1 **Modelling of long term Zn, Cu, Cd, Pb dynamics from soils fertilized with organic**

2 **amendments.**

4 Running head: Modelling of long-term trace element dynamics

6 Claudia Cagnarini[1,2], Stephen Lofts[3], Luigi Paolo D'Acqui[4], Jochen Mayer[5], Roman Grüter[6],

7 Susan Tandy[6,8], Rainer Schulin[6], Benjamin Costerousse[7], Simone Orlandini[1], Giancarlo Renella[9]

9 1, Dipartimento di Scienze e Tecnologie Agrarie, Alimentari, Ambientali e Forestali (DAGRI),

10 Piazzale delle Cascine, 18, 50144 Firenze, Italy

11 2, UK Centre for Ecology & Hydrology, Environment Centre Wales, Deiniol Road, Bangor,

12 Gwynedd, LL57 2UW, United Kingdom

13 3, UK Centre for Ecology & Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg,

14 Lancaster, LA1 4AP, United Kingdom

15 4, Istituto di Ricerca sugli Ecosistemi Terrestri, CNR, Area della Ricerca di Firenze, Via Madonna

16 del Piano 10, 50019 Sesto Fiorentino (Firenze), Italy

17 5, Agroscope, Dept Agroecology and Environment, Reckenholzstrasse 191, 8046 Zurich,

18 Switzerland

19 6, Institute of Terrestrial Ecosystems, ETH Zurich, Universitätstrasse 16, 8092 Zurich, Switzerland

20 7, Institute of Agricultural Sciences, ETH, Universitätstrasse 2, 8092 Zurich, Switzerland

21   8, Rothamsted Research, North Wyke, Okehampton, Devon, EX20 2SB, United Kingdom

22   9, Department of Agronomy, Food, Natural Resources, Animals and Environment (DAFNAE),

23   viale dell'Università 16, 35020 Legnaro (Pd), Italy

25   Corresponding author: Claudia Cagnarini, Email: ccagnar@ceh.ac.uk

27   Paper type: Research Article

29   Key words: trace elements, farmyard manure, sewage sludge, compost, sustainability, Switzerland

31   Declaration of interest: none.

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 used dynamic simulations carried out with the Intermediate Dynamic Model for Metals (IDMM) to describe the observed trends of topsoil Zn, Cu, Pb and Cd concentrations in a long-term (>60 year) crop trial in Switzerland, where soil plots have been treated with different organic amendments (farmyard manure, sewage sludge and compost).

The observed EDTA-extractable concentrations ranged between 2.6-27.1 mg kg^{-1} for Zn, 4.9-29.0 mg kg^{-1} for Cu, 6.1-26.2 mg kg^{-1} for Pb and 0.08-0.66 mg kg^{-1} for Cd. Metal input rates were initially estimated based on literature data. An additional, calibrated metal flux, tentatively attributed to mineral weathering, was necessary to fit the observed data. Dissolved organic carbon fluxes were estimated using a soil organic carbon model. The model adequately reproduced the EDTA-extractable (labile) concentrations when input rates were optimised and soil lateral mixing was invoked to account for the edge effect of mechanically ploughing the trial plots: the global average RMSE was 2.7 and the average bias (overestimation) was -1.66, -2.18, -4.34 and -0.05 mg kg^{-1} for Zn, Cu, Pb and Cd, respectively. The calibrated model was used to project the long term metal trends in field conditions (without soil lateral mixing), under stable climate and management practices, with soil organic carbon estimated by modelling and assumed trends in soil pH. Labile metal concentrations to 2100 were largely projected to remain near constant or to decline, except for some metals in plots receiving compost. Ecotoxicological thresholds (critical limits) were predicted to be exceeded presently under sewage sludge inputs, and to remain so to 2100. Ecological risks were largely not indicated in the other plots, although some minor exceedances of critical limits were projected to occur for Zn before 2100.

56 This study advances our understanding TEs long-term dynamics in agricultural fields, paving the

57 way to quantitative applications of modelling at field scales.

58

59 **1. Introduction**

60 Trace elements (TEs) are naturally present in soils due to mineral weathering and biogeochemical

61 cycles. Several TEs such as zinc (Zn), copper (Cu) and nickel (Ni) play important roles in

62 biochemical processes and are essential for living organisms at low concentrations, though they

63 can become toxic to biota at high concentrations; therefore, their presence in soil can be tolerable

64 in a relatively narrow range of values (Adriano, 2005). Wan et al. (2020) and Wang et al. (2015)

65 reported that the concentrations providing ecological safety in China ranged from 38.3 to 263.3

66 mg kg^{-1} for Zn and from 13.1 to 51.9 mg kg^{-1} for Cu when shifting from acidic soils to alkaline

67 non/calcareous soils. In contrast, other TEs such as lead (Pb) and cadmium (Cd), which are not

68 physiologically active, may be toxic to living organisms at low concentrations and their

69 accumulation in soil is of particular concern. For example, background cadmium levels in world

70 topsoils range from 0.01 to 2.7 mg kg^{-1}, and in Europe the mean cadmium concentration in

71 cultivated soils is 0.5 mg kg^{-1} (EFSA, 2009). Excessive uptake of trace elements by crop plants

72 and enrichment in edible parts can pose significant risks to human health by entering into the food

73 chain (McGrath et al., 2015).

74 Accumulation of TEs in cultivated soils is widespread and is mainly caused by application of low

75 grade agrochemicals, organic fertilizers and sewage sludge (Toth et al., 2016). In an European

76 Union-wide survey, Ballabio et al. (2018) reported that agricultural soils have among the highest

77 potential to become enriched in Cu compared with other land uses, and that land cover and

78 management are better predictors of soil Cu concentrations than natural soil formation factors.

79 Organic amendments are considered more sustainable than inorganic mineral fertilizers (Diacono

80 & Montemurro, 2010): in fact, current industrial processes for N-fertilizer production are based on

81 fossil fuels, and P-fertilizers are manufactured from phosphate rocks which are naturally limited

82 (Roberts, 2014). However, the application of organic amendments, such as farmyard manure,

83 compost and digestates of bio-wastes, can also introduce TEs into agricultural soils. In the

84 European Union, typical levels of trace elements in cattle manure are 63-175 mg kg^{-1} for Zn, 15-

85 75 mg kg^{-1} for Cu, 1.4-4.3 mg kg^{-1} for Pb and 0.1-0.4 mg kg^{-1} for Cd (NEBRA, 2015), but pig and

86 poultry manure can be much more enriched in trace metals. Mean concentrations of Zn, Cu, Pb

87 and Cd in greenwaste compost in Germany were reported to be 168, 33, 61 and 0.7 mg kg^{-1},

88 respectively (NEBRA, 2015). Application of sewage sludge into agricultural soils can be even

89 more problematic as sewage sludge can contain trace metals up to 30 times their concentrations in

90 soil (Hudcova et al., 2019).

91 Once in the soil, multiple factors may control TE speciation, solubility and mobility (Gu & Evans,

92 2008), such as soil pH, soil and dissolved organic matter (SOM, DOM) contents, the quantity and

93 chemical composition of clay minerals and metal (oxy)hydroxides. Furthermore, speciation can

94 influence the TE toxicological hazard, particularly to organisms that are directly exposed to soils

95 such as plants and earthworms: models, such as the Biotic Ligand Model (Paquin et al. 2002),

96 postulate that metal toxicity is related to uptake of specific metal species in competition with other

97 solution ions, rather than to total dissolved metals. Repeated applications of organic amendments

98 can lead to the accumulation of TEs in agricultural soils, particularly through direct reactions with

99 the soil solids (adsorption), formation of precipitates, or physical occlusion within the organo-

100   mineral aggregates (fixation). This can lead to TE concentrations exceeding environmental

101   legislation thresholds.

102   In the context of long term TE accumulation due to regular application of organic amendments or

103   other additions, predicting the long term speciation and dynamics of TEs is useful to support

104   decisions on ecosystem management and human health protection. Dynamic models, if reliable,

105   are essential for this purpose. Models for TE dynamics exist at a number of levels of complexity,

106   from those with a mechanistic approach requiring highly detailed input information and calibration

107   (Bonten et al., 2011), to simple mass balance approaches generally applicable at large scales but

108   relatively unsuitable to understand and unravelling complex metal dynamics (Six & Smolders,

109   2014). Empirical models have been used to simulate dynamics and uptake of TEs at specific

110   agricultural sites based on site–specific calibration, (Bergkvist & Jarvis, 2004; Ingwersen &

111   Streck, 2006), but such models can lack a reliable generalisation of the parameters to different

112   climatic conditions and hydrological and soil physio-chemical properties.

113   Among models for determining TE dynamics in soil, the Intermediate Dynamic Model for Metals

114   (IDMM) (Lofts et al., 2013; Xu et al., 2016) is an example of a semi-empirical dynamic model

115   which allows general application, given a reasonably parsimonious set of input data. It is intended

116   for long term application from decades to centuries. The IDMM describes metal dynamics from a

117   past year at which metal inputs can be assumed to be uninfluenced by anthropogenic activities.

118   Processes influencing metal dynamics, including solid/solution partitioning, fixation into soil solid

119   phases, and leaching, are described in a semi-empirical manner. Hydrological variables (e.g.

120   annual volume of soil drainage) are specified as time series. Similarly, key properties influencing

121   metal dynamics, such as the pH of the soil solution, dissolved organic carbon (DOC) flux, SOM

122   content and soil erosion rate, may be fixed to single values or varied annually.

123   The objective of this study was to assess the capability of the IDMM to reproduce metal dynamics

124   at a well-characterized location receiving a range of organic amendments. This application of the

125   model is at a smaller and more detailed scale than previous evaluations (Lofts et al., 2013; Xu et

126   al., 2016). We simulated the dynamics of Zn, Cu, Pb and Cd in the topsoil of a long term (>60 yr)

127   agricultural trial in Switzerland, comprising a series of plots receiving either farmyard manure,

128   sewage sludge, green waste compost, or no amendment. After optimising the model parameters

129   and driving data for the site, we then made projections of metal dynamics into the future under the

130   same agronomic practices, in order to assess their sustainability in terms of environmental risk.

2. Materials and Methods

2.1 The study site

The Zurich Organic Fertilization Experiment (ZOFE) is a long-term agricultural 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 mean annual precipitation is 1054 mm, and the mean annual temperature is 9.4°C. The soil is a carbonate-free, loamy (14% clay) Luvisol (IUSS, 2006), with a SOC content of 1.43% w/w and a pH (H_2O) value of 6.5 prior to the experiment. The field trial consists of twelve treatments replicated in five blocks of dimensions 7m × 5m in a systematic design. The same cultivation and plant protection regimes have been applied to all the treatments. In the present study we investigated the following four treatments: control (NIL#1) with no fertilization and no amendment, farmyard manure (FYM#2) with application of 5 t OM ha^{-1} every second year, sewage sludge (SS#3) with application of 2.5 t OM ha^{-1} every year, and green waste compost (COM#4) with application of 2.5 t OM ha^{-1} every year (Figure 1).

2.2 Trace element time series

The NIL, FYM, SS and COM soils (top 20cm, sieved to 2mm) were sampled from the Agroscope ZOFE soil archive and analysed for total and EDTA-extractable concentrations of Zn, Cu, Pb and Cd. Analysed soils were sampled from the years 1972, 1979, 1982, 1991, 1995, 2000, 2003, 2007

154 and 2011. Before 2011, samples from the five replicate plots per treatment had been bulked, so

155 variability among replicate plots could not be assessed. To determine the total and EDTA-

156 extractable soil TE concentrations respectively, soils were digested in aqua regia and extracted

157 using EDTA, and analysed by ICP-OES (Dv sequential Perkin Elmer Optima 2000). The EDTA-

158 extractable pools were obtained with the extraction protocol described by (Quevauviller, 1998).

