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SOIL Discussions

Modelling of long term Zn, Cu, Cd, Pb dynamics from soils fertilized with organic amendments.

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Abstract

Soil contamination by trace elements (TEs) is a major concern for sustainable land management. One potential source of excessive inputs of TEs into agricultural soils are organic amendments. Here, we use dynamic simulations carried out with the IDMM-ag model to describe observed trends of topsoil Zn, Cu, Pb and Cd concentrations in a long-term crop trial in Switzerland, where soils plots have been treated with differing organic amendments, particularly farmyard manure, sewage sludge and compost. IDMM-ag requires the definition of a parsimonious set of boundary conditions.

The model adequately reproduced the metal EDTA-extractable concentrations in ZOFE when site-specific soil lateral mixing, due to mechanically ploughing of small plots, was introduced. Calibration of an additional metal input flux was necessary to fit the measured data, indicating that knowledge gaps in quantifying historical metal inputs can affect field-scale simulations even in a well-characterized field. Projections of soil metal content in the long-term showed that, under stable organic amendment application rates, Zn and Cu labile concentrations might pose toxicological hazard for the soil ecosystem, particularly in the sewage sludge-amended plots. The sewage sludge topsoil was characterized by some variability in the organic matter composition, potentially due to the applied sewage sludge quality, which might affect the metal lability: this effect should be accounted for in models

This study takes a step forward in assessing potential and limitations of the IDMM-ag model to predict TEs long-term dynamics in agricultural fields, paving the way to quantitative applications of TEs modelling at field and larger scales.

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1. Introduction

Trace elements (TEs) are naturally present in soils due to mineral weathering and biogeochemical cycles. Many TEs, particularly cationic metals, are persistent in many topsoils, but can also leach to surface waters, with possible toxicological effects on the whole ecosystem. Several TEs such as zinc (Zn), copper (Cu) and nickel (Ni) play important roles in biochemical processes and are therefore essential for living organisms at low concentrations, though they can become toxic to biota at high concentrations; therefore, their presence in soil can be tolerable in a relatively narrow range of values (Adriano, 2005). In contrast, other TEs like lead (Pb) and cadmium (Cd), which are not physiologically active, are generally toxic to living organisms at low concentrations, and their accumulation in soil is of particular concern. Excessive uptake of trace elements by crop plants and their enrichment in edible parts can pose significant risks to human health by entering into the food chain (Mcgrath & Zhao, 2015). Accumulation of TEs in cultivated soils is widespread and is mainly caused by application of low grade agrochemicals, organic fertilizers and sewage sludge (Toth, Hermann, Da Silva, & Montanarella, 2016). In a European Union wide survey, Ballabio et al. (2018) reported that agricultural soils represent the environmental matrix with a high enrichment potential in TEs, and for example land cover and management are better predictors of soil Cu concentrations than natural soil formation factors. Due to limited natural availability of nutrient elements such as phosphorus (P), which is extracted from phosphate rocks (Roberts, 2014), and high energy consumption for the industrial production of mineral nitrogen (N) fertilizers, the application of organic amendments is considered a more sustainable option for agricultural soil management (Diacono & Montemurro, 2010). Organic amendments can have the additional benefit of increasing the soil organic matter (SOM) content, which usually enhances soil fertility and contributes to carbon sequestration from the atmosphere (Smith, 2016). However, the application of such amendments, such as farmyard manure, compost and digestates of bio-wastes, can also introduce TEs into agricultural soils. Application of sewage sludge into agricultural soils can be even more problematic, as sewage sludge often contains concentrations of various TEs such as Cd, Cu, Pb, and Zn up to 30 times their concentrations in soil (Hudcova, Vymazal, and Rozkosny, 2019; JRC, 2012; NEBRA, 2015).

Once in the soil, the fate of the TEs is controlled by multiple soil properties, as determined by land use history, climatic forcing and geological setting. The soil pH, soil and dissolved organic matter (SOM, DOM) contents, the quantity and chemical composition of reactive minerals such as clay minerals and metal (oxy)hydroxides, are all known to influence the speciation and solubility of TEs in soils (Gu & Evans, 2008). Furthermore, the TEs speciation can influence the toxicological hazard of the TEs, particularly to organisms that are directly exposed to soils, such as plants and earthworms. In the context of long-term TEs accumulation due to regular organic amendment or other additions, predicting the long-term speciation and dynamics of TEs is useful to support decisions on ecosystem management and human health protection. Overall, owing to the TEs reaction with the soil solid phases, repeated application of organic amendments can increase their concentrations in agricultural soils through direct reactions or their physical entrapment into the organo-mineral aggregates. This can lead to exceedance of their concentrations of the environmental legislation thresholds.

Dynamic models are useful in predicting the accumulation, bioavailability and potential uptake of TEs in soils, particularly for the projection of future trends. Reliable models can critically support land use and land management decisions, and regulatory initiatives. Models for TEs dynamics exist at a number of levels of complexity, from those with a site–specific, mechanistic approach requiring highly detailed input information and calibration (Bonten, Groenenberg, Meesenburg, &

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de Vries, 2011), to relative simple mass balance approaches applicable at large scale (Six & Smolders, 2014). Models have been used to simulate behaviour and uptake of TEs at specific agricultural sites subject to metal inputs (Bergkvist & Jarvis, 2004; Ingwersen & Streck, 2006), based on site–specific calibration, but such models are not readily applicable at large scale without generalisation of the parameterisation as a function of local climatic, hydrological and soil physico-chemical properties.

Among models for determining the TE dynamics in soil, The IDMM (Intermediate Dynamic Model for Metals) (Lofts, Tipping, Lawlor, & Shotbolt, 2013; Xu, Lofts, & Lu, 2016) is an example of a dynamic model which allows general application, given a reasonably parsimonious set of input data. It is intended for long term application from decades to centuries and describes metal dynamics by taking as a starting point a past year when metal dynamics can be assumed to be "pristine", that is uninfluenced by anthropogenic activities. Chemical processes influencing metal dynamics, solid/solution partitioning and fixation into soil solid phases, are described in a manner that seeks to reduce the number of variables required, while maintaining consistency with mechanistic understanding of the underlying processes. Soil hydrology intended as annual volume of drainage from a soil layer is specified, not modelled, and this allows for a range of complexity in the specification of hydrology, for example considering annual variation in drainage or fixing to a single value over time. Similarly, key properties influencing metal dynamics such as the pH value of the soil solution, dissolved organic carbon (DOC) concentration, SOM content and soil erosion rate, may be fixed to single values or varied annually.

The objective of this study was to apply the IDMM-ag model to a well-characterized location with ideally no site-specific calibration in order to assess its performance at larger scale. The hypothesis was that, if the model is successfully applied at field scale with no need of calibration, it might be

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used at larger scale as well, provided adequate inputs. We therefore assessed the dynamics of Zn, Cu, Pb and Cd in the topsoil of the ZOFE agricultural long-term trial in Switzerland, where the organic amendments farmyard manure, sewage sludge and green waste compost have been incorporated into soil for more than 60 years. Then, we applied the IDMM-ag model under the different organic amendment managements in order to (*i*) test the capability of the IDMM-ag model to reproduce the long-term changes in the labile pools of the TEs in the four treatments, and (*ii*) predict the labile and soluble concentration trends of the TEs in the next 100 years and assess any possible risk for the ecosystem and human health. At the current state of the art, large-scale modelling could be informative for both broad trends in TEs concentration and information on the time taken for a particular soil type to reach concentrations at which environmental risks occur.

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2. Materials and Methods

2.1 The study site

The Zurich Organic Fertilization Experiment (ZOFE) is an agricultural long-term plot trial started in 1949 by the Swiss Federal Agricultural Research Institute (Agroscope) at Zurich-Reckenholz, Switzerland, to compare different fertilization schemes in an 8-year crop rotation: 1) winter wheat/intercrop, 2) maize, 3) potato, 4) winter wheat/intercrop, 5) maize, 6) summer barley, 7) clover grass ley, 8) clover grass ley (Oberholzer et al., 2014). Ploughing has been carried out to a depth of at least 20 cm, from north-to-south and *vice versa*, alternating the direction of adjacent passes (Figure 1). The site is located at 420 m a.s.l., the annual precipitation has been 1054 mm in the long-term average, and the mean annual temperature 9.4°C. The soil is a carbonate-free, loamy (14% clay) Luvisol (IUSS, 2006), with a SOC content of 1.43% and a pH value of 6.5 at the beginning of the experiment. The field trial consists of twelve treatments replicated in five blocks in a systematic block design (Figure 1), and the same cultivation techniques and plant protection have been applied to all the treatments. In the present study we investigated the following four treatments: the control (NIL#1) with no fertilization and no amendment, the farmyard manure (FYM#2) with application of 5 t ha^{-1} of organic matter every second year, the sewage sludge (SS#3) with application of 2.5 t ha^{-1} of organic matter every year, and the green waste compost (COM#4) with application of 2.5 t ha^{-1} of organic matter every year.

