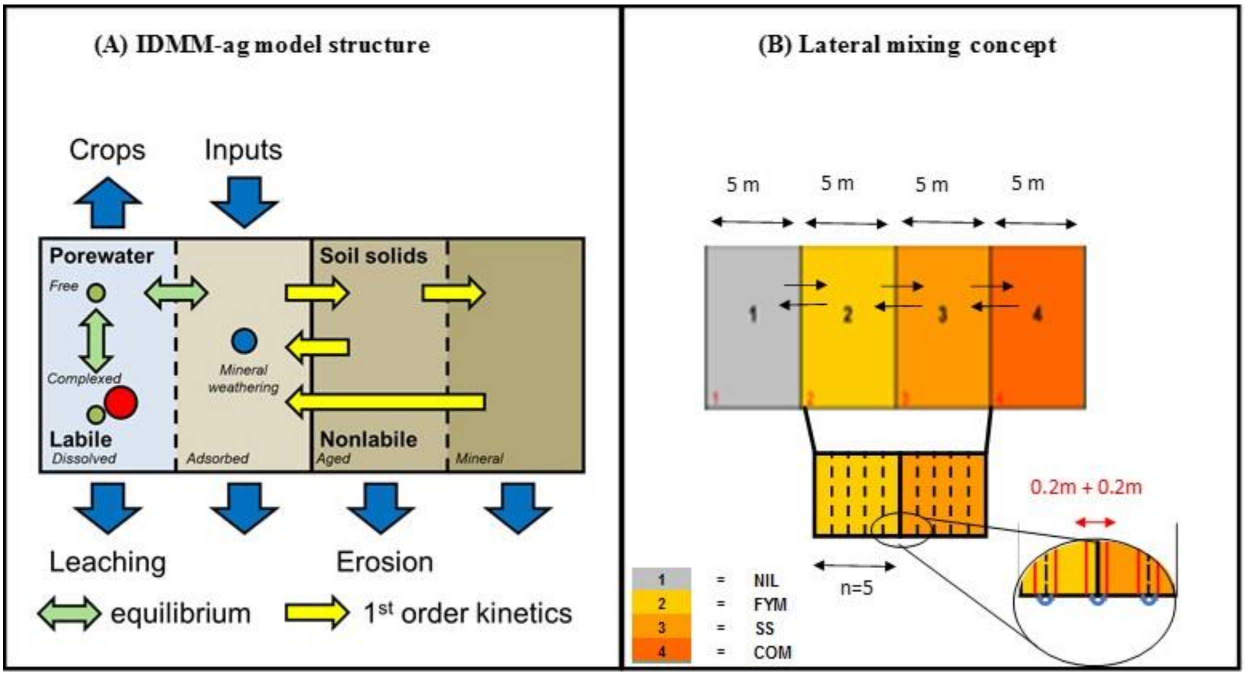
Referee #1

Below we answer to the main points raised by the Referee.

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 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.



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 (mol m^{-2} yr^{-1}) are computed by a flux balance:

$$\Delta M = M_t + F_{input} + F_{weath} - F_{drain} - F_{crop} \tag{S1}$$

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_{input}, F_{weath}, F_{drain}, F_{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:

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

Here $\log K_{f.m}$ is a Freundlich–type partition coefficient, defined as $\log\{\mathrm{M_{ads}}\} - n \cdot \log[\mathrm{M^{2+}}]$ where $\{\mathrm{M_{ads}}\}$ is the adsorbed metal concentration (mol g^{-1}), $[\mathrm{M^{2+}}]$ 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 $\{\mathrm{SOM}\}$ 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 $\{\mathrm{M_{ads}}\}$ from $[\mathrm{M^{2+}}]$ 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_1	γ_1	$\mathbf{n}$
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 SO_4, 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 SO_4, 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 Al^{3+} in the porewater on the basis of the pH and DOM concentration. The speciation of FeIII is handled by assuming the porewater Fe^{3+} 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) ΔLK_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 $K^{\ominus}$**	**$\Delta H^{\ominus}$ (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)
$Fe^{3+} + 2OH^- \rightleftharpoons Fe(OH)_2^+$	22.33	-40.25	Nordstrom et al. (1990)
$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3$	29.44	-63.97	Nordstrom et al. (1990)
$Fe^{3+} + 4OH^- \rightleftharpoons Fe(OH)_4^-$	34.4	-90.17	Nordstrom et al. (1990)
$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+$	4.04	16.36	Nordstrom et al. (1990)
$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$	1.48	23.43	Nordstrom et al. (1990)
$Fe^{3+} + 2Cl^- \rightleftharpoons FeCl_2^+$	2.13	–	Nordstrom et al. (1990)