159 The total metal concentrations were compared with the one-point-in-time measurements from the

160 same plots carried out with ICP-MS from an independent laboratory, so that interferences of As

161 with Cd in the readings (McBride, 2011) were ruled out as shown in Figure S1 of the Supporting

162 Information for Cd. Quality control of the ICP-OES was done every ten readings on the calibration

163 curve by measuring the TES concentrations in the blank samples and in the standard sample at

164 concentration of 1 ppm. The limits of quantification of total and EDTA-extractable concentrations

165 for each TE are given in Table S1 (Supporting Information).

166 Samples of farmyard manure from 2011 and 2014, sewage sludge from 2008 and 2012 and

167 compost from 2011, 2013 and 2014 were also analysed for total and EDTA-extractable

168 concentrations of Zn, Cu, Pb and Cd as described above.

169

170 **2.3 The Intermediate Dynamic Model for Metals with lateral mixing**

171 A detailed description of the Intermediate Dynamic Model for Metals (IDMM) is given in the

172 Supporting Information; here we present an overview of the most relevant concepts. The IDMM

173 simulates annual concentrations of total and geochemically active metals within a topsoil, and

174 metal fluxes from the soil due to porewater leaching and crop uptake. It distinguishes between a

175 pool of geochemically active (labile) TEs, comprising dissolved and adsorbed forms, and a non–

176 labile (aged) pool that comprises chemically less reactive and occluded forms (Figure 2A). The

177 labile metal pool is partitioned into dissolved and adsorbed forms assuming chemical equilibrium.

178 A Freundlich-type isotherm (Groenenberg et al., 2010) describes the relationship between free and

179 adsorbed TE ions, and the relationship between free TE ions and TEs complexes in the porewater

180 is computed using WHAM/Model VI (Tipping, 1998). Transformations between labile and aged

181 pools follow first-order kinetics. Two pools of aged metal are defined, termed 'weakly aged' and

182 'strongly aged'. The weakly aged pool has relatively rapid, reversible transformation kinetics with

183 the labile pool. Weakly aged metal may transfer into the strongly aged pool, and strongly aged

184 metal may transfer back into the labile pool. Both these transformations have relatively slow

185 kinetics compared to the transformations occurring between the labile and weakly aged pools.

186 The IDMM is driven by annual TE input rates, which we assume to be entirely in labile form.

187 Simulations start from a past year (1750 in this case), in which all metal inputs are assumed to be

188 natural, and where the soil is in steady state, i.e. metal input and output fluxes balance (Tipping,

189 1998). Metals can be removed from the soil due to leaching of the dissolved form in drainage

190 water, erosion of the soil, and uptake into the harvestable parts of crops. In this study erosion was

191 neglected in consideration of the site geomorphological characteristics (i.e. the site has negligible

192 slope). Since the soil samples were relevant to the homogenised ploughing depth, the soil was

193 modelled as a single well–mixed layer of 20 cm.

194 The work of McGrath (1987) and McGrath & Cegarra (1992) on plot experiments at Rothamsted

195 Experimental Station (U.K.) showed that lateral movement of soil among adjacent plots, due to

196 regular ploughing, exerted a significant influence on the temporal trends of metal concentrations

197 within the plough layer. Therefore, we extended the IDMM to enable the lateral transfer of metal

198 across the plots to be simulated. Figure 2B illustrates the lateral mixing model setup. The plots are

199 subdivided into a number of strips, within which the soil composition is physicochemically

200 homogeneous. Each year, a proportion of the topsoil, and its associated TEs, in each strip is

201 exchanged with the adjacent strip. Mean soil TE concentrations in each plot are computed as the

202 sum of the TE mass in each strip, divided by the sum of the soil mass in each strip. The number of

203 strips per plot, and the amount of soil exchanging, can be varied. Figure 2B shows an example

204 setup with five strips of 1m width and an exchange width of 0.2m, equal to the plough depth. For

205 simulations, we ordered the plots NIL-FYM-SS-COM. We fixed the exchange width to this value

206 for all simulations. A sensitivity analysis was carried out on the number of strips per plot, in order

207 to understand the impact of the choice of strip number on the predicted TE trends.

208

209 **2.4 Metal input rate estimation**

210 Besides TE inputs from the organic amendments, TE inputs to the plots were assumed to comprise

211 geogenic and anthropogenic deposition from the atmosphere, and mineral weathering from the

212 coarse (>2mm) fraction of soil. Estimation and optimisation of the input rates, as based on

213 available measurements and data from literature, are described in detail in the Supporting

214 Information. For the sewage sludge amendment only, two approaches were used to estimate the

215 metal inputs. The first approach, termed 'Swiss Trend', was derived from literature trends specific

216 to Switzerland; considering the unsatisfactory simulation results, the metal input rates were

217 adjusted to the ZOFE plots and this approach was termed 'Idealised Trend' (more details in the

218 Supporting Information).

219

220 **2.5 Model parameterisation**

221 The IDMM requires time series inputs of annual soil porewater pH, SOM, DOC fluxes in

222 porewater, and annual drainage volume, in order to simulate soil TE concentrations. For computing

223 TE losses by crop uptake and removal, annual crop yields and TE concentrations in the harvestable

224 parts of crops are required.

225 Soil porewater pH trends for 1949–2014 were obtained by firstly converting measurements in

226 aqueous extracts to porewater pH values, according to the formula provided by de Vries et al.

227 (2008) (Figure S7 in the Supporting Information). The trends in pH were then smoothed to reduce

228 the effect of noise on the simulations; a five-year period, four pass averaging approach was used

229 for smoothing. For future projections, we ran simulations assuming either (i) no change in pH from

230 2014 to 2100, or (ii) an exponential decline in pH from 2014 onwards to reach a constant pH 0.5

231 units below the 2014 value.

232 Prior to 1949, SOM was assumed to be constant and set to the mean of the first measurement in

233 each plot. Fitting of SOM observations before 2014 and projections to 2100 were done by applying

234 the two-pool SOM model ICBM (Andrén et al., 2004). Briefly, after fitting the NIL treatment with

235 the coefficients obtained by Menichetti et al. (2016) for ZOFE, the humification coefficient was

236 calibrated to fit the other amended treatments. Each plot was divided into five strips and the soil

237 lateral mixing approach described above was incorporated into the modelling. The resulting trends

238 are shown in Figure S7 (Supporting Information). The SOC was converted to SOM by assuming

239 the latter to be 50% C by mass.

240 No porewater dissolved organic carbon (DOC) concentration or flux data were available for ZOFE.

241 The total carbon respiration flux from 1949 onwards, obtained from the ICBM modelling, was

242 assumed to be proportional to the DOC loss flux. The annual DOC flux prior to the start of the

243 experiment was estimated, and DOC fluxes during the experiment were then estimated by scaling.

244 As the site was grassland prior to the experiment, we collated published data on DOC fluxes from

245 improved grasslands (Fu et al., 2019; Kindler et al., 2011; Buckingham et al., 2008), and derived

246 a median flux of 8.1 g m^{-2} a^{-1} for scaling. The computed flux trends were divided by the annual

247 drainage to obtain DOC concentration trends (Figure 3). The annual drainage was assumed to be

248 constant, and calculated by averaging the difference between rainfall measurements at local

249 stations and evapotranspiration estimated with a locally calibrated Primault equation.

250 Crop metal removal was assumed to be a function of crop biomass (Figure S7 in the Supporting

251 Information), as crop metal concentrations were assumed not to vary. Crop yields have been

252 measured in ZOFE yearly, based on the harvest from a sub-plot in each plot. Shoot biomass was

253 estimated by scaling the crop yields linearly according to the functions provided by Bolinder et al.

254 (2007). The Zn, Cu and Cd concentrations in winter wheat grains and shoots were measured at

255 harvest in 2014 and 2015 and the average values were taken to represent the respective metal

256 contents in the grains and shoots of wheat and barley, over the entire simulation period. The TE

257 concentrations for Pb, and for the other crops in the 8-year rotation, were estimated from previous

258 reports (de Vries et al., 2008; EFSA, 2009, 2010; SAEFL, 2003; SCAN, 2003a,b). Table S8

259 (Supporting Information) reports the assumed TE concentrations for all crops.

260

261 **2.6 Analysis of the soil and organic amendment FTIR and XRD**

262 NIL, FYM, SS and COM amended soil samples from 1972 and 2011 and SS sample from 2013

263 were analysed by Fourier Transform Infrared Spectroscopy (FTIR) to detect any change in time of

264 the soil organic fraction between the treatments. The DRIFT spectra were obtained using a rapid-

265 scan Spectrum-GX (Perkin Elmer, Monza, Italy) Fourier transform infrared spectrometer (FTIR)

266 in the mid-infrared spectral range (4000 to 450 cm^{-1}). The spectrometer was equipped with a

267 Peltier-cooled deuterated triglycine sulphate (DTGS) detector and an extended range KBr beam

268 splitter. Soil samples of 50 mg were placed in a stainless steel sample cup, located in a Perkin

269 Elmer diffuse reflectance accessory and scanned for 60 s. A silicon carbide (SiC) reference disk

270 was used as the background sample (Perkin-Elmer). The most noticeable peaks were attributed

271 according to D'Acqui et al. (2015) and Niemeyer et al. (1992), as reported in the Supporting

272 Information. The same soil samples were also analysed by X Ray Diffraction (XRD) to investigate

273 the soil mineral fraction, as also described in the Supporting Information.

274

275 **2.7 Projections of the long-term effects of organic amendment applications**

276 After evaluating and calibrating the IDMM for the period 1949-2014, the model was run in

277 predictive mode from 1750 to 2100 to derive projections of the long term influence of organic

278 amendment application on topsoil TE concentrations. For the period 2015–2100, the following

279 modelling assumptions were made: *i)* stable annual temperature and topsoil drainage; *ii)* constant

280 rates of TE input rates *via* all sources, at the 2014 rates, including the 'Idealised Trend' inputs via

281 sewage sludge addition; *iii)* constant crop yields at the 2014 values. Future SOM, DOC flux and

282 pH trends were generated as previously described.

283 The projected labile TE concentrations were compared against ecotoxicological critical limits

284 calculated for each metal according to the methodology of Lofts et al. (2004). This method assumes

285 that the free metal ion concentration is the most appropriate indicator of toxicity, combined with a

286 protective effect of the soil porewater pH. The resulting critical limit functions, expressed as labile

287 metal concentrations and functions of soil pH and SOM, aim to be protective of 95% of soil

288 species. The critical limit functions are reported in the Supporting Information.

289

290 **2.8 Statistical analysis**

291 All statistical analyses were carried out in R (version 3.5.0). The Mann-Kendall test (package

292 "Kendall") was used to assess monotonic trends in the TE time series. Increasing trends (Kendall's

293 tau statistic > 0) and decreasing trends (Kendall's tau statistic < 0) were considered significant

294 when the two-sided P-value was less than 0.05. The *bias* function and the "dplyr" package were

295 used to calculate the bias and the root mean squared error, respectively, of the simulated labile

296 concentrations versus the observed data.

