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1	Ageing of copper, zinc and synthetic pesticides
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26 Abstract

27 The transformation and mobility of heavy metals and synthetic pesticides in soil 28 depend on ageing, involving their chemical and physical distributions among soil fractions 29 over time. Heavy metals and synthetic pesticides often co-occur in soil, although their ageing 30 is usually evaluated separately and in bulk soil. Here, contrasting vineyard and crop soils were spiked with copper (Cu; 700 mg kg⁻¹) and zinc (Zn; 200 mg kg⁻¹) and/or synthetic pesticides 31 (5 mg kg⁻¹), i.e., the fungicide metalaxyl (MTY) and herbicide S-metolachlor (SMET), to 32 33 evaluate within 200 days their distribution among soil physical and chemical fractions. More 34 than 90% of MTY and SMET in soil was released into water, even 200 days after spiking. MTY, SMET, Cu and Zn were associated mainly with the silt fraction and to a lesser extent 35 36 (<30%) with the sand and clay fractions. Overall, the ageing of MTY, SMET, Cu and Zn in 37 agricultural soil was affected by the soil type and sterilization and only to a minor extent by 38 their co-occurrence. Sorption controlled the dissipation of MTY and SMET in soil, while biodegradation contributed to <10%. Cu was mainly $(37 \pm 2\%)$ associated with Fe oxides 39 40 after 200 days, while Zn was found $(33 \pm 2\%)$ in the residual fraction. The silt fraction of the nonsterile vineyard soil became enriched in 65 Cu over time ($\Delta \delta^{65}$ Cu = 0.25 ± 0.07 ‰), 41 whereas the clay fraction was depleted in ${}^{65}Cu$ ($\Delta\delta^{65}Cu = -0.20 \pm 0.07$ ‰). Cu isotope 42 43 fractionation mirrored the Cu distribution in soil chemical fractions, suggesting that Cu stable 44 isotopes may help to follow-up Cu ageing. In contrast, no significant Zn isotope fractionation 45 was observed among experiments or over time. Overall, our study emphasizes the variability in ageing of synthetic pesticides and heavy metals co-occurring in agricultural soils and their 46 47 interplay in soil fractions.

48 Keywords: agricultural soils; heavy metals; pesticides; ageing; particle-size fractions;
49 sequential chemical extraction; stable isotope analysis.

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51 Highlights	s:
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52	•	MTY, SMET, Cu and Zn were associated (>40%) with the silt fraction of agricultural soils
53	•	MTY, SMET, Cu and Zn distribution among soil fractions reflected ageing within 200
54		days
55	•	Sorption is a major process of MTY and SMET dissipation in crop and vineyard soils
56	•	MTY, SMET, Cu and Zn ageing was mainly affected by soil texture and organic content
57	•	δ^{65} Cu values in the silt and clay fractions of the soil mirrored chemical fractionation of Cu
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Graphical abstract



94 **1. Introduction**

95 The use of fertilizers, pesticides and sewage sludge has led to mixtures of synthetic 96 pesticides and heavy metals in agricultural soils. Synthetic pesticides and heavy metals often 97 co-occur in soil and can adversely affect nontarget organisms (Imfeld and Vuilleumier, 2012; 98 Muturi et al., 2017; Wyszkowska et al., 2012). Vineyard soils are of particular concern 99 because synthetic pesticides, inorganic copper (Cu) fungicides and zinc (Zn) amendments are 100 regularly applied (Komárek et al., 2010a; Imfeld et al., 2020). The physical and chemical 101 distribution and diffusion of synthetic pesticides and heavy metals over time in soil porewater, 102 minerals and organic matter are referred to as ageing (Komárek et al., 2010b; Ma et al., 2006). 103 Ageing depends on both the physicochemical characteristics of the soil and pollutant 104 properties (Komárek et al., 2010b; Swarcewicz and Gregorczyk, 2012; Zhang et al., 2014). Ageing increases pollutant sequestration and persistence, and reduces pollutant availability 105 106 and toxicity (Hatzinger and Alexander, 1995). Ageing also controls pollutant export from 107 agricultural soil since rainfall patterns influence the preferential mobilization of specific soil 108 fractions (Babcsányi et al., 2016; Meite et al., 2018). However, the concomitant ageing of 109 synthetic pesticides and heavy metals in agricultural soils remains poorly understood.

110 Dissolution, precipitation, complexation, sorption, diffusion and entrapment control 111 the sorption and ageing of synthetic pesticides and heavy metals in soil. The sorption of 112 synthetic pesticides involves hydrophobic binding to soil organic matter (SOM) and/or oxides 113 and clay minerals (Clausen et al., 2001; Cornejo et al., 2008; Đurović et al., 2009; Helal et al., 114 2006). During ageing, Cu and Zn sorb onto oxides, mainly retained by clay minerals 115 (Komárek et al., 2010b; Ma et al., 2006). The slow diffusion of Cu and Zn in Fe oxides 116 (Bruemmer et al., 1988), Al oxides and Mn oxides, clay minerals (Ma and Uren, 1998) and carbonate precipitation (Nakhone and Young, 1993; Ma et al., 2006) governs their 117

sequestration in soil. Cu and Zn also present high affinity for organic matter (Duplay et al., 2014; Néel et al., 2007; Quenea et al., 2009). It is worth noting that the ageing of synthetic pesticides and heavy metals is generally examined separately and in bulk soil. However, their concomitant occurrence may affect their distribution among soil fractions due to competition for sorption sites, the formation of complexes between pollutants (e.g., El Azzi et al., 2018), or the alteration of soil biogeochemistry and microbial activities impacting pollutant sorption.