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

Equilibrium	**log K$^{\ominus}$**	**ΔH$^{\ominus}$ (kJ mol^{-1})**	**Reference**
$Cu^{2+} + OH^{-} \rightleftharpoons CuOH^{+}$	6.48	–	Sunda and Hanson (1979)
$Cu^{2+} + 2OH^{-} \rightleftharpoons Cu(OH)_2$	11.78	–	Sunda and Hanson (1979)
$Cu^{2+} + H^{+} + CO_3^{-} \rightleftharpoons CuHCO_3^{+}$	14.62	–	Mattigod and Sposito (1979)
$Cu^{2+} + CO_3^{2-} \rightleftharpoons CuCO_3$	6.75	–	Smith and Martell (1976)
$Cu^{2+} + 2CO_3^{2-} \rightleftharpoons Cu(CO_3)_2^{2-}$	9.92	–	Smith and Martell (1976)
$Cu^{2+} + SO_4^{2-} \rightleftharpoons CuSO_4$	2.36	8.8	Smith and Martell (1976)
$Cu^{2+} + Cl^{-} \rightleftharpoons CuCl^{+}$	0.4	6.7	Smith and Martell (1976)
$Zn^{2+} + OH^{-} \rightleftharpoons ZnOH^{+}$	5.04	–	Baes and Mesmer (1976)
$Zn^{2+} + 2OH^{-} \rightleftharpoons Zn(OH)_2$	11.1	–	Baes and Mesmer (1976)
$Zn^{2+} + H^{+} + CO_3^{-} \rightleftharpoons ZnHCO_3^{+}$	13.12	–	Mattigod and Sposito (1979)
$Zn^{2+} + CO_3^{2-} \rightleftharpoons ZnCO_3$	4.76	–	Mattigod and Sposito (1979)
$Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4$	2.38	6.3	Smith and Martell (1976)
$Zn^{2+} + Cl^{-} \rightleftharpoons ZnCl^{+}$	0.4	5.4	Smith and Martell (1976)
$Cd^{2+} + OH^{-} \rightleftharpoons CdOH^{+}$	3.92	–	Baes and Mesmer (1976)
$Cd^{2+} + 2OH^{-} \rightleftharpoons Cd(OH)_2$	7.65	–	Baes and Mesmer (1976)
$Cd^{2+} + H^{+} + CO_3^{-} \rightleftharpoons CdHCO_3^{+}$	11.83	–	Parkhurst and Appelo (1999)
$Cd^{2+} + CO_3^{2-} \rightleftharpoons CdCO_3$	4.37	–	NIST (2003)
$Cd^{2+} + 2CO_3^{2-} \rightleftharpoons Cd(CO_3)_2^{2-}$	7.26	–	NIST (2003)
$Cd^{2+} + SO_4^{2-} \rightleftharpoons CdSO_4$	2.46	9.6	Smith and Martell (1976)
$Cd^{2+} + Cl^{-} \rightleftharpoons CdCl^{+}$	1.98	1.3	Smith and Martell (1976)
$Cd^{2+} + 2Cl^{-} \rightleftharpoons CdCl_2$	2.6	3.8	Smith and Martell (1976)
$Pb^{2+} + OH^{-} \rightleftharpoons PbOH^{+}$	6.29	–	Baes and Mesmer (1976)
$Pb^{2+} + 2OH^{-} \rightleftharpoons Pb(OH)_2$	10.88	–	Baes and Mesmer (1976)
$Pb^{2+} + 3OH^{-} \rightleftharpoons Pb(OH)_3^{-}$	13.94	–	Baes and Mesmer (1976)
$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3$	7.2	–	Buffle, Chalmers, Masson, Midgley (1988)
$Pb^{2+} + 2CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-}$	10.5	–	Buffle, Chalmers, Masson, Midgley (1988)
$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4$	2.75	–	Smith and Martell (1976)

Equilibrium	**log K[⊖]**	**ΔH[⊖] (kJ mol⁻¹)**	**Reference**
$Pb^{2+} + Cl^{-} \rightleftharpoons PbCl^{+}$	1.59	18.4	Smith and Martell (1976)
$Pb^{2+} + 2Cl^{-} \rightleftharpoons PbCl_2$	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 $k_{\mathrm{f,a}}$, $k_{\mathrm{f,b}}$, $k_{\mathrm{f,m}}$ and $k_{\mathrm{b,m}}$ respectively. These are summarised in Table S5.

