

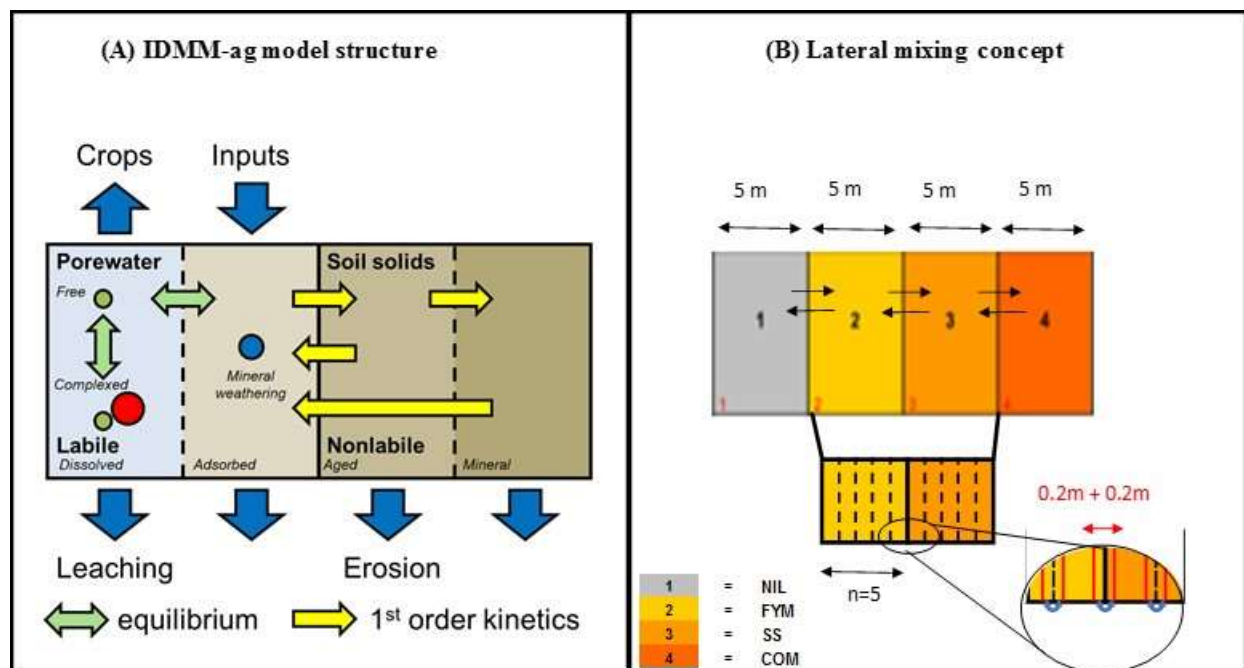
Referee #1

R1: The manuscript presented here deals with the model prediction/description of measured data that reflect the Zn, Cu, Cd and Pb dynamics in a long-term field trial amended with different organic amendments. Then, after evaluation, the used model is extrapolated to the future, to evaluate the possible risks of TEs by long-term application of organic amendments on agricultural fields. The advantage of this model is, according to the authors, that it has a restricted amount of input parameters. However, there are several issues with the manuscript in its current state.

1) The model description is not sufficient and scattered over different sections, which makes it difficult to link the different parts in the model. In addition, it should be much more clear which input parameters are needed for each part of the model (i.e., SOM and pH are likely used to calculate K_f 's? What are input parameters for the WHAM + which complexes are considered?) + references for ageing parameters are not presented. At least an overview of considered reactions should be presented in the SI, to allow the reader to evaluate the restrictions of the model.

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 Referee to present a model overview is very valuable. In particular, we will review the model description in the M&M and add the following paragraph in the SI.

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The IDMM simulates a topsoil as a single, fully-mixed soil layer and computes concentrations of metals associated with the soil and in the soil porewater on an annual basis. The soil layer has a defined depth and comprises fine earth material (the soil material itself), coarse matter (stones) and pore space, which is partly filled by water. Annual gains and losses of metal ($\text{mol m}^{-2} \text{yr}^{-1}$) are computed by a flux balance:

$$\Delta M = M_t + F_{input} + F_{weath} - F_{drain} - F_{crop} \quad (\text{S1})$$

where ΔM is the change in metal pool (mol m^{-2}), M_t is the metal pool in the soil before calculation (mol m^{-2}) and $F_{\text{input}}, F_{\text{weath}}, F_{\text{drain}}, F_{\text{crop}}$ are respectively the fluxes of metal into the soil in external input and weathering of metal the coarse fraction, and losses in porewater drainage and due to cropping.

Within the soil, metal is subdivided into a number of forms according to Figure 2A. These are:

1. Metal in porewater, comprising the free metal ion and metal complexed to solution ligands, including dissolved organic matter (DOM);
2. Adsorbed metal, comprising metal reversibly adsorbed to binding sites on the surface of the fine earth material. The sum of the adsorbed metal and the metal in porewater is the ‘labile’ or ‘geochemically active’ metal, considered measurable by extraction using a strong ligand or dilute acid (e.g. 0.1M EDTA, 0.43M HNO_3).
3. Two pools of ‘aged’ metal. This is metal in the fine earth that is considered ‘fixed’ within the solid phase and only slowly exchangeable with the labile pool. The two pools are characterised by relatively fast and slow exchange kinetics and are termed the ‘aged’ and ‘mineral’ pools.

Chemical speciation of the labile metal, including its distribution between the solid phase and porewater, is handled by equilibrium, while exchanges of metal among the labile, weakly aged and strongly aged pools are handled by kinetics.

Speciation and distribution of the labile metal pool

The equilibrium speciation and solid–porewater distribution of the labile metal pool is computed annually by a combination of empirical modelling and application of the WHAM/Model VI speciation code (Tipping, 1998). Empirical modelling, following the approach of Groenenberg et al. (2010), is used to derive the relationship between the free metal ion concentration in the porewater and the adsorbed metal concentration, as a function of key soil properties:

$$\log K_{f,m} = \log\{M_{\text{ads}}\} - n \cdot \log[M^{2+}] = \gamma_1 + \gamma_2 \cdot pH_{pw} + \gamma_3 \cdot \log\{SOM\}. \quad (\text{S2})$$

Here $\log K_{f,m}$ is a Freundlich–type partition coefficient, defined as $\log\{M_{\text{ads}}\} - n \cdot \log[M^{2+}]$ where $\{M_{\text{ads}}\}$ is the adsorbed metal concentration (mol g^{-1}), $[M^{2+}]$ is the free metal ion concentration in porewater (mol dm^{-3}) and n is a fitted constant in the range zero to unity. The terms pH_{pw} and $\{SOM\}$ are the porewater pH and the soil organic matter content (% w/w) respectively, and the γ terms are fitted constants. The model is optimised by fitting to the error in $\log K_{f,m}$; this drives a set of constants that provide consistent computation of $\{M_{\text{ads}}\}$ from $[M^{2+}]$ and vice versa. The constants used are taken from Groenenberg et al. (2010) and are shown in **Table S1**.

