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1 **Ageing of copper, zinc and synthetic pesticides**
2 **in particle-size and chemical fractions of agricultural soils**

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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
31 spiked with copper (Cu; 700 mg kg⁻¹) and zinc (Zn; 200 mg kg⁻¹) and/or synthetic pesticides
32 (5 mg kg⁻¹), i.e., the fungicide metalaxyl (MTY) and herbicide *S*-metolachlor (SMET), to
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.
35 MTY, SMET, Cu and Zn were associated mainly with the silt fraction and to a lesser extent
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
39 biodegradation contributed to <10%. Cu was mainly (37 ± 2%) associated with Fe oxides
40 after 200 days, while Zn was found (33 ± 2%) in the residual fraction. The silt fraction of the
41 nonsterile vineyard soil became enriched in ⁶⁵Cu over time ($\Delta\delta^{65}\text{Cu} = 0.25 \pm 0.07 \text{ ‰}$),
42 whereas the clay fraction was depleted in ⁶⁵Cu ($\Delta\delta^{65}\text{Cu} = -0.20 \pm 0.07 \text{ ‰}$). Cu isotope
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
46 in ageing of synthetic pesticides and heavy metals co-occurring in agricultural soils and their
47 interplay in soil fractions.

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

50

51 **Highlights:**

- 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 • $\delta^{65}\text{Cu}$ values in the silt and clay fractions of the soil mirrored chemical fractionation of Cu

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77 Graphical abstract

Contrasting soils



Soil microcosm experiments



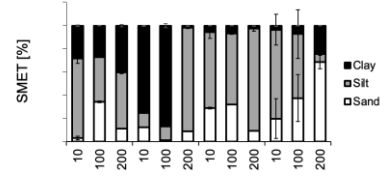
Nonsterile



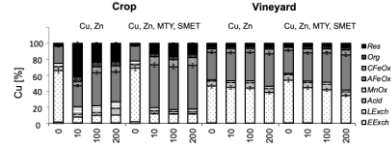
Ageing
Days: 0, 10, 100, 200

Physical and chemical distribution

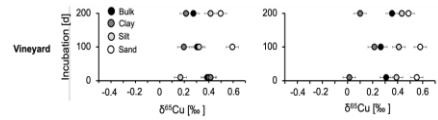
Pollutant mainly associated with the silt fraction



Ageing mainly affected by soil characteristics



$\delta^{65}Cu$ silt and clay fractions: mirror chemical fractionation of Cu



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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; Wyszowska 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).
105 Ageing increases pollutant sequestration and persistence, and reduces pollutant availability
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 (Brummer et al., 1988), Al oxides and Mn oxides, clay minerals (Ma and Uren, 1998) and
117 carbonate precipitation (Nakhone and Young, 1993; Ma et al., 2006) governs their

118 sequestration in soil. Cu and Zn also present high affinity for organic matter (Duplay et al.,
119 2014; Néel et al., 2007; Quenea et al., 2009). It is worth noting that the ageing of synthetic
120 pesticides and heavy metals is generally examined separately and in bulk soil. However, their
121 concomitant occurrence may affect their distribution among soil fractions due to competition
122 for sorption sites, the formation of complexes between pollutants (e.g., El Azzi et al., 2018),
123 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
127 exhibit distinct isotopic signatures in soil fractions. Cu isotope ratios ($^{65}\text{Cu}/^{63}\text{Cu}$) change
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,
132 2002), and complexation with organic matter (Bigalke et al., 2010; Ryan et al., 2014). $\delta^{65}\text{Cu}$
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.,
138 2005). $\delta^{66}\text{Zn}$ also varied during Zn complexation with humic acids (Jouvin et al., 2009) and
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
163 a purity ≥97%. Ultrapure water and dichloromethane (DCM), BaCl₂ (0.1 M), Pb(NO₃)₂ (0.05
164 M), CH₃COONa (1 M), NH₂OH·HCl (0.01 M), H₂C₂O₄ (0.1 M), Na₂C₂O₄ (0.175 M) and
165 Na₄P₂O₇ (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
174 calcareous vineyard topsoil were collected from a 1486 m² plot managed under conventional
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
188 higher contents of organic matter (5.5%), sand (10.3%) and silt (61.5%) than the vineyard
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;

193 (ii) nonsterile soils spiked with Cu and Zn; (iii) nonsterile soils spiked with MTY, SMET, Cu
194 and Zn; (iv) sterile (autoclaved) soils spiked with MTY and SMET; (v) sterile soils spiked
195 with Cu and Zn; (vi) sterile soils spiked with MTY, SMET, Cu and Zn; and (vii) nonsterile
196 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, CuCl_2 , and ZnCl_2 were filter-sterilized separately for soil spiking.