3. Results and Discussion

3.1 TE measurements in soil and organic amendments

Despite the continuous application of organic amendments, total TE concentrations (Figure 4) showed no significant ($P < 0.05$) accumulation patterns over time in the topsoil according to the Mann-Kendall trend test, except for the Pb concentration in the NIL treatment topsoil, which increased significantly due to atmospheric deposition. While the total concentrations were basically stable, the trends were decreasing for Zn in the SS treatment and for Cu in all the treatments, with Cu displaying large decreases, 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), in which an average total Cu concentration of ca.17 mg kg^{-1} was reported from more than 21,000 topsoils of EU countries. The observed higher Cu concentration in 1972 could be ascribed to past anthropogenic contamination, such as application of Cu-based fungicides. The reasons for the extensive loss of total Cu are unknown, as the rate of loss (5-8 mg kg-1 in 35 years) was larger than expected by leaching, which is of the order of 0.2-0.3 mg kg-1 per year (Vulkan et al., 2000 For comparison, the temporal trend of the total P concentration in the topsoil (Figure 4) exhibited lower temporal variability than the TE concentrations. Phosphorus showed significant accumulation over time in the FYM and SS treatments, but not in the NIL and COM treatments.

Increases in the EDTA-extractable concentrations (Table 1) were significant for Zn and Cd in the NIL and FYM treatments, and for Cu in the NIL treatment ($P < 0.05$). Conversely, in the SS treatment all the metals showed steady declines in their EDTA-extractable concentrations over the measurement period. Observed metal lability, calculated as the ratio of the EDTA-extractable concentration and total concentration in the same year, is reported in Figure S8.

319 The total TE concentrations of the organic amendments are reported in Table 2. The farmyard

320 manure and compost samples had comparable levels of total TE concentrations, with the green

321 waste compost presenting higher Pb enrichments. The sewage sludge had higher total TE

322 concentrations than the compost and farmyard manure, explaining why the magnitude of all total

323 TE concentrations ranked in the order NIL< COM = FYM < SS in 2011. The analysed sewage

324 sludge showed also the highest variability of the TE lability (Figure S8), with Zn lability varying

325 from 0.39 to 0.15 and Cu from 0.48 to 0.22 in the samples from 2008 and 2012. The lower lability

326 of Cu and Pb in the organic amendments than in the topsoil could be ascribed to their stronger

327 affinity for organic matter (McBride et al., 1999).

328

329 **3.2 Simulations of the metal trends**

330 The IDMM model was run from 1750 (pristine conditions) to simulate the observed metal

331 concentrations data between up to 2014. The observed and simulated total concentrations are

332 shown for reference in the Supporting Information (Figure S9). Here we focus firstly on the

333 predicted labile metal concentrations, and briefly discuss the modelling of the total metal

334 concentrations.

335 From a mechanistic point of view, the IDMM does not directly simulate the total soil metal

336 concentration, but explicitly considers separate labile, weakly aged and strongly aged forms, each

337 with their own dynamics. The IDMM sets the initial labile concentration assuming a steady state

338 balance of natural input and output metal fluxes, including kinetic transfers to and from the

339 nonlabile pool. In a dynamic simulation, changes in the labile concentration are then driven by

340 changes in inputs and the soil parameters influencing solid-solution partitioning and rate of net

341   aging (pH, soil organic matter, DOC flux). The initial aged concentrations are set by a combination

342   of equilibrium with the initial labile concentration, coupled with the adjust of one kinetic constant

343   (see Supporting Information for details). Changes in the aging concentration are then driven by

344   aging transformations of the labile form. Transformations between the labile and weakly aged

345   forms are sufficiently rapid that the weakly aged form responds rapidly to changes in the labile

346   concentration, but the slower transformations involving the strongly aged pool result in a highly

347   delayed response to changes in the labile pool. An example of predicted trends in the three pools

348   is shown in Figure S10 (Supporting Information).

349   Using five strips of dimension $1m \times 7m$ to simulate each plot when considering lateral mixing, the

350   IDMM gave the predictions shown in Figure 5 when using the 'Swiss Trend' and 'Idealised Trend'

351   inputs, both with and without lateral mixing.

352   Fitting of apparent model weathering rates was done for each scenario. Only small differences

353   were seen among the fitted rates, so here we focus only on the rates obtained when assuming lateral

354   mixing and using the 'Idealised Trend'. Fitted apparent weathering rates were 9.28, 1.62, 0.0798

355   and 0.914 mg m^{-2} a^{-1} for Cu, Zn, Cd and Pb respectively. These are generally higher than the

356   natural atmospheric deposition rates of 0.0699, 0.0752, 0.0109 and 0.522 mg m^{-2} a^{-1}. Clearly the

357   contribution of the apparent weathering rate is not negligible relative to other natural inputs.

358   Estimates of topsoil metal weathering inputs are uncommon in the literature, but Imseng and co–

359   workers (Imseng et al., 2018, 2019) have published estimates of Zn and Cd weathering at Swiss

360   grassland locations. Generally, the weathering rates they estimate (0.001–0.5 mg m^{-2} a^{-1} for Zn,

361   <0.01–0.39 mg m^{-2} a^{-1} for Cd) are lower than our fitted Zn rate but comparable for Cd. It is

362   reasonable to assume our fitted rates to be apparent weathering rates only, subject to a number of

363   uncertainties, particularly the lack of knowledge regarding anthropogenic metal additions to the

364   field prior to setting up the ZOFE experiment. This is particularly clear for copper, for which the

365   apparent rate looks unrealistically high and is likely to be compensating for unquantified past

366   inputs, as per what is known of the site history. Nonetheless, the fitting exercise is useful in

367   allowing us both to calibrate model predictions to observations, and to emphasise where the key

368   gaps in knowledge exist, that should be tackled to allow more comprehensive and plausible future

369   applications of the IDMM.

370   The 'Swiss Trend' of metal inputs predicted neither the magnitude nor the trends in labile metal

371   concentrations in the SS plot with or without lateral mixing enabled, with the partial exception of

372   Cd (Figure 5). The downward trend in labile metal concentrations in SS cannot be explained due

373   to metal removal in leaching and/or crop uptake using the key variables (porewater pH and DOC

374   concentration, metal contents of harvestable crops). Simulations were therefore repeated with

375   lateral mixing and optimisation of the inputs to SS (the 'Idealised Trend'). The optimised inputs

376   (total inputs from 1949 to 2014) were factors of 3.2, 2.3, 1.5 and 6.6 times higher than the

377   literature–derived inputs. With lateral mixing invoked, the model was reasonably successful in

378   describing the downwards observed trends in labile metal in the SS plot, although there was a

379   tendency to overestimate post–1990 observed concentrations, particularly for Pb. To illustrate the

380   influence of lateral mixing on predictions, we also ran a simulation using the 'Idealised Trend'

381   inputs without lateral mixing. The results suggest that lateral mixing due to ploughing has been a

382   key determinant of the observed metal concentrations in SS. In the absence of lateral mixing,

383   higher labile metal concentrations are consistently predicted from 1949 onwards (Figure 5), and

384   the observations are consistently overestimated. For example, in 2011, the observed labile metal

385   concentrations were 17.6, 18.5, 0.36 and 12.8 mg/kg for Cu, Zn, Cd and Pb respectively. The

386   model predictions when invoking lateral mixing were 21, 20, 0.46 and 25.2 mg/kg respectively,

387   which are reasonable agreement with the exception of Pb. By contrast, the predicted concentrations

388   when lateral mixing was not invoked were 40.6, 42.2, 0.87 and 49.7 mg/kg respectively, which are

389   all approximately double the concentrations predicted in the presence of lateral mixing. These

390   results are consistent with the lateral distribution of metals in ploughed experimental plots at

391   Rothamsted Experimental Station previously (McGrath, 1987). This influence of ploughing on

392   metal distribution is, however, likely to be confined to the specific management conditions of

393   experimental plots such as ZOFE, and not to be relevant for modelling commercial agricultural

394   systems at field and higher scales.

395   Observed labile metal concentrations in NIL, FYM and COM are consistently lower than those in

396   SS due to the lower rates of input. The IDMM generally reproduces the magnitude and trends in

397   concentrations reasonably well in these plots, but tends to slightly underestimate concentrations,

398   particularly in the FYM and COM plots. In the absence of lateral mixing, there is negligible

399   distinction between the 'Swiss Trend' and 'Idealised Trend' for these plots. Invoking lateral

400   mixing increases the predicted labile concentrations somewhat due to the predicted net transfer of

401   metal from the SS plot to the other plots. This results in an overestimation of the observed labile

402   metal in FYM and COM. The effect of lateral mixing on the predictions for NIL is smaller, since

403   it is not immediately adjacent to SS. There are marginal improvements to the predictions,

404   particularly for Cu and to an extent Zn, when lateral mixing is invoked and the 'Idealised Trend'

405   SS input trend is applied.

406   Model performance with soil lateral mixing under both the 'Swiss Trend' and the 'Idealized

407   Trend" is reported in Table 3: the model adequately reproduced the EDTA-extractable

408   concentrations when the input rates were optimised ('Idealized Trend'), resulting in a global

409   average RMSE of 2.7 and an average bias (overestimation) of -1.66, -2.18, -4.34 and -0.05 mg kg-

410   1 for Zn, Cu, Pb and Cd, respectively.

411   Total metal simulations are shown in Figure S9. Generally, the model predictions are similar in

412   trend to the prediction of labile metal, with increases after 1949 due to ZOFE inputs, and in SS, a

413   decline from the late 1970s onwards as a result of lateral mixing. Trends in total zinc are well

414   reproduced, although there is a bias to low predictions in SS and marginally high predictions in

415   COM. For Pb, particularly in FYM, SS and COM, temporal trends in observed concentrations are

416   unclear. For example, there is no clear trend to decreasing concentrations in SS, as predicted by

417   modelling. Generally, concentrations in FYM, SS and COM are overestimated, while the trend in

418   NIL is well reproduced. Observed cadmium concentrations also show appreciable noise; a clear

419   (declining) trend is seen only in SS. Modelled cadmium concentrations are almost consistently

420   biased high, although the trend in SS is reproduced. Inspection of the fit for the NIL plot suggests

421   that the initial total Cd may be overestimated as a result of the fitting approach, as the mean of the

422   first three observations is greater than the subsequent measurements. Total copper exhibits a

423   distinctive declining trend in all the plots, as noted previously, but the reason for these observed

424   trends is unclear. The rates of decline cannot be explained by any of the metal loss processes in

425   the IDMM. The concentrations in SS, while showing the same declining trend as the other plots,

426   stabilise at higher concentrations, reflecting the higher copper input.

427

3.3 Lateral mixing sensitivity analysis

429   We investigated the sensitivity of the predictions with lateral mixing to the number of

430   homogeneous soil strips used per plot (Section 2.3), by running simulations using the 'Idealised

431 Trend' and either two or ten soil strips per plot, maintaining a margin width of 0.2m. Figure 6

432 shows the simulated labile concentrations of Zn, Cu, Pb and Cd in 2014 across the transect. With

433 two strips per plot, the labile concentrations in SS were on average 28% lower than with five strips

434 when considering all the metals; the concentrations were comparable in FYM and COM but were

435 higher in NIL by on average 81%. With 10 strips per plot, the labile concentrations in SS were on

436 average 40% higher than with five strips, but lower in NIL, FYM and COM. Therefore, increasing

437 the number of strips per plot reduced the predicted redistribution of the TEs from the SS to the

438 adjacent plots. The choice of the number of strips per plot has clearly an effect on both the

439 determination of the 'Idealised Trend' inputs and the simulation performance. The pragmatic

440 choice of five strips for modelling provides an example of the magnitude of the effect of ploughing

441 on the redistribution of metals across the treatments, but in general the presence of the lateral

442 mixing effect does somewhat limit the usefulness of the plot data for model evaluation, by

443 requiring additional modelling and parameterisation not necessary for true field application.