Table S1. Parameters for adsorbed metal–free ion relationships, adapted from Groenenberg et al., 2010

Metal	γ_1	γ_2	γ_3	n
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Cu	-6.37	0.64	0.87	0.57
Zn	-4.67	0.46	0.84	0.84
Cd	-5.71	0.41	0.91	0.70
Pb	-6.46	0.96	1.35	0.84

The relationship between the free metal ion and dissolved metal in the porewater is handled by WHAM/Model VI. Inputs to the model comprise the porewater pH and dissolved concentrations of Na, Mg, Ca, Cl and SO₄, and the DOM concentration. These variables are all specified. An initial adjustment is made, whereby either the concentration of Ca, or those of Cl and SO₄, are adjusted to achieve charge balance at the specified pH. The speciation of Al is handled using the approach of Tipping (2005) to estimate the activity of Al³⁺ in the porewater on the basis of the pH and DOM concentration. The speciation of FeIII is handled by assuming the porewater Fe³⁺ to be in equilibrium with Fe(OH)₃, having a standard solubility constant of 2.5 and a standard enthalpy of -102 kJ mol⁻¹.

The equilibrium constants used are shown in Table S2 and Table S3.

Metal binding to DOM is simulated by assuming it to comprise 65% fulvic acid. Each metal has two binding constants, (i) log *K*_{MA} which is used to derive binding constants for carboxylic and phenolic binding sites, and (ii) Δ*LK*₂, which is used to generate constants for high affinity binding sites.

Table S2. Solution equilibrium parameters for Ca, Al, FeIII and carbonate.

Equilibrium	log <i>K</i>^o	Δ<i>H</i>^o (kJ mol⁻¹)	Reference
$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$	10.329	-14.899	Nordstrom et al. (1990)
$2H^+ + CO_3^{2-} \rightleftharpoons H_2CO_3$	16.681	-24.008	Nordstrom et al. (1990)
$Mg^{2+} + H^+ + CO_3^- \rightleftharpoons MgHCO_3^+$	11.4	-11.59	Nordstrom et al. (1990)
$Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3$	2.98	11.34	Nordstrom et al. (1990)
$Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4$	2.37	19.04	Nordstrom et al. (1990)
$Al^{3+} + OH^- \rightleftharpoons AlOH^{2+}$	9.01	-6.44	May, Helmke, Jackson (1979)
$Al^{3+} + 2OH^- \rightleftharpoons Al(OH)_2^+$	17.87	-15.40	May, Helmke, Jackson (1979)
$Al^{3+} + 4OH^- \rightleftharpoons Al(OH)_4^-$	33.84	-45.44	May, Helmke, Jackson (1979)
$Al^{3+} + SO_4^{2-} \rightleftharpoons AlSO_4^+$	3.2	9.6	Izatt, Eatough, Christensen, Bartholomew (1969) Sillen and Martell (1971)
$Al^{3+} + 2SO_4^{2-} \rightleftharpoons Al(SO_4)_-$	5.11	13.0	Izatt, Eatough, Christensen, Bartholomew (1969) Sillen and Martell (1971)
$Ca^{2+} + H^+ + CO_3^- \rightleftharpoons CaHCO_3^+$	11.44	-3.64	Nordstrom et al. (1990)
$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$	3.22	14.85	Nordstrom et al. (1990)
$Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4$	2.30	6.90	Nordstrom et al. (1990)
$Fe^{3+} + OH^- \rightleftharpoons FeOH^{2+}$	11.81	-12.39	Nordstrom et al. (1990)

$\text{Fe}^{3+} + 2\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2^+$	22.33	-40.25	Nordstrom et al. (1990)
$\text{Fe}^{3+} + 3\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_3$	29.44	-63.97	Nordstrom et al. (1990)
$\text{Fe}^{3+} + 4\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_4^-$	34.4	-90.17	Nordstrom et al. (1990)
$\text{Fe}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeSO}_4^+$	4.04	16.36	Nordstrom et al. (1990)
$\text{Fe}^{3+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^{2+}$	1.48	23.43	Nordstrom et al. (1990)
$\text{Fe}^{3+} + 2\text{Cl}^- \rightleftharpoons \text{FeCl}_2^+$	2.13	–	Nordstrom et al. (1990)

Table S3. Solution equilibrium parameters for Cu, Zn, Cd and Pb

Equilibrium	log K ^o	ΔH° (kJ mol ⁻¹)	Reference
$\text{Cu}^{2+} + \text{OH}^- \rightleftharpoons \text{CuOH}^+$	6.48	–	Sunda and Hanson (1979)
$\text{Cu}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cu}(\text{OH})_2$	11.78	–	Sunda and Hanson (1979)
$\text{Cu}^{2+} + \text{H}^+ + \text{CO}_3^- \rightleftharpoons \text{CuHCO}_3^+$	14.62	–	Mattigod and Sposito (1979)
$\text{Cu}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CuCO}_3$	6.75	–	Smith and Martell (1976)
$\text{Cu}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-}$	9.92	–	Smith and Martell (1976)
$\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4$	2.36	8.8	Smith and Martell (1976)
$\text{Cu}^{2+} + \text{Cl}^- \rightleftharpoons \text{CuCl}^+$	0.4	6.7	Smith and Martell (1976)
$\text{Zn}^{2+} + \text{OH}^- \rightleftharpoons \text{ZnOH}^+$	5.04	–	Baes and Mesmer (1976)
$\text{Zn}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_2$	11.1	–	Baes and Mesmer (1976)
$\text{Zn}^{2+} + \text{H}^+ + \text{CO}_3^- \rightleftharpoons \text{ZnHCO}_3^+$	13.12	–	Mattigod and Sposito (1979)
$\text{Zn}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{ZnCO}_3$	4.76	–	Mattigod and Sposito (1979)
$\text{Zn}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{ZnSO}_4$	2.38	6.3	Smith and Martell (1976)
$\text{Zn}^{2+} + \text{Cl}^- \rightleftharpoons \text{ZnCl}^+$	0.4	5.4	Smith and Martell (1976)
$\text{Cd}^{2+} + \text{OH}^- \rightleftharpoons \text{CdOH}^+$	3.92	–	Baes and Mesmer (1976)
$\text{Cd}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_2$	7.65	–	Baes and Mesmer (1976)
$\text{Cd}^{2+} + \text{H}^+ + \text{CO}_3^- \rightleftharpoons \text{CdHCO}_3^+$	11.83	–	Parkhurst and Appelo (1999)
$\text{Cd}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CdCO}_3$	4.37	–	NIST (2003)
$\text{Cd}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Cd}(\text{CO}_3)_2^{2-}$	7.26	–	NIST (2003)
$\text{Cd}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CdSO}_4$	2.46	9.6	Smith and Martell (1976)
$\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+$	1.98	1.3	Smith and Martell (1976)
$\text{Cd}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CdCl}_2$	2.6	3.8	Smith and Martell (1976)
$\text{Pb}^{2+} + \text{OH}^- \rightleftharpoons \text{PbOH}^+$	6.29	–	Baes and Mesmer (1976)
$\text{Pb}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_2$	10.88	–	Baes and Mesmer (1976)
$\text{Pb}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_3^-$	13.94	–	Baes and Mesmer (1976)