2.2 Trace element time series

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,

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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 1 M nitric acid 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. 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 for, and compost of years 2011, 2013 and 2014 were also analysed for total and EDTA-extractable concentrations of Zn, Cu, Pb and Cd with the extraction procedures described above.

2.3 The Intermediate Dynamic Model for Metals with lateral mixing

The IDMM-ag predicts annual concentrations of metals within topsoil and fluxes of metal from soil due to porewater leaching and crop uptake, and distinguishes between a pool of labile (geochemically active) TEs, comprising dissolved and adsorbed metal, and a non-labile (aged) pool that accounts for chemically-less reactive and physically-protected solid forms of metals (Figure 2A). The labile metal pools are partitioned into dissolved and adsorbed forms assuming chemical equilibrium. A Freundlich-type isotherm (Groenenberg et al., 2010) is used to describe the relationship between free TEs and adsorbed TEs ions, and the relationship between free TEs ions and TEs complexes in the porewater is computed using WHAM/Model VI (Tipping, 1998).

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Transformations between labile and aged pools are assumed to follow first-order kinetics. Labile TEs may reversibly transfer into a 'weakly aged' pool, from which metal may subsequently transfer irreversibly into a 'strongly aged' pool that can transfer directly into the labile pool. The IDMM-ag is driven by annual TEs input rates: all the metal inputs were considered fully labile and added into the model labile pool. The model simulations start from a past year in which all metal inputs are assumed to be natural, and where the soil is in steady state, i.e. metal input and output fluxes balance (Tipping, 1998). In this study erosion was neglected in consideration of the site geomorphological characteristics that make it negligible. Since the soil samples were relevant to the homogenised ploughing depth, the soil was modelled as a single well–mixed layer of 20 cm.

Based on the experimental work of Mcgrath & Cegarra (1992) and McGrath (1987) on the influence of ploughing on lateral mixing of soil metals across plot boundaries, and based on initial IDMM–ag simulations, the effect of lateral mixing was explored through a model modification that allowed the plots to be simulated as sets of strips, with annual exchange of soil and TEs across the strips (Figure 2B). In particular, lateral soil exchange was assumed to occur at the margins of the strips across a width of 0.2 m, equal to the ploughing depth. A sensitivity analysis was carried out on the number of strips per plot from five to ten, in order to understand its impact on the simulations.

2.4 Estimation of metal input fluxes for the model

In the absence of anthropogenic sources, the metal inputs occurring naturally via geogenic deposition (mainly volcanic eruptions) and soil mineral weathering are considered to be in balance with the output fluxes. The natural inputs were assumed to be constant over time. In analogy to the work by Rieder et al. (2014) for a Swiss forest, the geogenic deposition was estimated by

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averaging the metal enrichment factors reported for Zn, Cu, Pb, Cd by Shotyk et al. (2002) in deep layers (deposited before 1905) of a peat bog in the Jura Mountains, Switzerland. Mean Enrichment Factors (EFs) were converted to actual atmospheric depositions by using moss concentration data described later for anthropogenic atmospheric deposition. The estimated geogenic deposition rates were: $1.1 \cdot 10^{-6}$ mol m^{-2} yr^{-1} for Zn, $1.15 \cdot 10^{-6}$ mol m^{-2} yr^{-1} for Cu, $2.52 \cdot 10^{-6}$ mol m^{-2} yr^{-1} for Pb, $9.74 \cdot 10^{-8}$ mol m^{-2} yr^{-1} for Cd. The required magnitude of the mineral weathering flux was estimated by fixing it to be constant over the simulation period, and adjusting it to make the modelled labile TEs concentrations in 1972 equal to the observed values. The fitted additional fluxes were used in all simulations, assuming them to be the same for all the plots.

Rates of anthropogenic atmospheric deposition of Zn, Cu, and Cd before c.a. 1990 were estimated by means of the EFs reported by Shotyk et al. (2002). For Pb, the EFs before 1990 were taken from Weiss et al. (1999), averaging peat bog sites with annual precipitation similar to ZOFE. From 1990 to 2014, atmospheric deposition data were estimated from the metal concentrations in mosses measured in Northern Switzerland sites (BAFU 2018). These concentration values were converted into atmospheric deposition rates by means of the transfer functions reported by Thoni et al. (1996) for Switzerland (Figure S1 in Supporting Information).

Since farmyard manure P content has been measured in ZOFE throughout the experiment, Zn and Cu inputs were calculated by multiplying the Zn:P and Cu:P ratios with the actual P loading from the manure relying on the data by Menzi and Kessler (2009), who reported stable average concentrations of Zn and Cu per unit of P in 1100 FYM samples. 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. To take into account the strong reduction of the Zn and Cu contents in FYM observed from 1999s as a consequence of the decreased supply of TEs in the animal forage (de

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Vrie et al., 2004; Groenenberg et al., 2006; Menzi and Kessler, 1999), Zn and Cu inputs with farmyard manure application were reduced by factors of 0.7 and 0.52, respectively, starting from 1999 onwards. 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 of Menzi and Kessler (2009) ,because the total Pb and Cd concentrations in the farmyard manure samples from 2011 and 2014 (Table 1) were below the ICP-OES detection limit (Figure S2 in Supporting Information).

The TEs concentrations measured in the green waste compost samples applied in 2011, 2013 and 2014 (Table 1) were averaged and assumed to be constant throughout the experiment. For Cd, which was below the instrument detection limit, a value of 0.13 mg kg^{-1} was used, based on a nation-wide investigation of compost quality in Switzerland (Kupper et al., 2014) (Figure S2 in the Supporting Information).

For the sewage sludge tTEs inputs, we followed two approaches. In a first approach termed '*Swiss Sludge Trend*', we averaged the metal concentrations in the SS samples from 2008 and 2012 (Table 1) and assumed that they were representative for the period 2000-2014. For the 1975-2000 period, the exponential decrease in metal contents reported by Kulling et al. (2001) for sewage sludge in Switzerland was applied to the measured values; before 1975, the metal concentrations were kept constant and equal to the values calculated in 1975. In the second approach termed '*Idealized Trend*' we kept the measured metal concentrations constant for the period 1975-2014 and fitted the inputs for the period 1965-1975 to match the peaks measured in the EDTA-extracted concentration trends. Before 1965, the soil metal concentrations were considered negligible. The metal loading time trends were determined by multiplying the metal concentrations, as estimated

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according to the two approaches described above, by the amount of sewage sludge applied (Figure S3 in the Supporting Information).

2.5 Metal outputs and other driving variables

The two routes for metal output were leaching and crop uptake. Average water drainage was calculated from rainfall measured at local stations and evapotranspiration estimated with a locally calibrated Primault equation. Since no porewater dissolved organic carbon (DOC) concentration data were available, a constant value of 7 mg C l^{-1} was assumed, a reasonable value for agricultural soils with low SOC content as reported by De Troyer et al. (2014). Furthermore, a preliminary sensitivity analysis showed that varying the DOC concentration in the plausible range of 7-12 mg C l^{-1} had little effects on the results, with minor increase for the fitted additional input flux in case of higher DOC concentrations. Crop metal removal was assumed to be a function of crop biomass (Figure S4 in the Supporting Information), as crop metal concentrations were assumed not to vary. Crop yields have been measured in ZOFE yearly based on the harvest from a sub-plot in each plot. Shoot biomass was estimated by scaling linearly with crop yields. The Zn, Cu, Cd concentrations in winter wheat grains and shoots were measured at harvest in 2014 and 2015 and the average values were taken to represent the respective metal contents over the entire duration of the simulated experiment in the grains and shoots of wheat and barley. The TEs concentrations for the other crops were estimated by previous reports (de Vries et al., 2008; EFSA, 2009, 2010; SAEFL, 2003; SCAN, 2003a,b)..

The IDMM–ag model uses SOM and porewater pH as key variables controlling metal solid/solution partitioning, aging and speciation, and both soil pH values and SOC content data were available for soils from all ZOFE plots since 1949. The SOM contents were estimated assuming that SOC is 50% by weight of the measured SOM. Values of pH from aqueous extracts

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were converted into porewater pH values according to de Vries et al. (2008). The SOM content and porewater pH values were provided to the model for all available years and linearly interpolated when missing (Figure S4 in the Supporting Information).

