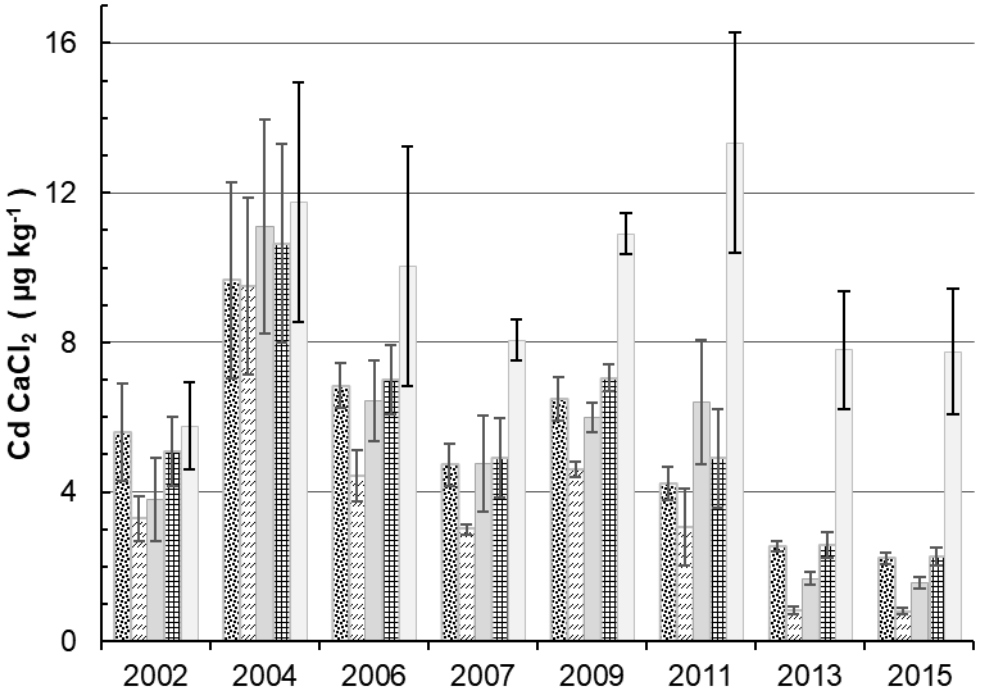
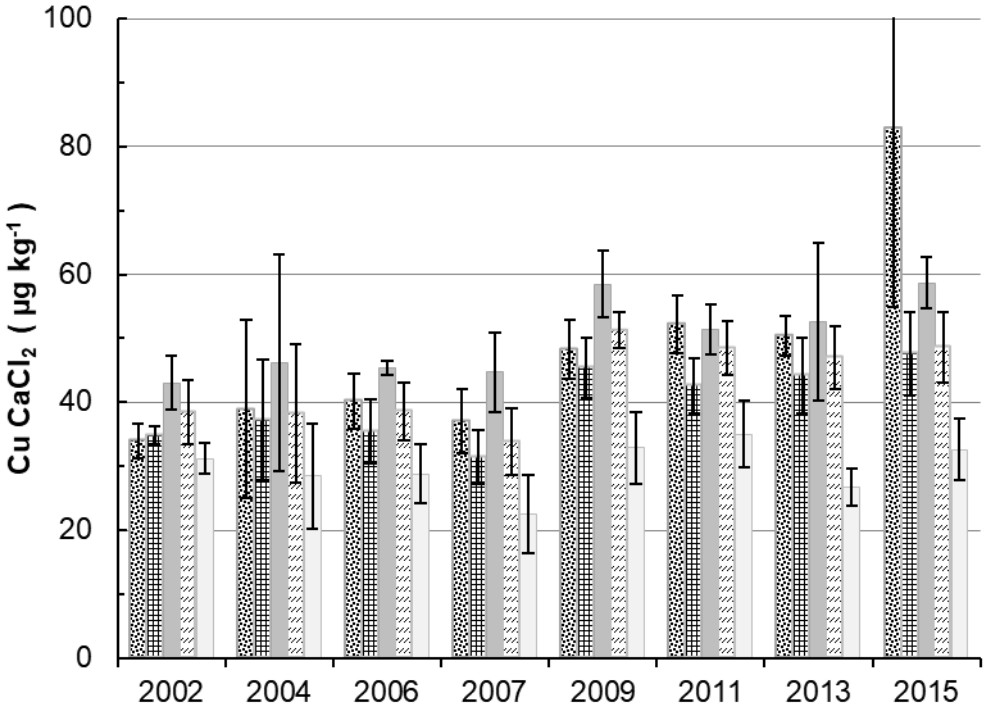
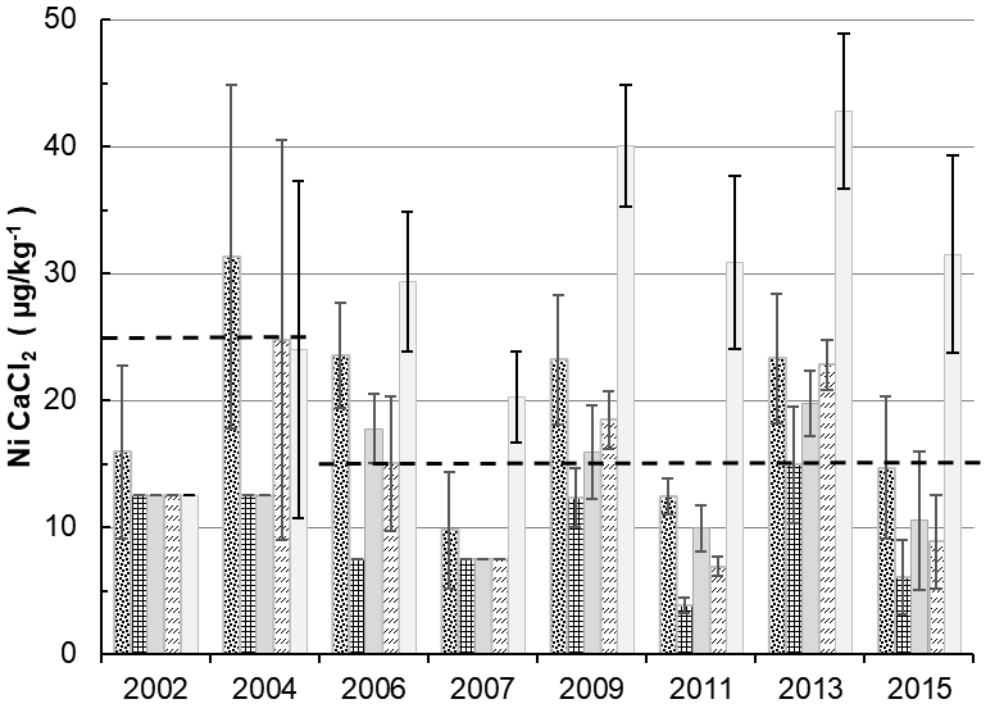
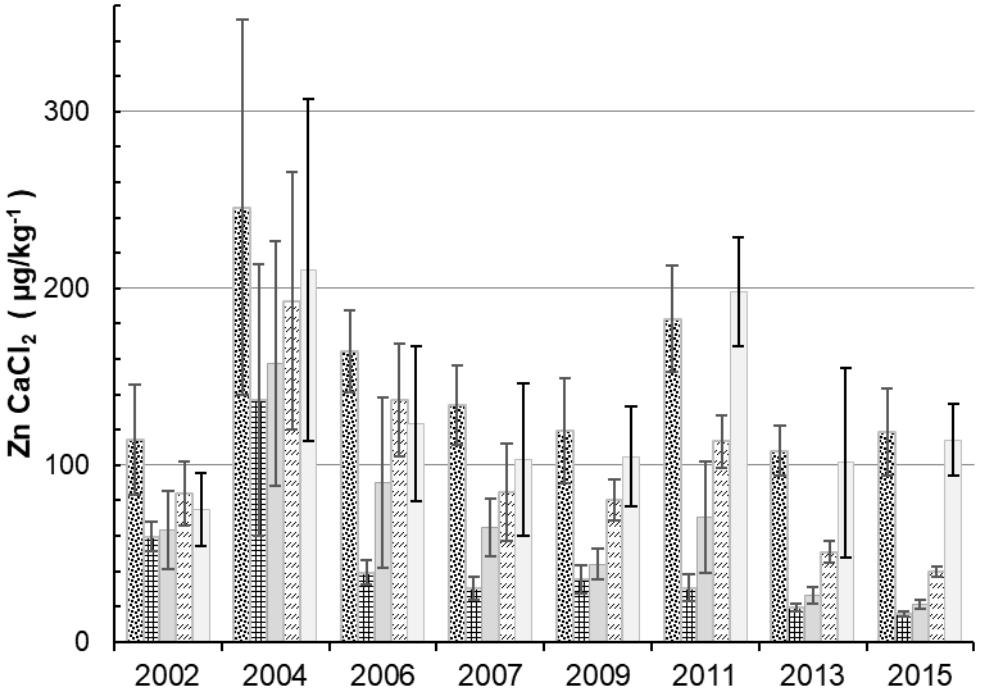


FIGURE 4 Black & Grey


16
12
8
4
0
Cd CaCl2 (µg kg-1)
2002
2004
2006
2007
2009
2011
2013
2015


100
80
60
40
20
0
Cu CaCl2 (µg kg-1)
2002
2004
2006
2007
2009
2011
2013
2015


50
40
30
20
10
0
Ni CaCl2 (µg/kg-1)
2002
2004
2006
2007
2009
2011
2013
2015


300
200
100
0
Zn CaCl2 (µg/kg-1)
2002
2004
2006
2007
2009
2011
2013
2015

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