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Interactive comment on "Modelling of long term Zn, Cu, Cd, Pb dynamics from soils fertilized with organic amendments" *by* Claudia Cagnarini et al.

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We tackle below the five main observations raised by the Reviewer. 1) We recognize that the description of IDMM-ag given in the M&M is not sufficient to capture the model details, unless the cited references are checked. This was done partly by purpose to simplify the reading of an already-long manuscript. Therefore, we think that the suggestion given by the Reviewer to present a model overview, like in the form of a table, is very valuable and we will implement it. Also, we will edit the current layout of the model description in the M&M to give more details. 2) The Reviewer is making a good comment. In fact, ICP-OES could have interferences with As, particularly when this is present at medium/high concentration while Cd is close to the background value (see McBride. 20011. A comparison of reliability of soil Cd determi-

nation by standard spectrometric methods. J Environ Qual. 2011; 40(6): 1863–1869. doi:10.2134/jeq2011.0096). We didn't measure As concentration in the test field, but we made a comparison of the total metal concentrations obtained by extraction with aqua regia and analysis of the extracts with ICP-OES (by the lab that conducted all the measurements presented in the manuscript) and ICP-MS (in another lab in Zurich). In fact, ICP-MS is recognized to have greater sensitivity in Cd determination. The measurements of Cd concentrations in four different treatments obtained by ICP-OES and ICP-MS are in good agreement (see below). This test, which was carried out also for other trace elements, can be taken as a validation of the ICP-OES measurements, ruling out any possible interference with As. Please note that for determination of metal total concentrations in soils, the extractions have always been done with aqua regia; HNO3 was used only for extraction of the organic amendments. As to quality control of the ICP-EOS instrument, it is done on the calibration curve every 10 readings by measuring the TES concentrations in the blanks and in the standard sample at intermediate concentration of 1 ppm. The limit of quantification for every element is taken as 3 standard deviation of the readings from the blank samples. We will include more details of the analytical procedures in the M&M. 3) As correctly pointed by the Reviewer, we didn't have any DOC measurements available. The hypothesis that DOC concentration increases with organic amendment application is very likely, though the magnitude of this increase is dependent on many factors, such as application rate (maybe a threshold effect?), type of organic amendment, soil properties and local environmental factors. Since the inconsistency/scatter of the data in the literature (see a recent meta-analysis by Li et al (2019). "Effect of land management practices on the concentration of dissolved organic matter in soil: A meta-analysis". Geoderma 344 (2019) 74–81), it is very difficult to make an educated guess. However, since the reviewer's comments are valid, we have made additional analysis on the DOC contribution to TEs simulations. As a forward, the Reviewer suggests that DOC might peak after amendment application to slowly decrease until next application; this cycle is likely to happen, however IDMM-ag has an annual time step that requires an "aver-

age" DOC value to be specified. As a first test, we increased the DOC from 7 mgC/l to 33 mgC/l from pristine conditions to 2014 and applied this fixed concentration to all the treatments. These values come from the paper by De Troyer et al (2014). Factors Controlling the Dissolved Organic Matter Concentration in Pore Waters of Agricultural Soils. Vadose Zone J., which reports a large DOC dataset from European agricultural soils. In the ms we decided to apply a very low DOC value correspondent to the control treatment, characterized by big SOC loss and mechanical ploughing. Here we tested 33 mg C/l, the median value reported by De Troyer et al. (2014). The simulations with a fixed 33 mg C/l as DOC concentration did not differ from the ones with 7 mg C/l, with the only difference that we had to increase the additional input term (mineral weathering as we suggested in the ms) to fit the metal concentrations in 1972 for the control treatment. Except for Zn, the new fitted inputs are one order of magnitude bigger than the old ones: 3.99 mg m-2 yr-1 for Zn, 27.3 mg m-2 yr-1 for Cu, 3.52 mg m-2 yr-1 for Pb and 0.157 mg m-2 yr-1 for Cd. The higher values of this additional input term suggest that a five-fold increase in DOC concentration in the control treatment might be unrealistically high. Therefore, as a second trial we kept 7 mg C/l in the control treatment and in the other treatments before 1949 when the trial started. In particular, we applied a linear increase up to the following DOC concentration values in 2014: 56 mg C/l in the farmyard manure treatment, 70 mg C/l in the sewage sludge treatment, and 35 mg C/l in the compost treatment. We present below the results only with lateral mixing and the "idealized trend" as a simulation of the sewage sludge metal inputs. The model predictions slightly improved when increasing the DOC concentration with organic amendment applications: while the control treatment was barely affected, in FYM and COM the overestimation in labile concentrations, particularly for Cu and Pb, got smaller. Even in the sewage sludge treatment the TEs decreasing trends were better simulated. We can conclude that increasing the DOC concentration under organic amendment applications does not substantially modify the simulations, thus confirming the assumptions we made in the ms, but slightly improved them. So, we think it is valuable to add at least the second trial in the ms, presenting it as a test on DOC