2.6 Analysis of the soil and organic amendment FTIR and XRD

The NIL, FYM, SS and COM amended soil samples from 1972 and 2011 were analysed by Fourier Transform Infrared Spectroscopy (FTIR) and by X-Ray Diffraction (XRD) to detect compositional changes in the soil organic and inorganic components. The DRIFT spectra were obtained using a rapid-scan Spectrum-GX (Perkin Elmer, Monza, Italy) Fourier transform infrared spectrometer (FTIR) in the mid-infrared spectral range (4000 to 450 cm^{-1}). The spectrometer was equipped with a Peltier-cooled deuterated triglycine sulphate (DTGS) detector and an extended range KBr beam splitter. Soil samples of 50 mg were placed in a stainless steel sample cup, located in a Perkin Elmer diffuse reflectance accessory and scanned for 60 s. A silicon carbide (SiC) reference disk was used as the background sample (Perkin-Elmer). The most noticeable pecks were attributed according to (D'Acqui, Santi, Vizza, & Certini, 2015; Niemeyer, Chen, & Bollag, 1992) as reported in Supporting Information. Chemometric PCA analysis were carried out by the Unscrambler X® Version X 10.4 (Camo Software) with spectra pre-processed with Extended Multiplicative Scatter Correction (EMSC). The X-ray diffractometry (XRD) investigation was conducted on randomly-oriented powders of bulk soil by a Philips PW3830 X-ray diffractometer with CoKα radiation, 0.02° step size, and 1s step time each point over a 2θ range of 5-75°. The SS soil sample from 2013 was also analysed.

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2.7 Evaluation of long-term effects of organic amendment applications and concentration limits

We assessed the long-term effects of organic fertilization under the ZOFE trial environmental conditions. After validating IDMM-ag against the measured EDTA-extractable data, the model was run in predictive mode for 100 years, starting from pristine conditions until year 2114. The lateral mixing effect was removed as we aimed at simulate a real agricultural scenario with bigger plots than in ZOFE. In particular, the following boundary conditions were applied: *i*) stable TE input rates *via* anthropogenic deposition and organic amendment applications as recorded in 2014 (geogenic deposition and weathering rates were kept constant as previously described), and the *'Idealized Trend'* approach to estimate the metal inputs with the sewage sludge application, *ii*) stable SOM and soil pH as recorded in 2014, stable crop yields as recorded in the last rotation before 2014, and *iii*) stable temperature and rainfall, no climate change was taken into account.

Measured total TEs concentrations were compared with threshold values expressed as soil total concentrations reported in the Swiss Ordinance Relating to Impact on the Soil (OIS, 1998). The soluble concentrations from OIS (1998) extracted with 0.01 M $NaNO_3$ solution were used as indicators of potential soil ecotoxicity, and assessed with the projected pore water concentrations from the long-term IDMM-ag simulations. The projected labile concentrations were compared against the critical limits calculated for each metal according to the method proposed by Lofts et al. (2005) and based on the free ion approach: basically the ecosystem critical limits, expressed as labile metal pools, are determined by soil solution pH value, SOM and multispecies fraction affected, which was set to 0.1 in this study.

2.8 Statistical analysis

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All statistical analyses were carried out in R (version 3.5.0). The Mann-Kendall test (package "Kendall") was used to assess monotonic trends in the TE time series. Increasing trends (Kendall's tau statistic > 0) and decreasing trends (Kendall's tau statistic < 0) were considered significant when the two-sided *P*-value was less than 0.05. The "dplyr" package was used to calculate the root mean squared error (*RMSE* with the "rmse" function) of the simulated labile concentrations versus the measured data. The linear correlation between metal simulations and measurements was assessed with the Pearson correlation coefficient (*r* with the "cor" function).

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3. Results and Discussion

3.1 Temporal trends of total and labile TEs

Despite the continuous application of organic amendments, the TEs total concentrations had no significant ($P < 0.05$) accumulation patterns over time in the topsoil according to the Mann-Kendall trend test, except for Pb concentration that increased significantly ($P < 0.05$) in the NIL treatment topsoil due to the atmospheric deposition (Figure 3). The total concentration trends were decreasing for Zn in the SS treatment and for Cu in all the treatments ($P < 0.05$), with Cu that displayed the strongest decrease from 60–102 mg kg^{-1} in 1972 to 30–57 mg kg^{-1} in 1995. The concentrations measured in 1972 were clearly elevated when compared to Ballabio et al. (2018), where an average total Cu concentration of ca.17 mg kg^{-1} was reported from more than 21000 topsoils of EU countries. The observed higher Cu concentration in 1972 could be ascribed to the previous historic application of Cu-based fungicides, although we have no information on the duration and rates of fungicide application. The rate of total Cu loss from the studied soil was larger than that expected by leaching which is in the order of 0.2-0.3 mg kg^{-1} of Cu per year amounting to 5-8 mg kg^{-1} in 35 years (Vulkan et al., 2000). Mixing of the top 20 cm of soil with less contaminated deeper soil due to bioturbation could have caused a 'dilution' effect in the topsoil (Jarvis et al., 2010; MullerLemans & vanDorp, 1996).

In the SS treatment the total Zn, Cu and Pb concentrations exceeded the thresholds of the Swiss environmental legislation (OIS, 1998) set to 150, 40 and 50 mg kg^{-1} for Zn, Cu and Pb, respectively. The Cu concentrations exceeded the thresholds of the Swiss environmental legislation in the soils of NIL, FYM and COM treatments during the 1970s then returned fully compliant to the legislation in the 1990s, whereas the total Cd concentrations never exceeded the guide value of 0.8 mg kg^{-1}. For comparison, the temporal trends of total P concentrations in the

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topsoils were also analysed, and they showed less variability than the TE concentrations, a significant accumulation over time in the FYM and SS treatments ($P < 0.05$), not in the NIL and COM treatments (Figure 3).

The TEs lability in the ZOFE soils, here defined as the ratio between the EDTA-extractable concentration and the total concentration is shown in Figure 4A. The Zn lability increased significantly ($P < 0.05$ according to the Mann-Kendall test) only in the FYM treatment. This could be due to the fact that the EDTA-extractable Zn, Cu and Cd showed significant increasing trends over time in the NIL and FYM treatments except for Cu in the FYM treatment (Figure 5S in Supporting Information) as a consequence of labile metal inputs, but also to soil acidification and SOM loss observed in the NIL and FYM treatments (Figure 4S in Supporting Information). The lack of significant increases in EDTA-extractable pools for Zn, Cu and Cd in the COM soil could be due to the increase of the pH value over time. The lability of Cu significantly increased ($P < 0.05$) in the NIL and FYM treatments due to the decrease of its total concentrations. In the SS soil the EDTA-extractable TEs decreased significantly ($P < 0.05$) despite soil acidification and SOM loss also occurred in this treatment (Figure 5S in Supporting Information). Whereas EDTA-extractable trends paralleled similar trends of decreasing total concentrations in the SS treatment for the other metals, this was not the cases for soil Pb. Therefore, Pb lability trend was decreasing. The Cd lability was generally the highest of all the metals across the treatments which is consistent with its known lower affinity for the soil inorganic and organic soil colloids (McBride, Richards, Steenhuis, & Spiers, 1999).

The total TE concentrations of the organic amendments are reported in Table 1. The farmyard manure and compost samples had comparable levels of total TE concentrations, with the green waste compost presenting higher Pb concentrations (Table 1). The sewage sludge had higher total

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TE concentrations than the compost and farmyard manure, explaining why the magnitude of all total TE concentrations ranked in the order NIL< COM = FYM < SS in 2011, and SS amended soil also showed P overfertilization. The analysed sewage sludge showed the highest variability in TEs lability over time, with Zn lability varying from 0.39 to 0.15 and Cu from 0.48 to 0.22 in the samples from 2008 and 2012, respectively (Figure 4B). The lower lability of Cu and Pb in the organic amendments than in the topsoil could be ascribed to their stronger affinity for the organic matter (McBride et al., 1999).

3.2 Simulations of soil metal dynamics

The IDMM-ag model was run to simulate the measured EDTA-extractable concentrations with the model-derived labile metal pools. However, to force model agreement with the measured EDTA-extractable metals for the NIL plots in 1972, we had to enter additional input rates of TE as constant in time. The fitted additional inputs were: 2.5 mg m^{-2} yr^{-1} for Zn, 5.5. mg m^{-2} yr^{-1} for Cu, 0.35 mg m^{-2} yr^{-1} for Pb and 0.07 mg m^{-2} yr^{-1} for Cd. This additional TE term, being a calibrated variable, was attributed to mineral weathering, although the site history also suggests that there is likely to be a contribution from inputs of fungicides to the labile Cu concentrations at the beginning of the measurement period. Estimates of TE weathering rates of 0.001-0.86 mg m^{-2} yr^{-1} for Zn and 0.0-0.039 mg m^{-2} yr^{-1} for Cd in Swiss agricultural soils have been reported (Imseng et al., 2018; Imseng et al., 2019), which were consistent with the fitted values. However, there is a need for more research on topsoil metal weathering rates and their contribution to determining labile metal concentrations in order to reduce the overall uncertainty on historic TEs inputs.