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

213 All experiments were incubated in the dark at 20 °C. Sampling was carried out using a
214 sacrificial approach on days 1 (following an equilibration of 24 h), 10, 100, and 200. In total,
215 16 experiments were set up, each in independent triplicate microcosms, and for each of the
216 four sampling days, yielding a total of 192 individual soil microcosms (Table S3).

217 *2.4. Physical separation of soil particle-size fractions*

218 To separate the water and soil fractions for MTY and SMET analysis, soil suspensions
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 μm) 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
226 $\pm 5\%$) for Cu or Zn was verified. The sand, silt and clay fractions were stored at $-4\text{ }^{\circ}\text{C}$ prior to
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
234 gas chromatography (GC, Trace 1300, Thermo Fisher Scientific) coupled with a mass
235 spectrometer (MS, ISQTM, Thermo Fisher Scientific). Recoveries, limits of detection (LODs),
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*

239 The distribution of Cu and Zn among soil chemical fractions was quantified with a
240 sequential extraction procedure adapted from Rao et al. (2008) and summarized in Table S5.
241 Eight fractions were extracted sequentially: (i) easily exchangeable (*EExch*); (ii) less easily
242 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
248 extract the *LExch* and *Acid* fractions, respectively. The *MnOx*, *AFeOx* and *CFeOx* fractions
249 were extracted with hydroxylamine in hydrochloric acid NH₂OH·HCl, oxalate H₂C₂O₄ and
250 ammonium oxalate (NH₄)₂C₂O₄, 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 MΩ
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

264 For Cu and Zn quantification, soil samples were first oven-dried (60 °C) and powdered
265 using an agate disk mill (<100 μm) prior to total dissolution in acids under a laminar fume
266 hood in a clean room, as described previously (Babcsányi et al., 2016). Measurements were
267 carried out by ICP-AES (ICAP6500, Thermo Fisher Scientific) with geological standards,

268 BCR-2 (US Geological Survey, Reston, VA, USA) and SCL-7003 (Analytika, Prague, Czech
269 Republic), for quality control (Babcsányi et al., 2014). The total analytical uncertainty of
270 measurements was $\pm 5\%$, and the detection limit was <3 ppb.

271 *2.7. Cu and Zn isotope analysis and notations*

272 For Cu and Zn isotope analysis, 100 mg of bulk soil, sand, silt or clay powder (<63
273 μm) was weighed in PFA vials. Liquid samples were evaporated to reach at least 200 ng of
274 Cu and Zn. All samples were dissolved in successive acid baths: HF-HNO₃ acid (v:v = 4:1) at
275 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 $\mu\text{g L}^{-1}$ of Cu and 200 $\mu\text{g L}^{-1}$ of Zn. The total procedure
281 contributed to $\leq 1\%$ of the total Cu and Zn content in the soil samples (data not shown).

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

288 The total analytical uncertainty for digestion, purification and isotope analysis was
289 $\leq 0.05\text{‰}$ (2σ , $n=15$) for $\delta^{65}\text{Cu}$ values and $\leq 0.09\text{‰}$ (2σ , $n=15$) for $\delta^{66}\text{Zn}$ values. The total
290 analytical uncertainty was determined using the soil reference material CRM-7003 ($\delta^{65}\text{Cu} =$
291 $0.18 \pm 0.05\text{‰}$ and $\delta^{66}\text{Zn} = -0.25 \pm 0.09\text{‰}$, including 3 samples digested separately and 15
292 isotope measurements), in agreement with the literature (Bigalke et al., 2010). Cu and Zn

293 isotope ratios were expressed as $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ values [‰] relative to the NIST 976 and
294 IRMM 3702 reference materials, respectively.

295 2.8. Data analysis

296 2.8.1. Pesticide dissipation and biodegradation

297 The contribution of abiotic and biotic dissipation of MTY and SMET in soil was
298 estimated by comparing dissipation in nonsterile (biotic) soils and in sterile (abiotic) soils.
299 The dissipated fractions [%] of pesticides after 200 days in sterile soils ($D_{abiotic, 200}$) define the
300 contribution of ageing and abiotic degradation, while dissipation in nonsterile experiments
301 ($D_{biotic, 200}$) additionally features biotic degradation. Thus, the extent of biodegradation (B_{diss})
302 [%] of MTY or SMET at 200 days was estimated as the difference between $D_{abiotic, 200}$ and
303 $D_{biotic, 200}$.

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.