444

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

446 The IDMM model assumes that the TEs present in the organic amendments are fully labile, so they

447 are added to the labile pool when they are introduced in the soil. While metal lability observations

448 in the organic amendment samples (Figure S8) show that the metals are not entirely labile, they

449 also indicate high variability of the metal lability in the SS amendment samples from 2008 and

450 2012. Additionally, Figure S9 shows that Pb lability in the SS-amended soils decreased over time,

451 while for the other metals in the SS treatment the lability remained constant despite a significant

452 pH decrease. At least for Pb, a consistent decrease of the incoming- metal lability would improve

453 the simulations of the labile metal concentrations in the SS treatment, also under the 'Idealised

454   Trend' inputs and soil lateral mixing. To support this hypothesis, the soil mineral and organic

455   fractions of soil samples from 1972 and 2011 were investigated to detect eventual changes between

456   treatments and over time caused by the application of the organic amendments.

457   The XRD diffractograms from 1972 and 2011 (and 2013 only for SS) did not reveal noticeable

458   differences among the soil samples (Figure S11 in the Supporting Information). This would

459   indicate that the long-term application of the organic amendments, including the sewage sludge,

460   did not introduce any exogenous minerals, such as clay minerals and Fe-(oxy) hydroxides, capable

461   to modify the TE lability in the soil, with particular reference to the decrease in the SS plots.

462   The FTIR spectra from 1972 and 2011 were also not suggestive of differing organic fraction

463   composition between treatments and over time, except for a varying peak in the sewage sludge

464   samples. To focus on the time change of the soil organic fraction composition, the FTIR spectra

465   from the 2011 and 2013 SS samples were subtracted from the 1972 spectra, thus resulting in

466   differential spectra. As shown in Figure 7, the differential spectra from 1972-2011 evidenced a

467   peak at 1040 cm^{-1}, associated to the functional group of polysaccharide-like compounds, that was

468   not present in the differential spectra from 1972-2013. This means that polysaccharide-like

469   compounds, which are reported to have high affinity for TEs (Geddie & Sutherland, 1993; Veglio,

470   Beolchini, & Gasbarro, 1997), were present in the soil in 1972 and 2013, but not in 2011.

471   In conclusion, the scarce observations available are more suggestive of organic fraction variability

472   in the sewage sludge amendments applied to ZOFE rather than to any consistent (in time) metal

473   lability trend. This organic matter composition change could have an impact on the lability of the

474   incoming TEs, and hence on simulation of labile TE dynamics, but more research is needed on the

475   lability of metal in organic amendments and the response of that lability following addition to soil.

3.5 Long-term effects of organic amendment applications

Figure 8 presents the projected labile metal concentrations from 1940 to 2100 under the model conditions described in Section 2.7. In NIL, FYM and SS, labile metal concentrations are projected to be steady or declining, regardless of the pH trend. In COM, steady increases of Cu, Zn and Pb are projected, but a small decline in Cd. The projected increases in COM are likely to be due at least in part to the smaller decline in soil OM in this plot, relative to the other plots. Soil–porewater partitioning in the IDMM is a function of soil OM, and so a temporal decline in organic matter will lower soil-solution partition coefficients and increase metal leaching. The proportional declines in labile metal concentration in NIL, FYM and SS are consistently in the order Cd > Zn > Pb ~ Cu. This reflects the higher tendency of Zn and Cd to be lost from the soils, due to their lower binding affinities for the soil OM.

Projecting a decline in porewater pH to 2100 produces varying results across different metals and plots. In NIL, FYM and SS, Zn, Cu and Cd are consistently projected to be lower in 2100 as a result of lower pH. Conversely, in COM the same metals are projected to increase slightly under the declining pH trend. This is also observed for Pb in SS. In a number of further cases, notably Zn in FYM and SS, Cu in SS and Pb in FYM, the labile metal concentration under declining pH is projected to be higher than that under constant pH initially, but then to drop to or below the constant pH projection in 2100. These observations can be rationalised by considering the interplay among the metal input rate, the rate of labile metal loss in leaching, and the pH dependence of the aging rate of added labile metal. In COM, the metal input rates are sufficiently high to project continued net metal accumulation, given the soil chemistry, while in the other plots input rates are insufficient to allow continued accumulation under the changing soil chemical conditions. Increased leaching losses with declines in pH are expected to be most important for Zn and Cd.

499   For Cu, and to an extent Pb, the distribution of organic matter between solid and solution is

500   expected to drive partitioning and hence leaching losses. In all the plots except NIL, the ratio of

501   DOC flux to SOC pool is projected to increase between 2014 and 2100. This trend will have a

502   positive influence on metal leaching by driving an increase in the proportion of metal complexed

503   with DOC in soil porewaters, relative to the proportion adsorbed to the soil solids. In contrast to

504   the other factors, declining pH will reduce the rate at which input metal is projected to age and so

505   drive greater retention within the labile pool. This latter process is projected to be particularly

506   important for Pb, but can also be seen influence projections of the other metals, particularly in

507   COM.

508   Figure 9 clearly shows that the largest projected risks occur in SS, driven by the relatively high

509   metal inputs. In particular, it is notable that for all metals exceedance of the critical limit is

510   predicted to have occurred prior to 2014 and to be maintained until 2100. The risk characterisation

511   ratios (RCRs; the ratio of modelled to critical labile concentration) for Zn are projected to exceed

512   11 around the present day and then to decline under projected constant pH, but to remain relatively

513   high (~9) in 2100. A similar pattern is seen for Cd, but the RCRs are smaller, approaching ~1.2

514   around the present day and declining to ~0.7 in 2100. In contrast, RCRs for Cu and Pb are predicted

515   to continuously increase from 1949 to 2100, although the rate of increase is projected to be

516   relatively low under the assumptions of future conditions.

517   The declining future pH trend results in higher projected risks for Pb in SS after 2014. The labile

518   Pb concentration is projected to be lower after 2014 in the declining pH scenario (Figure 8).

519   Therefore, the increased risk must be due to the lowering of the critical limit concentration due to

520   the decline in pH. Similar considerations can explain the slightly higher risk predicted for Zn and

521   Cd, but the interplay among the driving factors appears more complex, since the projected labile

522   metals are not initially lower in the declining pH scenario (Figure 8). For Cu, the decline in pH has

523   a relatively small influence on the critical limit concentration and so only marginal differences in

524   risk are projected.

525   Predicted risks to 2100 in NIL, FYM and COM are small and only limited to Zn; only marginal

526   differences between the constant and declining pH scenarios are seen. Notably, exceedance for Zn

527   is projected to occur in the future (around 2030), but RCR remains relatively small (RCR < 1.5 in

528   2100).

529

4 Conclusions

- We applied the dynamic soil metal model IDMM to simulate long term soil metal trends in the Zurich Organic Fertiliser Experiment trial, Switzerland, using metal chemistry parameters derived from independent datasets;

- Following calibration of inputs and account for lateral soil mixing, the IDMM reproduced the observed EDTA-extractable concentrations of Zn, Cu, Pb and Cd with average overestimation by -1.66, -2.18, -4.34 and -0.05 mg kg^{-1} for Zn, Cu, Pb and Cd, respectively.

- Considerable amounts of data are required to run the model. In particular, we used modelling to fit observations and estimate future trends in the soil OM content, and to estimate DOC fluxes from the topsoil;

- Estimating historic TE inputs as robustly as possible is important for the modelling. Where estimated inputs give biased predictions of soil TEs, optimisation may be useful within plausible limits if it aids in evaluation of the model;

- Mineral weathering inputs of TEs to soils are key in supporting the modelling. Knowledge of metal weathering rates is generally poor, however. Optimisation of weathering rates is possible, but must be interpreted cautiously. More research is required on robust determination and modelling of weathering rates in the field;

- Under the specific conditions of the ZOFE experiment, lateral mixing of soil due to ploughing appears to be a significant influence on the observed metal concentrations, due to net redistribution of TEs from plots with relatively high concentrations to those with relatively low concentrations;

- Changes in the soil chemistry of the plots since the inception of the ZOFE experiment, notably acidification and loss of soil OM, make the soils more vulnerable to the ecological impacts of metals;

- Projections of metal concentrations, including under future conditions of constant climate and metal inputs, suggest that historic inputs of sewage sludge would result in present day exceedances of threshold concentrations (critical limits) for all the TEs and that exceedances would remain until at least 2100. Some minor exceedance of Cu and Zn critical limits would be expected by 2100 under manure and compost application.

- The application of the IDMM model to the ZOFE trial is a promising step towards understanding the key processes controlling past, current and future TE dynamics at field scale;

- While long term trials such as ZOFE have the advantage of being well characterized, their soil metal concentrations can be influenced by their distinctive management practice, as this example shows;

- This study has identified some key knowledge gaps that need to be addressed for large scale model application: characterization metal weathering rates and DOC fluxes, and the metal contents of organic amendments;

- Because of the complexity of the model data requirements and likely resulting uncertainties in predictions, large scale application is likely to be most useful in assessing broad spatial and temporal trends in metal concentrations and risks.

573 **Author Contribution**

574 CC and SL run the model and wrote the ms. RS, ST, RG and BC run the soil experiments and LD

575 the FTIR and XRD analysis. GR and SO set up the research. All the co-authors revised the ms.

576

577 **Acknowledgements**

578 We thank Lucie Gunst from Agroscope for making possible the resampling of soils and

579 amendments from the archive. Also, we gratefully acknowledge Dr. Susanna Pucci and Dr. Luisa

580 Andrenelli who carried out the TE concentration analysis, Mr. Alessandro Dodero for sample

581 preparation for spectroscopic analysis and Dr. Alessandra Bonetti for FTIR analysis. We are

582 indebted to two anonymous reviewers for providing insightful comments. This research has been

583 partially funded by the Doctoral Program of the DISPAA of the University of Florence.

584

585 **Competing Interests**

586 The authors declare that they have no conflict of interest

587

Year	EDTA-extractable concentrations [mg kg^{-1}]			
	Zn	Cu	Pb	Cd
	NIL Treatment			
1972	3.1	6.2	7.5	0.14
1979	2.6	6.3	7.8	0.13
1982	2.9	6.1	8.8	0.08
1991	4.5	6.2	8.0	0.13
1995	4.3	6.2	8.9	0.14
2000	6.5	6.9	9.6	0.16
2003	6.4	6.7	8.4	0.17
2007	6.1	7.1	7.8	0.15
2011*	6.3	7.6	9.2	0.18
	FYM Treatment			
1972	3.5	8.3	8.9	0.17
1979	5.1	10.1	4.9	0.22
1982	5.1	9.6	11.5	0.23
1991	6.6	9.0	9.9	0.23
1995	8.5	11.0	11.5	0.24
2000	8.4	10.9	11.8	0.25
2003	7.7	10.5	10.8	0.25
2007	11.2	10.5	9.7	0.24
2011*	8.4	9.7	10.2	0.25
	SS Treatment			
1972	20.7	24.6	28.2	0.61
1979	26.7	26.2	29.0	0.66
1982	27.1	24.2	26.0	0.58
1991	24.3	22.7	19.8	0.50
1995	20.4	19.5	16.2	0.40
2000	19.6	20.7	16.7	0.42
2003	13.8	14.8	12.9	0.31
2007	17.5	17.3	12.2	0.33
2011*	17.6	18.5	12.8	0.36
	COM Treatment			
1972	3.7	8.6	9.7	0.18
1979	4.6	9.5	10.3	0.20
1982	8.6	13.3	11.7	0.24
1991	10.3	13.4	14.3	0.29
1995	6.5	8.5	9.5	0.18
2000	6.9	10.4	11.7	0.21
2003	5.0	8.7	9.4	0.18
2007	n.a.	n.a.	n.a.	n.a.
2011*	7.3	10.0	10.8	0.28

588 *mean of five replicates

589

590 **Table 1:** Soil EDTA-extractable concentrations of Zn, Cu, Pb, Cd in ZOFE topsoil (0-20 cm) for

591 the treatments NIL, FYM, SS and COM.