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Using five strips per plot for simulating the lateral mixing, and the two approaches '*Swiss Sludge Trend*' and '*Idealized Trend*' for estimating the sewage sludge metal inputs, the IDMM-ag model produced the labile concentration time trends presented in Figure 5. The simulations without lateral mixing are shown only for reference (Figure 6S in Supporting Information), since their predictions of the measured data were unsatisfactory. With the '*Swiss Sludge Trend*' approach, the measured EDTA-extractable concentrations were well simulated for all TEs in the NIL, FYM and COM treatments. Consideration of the lateral mixing improved the agreement with the measurements for the FYM and COM treatments by predicting higher labile metal concentrations, as a result of metal transfer from the adjacent SS plots. In fact, the introduction of the soil lateral mixing levelled-off the concentration differences between adjacent plots through the redistribution of TEs from the most enriched SS plots to the adjacent FYM and C plots. The improvement of the simulations for the FYM and COM treatments supported the hypothesis that lateral mixing is a major transfer process in these experimental soils. The simulations were not fully adequate for the SS treatment, with r values of 0.22, 0.02, 0.02, 0.64 for Zn, Cu, Pb, Cd respectively, and a lack of declining trends in EDTA-extractable soil metal concentrations observed over the measurement period (Figure 5; Figure S6). However, for Cd the model predicted a slight decline in concentrations from the 1990s onward, possibly be due to the fact that Cd showed the largest differences in concentration among the treatments, making the influence of the lateral mixing more pronounced.

The model outcomes for the SS treatment, where the initial measurements in 1972 were underestimated by up to a factor of three, suggest that the historic TE inputs to this plot were underestimated. To investigate this, we adjusted the time trends of the metal inputs to the SS plots to match more closely the observed trends (the *'Idealized Trend'* approach). After adjusting the

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inputs the model was able to reproduce the downward trends in the EDTA-extractable TEs observed in the SS treatment, with r values of 0.75, 0.73, 0.92, 0.88 for Zn, Cu, Pb, Cd respectively (Figure 5). However, the measured EDTA-extractable soil TE concentrations were slightly overestimated in the FYM and COM treatments, particularly for Cu and Pb. In fact, the *'Idealized Trend'* approach implied high metal inputs with the sewage sludge applications from the 1960s to the 1980s (Figure S2). These TEs were then rapidly transferred from the SS plots to the adjacent FYM and COM plots due to ploughing, leading to an overestimation of the labile TEs concentrations. The NIL plots, which are not adjacent to the SS plots, remained unaffected by the approach used to estimate the TE inputs with the sewage sludge. We therefore hypothesize that the soil lateral mixing was not the only cause of the bump-shaped trends observed in the SS soil, because this TE input approach led to an overestimation of the labile concentrations in the FYM and COM soils.

3.3 Lateral mixing sensitivity analysis

Splitting each plot into strips and exchanging a fraction of soil between adjacent strips at each time step gave satisfactory results with the following best-fit operational parameters (Figure 2): *i*) each plot was split into five strips, ii) the margin of a strip that was swapped with the adjacent strip was 20cm wide. A sensitivity analysis was carried out varying the number of strips per plot from five (each strip being 1m wide) to ten (each strip being 0.5m wide), but keeping the same margin of 20cm to be swapped. The '*Idealized Trend*' approach was used because it gave better data fitting. Figure 6 shows the simulated labile concentrations of Zn, Cu, Pb and Cd in 2014 across a transect comprising the plots NIL, FYM, SS and COM in series, to replicate the order in the repetition blocks I, II and III (Figure 1). Increasing the number of strips per plot from five to ten resulted in

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a more pronounced bell-shaped pattern, with less redistribution of the TEs from the SS to the adjacent plots. In general, the higher the number of strips per plot the less the contribution of the soil lateral mixing, so that an adjustment of the '*'Idealized Trend*" approach would be required to fit the decreasing trends of the metal EDTA-extractable concentrations in the SS treatment consisting of a small metal enrichment before 1980 followed by a decline. The opposite effect was observed when a lower number of strips per plot than five was used. Unfortunately, because no detailed information of the TEs content time trend in the sewage sludge applied to ZOFE was available, we could not optimize the number of strips per plot via data fitting. Furthermore, the two parameters (the number of strips per plot and the margin of the plot to be swapped) are inter-connected but we tested the variation of only the first of them, thus neglecting another potential source of uncertainty which should be considered in a full sensitivity analysis.

3.4 Soil spectroscopy analysis and long-term effects of organic amendment applications

The first two components of the PCA of the FTIR analysis of organic and inorganic components of the ZOFE soil samples from 1972 and 2011, and from 2013 only for the SS plots, covered 86% of the total spectral variance, with PC1 and PC2 accounting for 52% and 34%, respectively. Soils from 1972 and 2011 clustered separately, and the separation was mainly due to the organic C content (Figure 7A). This was confirmed by the loading plot of FTIR peaks of organic matter (OM) and quartz (Q) minerals (Figure 8B). For PC1 the OM peaks were positively and the Q peaks negatively correlated, whereas the PC2 showed an opposite trend, with the Q peaks slight prevalent than in PC1 (Figure 8B). The PC1 indicated that the soils underwent to SOM depletion over time, and the PC2 signalled that all soils, except SS, had higher presence of sand (Q peaks) in 2011than 1972, possibly due to loss of fine materials like clays. Concerning the peculiar behaviour of the

SS soil along the PC2, the differential FTIR spectra of the soils from 1972, 2011 and 2013 (the subtraction of the spectra of 2011 and 2013 from the spectra of 1972) resulted in a variable composition of the SOM between the soil from 2011 and 2013, regardless of the short time interval. The differential spectra of the SS samples from 1972-2011 evidenced a particular peak at 1040 cm^{-1} associated to the functional group of polysaccharide-like compounds that was not present in the differential spectra of the SS samples from 1972-2013. These compounds have potentially high affinity for TEs (Geddie & Sutherland, 1993; Veglio et al., 1997).

The XRD spectra did not reveal differences among soil samples regardless of sampling years and treatment (Figure S7, Supporting Information). This result indicate that the long term organic amendments, including the sewage sludge, did not introduce exogenous minerals such as clay minerals and Fe-(oxy)hydroxides that could have modified the TEs availability. Further work is needed to determine whether there was any time trend in the organic matter composition of the applied sewage sludge, as different sewage sludge quality can impact the lability of the freshly incoming TEs, overcoming the simplifying hypothesis that TEs present in the organic amendments are always fully labile. Such an improvement could explain the decreasing lability trend of Pb in the SS soil and reduce the over-prediction of Cu and Pb in the FYM and COM treatments when the '*'Idealized Trend*" approach was used with the lateral mixing. The importance of quantifying the adsorption capability of the sewage sludge applied to agricultural soils for TEs dynamic modelling, particularly for TEs with high affinity for the SOM such as Pb and Cu, was suggested also by Bergkvist & Jarvis (2004).

3.5 Long-term effects of organic amendment applications

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The long-term TEs labile concentrations (primary axis) and soluble concentrations in the pore water (secondary axis) predictions are shown in Figure 9. As no soil lateral mixing was considered, the labile TEs were predicted to accumulate in the SS plots beyond the measured concentrations; on the contrary, the predicted concentrations in the neighbouring FYM and COM treatments were predicted to become slightly lower than the measured values. The critical limits reported in Figure 9 (primary axis) for labile TE concentrations represent conservative estimations of biological chronic toxicity in the soil. The critical limits were close to the predicted labile concentrations of Zn and Cu in the NIL treatment though trends were declining on the long-term, and in the FYM and COM treatments where the limits could be exceeded on the long-term due to continuous TEs accumulation in the labile pool. In the SS treatment, Zn and Cu trends markedly exceeded the critical limits, although Zn labile concentration were declining on the long-term, but Cu labile concentration appeared to be stable over time. The Pb and Cd labile concentration trends were well below the critical limits in all the treatments, with the exception of Cd in the SS treatment. However, Cd was predicted to decline on the long-term in all the treatments, with the exception of the COM treatment. The Cd decline due to its high mobility is in line with the long-term predictions by Six & Smolders (2014) for the European agricultural soils. Globally, application of sewage sludge at current rate of 2.5 t ha^{-1} of organic matter every year appears unsustainable on the short and long-term for Zn and Cu accumulation in the labile pool, with particular reference to Cu whose labile concentration is projected to keep constantly high. Application of farmyard manure and compost at current rates might result in chronic toxicity effects on the long-term.

The predicted pore water concentrations paralleled those of the labile concentration trends but with a time-lag, and approximately by an order of magnitude below the Swiss legislation guide values of 0.5 mg l^{-1} for Zn, 0.7 mg l^{-1} for Cu, 0.02 mg l^{-1} for Cd, while no guide values are currently

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provided for Pb, and noteworthy Zn in the SS treatment was the same order of magnitude of the guide value. No calibration was done on the predicted soluble TE pools with measured data, so it is not possible to conclude that the guide values set in the Swiss policy would be actually matched in the future under stable conditions and current rates of soil organic amendment.