Equilibrium	log K ^o	ΔH ^o (kJ mol ⁻¹)	Reference
Pb ²⁺ + CO ₃ ²⁻ ⇌ PbCO ₃	7.2	–	Buffle, Chalmers, Masson, Midgley (1988)
Pb ²⁺ + 2CO ₃ ²⁻ ⇌ Pb(CO ₃) ₂ ²⁻	10.5	–	Buffle, Chalmers, Masson, Midgley (1988)
Pb ²⁺ + SO ₄ ²⁻ ⇌ PbSO ₄	2.75	–	Smith and Martell (1976)
Pb ²⁺ + Cl ⁻ ⇌ PbCl ⁺	1.59	18.4	Smith and Martell (1976)
Pb ²⁺ + 2Cl ⁻ ⇌ PbCl ₂	1.8	–	Smith and Martell (1976)

Table S4. Constants for metal binding to fulvic acid in WHAM/Model VI. All from Tipping (1998) except where noted.

Metal	log K _{MA}	ΔLK ₂
Mg	1.1	0.12
Al	2.5	0.46
Ca	1.3	0
FeIII ^a	2.6	2.20
Cu	2.1	2.34
Zn	1.6	1.28
Cd	1.6	1.48
Pb	2.2	0.93

^a log K_{MA} from Tipping, Rey-Castro, Bryan, Hamilton-Taylor, 2002.

Exchange between labile, aged and mineral pools

Metal exchanges between the labile, aged and mineral pools are handled by a first order kinetic schema as introduced by Xu, Lofts and Lu (2016). The schema allows the following transfers of metal among the pools: (i) labile to aged, (ii) aged to labile, (iii) aged to mineral, and (iv) mineral to labile. These transfers are described by the kinetic constants $k_{f,a}$, $k_{f,b}$, $k_{f,m}$ and $k_{b,m}$ respectively. These are summarised in Table S5.

Table S5. Kinetic constants for metals transfers among the labile, aged and mineral pools.

Metal	$k_{f,a}$	$k_{f,b}$	$k_{f,m}$	$k_{b,m}$	Reference
Cu	$10^{-2.5+10^{-3.3}e^{pH_{pw}}}$	$10^{-2.1+10^{-3.5}e^{pH_{pw}}}$	10^{-5}		a
Zn	$10^{-4.2+0.26pH_{pw}}$	$10^{-3.2}$	10^{-5}		a
Cd	$10^{-2.9+0.18pH_{pw}}$	$10^{-1.6}$	10^{-5}		a
Pb	$10^{-6.3+0.51pH_{pw}}$	$10^{-2.6}$	10^{-5}		this study

^a Xu, Lofts and Lu (2016)

Aging constants for Pb were derived by analysis of an ongoing long term experiment, comprising four UK soils. Soils were spiked with lead and incubated with maintenance of temperature and moisture content (55% of water holding capacity). Samples were periodically taken for quantification of lead spike lability using isotopic dilution. Fitting results are shown in Figure S1.

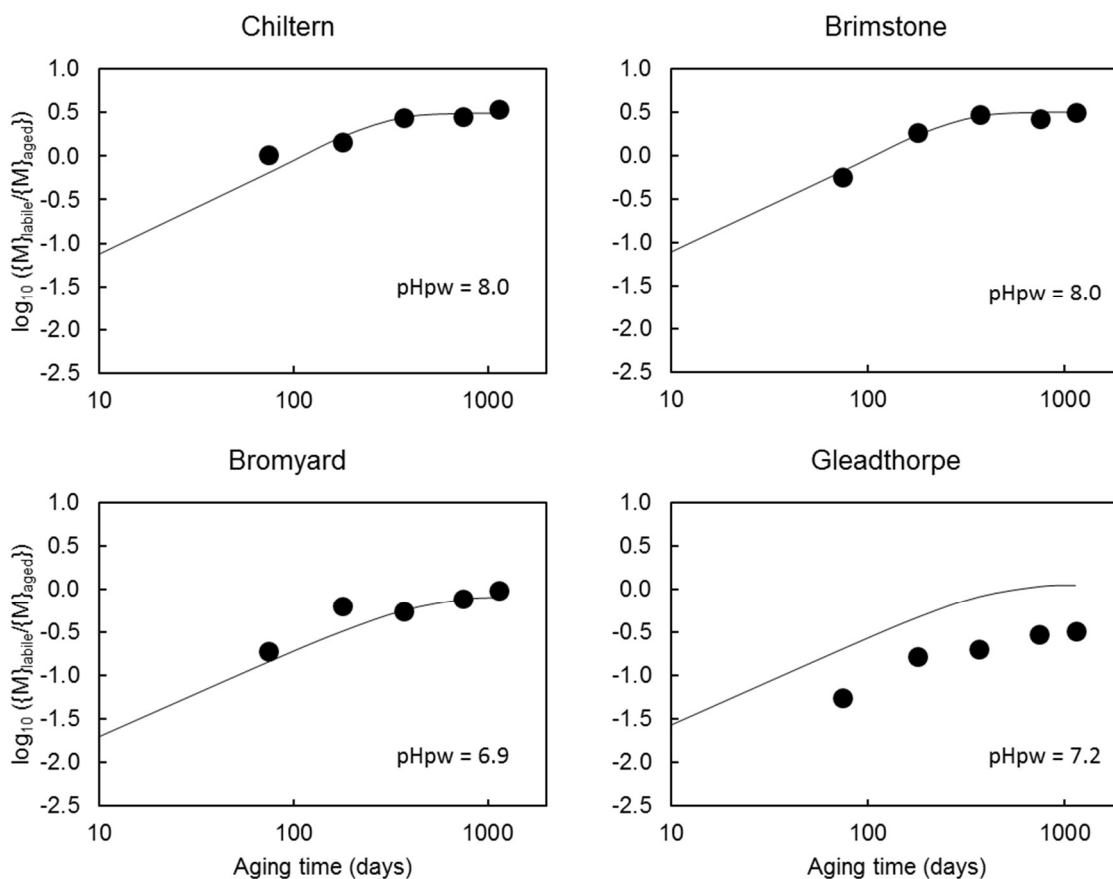


Figure S1. Aging of lead spikes in four UK soils and model fits using the expressions and parameters in Table S5.