concentrations since no DOC data are available to support the hypothesis. 4) Long-term experiments comparing different treatments are valuable sources of information, but here we showed a potentially unrecognized drawback: plots can be affected by soil mixing with the adjacent ones. This effect is hardly detectable unless elements present in trace concentrations are taken into account. Therefore, the lateral mixing was introduced to fit the data, since the 4 treatments considered were perfectly adjacent in 3 out of the 5 repetitions (in the other 2 repetitions the only compost treatment was separated from the "block"). In this sense, the lateral mixing is well represented by the considered treatments and collected data. Running another sampling campaign across the whole transect (12 treatments) is not feasible at the moment and, moreover, since some data are missing, it is not clear to know in advance the benefits of such an activity. However, we want to reinforce that lateral mixing serves the purpose of fitting the long-term trial data. The model, which is validated as long the simulations of historical data are satisfactory, should be run without lateral mixing when real fields are simulated. That's why we did not include the lateral mixing when projecting into the future the TEs accumulation as if ZOFE were a real field. 5) This comment is not very clear. In the pictures we showed the control treatment and the organic amendment treatments one next to the others because i) the control treatment takes part to the lateral mixing and it's worth showing the relevant simulations ii) absolute concentrations of TEs are useful on their own. However, we could show the concentrations of the organic amended treatments relative to the control treatment for the future projections. Regarding the other comments, we will review the English writing, include some quantitative data in the Abstract and Introduction and make clearer the last part of the paper. We thank the Reviewer for the useful suggestions throughout the paper.

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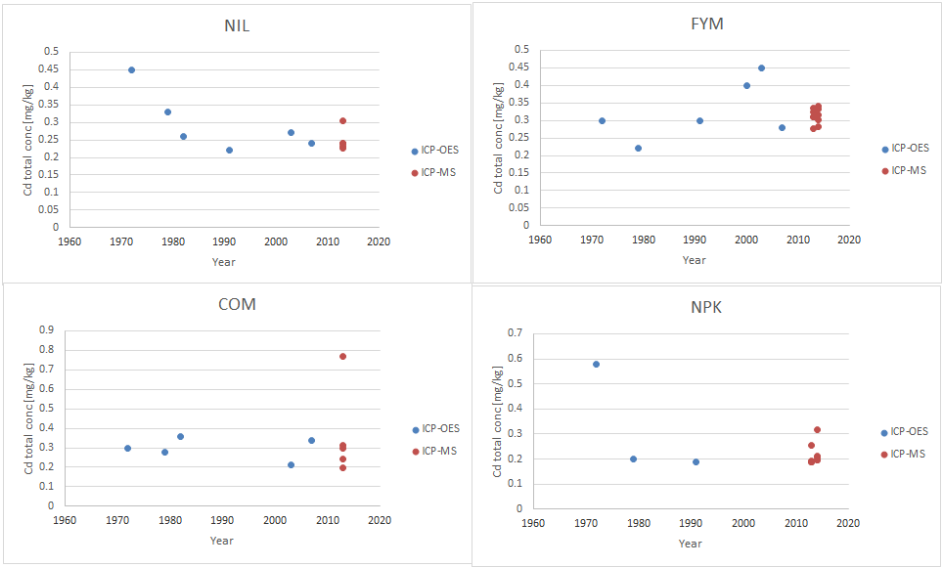

Fig. 1.

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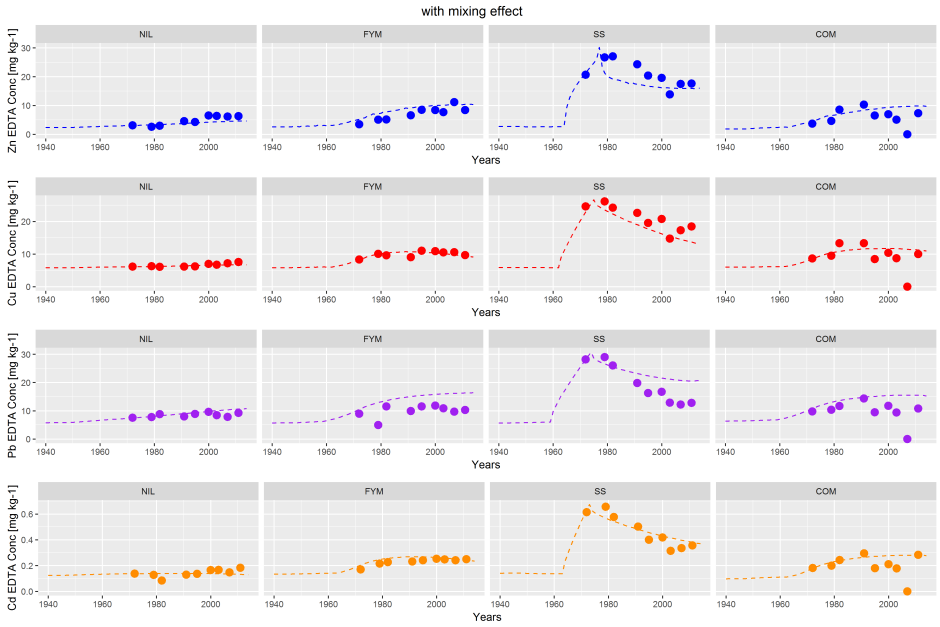

Fig. 2.

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