592

593

	Total Concentrations [mg kg^{-1}]					EDTA-extracted Concentrations [mg kg^{-1}]			
	Farmyard Manure								
Years	**Zn**	**Cu**	**Pb**	**Cd**	**P**	**Zn**	**Cu**	**Pb**	**Cd**
2011	109.5	23.6	traces*	traces*	6915	32.5	5.6	traces*	traces*
2014	158.9	27.8	traces*	traces*	8146	53.1	6.7	traces*	traces*
	Sewage Sludge								
2008	447.5	165.8	24.8	3.18	16110	173.1	78.8	9.1	0.26
2012	715.0	301.2	35.4	7.00	28870	105.7	66.2	8.6	0.16
	Compost								
2011	130.2	40.0	37.5	traces*	2238	30.8	6.1	12.8	traces*
2013	122.9	39.7	31.9	traces*	2118	30.2	6.5	13.0	traces*
2014	124.8	43.7	65.4	traces*	2242	28.7	5.6	12.5	traces*

594

595 *lower or close to the limit of detection.

596

597

598 **Table 2:** Total and EDTA-extractable concentrations of Zn, Cu, Pb, Cd and P relative to the total

599 dry matter of the organic amendment samples from available years.

Metals	Swiss Trend		Idealised Trend		Treatments
	RMSE	Bias	RMSE	Bias	
Zn	2.14	-1.71	1.73	1.45	NIL
Zn	1.87	-0.84	3.20	-2.95	FYM
Zn	11.03	10.00	3.62	-1.42	SS
Zn	2.45	-1.59	4.05	-3.72	COM
Cu	3.83	3.82	0.48	-0.36	NIL
Cu	4.00	3.93	2.98	-2.86	FYM
Cu	10.66	9.90	3.25	-2.25	SS
Cu	4.64	4.21	3.96	-3.23	COM
Pb	8.34	8.31	1.12	-0.61	NIL
Pb	9.90	9.70	5.47	-5.13	FYM
Pb	19.96	18.90	9.09	-7.28	SS
Pb	10.81	10.69	4.59	-4.32	COM
Cd	8.07	-8.07	0.03	0.01	NIL
Cd	8.53	-8.52	0.05	-0.05	FYM
Cd	9.40	-9.36	0.10	-0.08	SS
Cd	8.59	-8.59	0.10	-0.09	COM
Global Avg	7.76	2.55	2.74	-2.06	
Zn Avg	4.37	1.47	3.15	-1.66	
Cu Avg	5.78	5.47	2.67	-2.18	
Pb Avg	12.25	11.90	5.07	-4.34	
Cd Avg	8.65	-8.63	0.07	-0.05	

600

601 **Table 3:** Model performance in terms of Root Mean Square Error (RMSE) and Bias of simulated

602 labile concentrations vs observed EDTA-extractable concentrations with lateral mixing under the

603 'Swiss Trend' and the 'Idealised Trend'.

604

605

Figure Captions

Figure 1: The experimental design of ZOFE with 12 treatments replicated in five blocks. Only the 4 treatments highlighted in grey were investigated.

Figure 2: The IDMM model with lateral mixing. (A) The description of the model structure; (B) the description of the soil lateral mixing method.

Figure 3: Estimated DOC concentration time trends in ZOFE topsoil (20 cm) for the treatments NIL, FYM, SS and COM.

Figure 4: Total concentration time trends of Zn, Cu, Pb, Cd and P in ZOFE topsoil (20 cm) for the treatments NIL, FYM, SS and COM.

Figure 5: Observed EDTA-extractable concentrations (bullets), simulated labile concentrations with mixing (solid line) and without mixing (dashed line) with 'Swiss Trend' inputs (top) and 'Idealised Trend' inputs (bottom) for Zn, Cu, Pb, Cd in ZOFE topsoil (0-20 cm) for the treatments NIL, FYM, SS and COM.

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 five and 10 strips per plot with 'Idealised Trend' inputs.

Figure 7: 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 8: Projected labile concentrations for Zn, Cu, Pb and Cd to 2100 without lateral mixing and with 'Idealised Trend' inputs. Two scenarios are considered: constant pH (solid line), pH decreasing exponentially to 0.5 units below 2014 value (dotted line).

627 **Figure 9:** Projected Risk Characterisation Ratios (RCR) for Zn, Cu, Pb and Cd to 2100 without

628 lateral mixing and with 'Idealised Trend' inputs. Two scenarios are considered: constant pH (solid

629 line), pH decreasing exponentially to 0.5 units below 2014 value (dotted line).

630

631

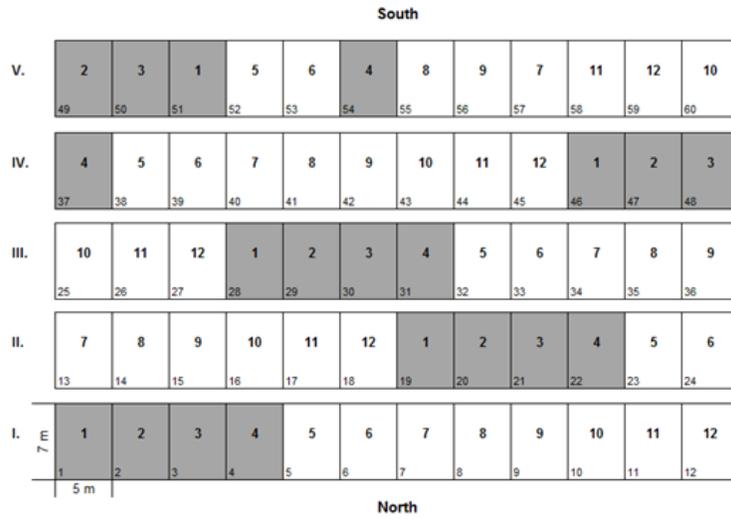
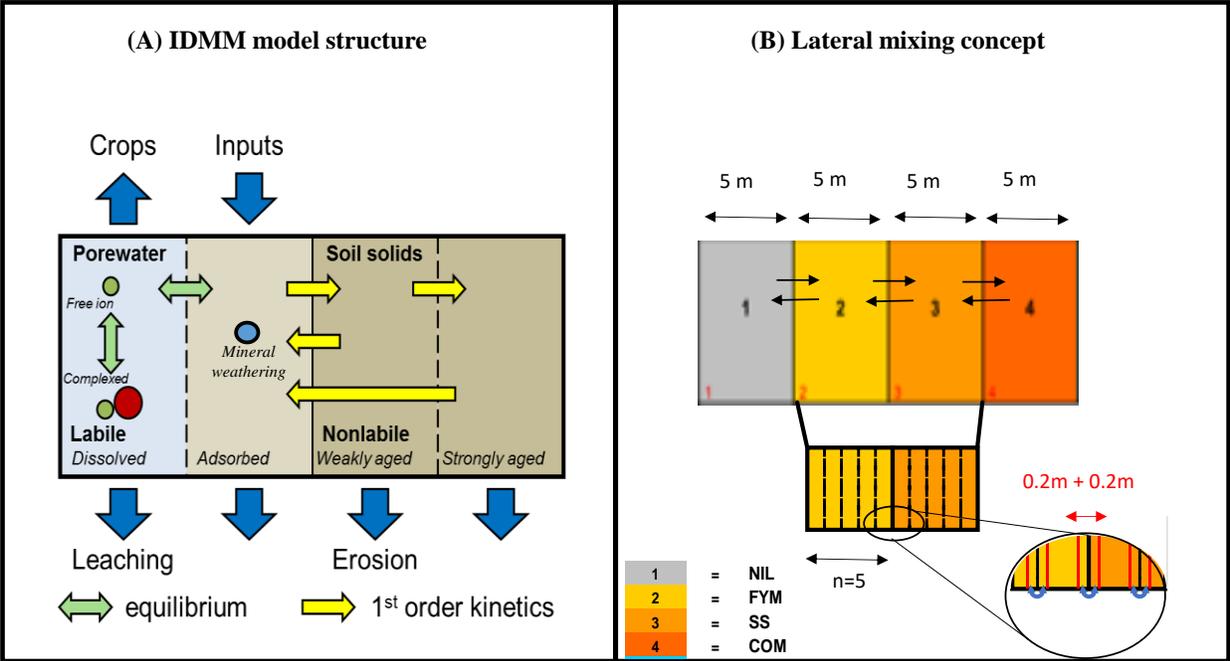