124 Compared with the physicochemical evaluation of soil fractions, the natural abundance 125 signatures of metal stable isotopes (Wiederhold, 2015) can reflect processes that metals 126 undergo in soil (Wang et al., 2021). In particular, transition metals such as Cu and Zn may exhibit distinct isotopic signatures in soil fractions. Cu isotope ratios (⁶⁵Cu/⁶³Cu) change 127 128 during Cu sorption onto Fe and Al oxy(hydr)oxides (Balistrieri et al., 2008a; Pokrovsky et al., 129 2008) or clay minerals (Li et al., 2015a), oxidation-reduction (Ehrlich et al., 2004; Zhu et al., 130 2002), uptake by plants (Jouvin et al., 2012; Ryan et al., 2013) or microorganisms (Navarrete 131 et al., 2011), precipitation as Cu mineral phases (Ehrlich et al., 2004; Maréchal and Albarède, 2002), and complexation with organic matter (Bigalke et al., 2010; Ryan et al., 2014). δ^{65} Cu 132 133 values significantly differ between particle-size soil fractions, including both SOM and 134 mineral phases (El Azzi et al., 2013; Vance et al., 2008; Babcsányi et al., 2016). Similarly, Zn 135 stable isotope fractionation has been observed following Zn sorption on carbonates (Schott et 136 al., 2014) and several oxides, including goethite and ferrihydrite Fe oxides (Lv et al., 2020; 137 Juillot et al., 2008), birnessite and pyrolusite Mn oxides, and Al oxides (Pokrovsky et al., 2005). δ^{66} Zn also varied during Zn complexation with humic acids (Jouvin et al., 2009) and 138 139 Zn sorption and bacterial incorporation (Kafantaris and Borrok, 2014). Although signals of 140 isotope fractionating processes of transition metals in soil may overlap, reference experiments 141 on Cu and Zn isotope fractionation during long-term ageing (>100 days) in agricultural soils 142 are missing thus far.

143 Here, we designed a laboratory microcosm study on contrasting vineyard and crop 144 soils to investigate the ageing of the widely used fungicides metalaxyl (MTY) and herbicides 145 S-metolachlor (SMET), as well as Cu and Zn. The objective of this study was to examine (i) 146 the influence of soil characteristics on the independent and concomitant ageing of synthetic 147 pesticides and heavy metals and (ii) the stable isotope fractionation of Cu and Zn during the 148 ageing of Cu and Zn in agricultural soils. Experiments with sterile (abiotic) and nonsterile 149 (biotic) soil were incubated separately for 1, 10, 100 and 200 days to recover soil particle-size 150 fractions for sequential chemical extraction and stable isotope analyses of Cu and Zn. We 151 hypothesized that (i) the ageing of synthetic pesticides and heavy metals in soil differs if they 152 co-occur or not, and (ii) the distribution of Cu and Zn among soil fractions during ageing is 153 associated with specific stable isotope fractionating processes in agricultural soil.

154

155 **2. Material and methods**

156 *2.1. Chemicals*

157 Metalaxyl (C₁₅H₂₁NO₄, methyl N-(methoxyacetyl)-N-(2,6-xylyl)-DL-alaninate) and S-158 metolachlor (C₁₅H₂₂ClNO₂, (S)-2-chloro-N-(2-ethyl-6-methyl-phenyl)-N-(1-methoxypropan-159 2-yl)acetamide) were purchased from Sigma-Aldrich (St. Louis, MO, USA), with purities of 160 99.8% and 98.2%, respectively. The physicochemical characteristics of MTY and SMET are 161 provided in Table S1. Copper (CuCl₂) and zinc (ZnCl₂) chlorides for soil spiking and salts for 162 preparing artificial rainwater were purchased from Sigma-Aldrich (St. Louis, MO, USA) with a purity \geq 97%. Ultrapure water and dichloromethane (DCM), BaCl₂ (0.1 M), Pb(NO₃)₂ (0.05 163 164 M), CH₃COONa (1 M), NH₂OH·HCl (0.01 M), H₂C₂O₄ (0.1 M), Na₂C₂O₄ (0.175 M) and 165 $Na_4P_2O_7$ (0.1 M) for the sequential extraction of soil chemical fractions were purchased from 166 Sigma–Aldrich.

167 *2.2. Experimental soils*

168 A vineyard and crop soil with contrasting physicochemical properties (Table S2) were 169 collected with a distilled water- and ethanol-cleaned shovel on August 6 and 7, 2015, from 170 well-characterized sites. The vineyard soil was collected from a plot in an experimental 171 catchment in Rouffach (Alsace, France) (Babcsányi et al., 2016; Duplay et al., 2014; Imfeld et 172 al., 2020). Fifty kg of topsoil (0 to 5 cm, Hor. A) were collected by random subsampling 173 (>50) at each site, since this soil layer is directly impacted by pesticides. Subsamples of calcareous vineyard topsoil were collected from a 1486 m² plot managed under conventional 174 175 wine-growing practices across seven vine inter-rows at ten locations in each inter-row. 176 Subsamples of arable crop soil were obtained from three transects in a field site cultivated 177 with sugar beet, corn and wheat at Alteckendorf (Alsace, France) (Lefrancq et al., 2017). 178 Subsamples of the crop soil were collected from a 47-ha crop catchment (corn and wheat) 179 across three transects.

180 Soil samples were transported in coolers to the laboratory, dried at 30 °C with an air-181 forced oven for soil analysis or at room temperature for further soil incubation, and sieved 182 using a 2-mm mesh. After complete homogenization by mixing four times in quarters, an 183 aliquot of each dried soil was weighed and dried at 105 °C to quantify the soil moisture 184 content. Soil physicochemical characteristics (Table S2) were measured following ISO 185 methods and procedures (Meite et al., 2018; Pérez-Rodríguez et al., 2021). Briefly, the clay-186 loamy vineyard soil was alkaline (pH 8.1), with a low content of organic matter (1.7%) and a 187 high content of carbonates (27.1%). The crop soil was neutral (pH 7.0), characterized by higher contents of organic matter (5.5%), sand (10.3%) and silt (61.5%) than the vineyard 188 189 soil.

190 2.3. Experimental set-up

191 Seven series of soil microcosm experiments were set up in parallel for both the 192 vineyard and crop soils (Table S3): (i) nonsterile (biotic) soils spiked with MTY and SMET;

(ii) nonsterile soils spiked with Cu and Zn; (iii) nonsterile soils spiked with MTY, SMET, Cu
and Zn; (iv) sterile (autoclaved) soils spiked with MTY and SMET; (v) sterile soils spiked
with Cu and Zn; (vi) sterile soils spiked with MTY, SMET, Cu and Zn; and (vii) nonsterile
and sterile soils adjusted with sterile distilled water only as controls.