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4 Conclusions

The IDMM-ag model provided adequate descriptions of the measured EDTA-extractable concentration trends for the ZOFE long term field trial, when soil lateral mixing (site-specific) and historic metal inputs adjusted to match observations were included. The labile concentrations of Zn and Cu exceeded the critical limits, with potential toxic effects to 10% of the ecosystem species in the SS amended soil, and it was predicted that their labile concentrations might exceed the critical limits also in the FYM and COM amended soils on the long-term. Simulation of the EDTA-extractable concentrations in the sewage sludge-amended plots and redistribution of the TEs to the adjacent plots was possibly affected by the high variability of the sewage sludge organic matter composition. This suggests that the metal input lability might vary and could be specified in the TEs dynamic models to improve the simulations. The need to adjust the inputs with an additional metal flux demonstrated that even for an experimental site with a well-known history, there may be gaps in knowledge affecting all the models, regardless of their structure. At larger scale than field-scale, such gaps are likely to exist also because the historic estimates might be inaccurate and not greatly amenable to fine scale resolution.

Great improvements in TEs modelling will be brought by access to other datasets for testing the model, quantifying the influence of bioturbation on the vertical redistribution of metals, assessing metal weathering rates and their control factors, and analysing metal lability in the organic amendments, particularly sewage sludge. Globally, the presented application of IDMM-ag is promising for TEs dynamic simulations at field and larger scale, particularly if the current limitation in the quality of the input data are overcome.

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	Total Concentration [mg kg^{-1}]					**EDTA-Extracted Concentration [mg kg^{-1}]**			
	Farmyard Manure								
Years	**Zn**	**Cu**	**Pb**	**Cd**	**P**	**Zn**	**Cu**	**Pb**	**Cd**
2011	109.5	23.59	bdl*	bdl*	6915	32.49	5.60	bdl*	bdl*
2014	158.9	27.78	bdl*	bdl*	8146	53.14	6.73	bdl*	bdl*
	Sewage Sludge								
2008	447.5	165.80	24.76	3.18	16110	173.06	78.78	9.06	0.26
2012	715.0	301.20	35.40	7.00	28870	105.72	66.18	8.60	0.16
	Compost								
2011	130.2	39.95	37.50	bdl*	2238	30.76	6.09	12.81	bdl*
2013	122.9	39.68	31.89	bdl*	2118	30.19	6.48	12.98	bdl*
2014	124.8	43.66	65.43	bdl*	2242	28.68	5.63	12.51	bdl*

*bdl=below detection limit (0.001 mg l^{-1})

Table 1: Total and EDTA-extractable Zn, Cu, Pb, Cd and P concentrations relative to the total dry matter of the organic amendment samples available.

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Figure Captions

Figure 1: Experimental design of ZOFE with 12 treatments replicated in five blocks. Only the 4 treatments highlighted in grey were investigated: control (NIL #1), farmyard manure (FYM #2), sewage sludge (SS #3), and green waste compost (COM #4).

Figure 2: IDMM-ag model with lateral mixing. (A) Description of the model structure; (B) description of the soil lateral mixing implemented.

Figure 3: Total concentration time trends of Zn, Cu, Pb, Cd and P in ZOFE topsoils (20 cm) for the treatments NIL, FYM, SS and COM.

Figure 4: Lability time trends of Zn, Cu, Pb and Cd, expressed as the ratio between the EDTA-extractable concentration and total concentration, (A) in ZOFE topsoils (0-20 cm) for the treatments NIL, FYM, SS and COM; (B) in the organic amendment samples available.

Figure 5: Measured EDTA-extractable concentrations (•), simulated labile pool concentrations with the '*Swiss Sludge Trend*' approach (—), simulated labile pool concentrations with the *'Idealized Trend'* approach (--), of Zn, Cu, Pb, Cd in ZOFE topsoils (0-20 cm) for the treatments NIL, FYM, SS and COM. All the simulations are carried out with the lateral mixing effect. The two approaches differ in the way the sewage sludge metal content over time is estimated. RMSE = Root Mean Square Error; r = Pearson correlation.

Figure 6: Simulated labile concentrations of Zn, Cu, Pb and Cd in 2014 across a transect comprising the plots NIL, FYM, SS and COM in series with 5 and 10 strips per plot with the *'Idealized Trend'* approach.

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Figure 7: PCA analysis of the FTIR spectra from the NIL, FYM, SS and COM topsoil samples in 1972 and 2011. (A) PCA score plot with blue marks for samples from 1972 and red marks for samples from 2011; (B) PCA loading plot with the most noticeable peaks classified as clay (Cl), organic matter (OM) and quartz (Q).

Figure 8: Differential FTIR spectra of the SS samples: SS 2011 spectra subtracted from the 1972 spectra (red line), SS 2013 spectra subtracted from the 1972 spectra (blue line).

Figure 9: Measured EDTA-extractable concentrations (•), critical limits for labile concentrations (primary axis), projections of labile concentrations (primary axis) and soluble concentrations (secondary axis), for Zn, Cu, Pb, Cd from pristine conditions to 2114 in a real field experiencing stable conditions and organic amendment applications as in ZOFE. All the simulations are carried out without lateral mixing effect and with the *'Idealized Trend'* approach.

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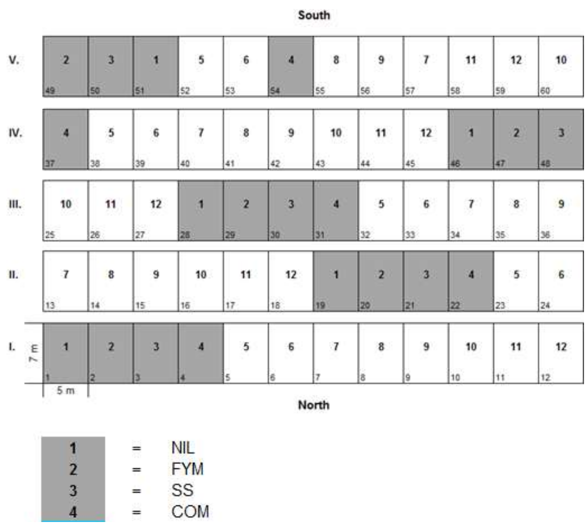

Figure 1

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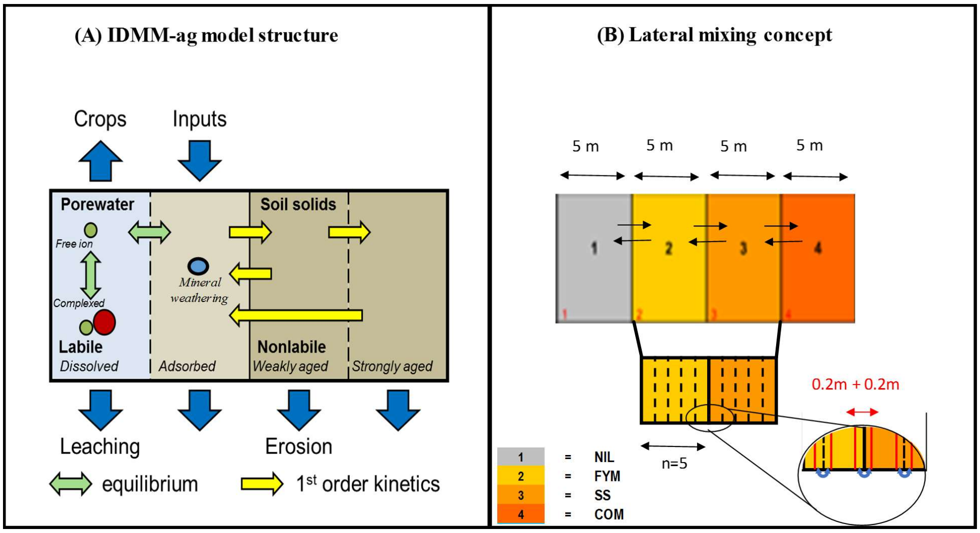

Figure 2

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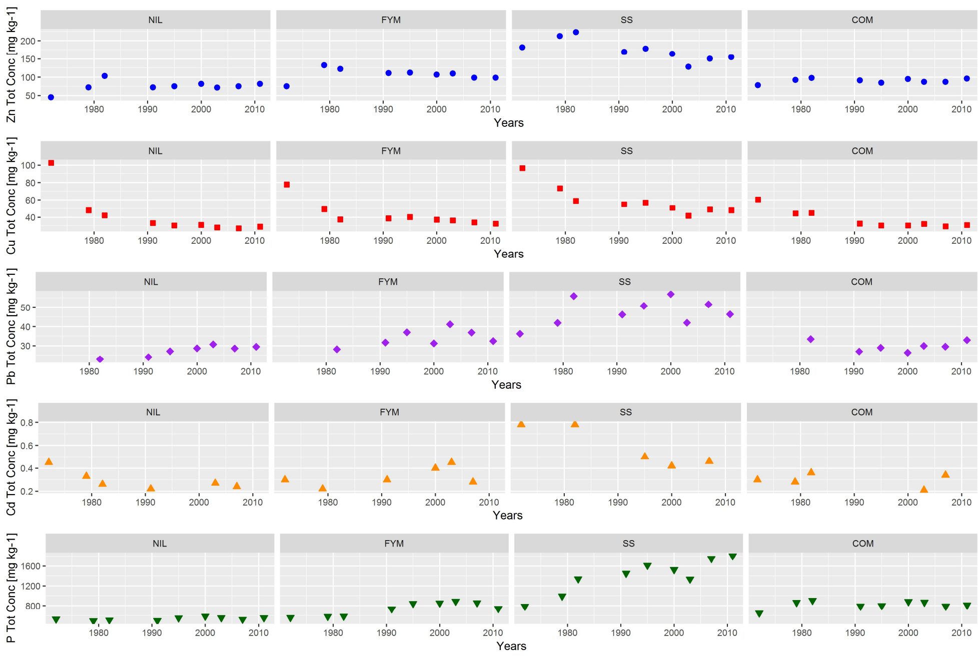