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

Metal	$\mathbf{k}_{f,a}$	$\mathbf{k}_{f,b}$	$\mathbf{k}_{f,m}$	$\mathbf{k}_{b,m}$	**Reference**
Cu	$10^{-2.5+10^{-3.3}\mathrm{e}^{pH_{pw}}}$	$10^{-2.1+10^{-3.5}\mathrm{e}^{pH_{pw}}}$	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.

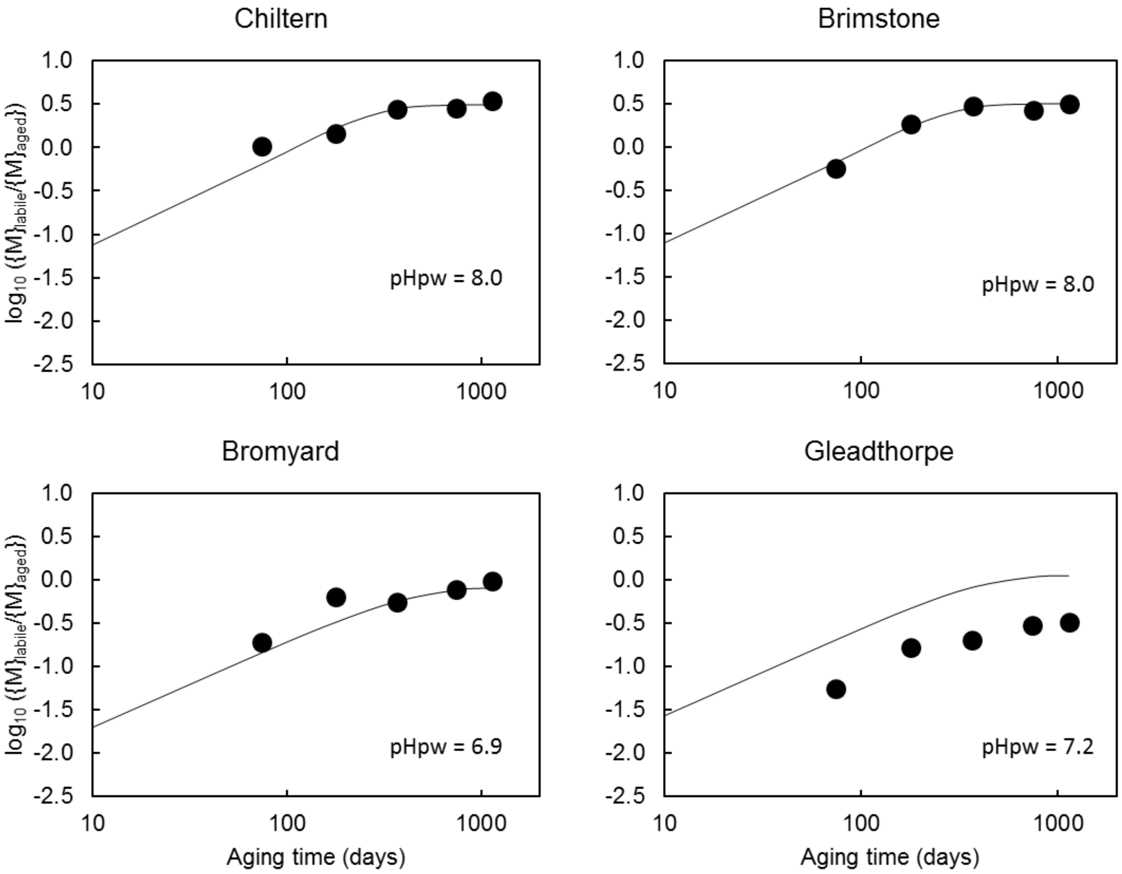


Figure S1. Aging of lead spikes in four UK soils and model fits using the expressions and parameters in Table S5.