197 The soil microcosms consisted of 60 g of air-dried soil in sterile 100 mL HDPE flasks. 198 A 0.2 µm syringe filter (Rotilabo®, Carl Roth®, France) was mounted on a syringe tip stuck 199 through the vial cap to allow oxic conditions in the vials through permanent soil-atmosphere 200 gas exchange while limiting water loss and avoiding contamination (Torabi et al., 2020). The 201 soil for sterile experiments was autoclaved three times at 12 h intervals. The soil microcosms 202 were prepared under laminar flow with sterile material, as described earlier (Torabi et al., 203 2020). Briefly, pesticide stock solutions of individual MTY and SMET in DCM were added 204 to distilled water and stirred until complete DCM evaporation. The aqueous solutions of 205 MTY, SMET, CuCl₂, and ZnCl₂ were filter-sterilized separately for soil spiking.

Experiments with nonsterile and sterile soils were spiked with MTY and SMET at 5 mg kg⁻¹ and/or Cu at 700 mg kg⁻¹ and Zn at 200 mg kg⁻¹, equivalent to high but environmentally relevant concentrations in agricultural soil (Imfeld et al., 2020; Komárek et al., 2010b). Solution spiking was adjusted to reach a final water content of 20% (w/w). To homogenize the soil microcosms, aqueous pesticide solution, or deionized water as a control, was added between soil layers, i.e., 4 layers of soil and 5 layers of aqueous solution. The microcosms were then vortexed for 30 s.

All experiments were incubated in the dark at 20 °C. Sampling was carried out using a sacrificial approach on days 1 (following an equilibration of 24 h), 10, 100, and 200. In total, 16 experiments were set up, each in independent triplicate microcosms, and for each of the four sampling days, yielding a total of 192 individual soil microcosms (Table S3).

217 2.4. Physical separation of soil particle-size fractions

To separate the water and soil fractions for MTY and SMET analysis, soil suspensions 218 219 with 1:5 bulk soil:ultrapure sterile water were agitated for 24 h at 60 rpm and centrifuged at 220 750 rpm for 5 min. The obtained supernatant constituted the water fraction. The sand (>63 221 μm), silt (2 and 63 μm) and clay (<2 μm) soil fractions were separated as described 222 previously (Wang and Keller, 2008). The sand fraction was wet-sieved (63 μ m) and carefully 223 rinsed with 18.2 M Ω water. The silt and clay fractions were separated by centrifugation at 750 224 rpm for 5 min. The obtained supernatant was eventually centrifuged (4000 rpm, 35 min) to 225 collect the clay fraction. The sand, silt and clay fractions were weighed, and the recovery (≥ 95 \pm 5%) for Cu or Zn was verified. The sand, silt and clay fractions were stored at -4 °C prior to 226 227 further treatments and quantification of Cu, Zn, MTY and SMET.

228

2.4.MTY and SMET quantification

229 MTY and SMET were extracted from water using SPE with SolEx C18 cartridges (1 g 230 phase, Dionex-Thermo Fischer) method described previously (Masbou et al. 2018). Extraction 231 from the particle-size fractions was carried out with ethyl-acetate using a modified 232 solid-liquid extraction protocol (Ivra et al. 2014). Extraction recoveries from water and 233 sediment samples were highly reproducible (SE<10%). MTY and SMET were quantified by gas chromatography (GC, Trace 1300, Thermo Fisher Scientific) coupled with a mass 234 spectrometer (MS, ISQTM, Thermo Fisher Scientific). Recoveries, limits of detection (LODs), 235 236 limits of quantification (LOQs) and accuracy of GC-MS measurements are provided in Table 237 S4 (Supporting Information).

238

2.5.Sequential chemical extraction of Cu and Zn

The distribution of Cu and Zn among soil chemical fractions was quantified with a sequential extraction procedure adapted from Rao et al. (2008) and summarized in Table S5. Eight fractions were extracted sequentially: (i) easily exchangeable (*EExch*); (ii) less easily exchangeable (*LExch*); (iii) acid-soluble, carbonate-bound (*Acid*); (iv, v and vi) reducible, 243 Mn- (MnOx), amorphous Fe- (AFeOx) and crystallized Fe-oxide bound (CFeOx); (vii) 244 oxidizable, organic matter-bound (Org); and (viii) residual (Res), associated with the silicate 245 matrix.

246 Homogenized soil samples (1 g) were extracted with 25 mL of extractant. A solution 247 of BaCl₂ extracted the *EExch*, followed by PbNO₃ and sodium acetate in acetic acid (pH 5) to extract the LExch and Acid fractions, respectively. The MnOx, AFeOx and CFeOx fractions 248 249 were extracted with hydroxylamine in hydrochloric acid NH₂OH·HCl, oxalate $H_2C_2O_4$ and 250 ammonium oxalate $(NH_4)_2C_2O_4$, respectively. The Org fraction was extracted with sodium 251 pyrophosphate (Na₄P₂O₇). Extraction of amorphous and crystallized Fe oxide-bound metals 252 was carried out in the dark and under UV light, respectively. The Res fraction was dissolved 253 twice in 10 mL of bidistilled HNO₃ heated at 200 °C on a hot plate, followed by dissolution in 254 10 mL of bidistilled HCl and 10 mL of supra-pure HF heated at 100 °C for 24 h. Acids were 255 evaporated at 120 °C and dissolved in 5 mL of HCl 7 M in an ultrasonic bath for 5 min and 256 heated at 70 °C for 12 h.

257 The fraction obtained after each extraction stage was washed with 20 mL of 18.2 M Ω 258 cm water with an end-over-end shaker and centrifuged for 30 min at 5000 rpm. The solution 259 containing the extracted elements was acidified with distilled HNO₃ (0.5 M) and stored in 260 polyethylene vials at 4 °C until analysis. The analytical uncertainty for the entire sequential 261 extraction procedure was <10% based on separate triplicate extractions and measurements 262 (Semhi et al., 2014).