Figure 1

633

634

635

636

637

638 **Figure 2**

639

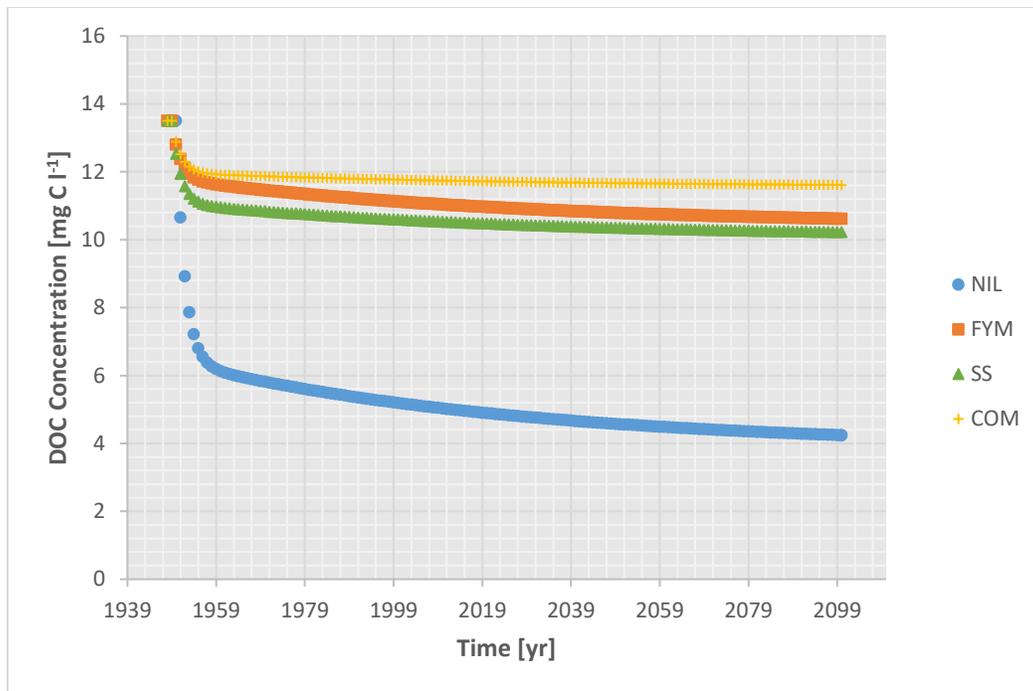



Figure 3

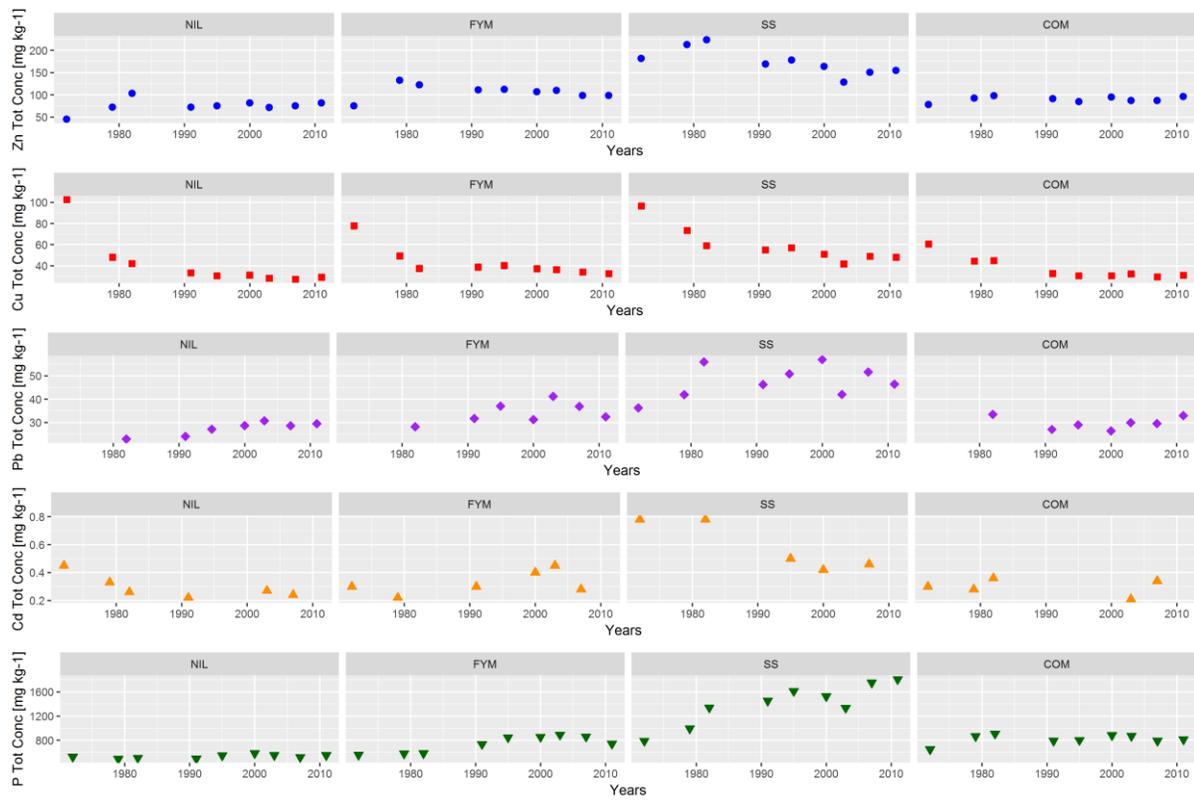
641

642

643

644

Figure S4

645

646

647

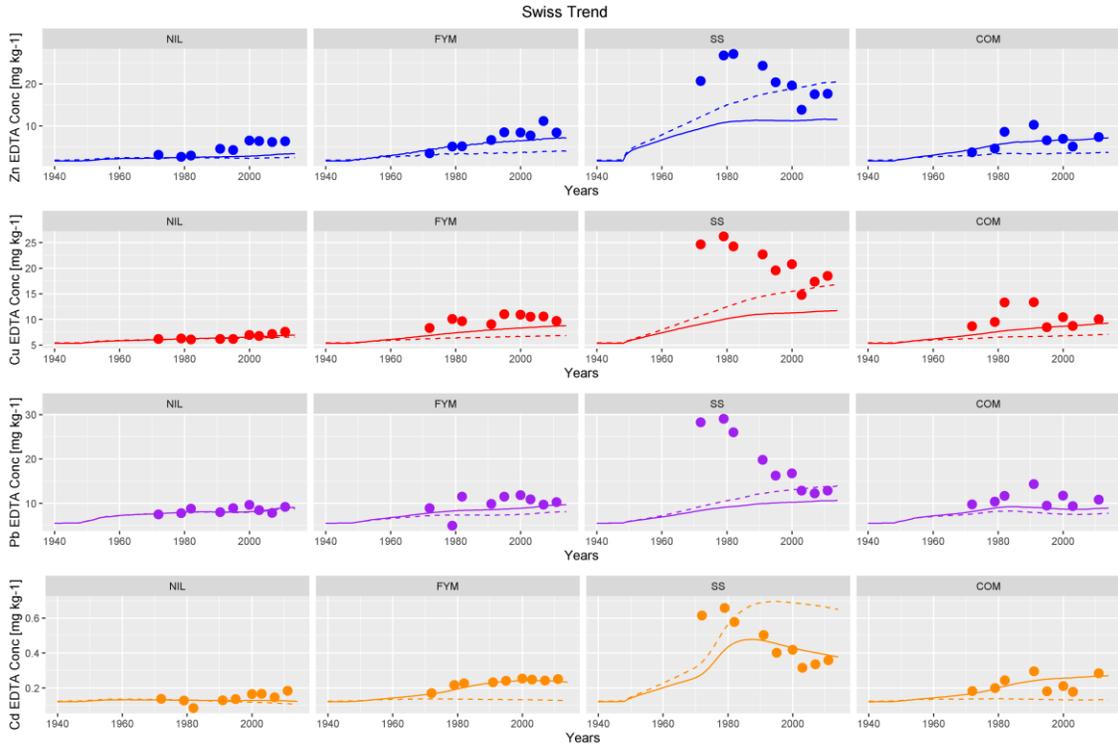
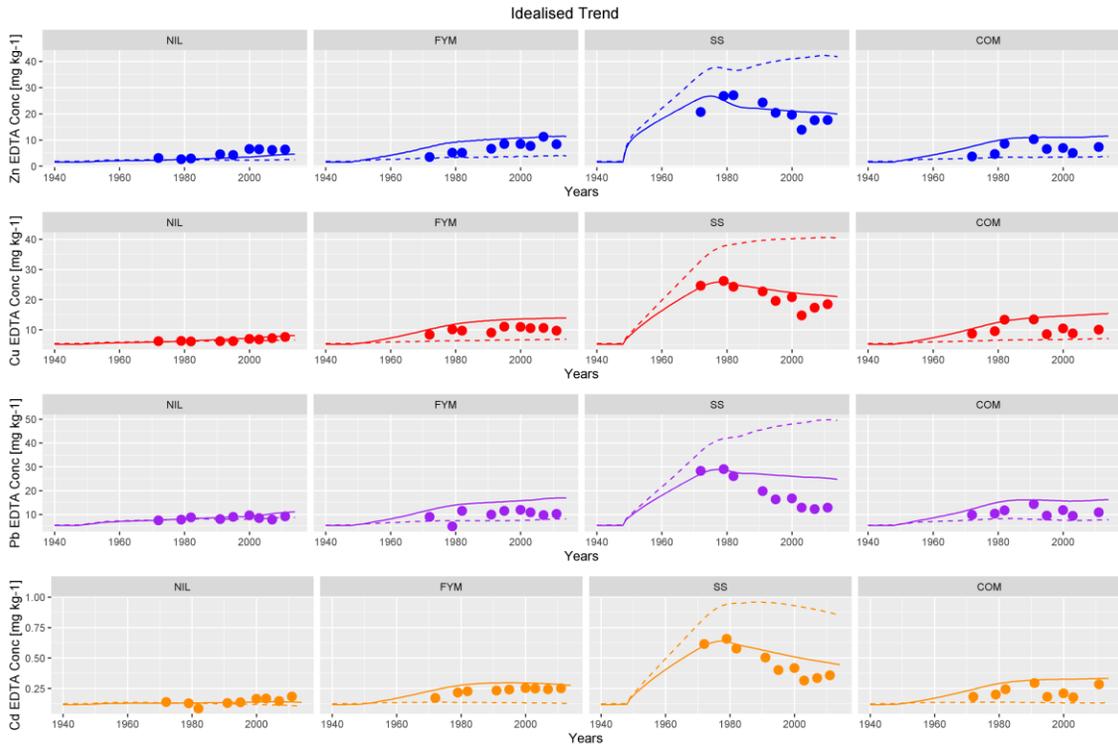
648

649

650

651

652

653

654

655

656 **Figure 5**

657

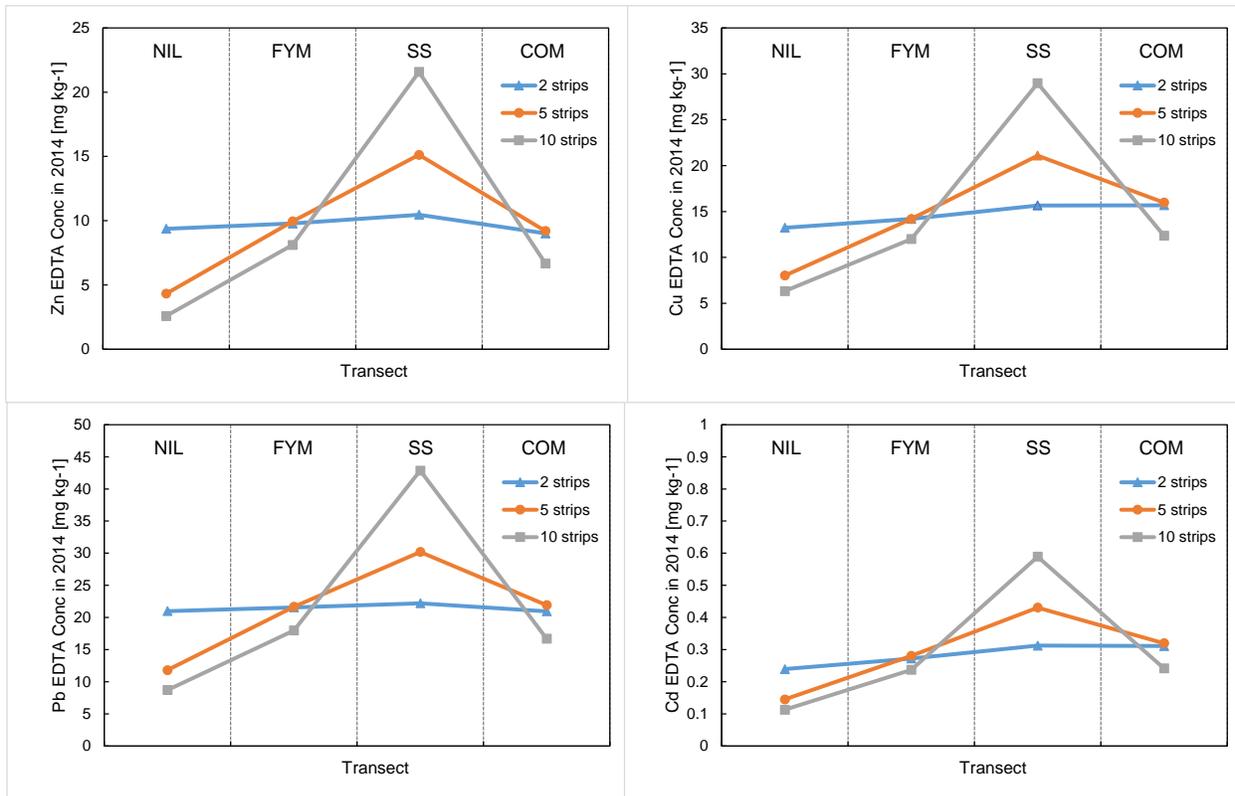
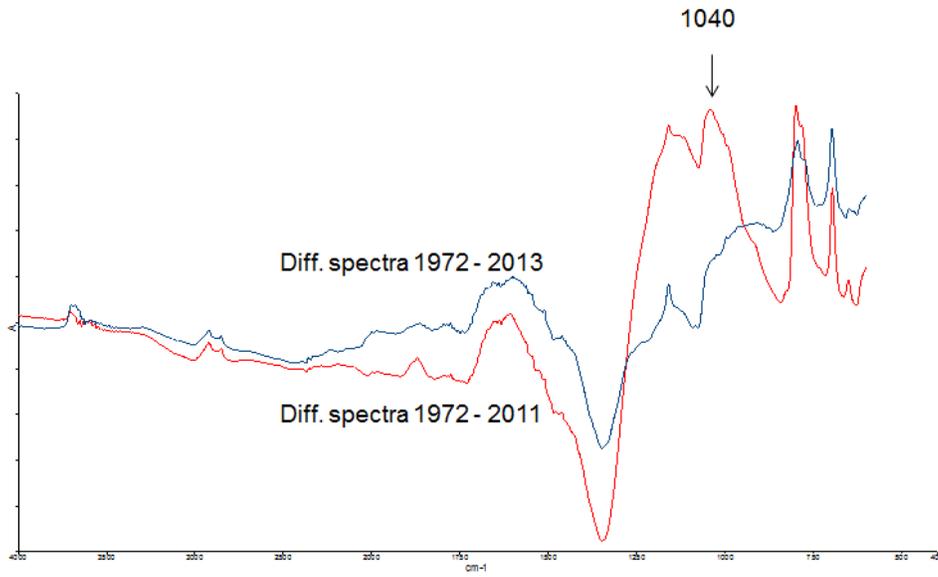