Figure 3

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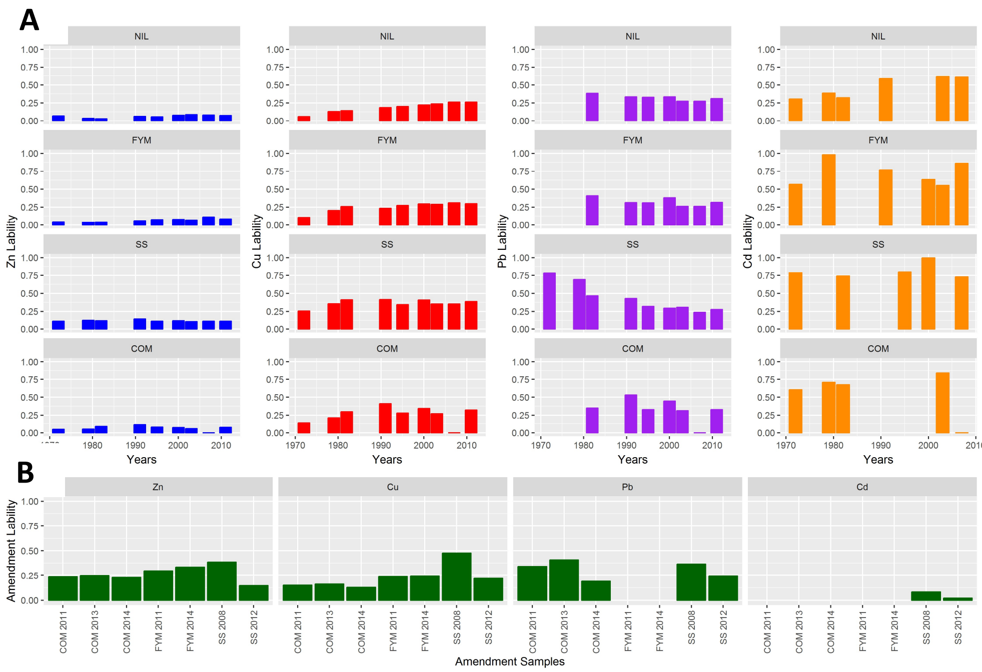

Figure 4

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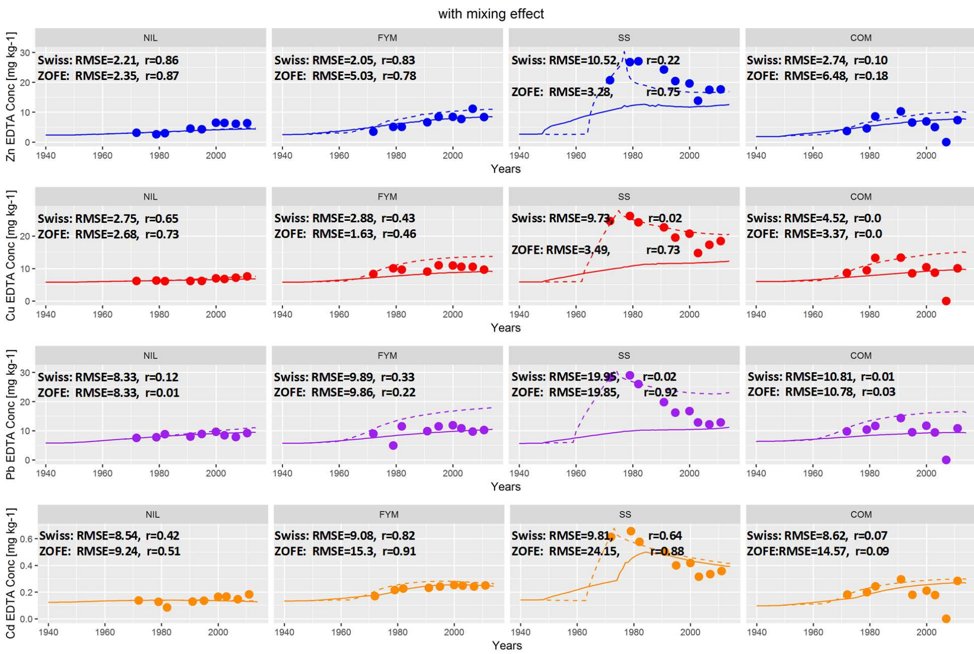

Figure 5

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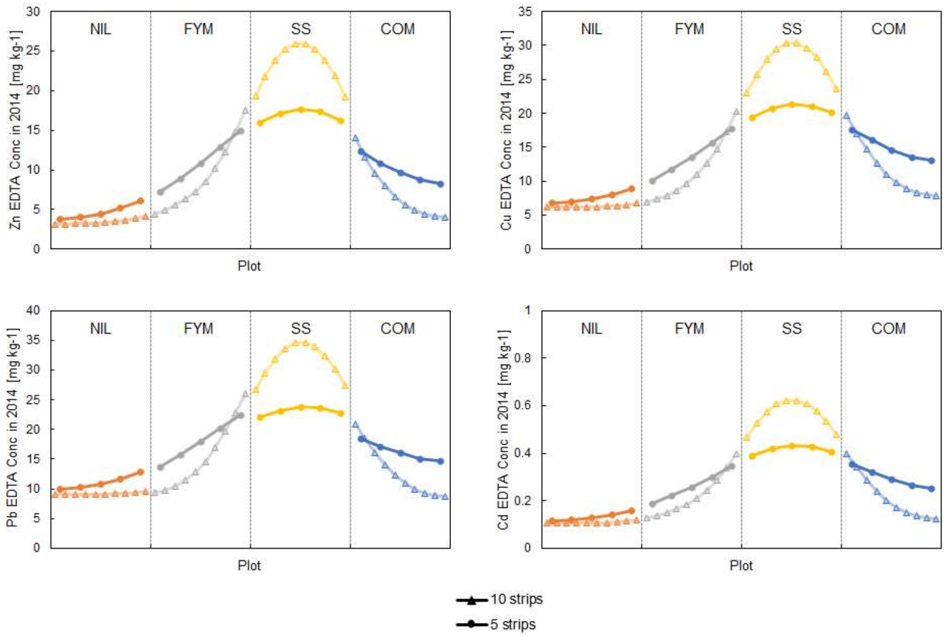

Figure 6

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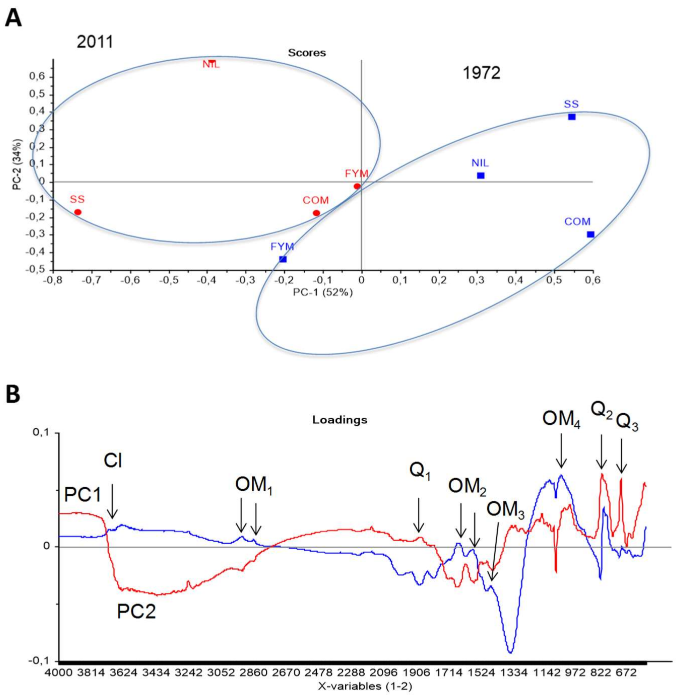