263 2.6.Quantification of Cu and Zn

For Cu and Zn quantification, soil samples were first oven-dried (60 °C) and powdered using an agate disk mill (<100 μ m) prior to total dissolution in acids under a laminar fume hood in a clean room, as described previously (Babcsányi et al., 2016). Measurements were carried out by ICP-AES (ICAP6500, Thermo Fisher Scientific) with geological standards, BCR-2 (US Geological Survey, Reston, VA, USA) and SCL-7003 (Analytika, Prague, Czech Republic), for quality control (Babcsányi et al., 2014). The total analytical uncertainty of measurements was \pm 5%, and the detection limit was <3 ppb.

271 2.7.Cu and Zn isotope analysis and notations

For Cu and Zn isotope analysis, 100 mg of bulk soil, sand, silt or clay powder (<63 μ m) was weighed in PFA vials. Liquid samples were evaporated to reach at least 200 ng of Cu and Zn. All samples were dissolved in successive acid baths: HF-HNO₃ acid (v:v = 4:1) at 70 °C, HClO₄ acid at 150 °C and a mixture of HCl and H₃BO₃ at 110 °C.

276 Protocols for double Cu and Zn purifications were adapted from Maréchal et al. (1999) 277 and Babcsányi et al. (2014) for Cu and from Moynier et al. (2009) for Zn (Table S6). Each Cu 278 purification step was followed by sample digestion in 1 mL of HNO₃ to mineralize the 279 organic matter recovered from the AGMP1 resin. Purified samples and standards were 280 dissolved in HNO₃ 0.5 M to reach 100 μ g L⁻¹ of Cu and 200 μ g L⁻¹ of Zn. The total procedure 281 contributed to \leq 1% of the total Cu and Zn content in the soil samples (data not shown).

Cu and Zn isotope ratios were measured with a Finnigan-Neptune MC-ICP-MS (Thermo Scientific, Waltham, MA, USA) using a Ni standard (NIST SRM 986) for Cu and a Cu standard (NIST SRM 976) for Zn. For Cu and Zn isotope ratio measurements, the Cu standard (NIST SRM 976) and Zn standard (IRMM 3702) were used for correction of instrumental mass biases as previously described (Li et al., 2009). Each measurement of stable isotope ratios consisted of 40 (Cu) and 30 (Zn) cycles of 8 s of integration.

The total analytical uncertainty for digestion, purification and isotope analysis was $\leq 0.05 \ \% \ (2\sigma, n=15)$ for δ^{65} Cu values and $\leq 0.09 \ \% \ (2\sigma, n=15)$ for δ^{66} Zn values. The total analytical uncertainty was determined using the soil reference material CRM-7003 (δ^{65} Cu = $0.18 \pm 0.05\%$ and δ^{66} Zn = $-0.25 \pm 0.09\%$, including 3 samples digested separately and 15 isotope measurements), in agreement with the literature (Bigalke et al., 2010). Cu and Zn isotope ratios were expressed as δ^{65} Cu and δ^{66} Zn values [‰] relative to the NIST 976 and IRMM 3702 reference materials, respectively.

- 295 2.8.Data analysis
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2.8.1. Pesticide dissipation and biodegradation

The contribution of abiotic and biotic dissipation of MTY and SMET in soil was estimated by comparing dissipation in nonsterile (biotic) soils and in sterile (abiotic) soils. The dissipated fractions [%] of pesticides after 200 days in sterile soils ($D_{abiotic, 200}$) define the contribution of ageing and abiotic degradation, while dissipation in nonsterile experiments ($D_{biotic, 200}$) additionally features biotic degradation. Thus, the extent of biodegradation (B_{diss}) (%] of MTY or SMET at 200 days was estimated as the difference between $D_{abiotic, 200}$ and $D_{biotic, 200}$.

304

2.8.2. Statistical analyses

305 Statistical tests were performed using the R program (Copyright 2005, The R 306 Foundation for Statistical Computing, Version 2.15.1). Nonparametric Wilcoxon and 307 Kruskal–Wallis tests were applied to compare the ageing of MTY, SMET, Cu and Zn 308 according to the soil type, sterilization or distribution in soil fractions.

309 Cluster analysis was used to visualize dissimilarities between the distribution patterns 310 of MTY, SMET, Cu and Zn in the particle-size fractions of soil and of Cu and Zn in the 311 chemical fractions. The distance between distribution patterns was calculated with the Bray-312 Curtis dissimilarity index. A hierarchical cluster analysis was performed on the resulting 313 dissimilarity matrix using Ward's method (Ward, 1963).

314

315 **3. Results and discussion**

316 *3.1. Distribution of MTY and SMET among particle-size fractions during ageing*

317 More than 96% of residual MTY and SMET was released from the soil into the water phase in all experiments and after all incubation times (Figure 1). The high solubility in water 318 319 and low sorption propensity of MTY and SMET (Table S1) favoured partitioning into the 320 water phase at all incubation times. Only a minor and constant portion of MTY and SMET 321 remained associated with soil over time. Since the water phase did not include soil particles, 322 MTY and SMET were mainly freely dissolved and associated to DOC. This emphasizes the potential of MTY and SMET mobilization from agricultural soils into runoff water and further 323 324 export to aquatic ecosystems, even 200 days after pesticide application. However, the 325 distribution of pesticides among particle-size fractions of the soil may also affect pesticide export into runoff since the rainfall pattern determines the preferential export of specific soil 326 327 fractions (Martínez-Casasnovas et al., 2002; Mohamadi and Kavian, 2015; Meite et al., 2018; Imfeld 2020). 328 et al.,



Figure 1. Distribution of (A) metalaxyl (MTY) and (B) *S*-metolachlor (SMET) among fractions of crop and vineyard soils, including water, sand $(x>50 \ \mu m)$, silt (2<x<50 \ \mu m) and clay (x<2 \ \mu m), in nonsterile and sterile experiments. The distribution of MTY and SMET among soil fractions does not reflect their dissipation extent (see section 3.2). Error bars denote 95% confidence intervals.