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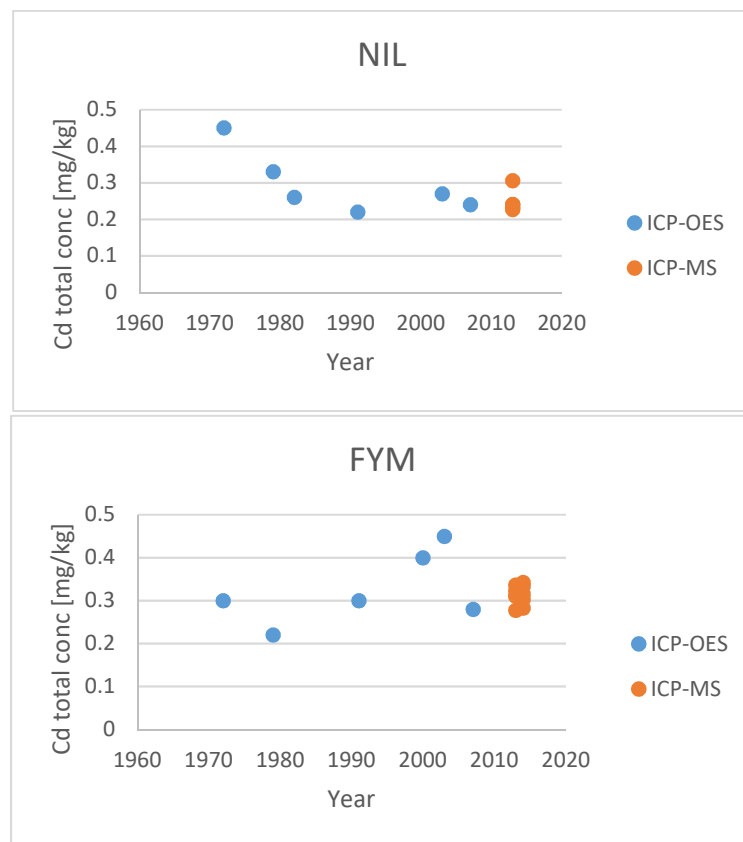
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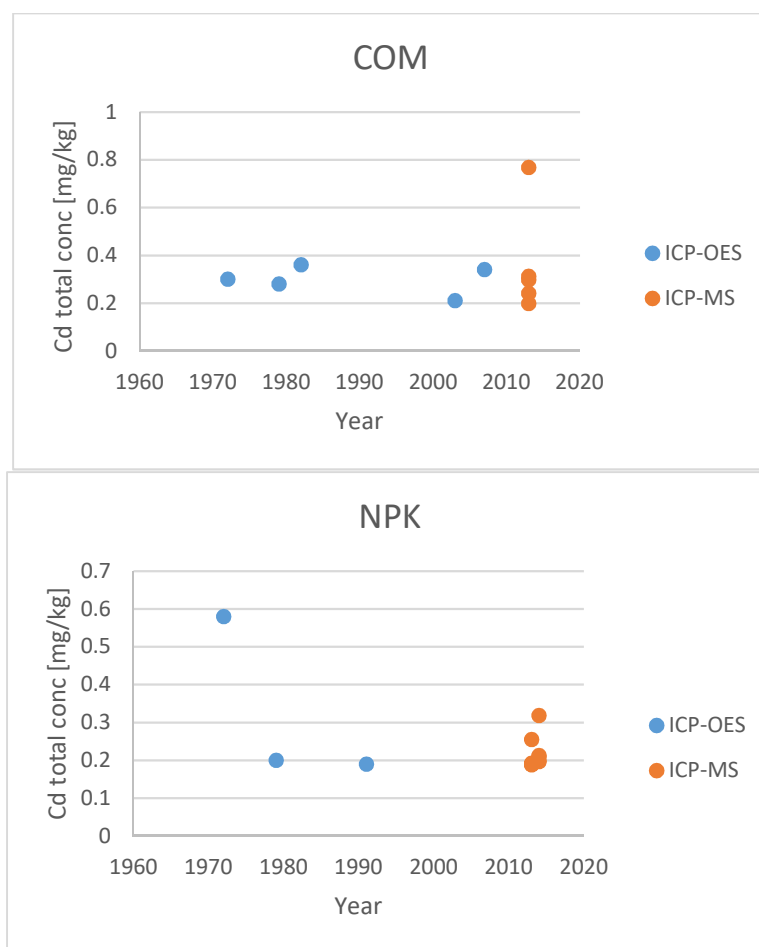
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R1: 2) The measurements of the TEs lack quality control, the limit of quantification of each element and the relation with the measured data should be presented and, maybe most importantly, the Cd concentrations in the extracts are measured with ICP-OES, what could be troublesome regarding the known interferences during ICP-OES measurements with As in soil extracts.

ICP-OES could give interference of As with Cd measurements, particularly when As is present at medium/high concentrations while Cd is close to the background values (see McBride. 2011. *A comparison of reliability of soil Cd determination by standard spectrometric methods. J Environ Qual. 2011; 40(6): 1863–1869. doi:10.2134/jeq2011.0096*). Unfortunately, we did not measure As concentrations in the field, though we do not expect high enrichment of As in ZOFE soil. However, as a validation of the analytic procedure, we compared the total metal concentration time trends obtained by extraction in aqua regia and analysis of the extracts with ICP-OES with the total metal concentrations obtained from another laboratory in Zurich which analysed the same plots in 2013 and partly in 2014 using extraction in aqua regia and analysis with ICP-MS. In fact, ICP-MS is recognized to have greater sensitivity in Cd determination. We show below the comparison for Cd: measurements from ICP-OES and ICP-MS are in good agreement. This test rules out any possible interference with As. Please note that for determination of total concentrations, the extractions were done with aqua regia and not with 1 M HNO₃ as erroneously indicated in the paper.





As to the quality control of the ICP-EOS measurements, it is done on the calibration curve every 10 readings by measuring the TES concentrations in the blanks and in the standard sample at the intermediate concentration of 1 ppm. The limit of quantification for every element is 3 standard deviations of the readings from the blank samples. Therefore, we propose to modify the paragraph in the M&M as follows:

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The NIL, FYM, SS and COM soils (top 20cm) were sampled from the Agroscope ZOFE soil archive and analysed for total and EDTA-extractable concentrations of Zn, Cu, Pb and Cd. Soils sampled were from years 1972, 1979, 1982, 1991, 1995, 2000, 2003, 2007 and 2011. Before 2011, the samples from the five replicate plots per treatment had been bulked, so that the variability between replicate plots could not be assessed. The archived samples comprised only the 2mm-sieved fraction. To determine total soil TEs concentrations, sample extracts in aqua regia were analysed by means of an inductively coupled plasma optical emission spectrometry (ICP-OES Dv sequential Perkin Elmer Optima 2000). The EDTA-extractable

pools were obtained with the extraction protocol described by Quevauviller (1998) followed by ICP-OES analysis. *Total metal concentration trends obtained with ICP-OES were compared with one-point-in-time measurements from the same plots carried out in other laboratory with ICP-MS, to rule out any interference of As with Cd readings (McBride, 2011). Quality control of the ICP-OES was done on the calibration curve every ten readings by measuring the TES concentrations in the blank samples and in the standard sample at the intermediate concentration of 1 ppm. The limit of quantification for each element was calculated as three standard deviations of the blank readings.* For each metal we took the ratio of the EDTA-extractable concentration and total concentration in the same year to define the metal lability as a measure of the biogeochemically-available fraction at that point in time.