Figure 7

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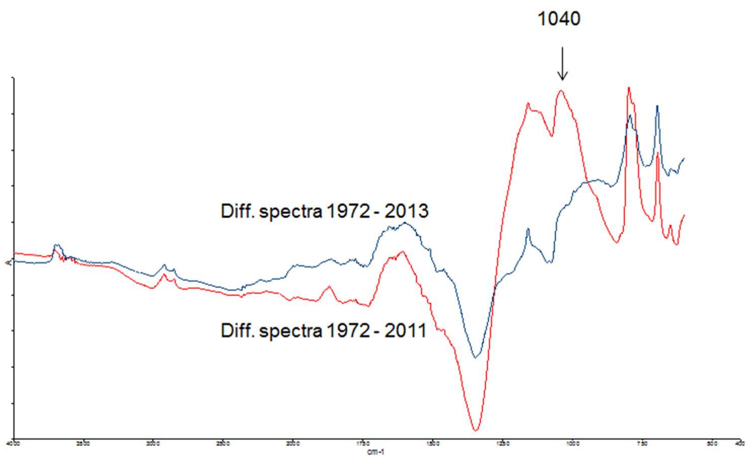

Figure 8

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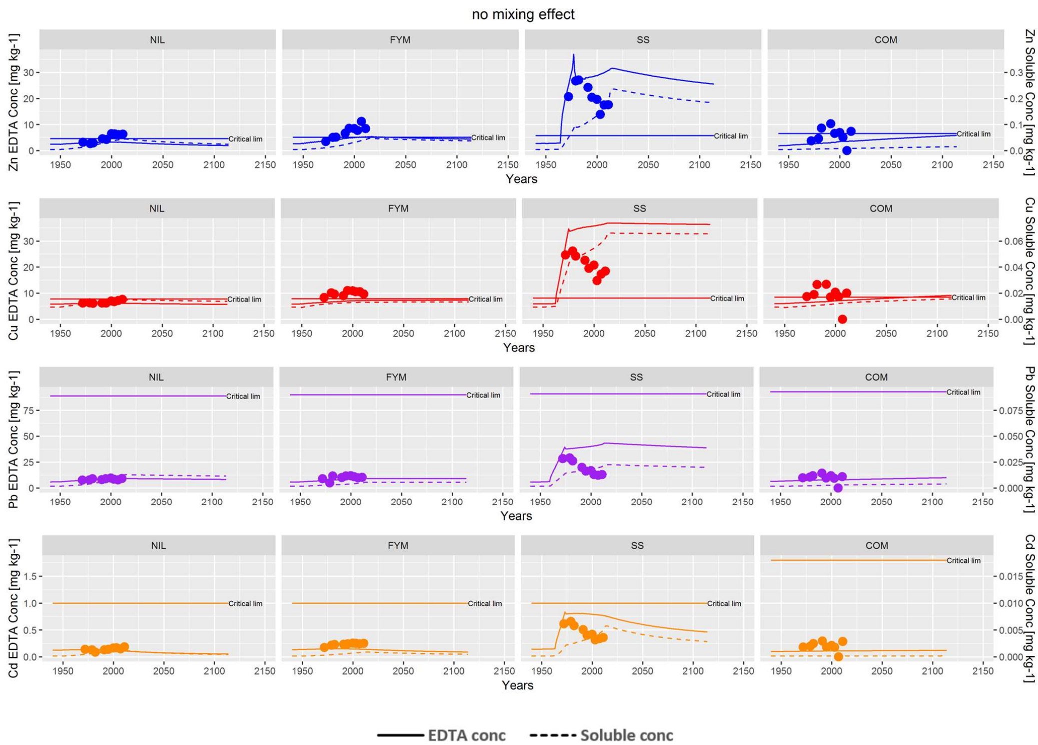

Figure 9

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Bibliography

Adriano, D.C., 2005. Trace elements in terrestrial environments. Biogeochemistry, Bioavailability, and Risks of Metals. Springer, New York.

BAFU (Hrsg.) 2018: Deposition von Luftschadstoffen in der Schweiz. Moosanalysen 1990 – 2015. Bundesamt für Umwelt, Bern. Umwelt-Zustand Nr. 1818: 134 S.

Ballabio, C., Panagos, P., Lugato, E., Huang, J. H., Orgiazzi, A., Jones, A., . . . Montanarella, L. (2018). Copper distribution in European topsoils: An assessment based on LUCAS soil survey. *Science of the Total Environment, 636*, 282-298. doi:10.1016/j.scitotenv.2018.04.268

Bergkvist, P., & Jarvis, N. (2004). Modeling organic carbon dynamics and cadmium fate in long-term sludge-amended soil. *Journal of Environmental Quality, 33*(1), 181-191. doi:DOI 10.2134/jeq2004.0181

Bonten, L. T. C., Groenenberg, J. E., Meesenburg, H., & de Vries, W. (2011). Using advanced surface complexation models for modelling soil chemistry under forests: Solling forest, Germany. *Environmental Pollution, 159*(10), 2831-2839. doi:10.1016/j.envpol.2011.05.002

D'Acqui, L. P., Santi, C. A., Vizza, F., & Certini, G. (2015). Living and dead soil organic matter under different land uses on a Mediterranean island. *European Journal of Soil Science, 66*(2), 298-310. doi:10.1111/ejss.12219

De Troyer, I., Merckx, R., Amery, F., & Smolders, E. (2014). Factors Controlling the Dissolved Organic Matter Concentration in Pore Waters of Agricultural Soils. *Vadose Zone Journal, 13*(7). doi:10.2136/vzj2013.09.0167

De Vries, W., Römkens, P.F.A.M., Voogd, J.C.H. (2004). Prediction of the long term accumulation and leaching of copper in Dutch agricultural soils: A risk assessment study (Rapport 1030), Alterra Green World Research, Wageningen, The Netherlands

de Vries, W., Romkens, P. F. A. M., & Bonten, L. T. C. (2008). Spatially explicit integrated risk assessment of present soil concentrations of cadmium, lead, copper and zinc in the Netherlands. *Water Air and Soil Pollution, 191*(1-4), 199-215. doi:10.1007/s11270-008-9617-z

Diacono, M., & Montemurro, F. (2010). Long-term effects of organic amendments on soil fertility. A review. *Agronomy for Sustainable Development, 30*(2), 401-422. doi:10.1051/agro/2009040

EFSA. 2009. Scientific Opinion of the Panel on Contaminants in the Food Chain on a request from the European Commission on cadmium in food. The EFSA Journal (2009) 980, 1-139.

EFSA Panel on Contaminants in the Food Chain (CONTAM); Scientific Opinion on Lead in Food. EFSA Journal 2010; 8(4):1570. [151 pp.]. doi:10.2903/j.efsa.2010.1570. Available online: www.efsa.europa.eu

Geddie, J. L., & Sutherland, I. W. (1993). Uptake of Metals by Bacterial Polysaccharides. *Journal of Applied Bacteriology, 74*(4), 467-472. doi:DOI 10.1111/j.1365-2672.1993.tb05155.x

Groenenberg, J.E., Römkens, P.F.A.M. & De Vries, W. (2006). Prediction of the long term accumulation and leaching of copper in Dutch agricultural soils: A risk assessment study (Rapport 1278), Alterra Green World Research, Wageningen, The Netherlands.

Groenenberg, J. E., Romkens, P. F. A. M., Comans, R. N. J., Luster, J., Pampura, T., Shotbolt, L., . . . de Vries, W. (2010). Transfer functions for solid-solution partitioning of cadmium, copper, nickel, lead and zinc in soils: derivation of relationships for free metal ion activities and validation with independent data. *European Journal of Soil Science, 61*(1), 58-73. doi:10.1111/j.1365-2389.2009.01201.x