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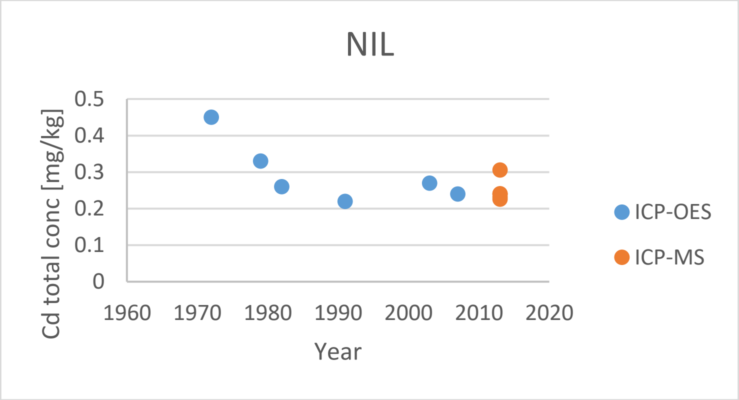
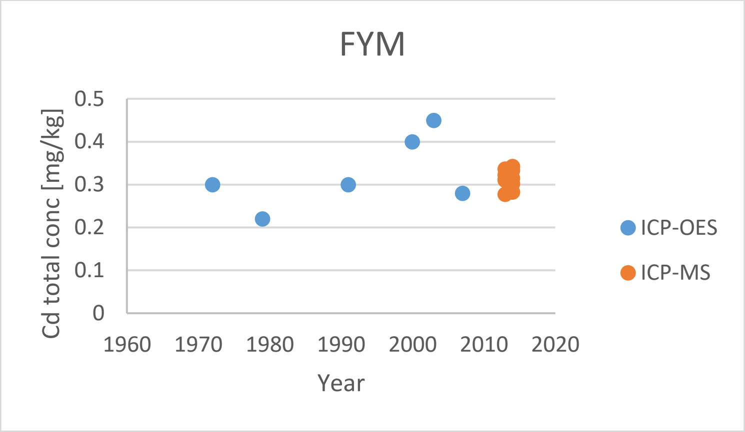
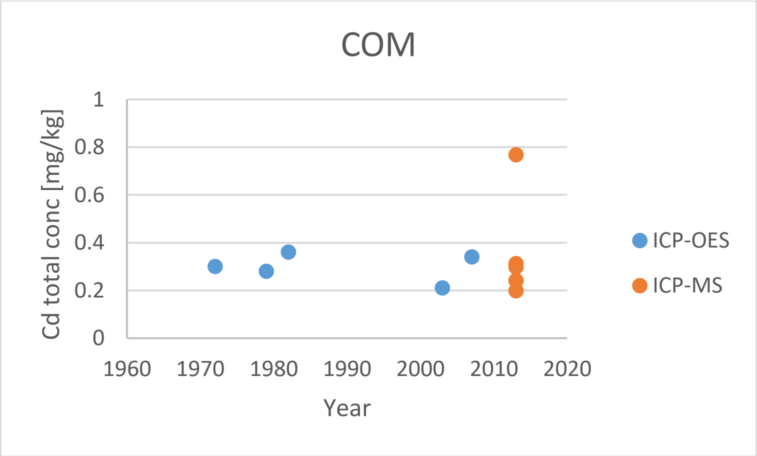
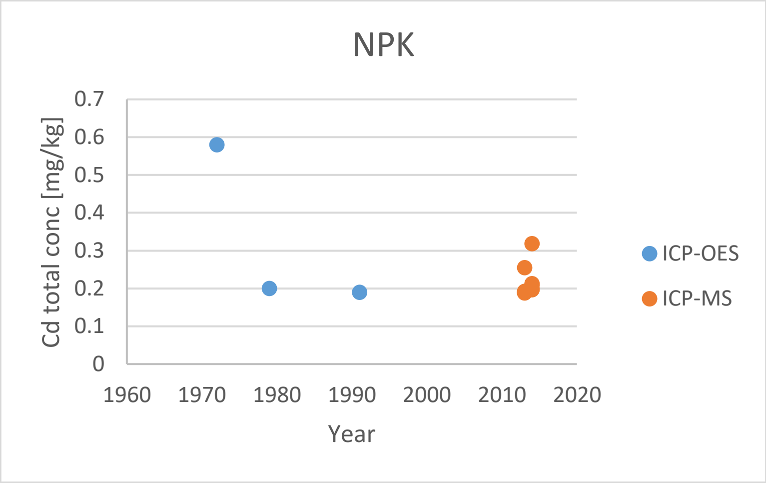
2) ICP-OES could give interference of As with Cd measurements, particularly when As is present at medium/high concentrations while Cd is close to the background values (see *McBride. 2011. A comparison of reliability of soil Cd determination by standard spectrometric methods. J Environ Qual. 2011; 40(6): 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 in the soils, the extractions were done with aqua regia and not with 1 M HNO3 as erroneously indicated in the paper, which was used only for extraction of the organic amendments.