Figure 6

672

673   **Figure 7**

674

675

676

677

678

Figure 8

680

681

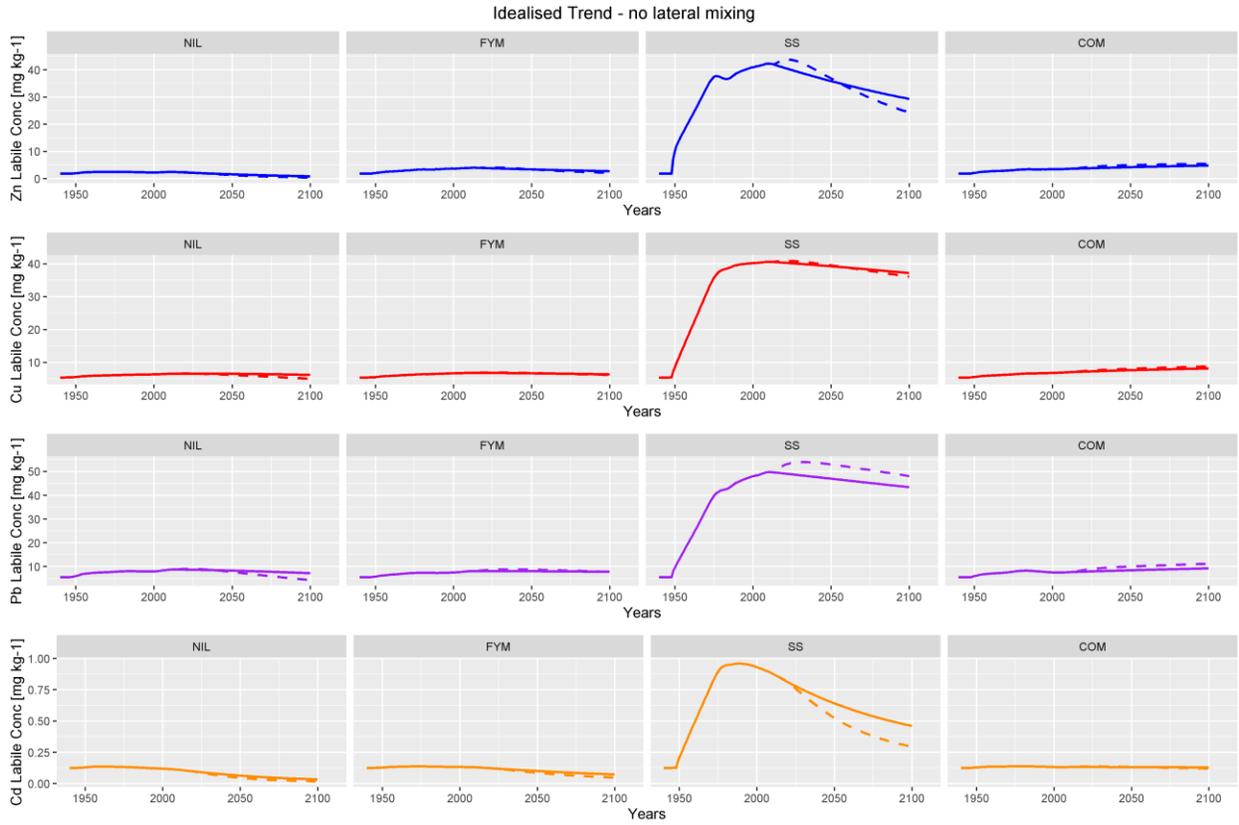
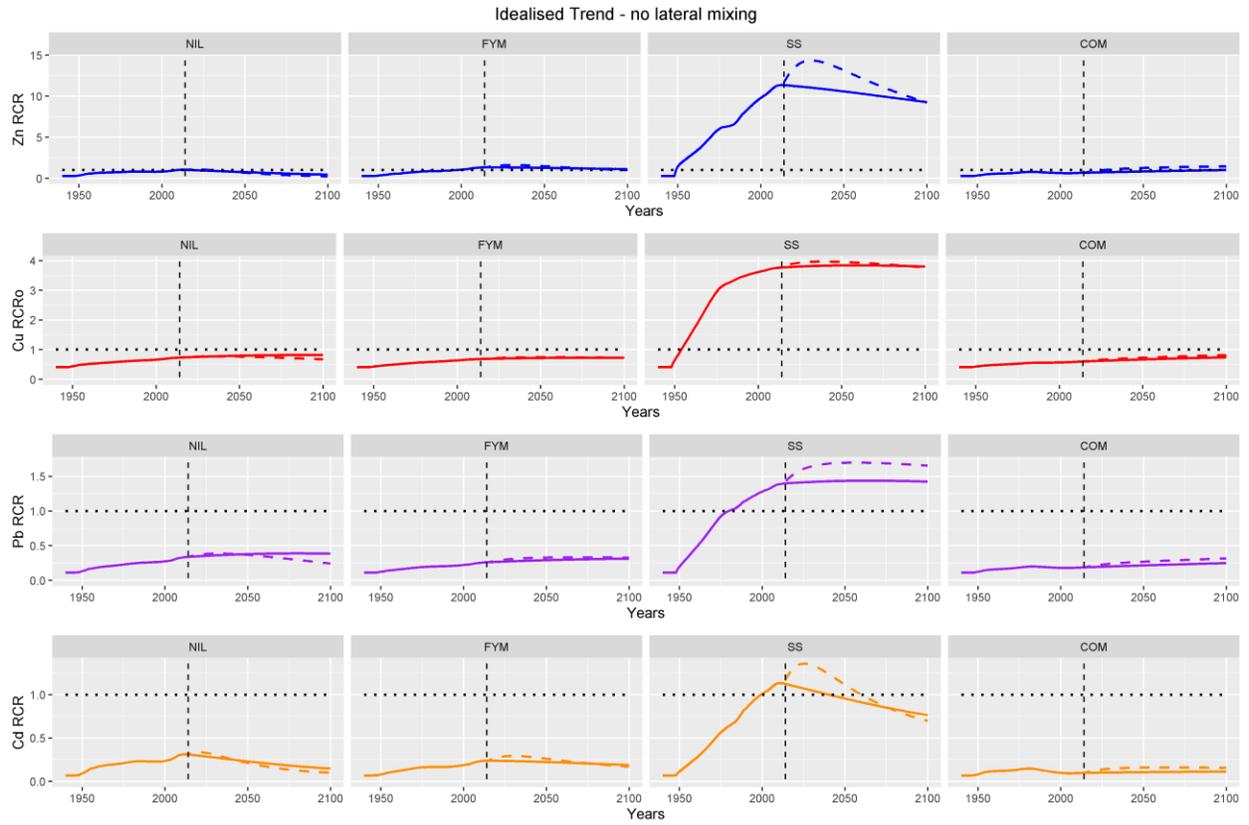



Figure 9

683

684 **Bibliography**

685 Adriano, D.C., 2005. Trace elements in terrestrial environments. Biogeochemistry, Bioavailability, and
686   Risks of Metals. Springer, New York.
687 Andrén, O., Kätterer, T. & Karlsson, T. (2004). ICBM regional model for estimations of dynamics of
688   agricultural soil carbon pools. Nutrient Cycling in Agroecosystems 70, 231–239 (2004).
689   https://doi.org/10.1023/B:FRES.0000048471.59164.ff
690 Ballabio, C., Panagos, P., Lugato, E., Huang, J. H., Orgiazzi, A., Jones, A., . . . Montanarella, L. (2018). Copper
691   distribution in European topsoils: An assessment based on LUCAS soil survey. *Science of the Total*
692   *Environment, 636*, 282-298. doi:10.1016/j.scitotenv.2018.04.268
693 Bergkvist, P., & Jarvis, N. (2004). Modeling organic carbon dynamics and cadmium fate in long-term
694   sludge-amended soil. *Journal of Environmental Quality, 33*(1), 181-191. doi:DOI
695   10.2134/jeq2004.0181
696 Bolinder, M. A., Janzen, H. H., Gregorich, E. G., Angers, D. A., & VandenBygaart, A. J. (2007). An approach
697   for estimating net primary productivity and annual carbon inputs to soil for common agricultural
698   crops in Canada. Agriculture Ecosystems & Environment, 118(1-4), 29-42.
699   doi:10.1016/j.agee.2006.05.013
700 Bonten, L. T. C., Groenenberg, J. E., Meesenburg, H., & de Vries, W. (2011). Using advanced surface
701   complexation models for modelling soil chemistry under forests: Solling forest, Germany.
702   *Environmental Pollution, 159*(10), 2831-2839. doi:10.1016/j.envpol.2011.05.002
703 Buckingham S., Tipping E., Hamilton-Taylor J. (2008). Concentrations and fluxes of dissolved organic
704   carbon in UK topsoils. *Sci total Envir., 407*(1):460-70
705 D'Acqui, L. P., Santi, C. A., Vizza, F., & Certini, G. (2015). Living and dead soil organic matter under different
706   land uses on a Mediterranean island. *European Journal of Soil Science, 66*(2), 298-310.
707   doi:10.1111/ejss.12219
708 de Vries, W., Romkens, P. F. A. M., & Bonten, L. T. C. (2008). Spatially explicit integrated risk assessment
709   of present soil concentrations of cadmium, lead, copper and zinc in the Netherlands. *Water Air*
710   *and Soil Pollution, 191*(1-4), 199-215. doi:10.1007/s11270-008-9617-z
711 Diacono, M., & Montemurro, F. (2010). Long-term effects of organic amendments on soil fertility. A
712   review. *Agronomy for Sustainable Development, 30*(2), 401-422. doi:10.1051/agro/2009040
713 EFSA. 2009. Scientific Opinion of the Panel on Contaminants in the Food Chain on a request from the
714   European Commission on cadmium in food. The EFSA Journal (2009) 980, 1-139.
715 EFSA Panel on Contaminants in the Food Chain (CONTAM); Scientific Opinion on Lead in Food. EFSA
716   Journal 2010; 8(4):1570. [151 pp.]. doi:10.2903/j.efsa.2010.1570. Available online:
717   www.efsa.europa.eu
718 Fu, J., Gasche, R., Wang, N., Lu, H. Y., Butterbach-Bahl, K., & Kiese, R. (2019). Dissolved organic carbon
719   leaching from montane grasslands under contrasting climate, soil and management conditions.
720   Biogeochemistry, 145(1-2), 47-61. doi:10.1007/s10533-019-00589-y
721 Geddie, J. L., & Sutherland, I. W. (1993). Uptake of Metals by Bacterial Polysaccharides. *Journal of Applied*
722   *Bacteriology, 74*(4), 467-472. doi:DOI 10.1111/j.1365-2672.1993.tb05155.x
723 Groenenberg, J. E., Romkens, P. F. A. M., Comans, R. N. J., Luster, J., Pampura, T., Shotbolt, L., . . . de Vries,
724   W. (2010). Transfer functions for solid-solution partitioning of cadmium, copper, nickel, lead and
725   zinc in soils: derivation of relationships for free metal ion activities and validation with
726   independent data. *European Journal of Soil Science, 61*(1), 58-73. doi:10.1111/j.1365-
727   2389.2009.01201.x