Gu, X. Y., & Evans, L. J. (2008). Surface complexation modelling of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) adsorption onto kaolinite. *Geochimica Et Cosmochimica Acta, 72*(2), 267-276. doi:10.1016/j.gca.2007.09.032
Hudcova, H., Vymazal, J., & Rozkosny, M. (2019). Present restrictions of sewage sludge application in agriculture within the European Union. *Soil and Water Research, 14*(2), 104-120. doi:10.17221/36/2018-Swr
Imseng, M., Wiggenhauser, M., Keller, A., Muller, M., Rehkamper, M., Murphy, K., . . . Bigalke, M. (2018). Fate of Cd in Agricultural Soils: A Stable Isotope Approach to Anthropogenic Impact, Soil Formation, and Soil-Plant Cycling. *Environmental Science & Technology, 52*(4), 1919-1928. doi:10.1021/acs.est.7b05439
Imseng, M., Wiggenhauser, M., Muller, M., Keller, A., Frossard, E., Wilcke, W., & Bigalke, M. (2019). The Fate of Zn in Agricultural Soils: A Stable Isotope Approach to Anthropogenic Impact, Soil Formation, and Soil-Plant Cycling. *Environmental Science & Technology, 53*(8), 4140-4149. doi:10.1021/acs.est.8b03675
Ingwersen, J., & Streck, T. (2006). Modeling the environmental fate of cadmium in a large wastewater irrigation area. *Journal of Environmental Quality, 35*(5), 1702-1714. doi:DOI 10.2134/jeq2005.0412
IUSS Working Group WRB. 2006. World reference base for soil resources 2006. World Soil Resources Reports No. 103. FAO, Rome
Jarvis, N. J., Taylor, A., Larsbo, M., Etana, A., & Rosen, K. (2010). Modelling the effects of bioturbation on the re-distribution of 137Cs in an undisturbed grassland soil. *European Journal of Soil Science, 61*(1), 24-34. doi:10.1111/j.1365-2389.2009.01209.x
JRC. 2012. Occurrence and levels of selected compounds in European Sewage Sludge Samples. RC76111, doi:10.2788/67153
Kulling D, Stadelmann F, Herter U (2001) Sewage Sludge-Fertilizer or Waste? UKWIR Conference, Brussels
Kupper, T., Burge, D., Bachmann, H. J., Gusewell, S., & Mayer, J. (2014). Heavy metals in source-separated compost and digestates. *Waste Management, 34*(5), 867-874. doi:10.1016/j.wasman.2014.02.007
Lofts, S., Spurgeon, D., & Svendsen, C. (2005). Fractions affected and probabilistic risk assessment of Cu, Zn, Cd, and Pb in soils using the free ion approach. *Environmental Science & Technology, 39*(21), 8533-8540. doi:10.1021/es048121c
Lofts, S., Tipping, E., Lawlor, A. J., & Shotbolt, L. (2013). An intermediate complexity dynamic model for predicting accumulation of atmospherically-deposited metals (Ni, Cu, Zn, Cd, Pb) in catchment soils: 1400 to present. *Environmental Pollution, 180*, 236-245. doi:10.1016/j.envpol.2013.05.030
McBride, M. B., Richards, B. K., Steenhuis, T., & Spiers, G. (1999). Long-term leaching of trace elements in a heavily sludge-amended silty clay loam soil. *Soil Science, 164*(9), 613-623. doi:Doi 10.1097/00010694-199909000-00001
McGrath, S.P., 1987. Long–term studies of meal transfers following application of sewage sludge. In: Pollutant transport and fate in ecosystems, Eds. Coughtrey, P.J., Martin, M.H., Unsworth, M.H.. Blackwell Scientific Publications, Oxford, U.K
Mcgrath, S. P., & Cegarra, J. (1992). Chemical Extractability of Heavy-Metals during and after Long-Term Applications of Sewage-Sludge to Soil. *Journal of Soil Science, 43*(2), 313-321. doi:DOI 10.1111/j.1365-2389.1992.tb00139.x
Mcgrath, S. P., & Zhao, F. J. (2015). Concentrations of metals and metalloids in soils that have the potential to lead to exceedance of maximum limit concentrations of contaminants in food and feed. *Soil Use and Management, 31*, 34-45. doi:10.1111/sum.12080

Menzi, H., Kessler,J., 1998. Heavy metal content of manures in Switzerland. In: Martinez,J., Maudet,M. (Eds.),RAMIRAN 98.Proc. 8th Int. Conference of the FAO ESCORENA Network on Recycling of Agricultural, Municipal, and Industrial Residues in Agriculture. Rennes, France, 26-29 May 1998, FAO and Cemagref, France, pp. 495-506

MullerLemans, H., & vanDorp, F. (1996). Bioturbation as a mechanism for radionuclide transport in soil: Relevance of earthworms. *Journal of Environmental Radioactivity, 31*(1), 7-20. doi:Doi 10.1016/0265-931x(95)00029-A

NEBRA. 2015. Metals in Biosolids, Other Soil Amendments, & Fertilizers

Niemeyer, J., Chen, Y., & Bollag, J. M. (1992). Characterization of Humic Acids, Composts, and Peat by Diffuse Reflectance Fourier-Transform Infrared-Spectroscopy. *Soil Science Society of America Journal, 56*(1), 135-140. doi:DOI 10.2136/sssaj1992.03615995005600010021x

Oberholzer, H. R., Leifeld, J., & Mayer, J. (2014). Changes in soil carbon and crop yield over 60 years in the Zurich Organic Fertilization Experiment, following land-use change from grassland to cropland. *Journal of Plant Nutrition and Soil Science, 177*(5), 696-704. doi:10.1002/jpln.201300385

OIS. 1998. Ordinance Relating to Impacts on the Soil. Swiss Federal Council

Quevauviller, P. (1998). Operationally defined extraction procedures for soil and sediment analysis - I. Standardization. *Trac-Trends in Analytical Chemistry, 17*(5), 289-298. doi:Doi 10.1016/S0165-9936(97)00119-2

Rieder, S. R., Tipping, E., Zimmermann, S., Graf-Pannatier, E., Waldner, P., Meili, M., & Frey, B. (2014). Dynamic modelling of the long term behaviour of cadmium, lead and mercury in Swiss forest soils using CHUM-AM. *Science of the Total Environment, 468*, 864-876. doi:10.1016/j.scitotenv.2013.09.005

Roberts, T. L. (2014). Cadmium and Phosphorous Fertilizers: The Issues and the Science. *Symphos 2013 - 2nd International Symposium on Innovation and Technology in the Phosphate Industry, 83*, 52-59. doi:10.1016/j.proeng.2014.09.012

SAEFL. 2003. Assessment of Risks to Health and the Environment from Cadmium in Mineral Fertilisers. Technical report.

SCAN. 2003a. Opinion of the Scientific Committee for Animal Nutrition on the use of copper in feedingstuffs. EUROPEAN COMMISSION, HEALTH & CONSUMER PROTECTION DIRECTORATE-GENERAL.

SCAN. 2003b. Opinion of the Scientific Committee for Animal Nutrition on the use of zinc in feedingstuffs. EUROPEAN COMMISSION, HEALTH & CONSUMER PROTECTION DIRECTORATE-GENERAL.

Shotyk, W., Krachler, M., Martinez-Cortizas, A., Cheburkin, A. K., & Emons, H. (2002). A peat bog record of natural, pre-anthropogenic enrichments of trace elements in atmospheric aerosols since 12 370 C-14 yr BP, and their variation with Holocene climate change. *Earth and Planetary Science Letters, 199*(1-2), 21-37. doi:Pii S0012-821x(02)00553-8

Six, L., & Smolders, E. (2014). Future trends in soil cadmium concentration under current cadmium fluxes to European agricultural soils. *Science of the Total Environment, 485*, 319-328. doi:10.1016/j.scitotenv.2014.03.109

Smith, P. (2016). Soil carbon sequestration and biochar as negative emission technologies. *Global Change Biology, 22*(3), 1315-1324. doi:10.1111/gcb.13178

Thoni, L., Schnyder, N., & Krieg, F. (1996). Comparison of metal concentrations in three species of mosses and metal freights in bulk precipitations. *Fresenius Journal of Analytical Chemistry, 354*(5-6), 703-708.

https://doi.org/10.5194/soil-2020-21
Preprint. Discussion started: 25 May 2020

Tipping, E. (1998). Humic ion-binding model VI: An improved description of the interactions of protons and metal ions with humic substances. *Aquatic Geochemistry, 4*(1), 3-48. doi:Doi 10.1023/A:1009627214459

Tipping, E. CHUM: a hydrochemical model for upland catchments. J Hydrol 1996;174: 305–30.

Toth, G., Hermann, T., Da Silva, M. R., & Montanarella, L. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. *Environment International, 88*, 299-309. doi:10.1016/j.envint.2015.12.017

Veglio, F., Beolchini, F., & Gasbarro, A. (1997). Biosorption of toxic metals: An equilibrium study using free cells of Arthrobacter sp. *Process Biochemistry, 32*(2), 99-105. doi:Doi 10.1016/S0032-9592(96)00047-7

Vulkan, R., Zhao, F. J., Barbosa-Jefferson, V., Preston, S., Paton, G. I., Tipping, E., & McGrath, S. P. (2000). Copper speciation and impacts on bacterial biosensors in the pore water of copper-contaminated soils. *Environmental Science & Technology, 34*(24), 5115-5121. doi:10.1021/es/0000910

Weiss, D., Shotyk, W., Appleby, P. G., Kramers, I. D., & Cheburkin, A. K. (1999). Atmospheric Ph deposition since the industrial revolution recorded by five Swiss peat profiles: Enrichment factors, fluxes, isotopic composition, and sources. *Environmental Science & Technology, 33*(9), 1340-1352. doi:DOI 10.1021/es980882q

Xu, L., Lofts, S., & Lu, Y. (2016). Terrestrial ecosystem health under long-term metal inputs: modeling and risk assessment. *Ecosystem Health and Sustainability, 2*(5), e01214. doi:10.1002/ehs2.1214