334 The MTY and SMET distribution among particle-size fractions largely varied among 335 conditions but did not change significantly (p>0.1) with ageing or soil type in nonsterile 336 experiments (Figure 1). However, both MTY and SMET dissipated in soil over time (see 337 section 3.2). Overall, MTY and SMET were mainly associated with the silt fraction in both 338 soil types, although the silt content was approximately three times lower in the vineyard soil 339 (23.1%) than in the crop (61.5%) (Table S2). In the silt fraction, both MTY and SMET 340 slightly increased over time in nonsterile experiments with vineyard soil. Differences in both 341 the content and nature of SOM and minerals among particle-size fractions can alter the 342 distribution of MTY and SMET. The SOM content generally increases with decreasing particle size (Guo et al., 2010; Quenea et al., 2009; Schmidt and Kögel-Knabner, 2002), 343 which may favour MTY and SMET sorption in the silt and clay fractions. In addition, the 344 345 proportion of particulate organic matter (POM, >50 µm) and mineral-associated organic 346 matter (MOM, <50 µm) constituting SOM is expected to differ among particle-size fractions 347 in crop and vineyard soils (Benoit et al., 2008; Guo et al., 2010; Moyo et al., 2014; Tirloni et 348 al., 2012).

349 We thus hypothesize that an intermediate degree of SOM alteration and the specific 350 POM/MOM ratio in the silt fraction favoured the sorption of nonionic pesticides, such as 351 MTY and SMET (Figure 1). In particular, less degraded SOM with a medium-density organic 352 fraction and a lower POM/MOM ratio in the silt than in the sand fraction may favour MTY 353 and SMET sorption in the silt fraction of the vineyard soil (Besnard et al., 2001; Parat et al., 354 2002; Quenea et al., 2009). Interactions with minerals in the silt and clay fractions can further 355 stabilize SOM in the form of organomineral complexes (Mertz et al., 2005; Poirier et al., 356 2005; Schmidt and Kögel- Knabner, 2002) and pesticide-SOM complexes. These results are 357 in agreement with previous studies showing fast incorporation of metalaxyl in silt- and clayorganic matter (Kalathoor et al. 2015). The binding mechanism may include hydrogen and ionic bonds between the oxygen-rich metalaxyl residues and the soil humic surface. In addition, nonionic pesticides can sorb onto soil oxides, especially on clay minerals (Clausen et al., 2001; Cornejo et al., 2008; Moyo et al., 2014; Remucal and Ginder-Vogel, 2014). This may explain the slight increase in MTY and SMET in the clay fraction of the crop soil after 200 days of ageing (Figure 1).

364 In comparison with the nonsterile experiments, both MTY and SMET significantly 365 increased over time in the silt and sand fractions of sterile crop and vineyard soils, respectively. Sterilization by autoclaving affected the distribution of MTY and SMET among 366 367 soil fractions, presumably due to changes in the availability of soil-binding sites and SOM 368 alteration. Autoclaving results in physical aggregate fractionation, decreasing soil aggregation and increasing the clay fraction (Berns et al., 2008). The lysis of microorganisms and 369 370 subsequent transformation of microbial carbon also alter the SOM structure. Thus, alteration 371 of SOM and lower soil aggregation following autoclaving likely favoured ageing of both 372 MTY and SMET in the sand fraction in sterile experiments with vineyard soil (Figure 1). 373 Indeed, the sand fraction generally contains higher POM, which is known as a light-density 374 organic fraction and the most accessible SOM fraction for pesticides (Quenea et al., 2009). 375 Overall, higher aggregate fractionation and SOM alteration, together with changes in 376 POM/MOM ratios across soil fractions, led to distinct distributions of MTY and SMET 377 among soil fractions in the nonsterile and sterile experiments.

378

379 *3.2. Dissipation of MTY and SMET in crop and vineyard soils*

Ageing also controlled the dissipation of MTY and SMT in agricultural soils. The extent of dissipation by irreversible sorption and biodegradation was estimated based on differences between the dissipated fraction of MTY and SMET in nonsterile and sterile

experiments (Table 1). Overall, soil type, sterilization and ageing did not significantly (p>0.1)383 384 affect MTY and SMET dissipation in soil. For all experiments and based on concentration decrease, more than 90% of MTY and SMET dissipated within 200 days (Table 1). The large 385 386 uncertainties associated with dissipation estimates in the crop than in the vineyard soil may 387 reflect higher heterogeneity of biological, physical and chemical characteristics. The contribution of MTY and SMT volatilization, dilution, plant uptake, export or 388 389 photodegradation can be safely discarded in our setup. Hence, biodegradation in the nonsterile 390 experiments ranged from <8 to <72 given the uncertainty associated with dissipation 391 estimates and generally accounted for dissipation of less than 10% (Table 1). Sorption was 392 thus identified as the major process responsible for MTY and SMET dissipation in all 393 experiments.

394

Table 1. Dissipated fractions of pesticides in nonsterile ($D_{biotic,t}$) and sterile soils ($D_{abiotic,t}$),

	Сгор			Vineyard		
	D _{biotic} [%] ±SE	D _{abiotic} [%] ±SE	<i>B_{diss}</i> [%] ±SE	D _{biotic} [%] ±SE	D _{abiotic} [%] ±SE	<i>B_{diss}</i> [%] ±SE
MTY	92 ± 68	96 ± 23	<72	97 ± 7	96 ± 7	<10
SMET	94 ± 23	95 ± 4	<23	99 ± 4	93 ± 7	<8

along with the extent of biodegradation (B_{diss}) at 200 days.

397

398 The contribution of sorption to the overall MTY and SMET dissipation is expected to 399 increase with lower water content in soil. The low (20%) water content in crop and vineyard soils limited sorption-desorption, MTY and SMET bioavailability and microbial activity, thus 400 401 decreasing the contribution from biodegradation. In contrast, with a lower water content, the 402 fraction of nonextractable residues (NER) may have increased, resulting in an apparent dissipation of MTY and SMET (Rodríguez-Liébana and Peña, 2020). It can be hypothesized 403 404 that a lower water content enhanced intraparticle diffusion over time through inner soil pores of more soluble and less hydrophobic pesticides, such as MTY and SMET (solubility >400 405

406 mg L⁻¹ and K_{dsoil}<2.5 mL g⁻¹; Table S1). In turn, this reduced MTY and SMET bioavailability 407 and biodegradation while increasing their half-lives in the soil. Sorption was thus the main 408 dissipation process controlling MTY and SMET extraction and dissipation during ageing in 409 soils with low water content. Our results also emphasize the persistence and strong binding of 410 pesticide NER in dryer soils (Odukkathil and Vasudevan, 2013) after 200 days, even for 411 soluble and nonionic pesticides, such as MTY and SMET.