728 Gu, X. Y., & Evans, L. J. (2008). Surface complexation modelling of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II)
729   adsorption onto kaolinite. *Geochimica Et Cosmochimica Acta, 72*(2), 267-276.
730   doi:10.1016/j.gca.2007.09.032
731 Hudcova, H., Vymazal, J., & Rozkosny, M. (2019). Present restrictions of sewage sludge application in
732   agriculture within the European Union. *Soil and Water Research, 14*(2), 104-120.
733   doi:10.17221/36/2018-Swr
734 Imseng, M., Wiggenhauser, M., Keller, A., Muller, M., Rehkamper, M., Murphy, K., . . . Bigalke, M. (2018).
735   Fate of Cd in Agricultural Soils: A Stable Isotope Approach to Anthropogenic Impact, Soil
736   Formation, and Soil-Plant Cycling. *Environmental Science & Technology, 52*(4), 1919-1928.
737   doi:10.1021/acs.est.7b05439
738 Imseng, M., Wiggenhauser, M., Muller, M., Keller, A., Frossard, E., Wilcke, W., & Bigalke, M. (2019). The
739   Fate of Zn in Agricultural Soils: A Stable Isotope Approach to Anthropogenic Impact, Soil
740   Formation, and Soil-Plant Cycling. *Environmental Science & Technology, 53*(8), 4140-4149.
741   doi:10.1021/acs.est.8b03675
742 Ingwersen, J., & Streck, T. (2006). Modeling the environmental fate of cadmium in a large wastewater
743   irrigation area. *Journal of Environmental Quality, 35*(5), 1702-1714. doi:DOI
744   10.2134/jeq2005.0412
745 IUSS Working Group WRB. 2006. World reference base for soil resources 2006. World Soil Resources
746   Reports No. 103. FAO, Rome
747 Jarvis, N. J., Taylor, A., Larsbo, M., Etana, A., & Rosen, K. (2010). Modelling the effects of bioturbation on
748   the re-distribution of 137Cs in an undisturbed grassland soil. *European Journal of Soil Science,
749   61*(1), 24-34. doi:10.1111/j.1365-2389.2009.01209.x
750 Kindler, R., Siemens, J., Kaiser, K., Walmsley, D. C., Bernhofer, C., Buchmann, N., . . . Kaupenjohann, M.
751   (2011). Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon
752   balance. Global Change Biology, 17(2), 1167-1185. doi:10.1111/j.1365-2486.2010.02282.x
753 Lofts, S., Tipping, E., Lawlor, A. J., & Shotbolt, L. (2013). An intermediate complexity dynamic model for
754   predicting accumulation of atmospherically-deposited metals (Ni, Cu, Zn, Cd, Pb) in catchment
755   soils: 1400 to present. *Environmental Pollution, 180*, 236-245. doi:10.1016/j.envpol.2013.05.030
756 Lofts, S., Spurgeon, D. J., Svendsen, C., & Tipping, E. (2004). Deriving soil critical limits for Cu, Zn, Cd, and
757   Ph: A method based on free ion concentrations. Environmental Science & Technology, 38(13),
758   3623-3631. doi:DOI 10.1021/es030155h
759 McBride, M. B., Richards, B. K., Steenhuis, T., & Spiers, G. (1999). Long-term leaching of trace elements in
760   a heavily sludge-amended silty clay loam soil. *Soil Science, 164*(9), 613-623. doi:Doi
761   10.1097/00010694-199909000-00001
762 McBride, M. B. (2011). A Comparison of Reliability of Soil Cadmium Determination by Standard
763   Spectrometric Methods. Journal of Environmental Quality, 40(6), 1863-1869.
764   doi:10.2134/jeq2011.0096
765 McGrath, S.P., 1987. Long–term studies of meal transfers following application of sewage sludge. In:
766   Pollutant transport and fate in ecosystems, Eds. Coughtrey, P.J., Martin, M.H., Unsworth, M.H..
767   Blackwell Scientific Publications, Oxford, U.K
768 Mcgrath, S. P., & Cegarra, J. (1992). Chemical Extractability of Heavy-Metals during and after Long-Term
769   Applications of Sewage-Sludge to Soil. *Journal of Soil Science, 43*(2), 313-321. doi:DOI
770   10.1111/j.1365-2389.1992.tb00139.x
771 Mcgrath, S. P., & Zhao, F. J. (2015). Concentrations of metals and metalloids in soils that have the potential
772   to lead to exceedance of maximum limit concentrations of contaminants in food and feed. *Soil
773   Use and Management, 31*, 34-45. doi:10.1111/sum.12080

774   Menichetti, L., Katterer, T., & Leifeld, J. (2016). Parametrization consequences of constraining soil organic
775   matter models by total carbon and radiocarbon using long-term field data. Biogeosciences,
776   13(10), 3003-3019. doi:10.5194/bg-13-3003-2016
777   NEBRA. 2015. Metals in Biosolids, Other Soil Amendments, & Fertilizers
778   Niemeyer, J., Chen, Y., & Bollag, J. M. (1992). Characterization of Humic Acids, Composts, and Peat by
779   Diffuse Reflectance Fourier-Transform Infrared-Spectroscopy. *Soil Science Society of America*
780   *Journal, 56*(1), 135-140. doi:DOI 10.2136/sssaj1992.03615995005600010021x
781   Oberholzer, H. R., Leifeld, J., & Mayer, J. (2014). Changes in soil carbon and crop yield over 60 years in the
782   Zurich Organic Fertilization Experiment, following land-use change from grassland to cropland.
783   *Journal of Plant Nutrition and Soil Science, 177*(5), 696-704. doi:10.1002/jpln.201300385
784   Paquin, P.R, Gorsuch, J.W., Apte, S., Batley, G.E., Bowles, K.C., Campbell, P.G.C., Delos, C.G., Di Toro, D.M.,
785   Dwyer, R.L., Galvez, F., Gensemer, R.W., Goss, G.G., Hogstrand, C., Janssen, C.R., McGeer, J.C.,
786   Naddy, R.B., Playle, R.C., Santore, R.C., Schneider, U., Stubblefield, W.A., Wood, C.M., Wu, K.B.,
787   (2002). The biotic ligand model: a historical overview. *Comparative Biochemistry and Physiology*
788   *Part C, 133*, 3-35.
789   Quevauviller, P. (1998). Operationally defined extraction procedures for soil and sediment analysis - I.
790   Standardization. *Trac-Trends in Analytical Chemistry, 17*(5), 289-298. doi:Doi 10.1016/S0165-
791   9936(97)00119-2
792   Roberts, T. L. (2014). Cadmium and Phosphorous Fertilizers: The Issues and the Science. *Symphos 2013 -*
793   *2nd International Symposium on Innovation and Technology in the Phosphate Industry, 83*, 52-59.
794   doi:10.1016/j.proeng.2014.09.012
795   SAEFL. 2003. Assessment of Risks to Health and the Environment from Cadmium in Mineral Fertilisers.
796   Technical report.
797   SCAN. 2003a. Opinion of the Scientific Committee for Animal Nutrition on the use of copper in
798   feedingstuffs. EUROPEAN COMMISSION, HEALTH & CONSUMER PROTECTION DIRECTORATE-
799   GENERAL.
800   SCAN. 2003b. Opinion of the Scientific Committee for Animal Nutrition on the use of zinc in feedingstuffs.
801   EUROPEAN COMMISSION, HEALTH & CONSUMER PROTECTION DIRECTORATE-GENERAL.
802   Six, L., & Smolders, E. (2014). Future trends in soil cadmium concentration under current cadmium fluxes
803   to European agricultural soils. *Science of the Total Environment, 485*, 319-328.
804   doi:10.1016/j.scitotenv.2014.03.109
805   Smith, P. (2016). Soil carbon sequestration and biochar as negative emission technologies. *Global Change*
806   *Biology, 22*(3), 1315-1324. doi:10.1111/gcb.13178
807   Tipping, E. (1998). Humic ion-binding model VI: An improved description of the interactions of protons
808   and metal ions with humic substances. *Aquatic Geochemistry, 4*(1), 3-48. doi:Doi
809   10.1023/A:1009627214459
810   Tipping, E. CHUM: a hydrochemical model for upland catchments. J Hydrol 1996;174: 305–30.
811   Toth, G., Hermann, T., Da Silva, M. R., & Montanarella, L. (2016). Heavy metals in agricultural soils of the
812   European Union with implications for food safety. *Environment International, 88*, 299-309.
813   doi:10.1016/j.envint.2015.12.017
814   Veglio, F., Beolchini, F., & Gasbarro, A. (1997). Biosorption of toxic metals: An equilibrium study using free
815   cells of Arthrobacter sp. *Process Biochemistry, 32*(2), 99-105. doi:Doi 10.1016/S0032-
816   9592(96)00047-7
817   Vulkan, R., Zhao, F. J., Barbosa-Jefferson, V., Preston, S., Paton, G. I., Tipping, E., & McGrath, S. P. (2000).
818   Copper speciation and impacts on bacterial biosensors in the pore water of copper-contaminated
819   soils. *Environmental Science & Technology, 34*(24), 5115-5121. doi:10.1021/es/0000910

820   Wan, Y. N., Jiang, B., Wei, D. P., & Ma, Y. B. (2020). Ecological criteria for zinc in Chinese soil as affected
821   by soil properties. Ecotoxicology and Environmental Safety, 194. doi:ARTN
822   11041810.1016/j.ecoenv.2020.110418
823   Wang, X. Q., Wei, D. P., Ma, Y. B., & McLaughlin, M. J. (2015). Derivation of Soil Ecological Criteria for
824   Copper in Chinese Soils. Plos One, 10(7). doi:ARTN e013394110.1371/journal.pone.0133941
825   Xu, L., Lofts, S., & Lu, Y. (2016). Terrestrial ecosystem health under long-term metal inputs: modeling and
826   risk assessment. *Ecosystem Health and Sustainability, 2*(5), e01214. doi:10.1002/ehs2.1214

827

828