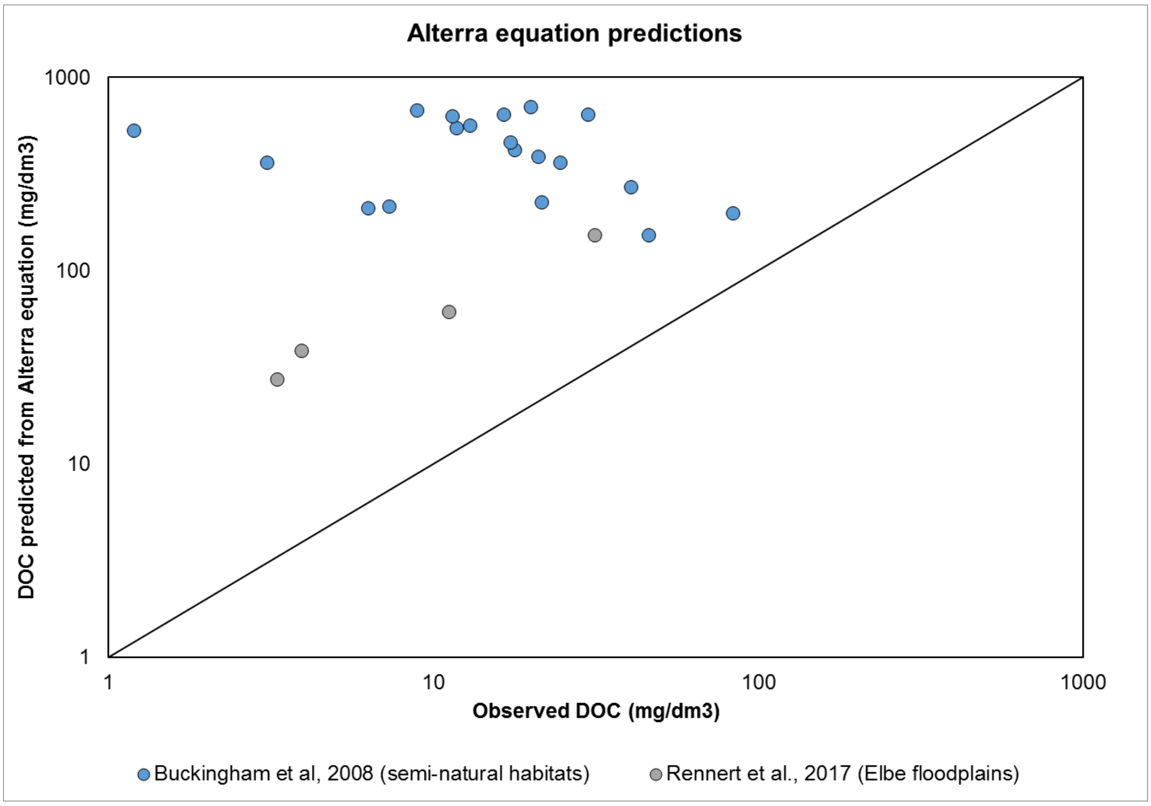


As to the quality control of the ICP-EOS measurements, it is done on the calibration curve every 10 readings by measuring the TES concentrations in the blanks and in the standard sample at the intermediate concentration of 1 ppm. The limit of quantification for every element is 3 standard deviations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

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 *(extraction with 1 M nitric acid)* and EDTA-extractable concentrations of Zn, Cu, Pb and Cd.

3) 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 produce 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 ZOFE), 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 od 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.

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4) 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.
5) 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.

Regarding the other comments, we thank the Referee for the valuable comments and we will take them in the ms.