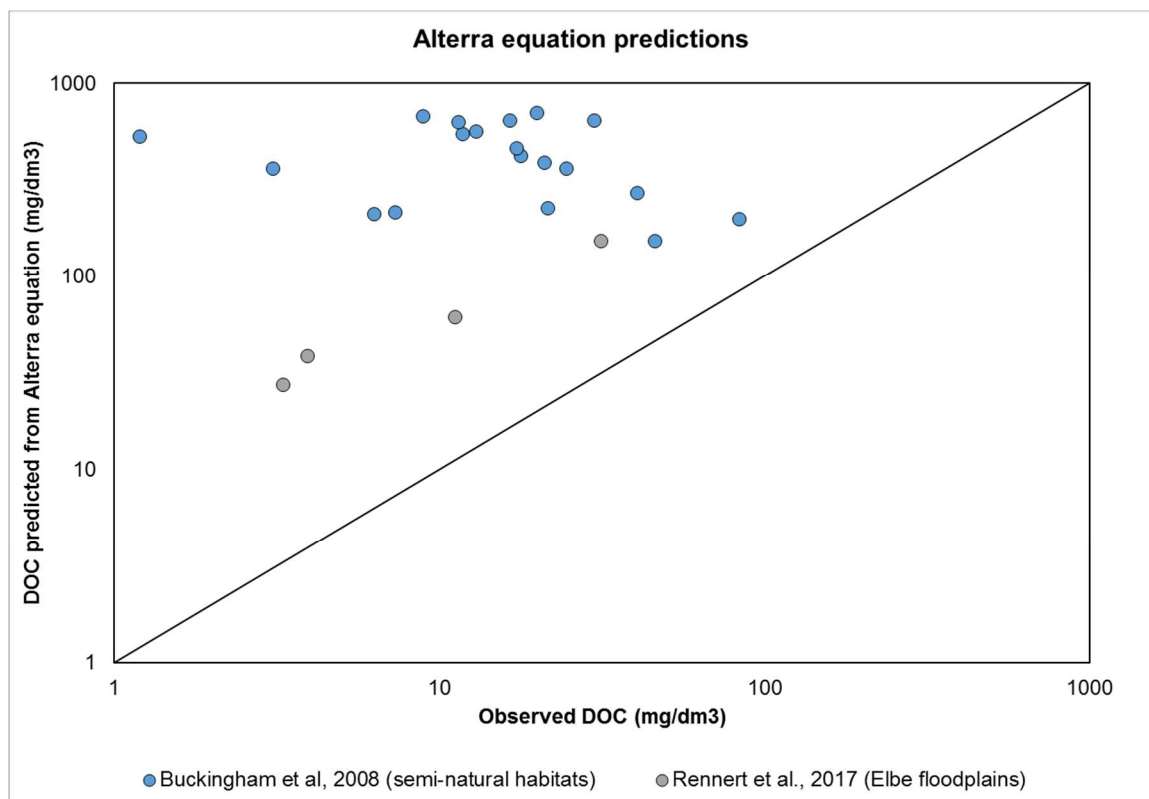
Samples of farmyard manure of years 2011 and 2014, sewage sludge of years 2008 and 2012 and compost of years 2011, 2013 and 2014 were also analysed for total (*by extracting 0.5 g of organic amendment in 10 ml of HNO₃*) and EDTA-extractable concentrations of Zn, Cu, Pb and Cd.

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R1: 3) The implementation of DOC in the model. Because no measurements were available, the DOC is fixed at 7 mg/L for all treatments (as in the beginning of the experiment) and remained constant, despite the application of different organic amendments. I am critical to this approach, due to the important effect of DOC to metal leaching. I would expect increasing (or changing between treatments) DOC concentrations over the years of the different organic amendment applications or at least increased DOC fluxes right after organic amendments that could increase metal leaching.

The Referee raises an important point on the role of the porewater DOC concentration, and we acknowledge that we have not justified the assumptions made regarding its concentrations. Therefore, we propose to introduce the following considerations into the ms.

Data on porewater DOC concentrations from arable soils are scarce and contradictory. To the best of our knowledge, there are no consistent data from long-term experiments. There are a small number of meta-analyses (for example Li et al., 2019; de Troyer et al., 2014), but they are not ideal, because: 1) they do not contain data on soils amended according to all the management approaches taken in ZOFE, so some residual assumptions on DOC would be required; 2) we could not find any data on long-term time trends of field DOC concentrations under arable soils; 3) DOC concentrations obtained from laboratory soil extractions differ from data collected directly from the field using lysimeters, with the latter usually showing lower concentrations; if this is the case, most of the available DOC data are likely to be overestimates of 'true' field concentrations and thus bias the model results. We compared the predictions of the equation suggested by Referee #2 to estimate DOC from pH and SOM (Derivation of Partition Relationships to Calculate Cd, Cu, Ni, Pb, Zn Solubility and Activity in Soil Solutions; Alterra: Wageningen, 2004; p 75) with data from two studies that measured DOC sampled in field using lysimeters:



There is a consistent trend to overestimation of the observed DOC concentration (up to at least two orders of magnitude) and no relationship between observed and predicted DOC concentrations. Therefore, we strongly conclude that the Alterra equation should at best be applied with great care. Application of the equation to the ZOFE plots produced predicted DOC concentrations in the range 60-80 mg/dm³, which we contend, on the basis of the chart above, is highly likely to overestimate DOC and thus not be useful for our purposes.