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3.3. Distribution of Cu and Zn among particle-size fractions during ageing

414 Cu partitioning between soil and water was mainly affected by soil sterilization and 415 ageing, whereas Zn partitioning only slightly varied during ageing. The fraction of Cu 416 released into the water phase $(36 \pm 2\%)$ was three times higher than that of Zn $(12 \pm 1\%)$ in 417 nonsterile experiments (Figure 2). Partitioning of both Cu and Zn into water only slightly decreased between 10 and 200 days of ageing. Overall, this emphasizes the potential release 418 419 of Cu- and Zn-DOM complexes from agricultural soils into the aqueous phase during Cu and 420 Zn ageing. The formation and dominance of Cu- and Zn-DOM complexes at pH>7 in aqueous 421 solution was supported by speciation modelling using Minteq with Nica-Donnan and 422 Stockholm Humic models (data not shown) (Vance et al., 2008). The amount of Cu in the 423 aqueous phase was generally approximately twice as high in sterile than in nonsterile 424 experiments (Figure 2). The higher release of Cu- and Zn-DOM complexes into the water 425 phase in sterile experiments was due to the physical aggregate fractionation of the soil during autoclaving, favouring DOM release. In addition, the quality of DOM has profound and 426 427 different effects on Cu and Zn binding (e.g., Baken et al., 2011). Different DOM qualities among experiments may have resulted in preferential Cu-DOM binding and release compared 428 429 with Zn-DOM complexes and distinct patterns of water-soil partitioning in sterile and 430 nonsterile experiments with crop and vineyard soils.

431 The Cu and Zn distribution among soil particle-size fractions in nonsterile and sterile 432 experiments did not significantly change during ageing (p>0.1); Figure 2). Cu and Zn distribution in both crop and vineyard soils followed a silt ($54 \pm 3\%$ of Cu and $51 \pm 3\%$ of Zn) 433 > clay (24 ± 1% of Cu and 34 ± 2% of Zn) > sand pattern (23 ± 1% of Cu and 15 ± 1% of Zn) 434 435 (Figure 2). This emphasizes that Cu and Zn were mainly associated with silt, despite the 436 larger proportion (68%; Table S2) of clay in the vineyard than in the crop soil. Less degraded 437 SOM and a lower POM/MOM ratio in the silt fraction possibly favoured Cu and Zn sorption, 438 especially in the vineyard soil. Similarly, POM associated with the sand fraction likely 439 favoured Cu and Zn binding (Quenea et al., 2009), whereas sorption to sand minerals, mainly 440 composed of quartz, remained limited (Nenadović et al., 2010).



441

Figure 2. Distribution of (A) Cu and (B) Zn among crop and vineyard soils, including water, sand (x>50 µm), silt (2 <x<50 µm) and clay (x<2 442 fractions in sterile 95% confidence intervals. 443 μm) nonsterile and experiments. Error bars denote

3.4. Distribution of Cu and Zn among chemical fractions

446 The Cu and Zn distribution among chemical fractions mainly differed with soil type 447 and more subtly over time (Figure 3). The cluster analysis highlighted that the distribution of 448 both Cu and Zn among chemical fractions differed between the crop and vineyard soils and 449 different distribution patterns between Cu and Zn (Figure 4). In particular, the *LExch*-Cu and Zn fractions were significantly higher (p < 0.001), whereas the *Res*-Cu and Zn fractions were 450 451 lower (p < 0.001) in the vineyard than in the crop soil. In both soils, Cu and Zn were mainly associated with *LExch* ($\overline{X} \pm$ SD across conditions: 34 ± 2% for Cu and 32 ± 2% for Zn), 452 AFeOx ($37 \pm 2\%$ for Cu and $15 \pm 1\%$ for Zn) and Res fractions ($11 \pm 1\%$ for Cu and $33 \pm 2\%$ 453 454 for Zn) (Figure 3). This distribution agrees with previous studies, showing that Cu and Zn in 455 the *LExch* fraction were mainly covalently bound to organic and inorganic sites (Rao et al., 456 2008). Clay minerals and organic matter controlling the cation exchange capacity (CEC) of 457 soil (Liu et al., 2017) may have favoured Cu and Zn release from vineyard soil (CEC=15.4 $\text{cmol}^+\text{kg}^{-1}$, Table S2) compared with crop soil (CEC=9.1 $\text{cmol}^+\text{kg}^{-1}$). In the *AFeOx* fraction, 458 459 Cu and Zn were generally associated with amorphous Fe oxides following coprecipitation, adsorption, surface complex formation, ion exchange and/or penetration into the mineral. In 460 461 contrast, Cu and Zn in the *Res* fraction were strongly bound or entrapped in minerals, 462 especially clays and oxides (Clausen et al., 2001; Đurović et al., 2009; Remucal and Ginder-Vogel, 2014; Ruggiero et al., 2002). Higher proportions of both Al₂O₃ and Fe₂O₃ in the crop 463 soil (Table S2) may explain the higher Res-Cu and Zn in the crop than in the vineyard soil. 464

465

466



469 Figure 3. Distribution of Cu and Zn among chemical fractions of nonsterile crop and vineyard soils spiked with Cu and Zn only or with Cu, Zn,
470 metalaxyl (MTY) and S-metolachlor (SMET). Error bars denote 95% confidence intervals.



472 Figure 4. Hierarchical cluster analysis (Ward's method) of Cu and Zn distribution in
473 chemical soil fractions (*EExch, LExch, Acid, MnOx, AFeOx, CFeOx, Org* and *Res*) in
474 nonsterile crop (C) and vineyard (V) soils spiked with Cu and Zn or with Cu, Zn, metalaxyl
475 (MTY) and S-metolachlor (SMET) for 0, 10, 100 or 200 days of ageing.

The distribution of Cu and Zn among chemical fractions also varied over time, 477 especially in the crop soil. For both Cu and Zn, EExch and LExch fractions and, to a lesser 478 extent, Org- and CFeOx fractions significantly differed (p < 0.05) between Days 0 and 10 in 479 480 the crop soil. This suggests a redistribution of Cu and Zn from LExch and EExch to Org and 481 *CFeOx* fractions in the early ageing stage, in agreement with previous studies (Ma et al., 482 2006; Jalali and Khanlari, 2008). Notably, the uncertainty associated with sequential chemical 483 extraction of Cu and Zn from the *EExch* and *LExch* fractions may be high since MgCl used to 484 extract exchangeable elements partly dissolves carbonates and releases Mg.

485

487 *3.5. Effect of co-contamination on the distribution of Cu and Zn among chemical fractions*

The distribution of Cu and Zn among chemical fractions slightly differed in experiments spiked with MTY, MET, Cu and Zn and with Cu and Zn only (Figure 3), particularly in the crop soil between Days 10 and 200 (Figure 4). Concomitant ageing of MTY, MET, Cu and Zn significantly (p<0.01) increased the *LExch* fraction and decreased the *MnOx* fraction for both Cu and Zn compared with experiments spiked with Cu and Zn only.

493 These results suggest that the co-occurrence of MTY, MET, Cu and Zn in soil affects 494 their complexation and competitive sorption to soil-binding sites and thus modifies their 495 sorption rates and distribution, mainly in the LExch and MnOx fractions. The less degraded 496 SOM and a lower POM/MOM ratio in the silt fraction is likely to control the sorption of non-497 ionic MTY and SMET and heavy metals in the studied soils (see section 3.1 and 3.3). First, 498 competitive sorption on SOM and minerals can affect the sorption rates of both organic 499 pollutants and metals. This has been observed previously for Cu and *p*-nitrophenol in soil (Pei 500 et al., 2006) or Cu and chlordimeform sorption on montmorillonite (Maqueda et al., 1998). 501 Although no experiments on competitive sorption with MTY and SMET and heavy metals 502 have been reported, Cu and Zn are expected to form stronger bounds at pH>6 and competition 503 between metals and non-ionic pesticides is expected to be limited (e.g., Jacobson et al. 2005). 504 In addition, the formation of pesticide-metal complexes may alter the sorption of MTY and 505 SMET in the presence of trace metals and vice versa. Metals can enhance the linkage between 506 synthetic pesticides and organic matter, with Cu linking SOM and soluble pesticides thus 507 facilitating their sorption (Zhou et al., 2004; Morillo et al., 2002). The introduction of 508 synthetic pesticides in soil can also alter the physicochemical characteristics of the solution, thereby modifying the sorption rates. For instance, reductive dissolution of oxides by 509 510 synthetic pesticides may enhance the release of Cu and Zn associated with oxides in the silt 511 and clay fractions in experiments with MTY, MET, Cu and Zn, as previously observed with 512 Mn oxides (Remucal and Ginder-Vogel, 2014). Finally, Cu or Zn ions in soil may also affect 513 the activity of microorganisms, thus decreasing MTY and SMET degradation (Liu et al., 514 2007) and altering ageing patterns.

515 Overall, our results show that the co-occurrence of synthetic pesticides and metals can 516 slightly affect their sorption behaviour and ageing, depending on the soil characteristics. 517 However, the order of pollutant addition in soil can also influence sorption and competition 518 for binding sites (Maqueda et al., 1998), although the effect of consecutive addition of 519 pollutants has not yet been explored.

520

521 *3.6. Cu and Zn stable isotope fractionation during Cu and Zn ageing in agricultural soils*

Stable isotope signatures of Cu (δ^{65} Cu) and Zn (δ^{66} Zn) were analysed from Day 10 522 onwards to evaluate the isotope fractionation and associated processes during long-term 523 524 ageing (>100 days) of Cu and Zn in soil fractions. Cu and Zn isotope fractionation was 525 analysed in experiments spiked with Cu, Zn, MTY and SMET, which are more representative 526 of multicontaminated agricultural soils. It is worth noting that Cu and Zn isotope fractionation 527 among soil fractions mainly resulted from ageing of fresh Cu and Zn since the Cu and Zn spikes represented >90% and >70% of the initial Cu and Zn mass in soil, respectively. As 528 expected, δ^{65} Cu and δ^{66} Zn values of bulk soils on Day 0 (data not shown) did not change 529 530 significantly over time or among experiments. The isotopic mass balance of Cu and Zn in soil 531 physical fractions fitted with the isotopic composition of the bulk soil, emphasizing the 532 accuracy of Cu and Zn isotopic analysis in soil physical fractions.

533 The δ^{65} Cu values differed mainly among soil fractions, particularly in the crop soil 534 experiments ($\Delta\delta^{65}$ Cu up to 1 ‰), and slightly over time in the clay fraction of the vineyard 535 soil (Figure 5). In contrast, δ^{66} Zn values did not vary significantly among soil types, 536 granulometric fractions or over time ($\Delta\delta^{66}$ Zn<0.4 ‰) (Figure S1). Both binding to organic

complexes and sorption to secondary minerals, such as clays and Fe-Mn oxyhydroxides, may 537 compete to control Cu and Zn behaviour in soils (Grybos et al., 2007) and is certainly key for 538 isotope fractionation in soil. Nevertheless, different chemical distributions of Cu and Zn 539 (Figures 3 and 4), and redox transitions in the case of Cu, and specific values of the stability 540 541 constant for each complex (Ryan et al., 2014) resulted in distinct Cu and Zn isotope fractionation in soil. Similar patterns of δ^{65} Cu and δ^{66} Zn values in nonsterile and sterile 542 experiments emphasize that slight differences in the physical and chemical distribution of Cu 543 544 and Zn and biotic processes did not significantly affect Cu and Zn stable isotope fractionation.



546

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Figure 5. δ^{65} Cu values in bulk soil and clay, silt and sand fractions of nonsterile and sterile crop and vineyard soils spiked with Cu, Zn, MTY and SMET. Error bars denote analytical uncertainty (± 0.05).