In conclusion, we think that sources of reliable DOC concentrations for agricultural fields are effectively missing, and so should be identified as key research priorities. Therefore, we suggest that (i) this knowledge gap should be openly confronted and emphasised in the ms; (ii) given this lack of knowledge, the most pragmatic approach is to carry out a systematic sensitivity analysis within a

plausible range of DOC concentrations, incorporating also time trends. We will do a mini-review of field measurements of annual DOC fluxes for temperate grassland sites (before 1949) and arable with/without organic amendments (after 1949) and we will perform simulations with the minimum, maximum and midpoint of our established range of DOC fluxes. To incorporate the time trends in the sensitivity analysis, we propose to apply to each plot a simplified SOC model (for example, a two-pool model like the one in Menichetti et al. (2016), which was previously applied to ZOFÉ), assuming that DOC correlates with the decomposition fluxes out of these pools. Clearly, this estimation of DOC is affected by the assumptions of C input decomposability when shifting the site management from grassland to arable in 1949; in addition, this approach does not include the effect of soil acidification, which is reported to control the adsorption/desorption of DOC. However, it could be considered a first estimation of DOC time trend.

We have already made some preliminary checks and the main conclusions are the following: increasing the DOC concentration in the control treatment has the effect of increasing the additional flux of metals that we hypothesized to be mineral weathering from the coarse fraction – this is to expected as the assumed DOC and weathering fluxes are not independent since the DOC controls the predicted soil labile concentration at steady state. Also, the impact of increasing five-fold the DOC concentration in the control treatment has a modest effect on the simulated labile concentrations (always <10%). On the other hand, increasing the DOC concentrations in the organic-amended treatments relative to the control treatment has the effect of lowering the metal concentration time-trends in these treatments, thus improving the overall simulation; yet, the effect is also modest.

Finally, the Referee suggests that DOC might peak after amendment application to slowly decrease until next application; this “cycle trend” is likely to happen, however since IDMM-ag has an annual time step, such short term effects are not modelled and an annual average DOC concentration, corresponding to the annual DOC flux, is what the model requires.

References:

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

De Troyer et al (2014). Factors Controlling the Dissolved Organic Matter Concentration in Pore Waters of Agricultural Soils. *Vadose Zone J.*

Menichetti et al. (2016.). Parametrization consequences of constraining soil organic matter models by total carbon and radiocarbon using long-term field data. *Biogeosciences*, 13, 3003-3019.

R1: 4) The artefacts associated with the experimental design of the ZOFÉ, namely plots touching each other + mixing of plots edges by ploughing. In the model evaluation, it appeared to be critical to introduce lateral mixing. This does not allow to evaluate the model without mixing, which is later used to extrapolate into the future. The lateral spread of TE concentration should be validated in a transect across plots in the ZOFÉ experiment by some new measurements, to underpin this model approach.

Long-term experiments comprising different treatments are valuable sources of information, but here we showed a potentially unrecognized drawback: plots can be affected by soil mixing with ploughing (plots have a separation space, but eventually it is too narrow for mechanical ploughing). This effect is hardly detectable unless elements present in trace concentrations are taken into account.

Therefore, lateral mixing was introduced to check whether we could fit the data with realistic mixing coefficients. The 4 treatments considered were perfectly adjacent in 3 out of the 5 repetitions (in the other 2 repetitions the compost treatment only was separated from the “block”), so we can argue that the lateral mixing is well represented by the considered treatments and collected data. Clearly, the specific conditions in the long-term experiments cannot be extrapolated to real field conditions, and this is why we did not include the lateral mixing when projecting into the future the TE accumulation. 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 the real benefits we will get out of such an activity.

R1: In the results, the treatment effects should be evaluated relative to the control data, to evaluate and contribute observed trends to the organic amendments solely, which is the scope of this study.

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 metal concentrations of the organic amended treatments relative to the control treatment for the projections into the future.

R1: In addition, both the abstract and introduction lack quantitative data, the English writing could be improved and the final discussion of the results becomes difficult to follow starting from lines 408 to the end.

We will introduce quantitative data as per points below, revise some English mistakes/typos and try to make clearer the ms from line 408.

R1: Further point-by-point comments are presented below.

Abstract

36: abbreviation of model.

Yes, we will give first the full name. thanks.

38: soil plots, different.

OK, we will use different.

Are there more organic amendments than the ones summed up here (particularly is not the best link word here).

Yes, there are other mixed treatments amended with organic amendments and mineral fertilizers.

39-40: link with previous sentence is missing, maybe this sentence can be declined here + don't start sentence with an abbreviation.

Ok, we will get rid of the sentence here.

41: better provide quantitative measure of model performance.

OK, we will report the r metric. Thanks.

41: abbreviation ZOFÉ.

Right, we will replace with full name.

Wouldn't it be interesting to add the range of EDTA-extractable concentrations here in the abstract?

We will.

46: labile = EDTA-extractable? + provide projections, i.e. after XX years, concentrations could increase to YY.

We will use EDTA-extractable here. Yes, we will provide quantitative projections.

Introduction

57-58: this sentence is too vague and is not really necessary here, can be skipped.

OK.

59-64: it would be interesting if you would add the concentration ranges at which the essential and the non-essential TEs become of a concern.

I can provide some mini literature review for the TEs of concern here.

68: an

Yes.

68-71: please rephrase to make the message more clear.

OK. Provisional: "In a European Union wide survey, Ballabio et al. (2018) reported that agricultural soils have one of the highest potential to become enriched in TEs compared with other land uses, and that land cover and management are better predictors of soil Cu concentrations than natural soil formation factors."

71-75: the link with the previous section is not clear. In addition, what do you mean with "limited natural availability of nutrient elements such as P"? Preferably start your sentence with the main message, for example "Organic amendments are considered to be more sustainable than inorganic mineral fertilizers, due to XX and YY".

We mean that P is a limited (not-renewable) natural resource. Provisional rephrase: "Organic amendments are considered to be more sustainable than inorganic mineral fertilizers: for example, current industrial processes for N-fertilizer production are energy-intensive and P-fertilizers are produced from phosphate rocks which are naturally limited (Roberts, 2014)".

77: isn't it just the transformation of the organic amendment to SOM that contributes to carbon sequestration as such, not additional C sequestration from atmosphere? If not, please explain more, but only if relevant for this study!

Soil fertility can give a positive feedback to carbon sequestration via vegetation growth.

Actually, line 71-77 could be skipped from this introduction and you could go right at the possible introduction of TEs into soil by organic amendments, to keep the introduction to the point and relevant for this study.

Ok.

77-81: please provide concentration ranges for the TEs in the different organic amendments.

OK. We'll make a mini-review for this.

83: fate? + please rephrase second part of sentence

ok

86: you mean mobility (for solubility)?

Meaning the partition between soil solids and soil solution. We'll rephrase.

87-89: please provide examples or more explanation of importance of TE speciation vs toxicity

Yes, we will.

93: direct reactions?

Binding to soil solids. We will rephrase.

90: I think you can even say that it is not only useful, but even necessary

Ok.

97-98: you already stated this in line 90-91

OK

99-100: Please rephrase: I would not say that mechanistic models are site specific. Indeed, models that predict TE mobility and transfers over time by using as much as possible underlying physical and chemical mechanisms are likely only useful on a limited size scale, due to the high input needed, but they can be used at every site (when data are available), so they are not site specific.

We see your point, therefore we will get rid of "site-specific".

And what about empirical models?

Indeed, IDMM is partly empirical, which alleviates some of the complexity of the mechanistic models. I will expand this concept and merge with the concepts expressed further below the text.

102: what do you mean with behaviour?

Dynamic, we will replace it.

102-106: Ah, here you talk about empirical models. Please merge with text above and try to be more concise.

OK.

112-115: this is vague, could you specify more what variables you are talking about, and which mechanistic level of understanding is wanted.

We will give full model description in the SI, as we answered above.

Has this model been used already (and at what scale)? If yes, please provide the current state-of-the-art of the performance on this model. What is the knowledge gap here for this study now?

Thanks for the comment. We will clarify that the model has been used previously at catchment scale, while here we considered a much finer scale.

121: IDMM-ag?

IDMM, I will correct the old naming IDMM-ag.

122: What is “larger scale” here?

Realistic field scale.

123-124: “The hypothesis was that, if the model is successfully applied at field scale with no need of calibration, it might be used at larger scale as well, provided adequate inputs.” -> can you test the second part of your hypothesis with this study? If not, please rephrase the hypothesis.

We agree. Provisional version: “The hypothesis was to be able to apply the model to the long-term experiment field with no need of site-specific calibration. Also, we assumed that we could apply the same model to realistic field conditions under same agronomic practices in order to assess their sustainability over time”.

125: ZOFÉ?

We will define the acronym first, thanks.

131-133: please clarify sentence: “large scale”, “broad trends”, TE concentrations in soil? + rephrase final part of sentence.

OK, we will rephrase, meaning field scale.

M&M

150-152: for TE accumulation, the total applied amendment will likely be important, depending on the data collected on the TE content (per kg of material, per kg of OM,... ?).

We wrote “5 t ha⁻¹ of organic matter every second year...”, so we can rephrase it in “5 t OM ha⁻¹ every second year...”

160: 1M HNO₃ extractable metals are not total TE concentrations, please just write 1M HNO₃ extractable metals. And please also provide more experimental details, L:S ratio, extraction time. In addition, it would be interesting if this 1M HNO₃ extracted TEs could be related somehow to “total” element concentrations, measured by aqua regia or XRF or other, more standardized extraction protocols for total soil metal concentration.

As already said above, we made a mistake and we will correct it: the extraction with aqua regia was used for determination of total concentrations.

162-163: please shortly describe, conc. of EDTA, L/S ratio, extraction time.

We wonder if it is really useful to report the protocol described by Quevauviller (1998), as we followed exactly it. Maybe we could spare some space for the results, as the ms is already quite long...

164: try to avoid the use of “we”

ok

164-166: on what is the use of EDTA:1MHNO₃ extractable metals as a measure of lability based? Please clarify. Is this already used/tested? If so, please provide references.

See above, we used EDTA/aqua regia extractable metals as a measure of lability.

What about quality control of these measurements, what is the limit of quantification of these methods and how do the measured soil samples relate to this? This could be described already here, or in the results section. In addition, the determination of Cd with ICP-OES in extracts from soil samples

is troublesome due to the interferences with As, even at relative low As soil concentrations. For example see: "A comparison of reliability of soil Cd determination by standard spectrometric methods, M. McBride, JEQ 2011 (40, 1863-1865, doi: 10.2134/jeq2011.0096) and likely many other publications. Did you take this into account? If not, the reliability of the Cd measurements from this study can be severely questioned.

See above for full answer and proposed changes in the ms.

178: preferably write : free and adsorbed TE ions, in contrast to "free TEs"

OK

176-179: please provide an overview of the Freundlich isotherms and TE complexes considered during this study in the supporting information. What are the input parameters for the Freundlich model (i.e. which extraction did you choose to represent the adsorbed fraction, and how does this relate to the adsorbed fraction represented in the initial models of Groenenberg (I think they used 0.43M HNO₃ acid extractable metals as "reactive" soil metals). In addition, what other soil properties were measured to calculate the KF by the transfer functions of Groenenberg and how are these soil properties measured? What are the input parameters of the WHAM model and how are they measured?

See above: we will add an extra explanation in the SI

180: please provide the first-order rate constants used for each element and explain wherefrom they are derived (references).

See above: we will add an extra explanation in the SI

184: please provide the start year used in the calculations

Yes, we will, it is 1750.

186-187: please rephrase this sentence, it is not clear what is stated here

Ok, we will. The message is that erosion was neglected as the field was flat.

204-206: please clarify, not clear.

Yes, we will add in the ms that we used the transfer functions reported by Thoni et al. (1996) for Switzerland (Figure S1 in Supporting Information).

207-208: please be consistent in choice of unit

Yes, we will, thanks.

208-211: please provide the data of these fitted mineral weathering fluxes and compare with literature data, if possible.

As said below, we will move this part here from the results.

217: on what are these transfer functions based? Please shortly describe.

Ok.

220: P loading from the manure? You mean addition of P to the fields by manure application? You could quickly give the data here.

Yes, we mean that. Ok we will add the data here.

222: not clear, did you take the X:P ratio's from literature (=1100 data points) or from own measurements (= 2 data points)? Was P also measured in the FYM? That is not been described previously. In addition, how does the measured X:P ratio related to the literature reported?

We will rephrase if not clear. Basically, for Zn and Cu ratios we used the measurements: "The Zn:P and Cu:P ratios were averaged from the values measured in the farmyard manure samples applied in 2011 and 2014 as reported in Table 1". For Pb and Cd we used ratios from literature: "The Pb and Cd inputs with FYM application were also calculated from the P content, using Pb:P and Cd:P ratio values of 0.495 and 0.027, respectively, taken from the work 230 of Menzi and Kessler (2009)"

227: derivation of these factors? One time decrease or decrease linearly with time? Not clear.

These factors were derived from surveys in the cited references. We used a stepwise reduction from 2000 onwards.

231: the detection limit in the caption of table 1 is expressed in mg/L while the concentration data are expressed in mg/kg. Please provide detection limit in mg/kg, to provide a clear idea of the lowest measureable concentration in the FYM. See comment above on the analytics of soils and organic amendments.

Yes, we will change the units. See answer above for detection limits.

232: written like this, Figure S2 is about detection limits, which is not. Please rephrase.

OK

238: tTEs + avoid "we"

OK

245: which peaks? In the soils?

"the peaks measured in the EDTA-extracted concentration trends". We'll add reference to Figure 5 to make it clearer.

246: soil metal concentrations negligible?

It is a typo, we meant sewage sludge metal concentration. Thanks, we will correct it.

Figure S3: in the swiss sludge trend, the Cd fluxes trend is deviating from the other metals. Why?

For Cd, the concentration before 1975 was decreased by a factor of 0.2 because it would give unrealistically/high concentrations. To be added in the explanation.