550

551 The difference in δ^{65} Cu in the soil fractions of the crop and vineyard soils suggests 552 that different processes affected Cu isotope fractionation. In both soils, the clay fraction was 553 depleted in ⁶⁵Cu, whereas the silt and sand fractions were enriched in ⁶⁵Cu compared with the 554 bulk soil. The formation of SOM-Cu complexes and Fe-oxide and organo-clay complexes 555 generally drives Cu sorption in soil, although Cu precipitation as carbonate or hydroxide may 556 prevail in calcareous vineyard soil (El Azzi et al., 2013; Komárek et al., 2010a). Our results are in agreement with previous results insofar as Cu sorption to Fe oxides (Balistrieri et al., 557 2008b) and SOM (Bigalke et al., 2010) is expected to enrich Cu in ⁶⁵Cu, whereas Cu sorption 558 to clay minerals may deplete Cu in ⁶⁵Cu (Li et al., 2015b). In particular, the formation of Cu-559 SOM complexes at pH above 7 may affect δ^{65} Cu among soil fractions (Quenea et al., 2009). 560 However, the SOM quality varies in grain-size fractions, with more altered (oxidized) SOM 561 562 and stabilized organomineral complexes generally prevailing in the clay fraction (Poirier et 563 al., 2005). We thus hypothesize that the larger Res-Cu fraction in the crop than in the vineyard 564 soil (Figure 3) is characterized by strongly bound or entrapped Cu in clays, explaining the higher Cu enrichment in ⁶⁵Cu in the clay fraction of crop soil. In addition, Cu precipitation in 565 carbonates is also expected to deplete the clay fraction in ⁶⁵Cu (Maréchal and Sheppard, 2002) 566 567 in the vineyard soil since CaCO₃ contributed to 27.1% of the soil content (Table S2). However, XRD data showed that carbonate phases prevailed in the silt fraction of the 568 vineyard soil that was enriched in ⁶⁵Cu, whereas only traces of calcite were found in clays 569 570 (Babcsányi et al., 2016), and <1% of carbonates were found in the crop soil (Table S2). 571 Hence, it is unlikely that Cu precipitation in carbonate enriched the silt fraction and depleted the clay fraction in ⁶⁵Cu. 572

573 The δ^{65} Cu values of the soil fractions did not change much over time, especially after 574 100 days of ageing. This suggests that the Cu distribution among soil fractions was stable 575 from Day 10 onwards (Figures 2 and 3), reflecting limited Cu redistribution among chemical 576 fractions during longer-term ageing in both soil types. However, a redistribution of Cu 577 associated with Cu isotope fractionation in the early ageing stage, i.e., from Day 0 to 10, 578 cannot be excluded, and the signature may be acquired in the early stages of ageing. 579 Moreover, the silt fraction was gradually enriched in ⁶⁵Cu from Day 10 to 200 ($\Delta\delta^{65}$ Cu = 0.25 580 \pm 0.10 ‰) in nonsterile experiments with vineyard soil, whereas the clay fraction was depleted in 65 Cu ($\Delta \delta {}^{65}$ Cu = -0.20 ± 0.10 ‰) (Figure 5). Interestingly, the enrichment in 65 Cu 581 of the silt fraction mirrored the increasing contribution of the AFeOx fraction of nonsterile 582 vineyard soil over time (Figure 3). Since the AFeOx fraction involved Cu association with 583 amorphous Fe oxides, it may be inferred that Cu sorption to Fe oxides gradually increased 584 during ageing in the silt fraction of vineyard soil to reach δ^{65} Cu typically ranging between 585 586 0.24 0.98 ‰ (Balistrieri et al., 2008a; Pokrovsky and et al., 2008).

588 4. Conclusion

589 Current research issues in the field of pollutant dissipation in agricultural soils include 590 (i) how soil characteristics affect the ageing of synthetic pesticides and heavy metals and (ii) 591 how the co-occurrence of synthetic pesticides and heavy metals affects their distribution 592 among soil fractions during ageing. It is our contention that studies such as ours may help to 593 address these issues and enable more systematic examinations of concomitant ageing of 594 synthetic pesticides and heavy metals in soil fractions rather than in bulk soil. Specifically, 595 our study emphasised that the distribution of MTY and SMET among particle-size fractions 596 varied during ageing, thereby controlling the sorption of MTY and SMT and the potential 597 release of MTY and SMET into water. In contrast, the physical and chemical distributions of 598 Cu and Zn differed with soil type and more subtly over time.

599 Most importantly, we showed that the co-occurrence of synthetic pesticides and heavy 600 metals may slightly alter metal distribution in soil fractions, depending on soil characteristics. 601 Thus, the simultaneous evaluation of synthetic pesticides and heavy metals in soil physical 602 and chemical fractions can reinforce the evaluation of ageing in agricultural fields and help identify risks associated with pollutant distribution among soil fractions in multiple-603 604 contaminated areas. Here, we could identify field plots where preferential release into water 605 and export of aged pollutants associated with specific soil fractions occurred, thereby 606 allowing us to focus remediation efforts in these areas. Our results also provide new insights into Cu isotope fractionation during ageing in soils, emphasizing that δ^{65} Cu partly mirrored 607 608 the Cu distribution among chemical fractions of the soils, potentially involving Cu binding in 609 SOM and Fe oxides in specific soil fractions. Overall, our study illustrates the usefulness of 610 integrating approaches to jointly evaluate the ageing of micropollutant molecules and heavy 611 metals in soil for more robust assessment and remediation of multiple polluted sites.

613 Credit authorship contribution statement

Fatima Meite: Conceptualization, Investigation, Methodology, Data curation, Writing
- review & editing. Mathieu Granet: Investigation, Methodology, Data curation, Writing review & editing. Gwenaël Imfeld: Conceptualization, Methodology, Funding acquisition,
Project administration, Supervision, Formal analysis, Writing - original draft.

618

619 **Declaration of competing interest**

620 The authors declare that they have no known competing financial interests or personal 621 relationships that could have appeared to influence the work reported in this paper.

622

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