253-255: Ok at the start of the experiment, but I would expect increasing or changing DOC concentrations over the years of organic amendment applications (or between treatments) or at least DOC fluxes right after organic amendments. I think this approach (constant & low DOC over time) is not a good approach to simulate metal leaching over time in organic amendment treated plots (I assume this constant DOC is then the WHAM input?).

See the answer above.

256: on what is this plausible range based?

We proposed to include a sensitivity analysis on a broad range of DOC values. Still, we think that most DOC measurements in the lab overestimate the field DOC concentrations and that a low DOC value in the NIL treatment is plausible.

257: minor increase for fitted additional input flux? Not clear. + what is minor?

We will change this part with a full sensitivity analysis on DOC (and relevant fitted mineral weathering fluxes)

261: not clear

261: measurements of plant material has not been presented + data for Pb? In addition, changes of plant TE concentrations with changes in labile TE concentration in soils were not considered?

We actually showed estimated crop biomass (from measured product yield) over the course of the long-term experiment in Figure S4. The plant absorption flux in IDMM is calculated, as written, from plant material and fixed plant concentration of TEs.

267-268: It is not clearly explained how SOM and pH affect soil/solution partitioning, aging and speciation, because the input data/model description for the Freundlich, WHAM model and aging model are not well specified.

We will give full model explanation in the SI, see above.

284: pecks?

Typo, it is peaks.

290-291: why?

It is a description of the instrument capabilities...

305-306: Please state how the soil total concentrations are/should be measured in this Swiss Ordinance and comment on own measurement data.

Yes, thanks. Total concentration should be determined by extraction with 2 M HNO₃ with a proportion of 1:10 (w/v). We'll make it clear.

311-313: not clear + why 0.1?

We report the answer to Referee #2. We will slightly change the approach and explain it more in details.

We will use a slightly different but more standardized approach to estimate trace element critical limits. This time we will apply: *Lofts et al. (2004). Deriving Soil Critical Limits for Cu, Zn, Cd, and Pb: A Method Based on Free Ion Concentrations. Environ. Sci. Technol. 2004, 38, 3623-3631.* Furthermore, in the future projections we will show the variation of the critical limits over time together with pH and SOM changes. We agree with the Referee that the background concentrations should be subtracted for the calculation of the critical limits; therefore, we propose to subtract the trace element concentrations estimated by the model before 1949 (the start of the experiment).

Results and discussion

324: the trends in the organic amendment plots should be investigated relative to the trends in the control plots, to exclude all other enrichment/losses other than use of organic amendments, which is the core of this study. Then, the statistical analysis should be repeated on these relative data.

As suggested before, considering that the control treatment is involved in the lateral mixing, we propose to keep it separate in the simulations of the long-term data, and to show the relative trends, as suggested by the Referee, only in the future projections.

334-336: compare the measured Cu loss with the literature values + on what is this “expected” Cu leaching based.

OK, we will carry out a mini-literature review on CU losses and we will specify what the leaching is based on (which basically depends on the concentration of dissolved Cu and water leaching from the topsoil).

348-364: same comment, compare treatment effects relative to control.

Same as above.

350-357: you should test correlations between the data to underpin these suggestions.

We will remove most of the text from 322 to 374, and also the suggestions in 350-357.

370: P-overfertilization? Based on what?

We agree. We will rephrase the sentence just saying that P concentration in the sewage sludge was more than twice the P in the farmyard manure and compost.

378-388: this was already (partly) described in the M&M section (and provides answer to above comments), please move this section to the M&M.

Ok.

390: in the figures (also in SI), the ZOFÉ trend is mentioned. Is this the “Idealized trend”?

Thanks for the comment, yes we improperly used “ZOFÉ Trend” instead of “Idealized Trend”; we will correct it.

399-401: I have severe doubts of the applicability of the modelling results of TE dynamics to a realistic scale, as the experimental conditions of the field experiment are so specific, i.e., high TE concentration plots “contaminate” low TE concentration plots, so all the treatment effects are obscured by an experimental artefact (i.e. the plowing, the plots being so close to each other...). To be more clear -> the model was not capable to predict the measured concentrations, because the measured concentrations are affected due to the specific design and maintenance of the experimental plots, but such experimental plot are not relevant for real agricultural fields (i.e. narrow soil strips with different amendments that are influenced by lateral mixing), which makes the “fixing” of the model with the lateral mixing not really important for real situations. In addition, due to the fixing of the model by lateral mixing, the true performance of the model cannot be evaluated, and the extrapolation (done in figure 9) to real fields is questionable. However, I understand that this is related to the specific nature of this experimental design and that it is nevertheless worth to investigate the data available, due to the valuable information present from these long-term experiments. However, to verify the overall modelling approach (including lateral mixing and excluding it again to extrapolate the model), I think a simulated transect from figure 6 should be validated by measurements-> i.e. sample along a transect in the ZOFÉ experiment, measure labile concentrations and remodel for the sampling year.

We already provided an answer to this comment that we report below for convenience.

Long-term experiments comprising different treatments are valuable sources of information, but here we showed a potentially unrecognized drawback: plots can be affected by soil mixing with ploughing (plots have a separation space, but eventually it is too narrow for mechanical ploughing). This effect is hardly detectable unless elements present in trace concentrations are taken into account. Therefore, lateral mixing was introduced to check whether we could fit the data with realistic mixing coefficients. The 4 treatments considered were perfectly adjacent in 3 out of the 5 repetitions (in the other 2 repetitions the compost treatment only was separated from the “block”), so we can argue that the lateral mixing is well represented by the considered treatments and collected data. Clearly, the specific conditions in the long-term experiments cannot be extrapolated to real field conditions, and this is why we did not include the lateral mixing when projecting into the future the TE accumulation. 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 the real benefits we will get out of such an activity.

402: I guess only the r-value of the Cd is significant? Provide significance of r-values.

Thanks for the suggestion, we will provide the p-value.

408 and further: not clear anymore. Initial measurements underestimated? I've understand that these were fitted?

It was underestimated by a factor of three with the “Swiss Sludge Trend” as opposed to the “Idealized Trend”. We will be clearer in the sentence.

471-472: but the EDTA-extractable concentrations were measured? Couldn't this provide information of the “lability” of the TE input by the organic amendments.

We measured the “lability” of the TE input by the organic amendments only in the few available samples: in 2011 and 2014 for farmyard manure, in 2008 and 2012 for sewage sludge and in 2011, 2013, 2014 for compost (see Figure 4). The TE lability in the sewage sludge was highly variable; we found that the organic fraction of the sewage sludge was variable as well. Unfortunately, we didn't have a full time trend to fit in the model, therefore we considered the lability data as qualitative. Furthermore, the TE lability measured in the organic amendments did not always have a good match with the lability measured in the soil (for example, for Zn).