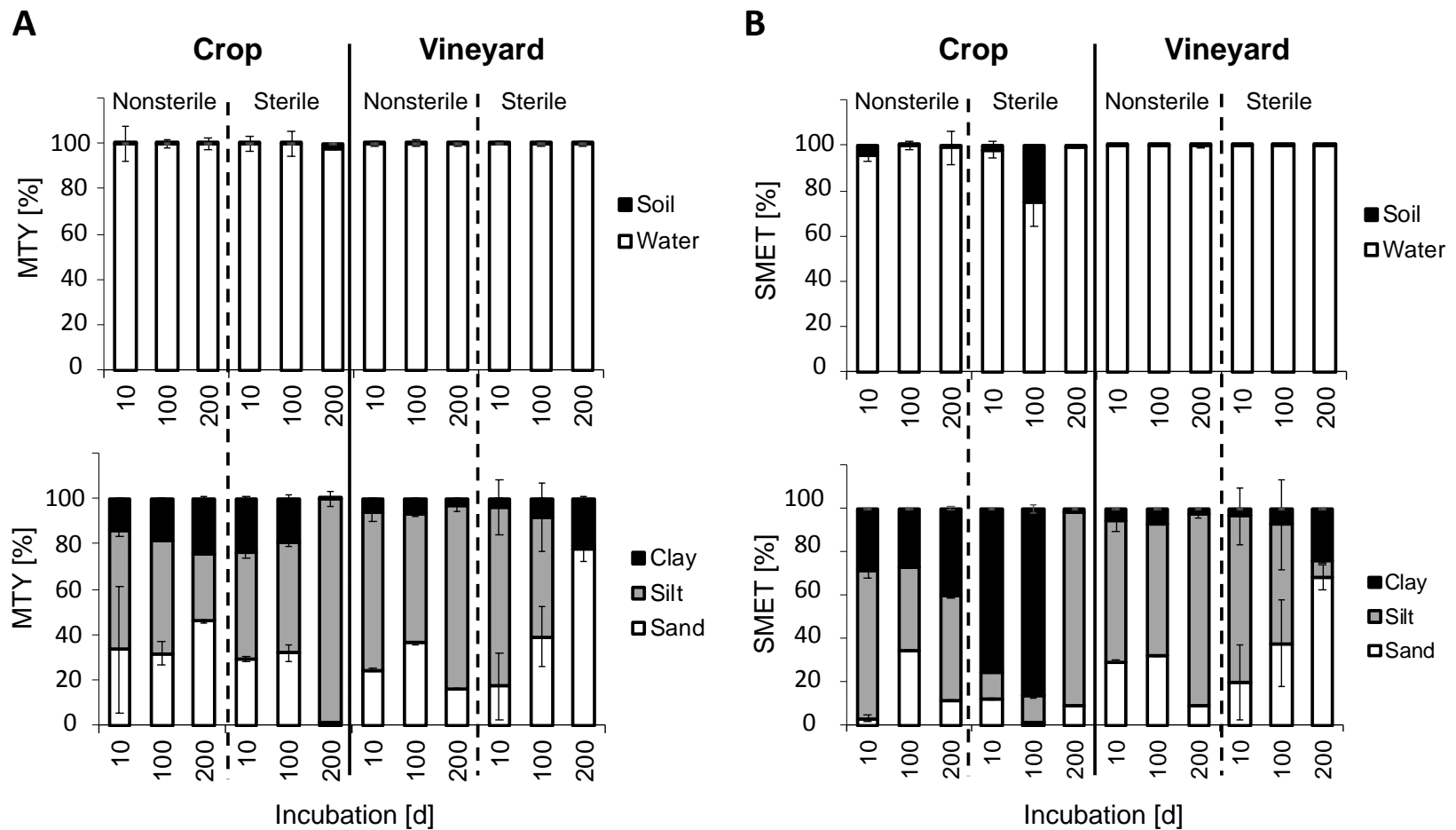
309 Cluster analysis was used to visualize dissimilarities between the distribution patterns
310 of MTY, SMET, Cu and Zn in the particle-size fractions of soil and of Cu and Zn in the
311 chemical fractions. The distance between distribution patterns was calculated with the Bray-
312 Curtis dissimilarity 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
318 phase in all experiments and after all incubation times (Figure 1). The high solubility in water
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
323 potential of MTY and SMET mobilization from agricultural soils into runoff water and further
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
326 export into runoff since the rainfall pattern determines the preferential export of specific soil
327 fractions (Martínez-Casasnovas et al., 2002; Mohamadi and Kavian, 2015; Meite et al., 2018;
328 Imfeld et al., 2020).



329

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

333

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
343 particle size (Guo et al., 2010; Quenea et al., 2009; Schmidt and Kögel-Knabner, 2002),
344 which may favour MTY and SMET sorption in the silt and clay fractions. In addition, the
345 proportion of particulate organic matter (POM, $>50\ \mu\text{m}$) and mineral-associated organic
346 matter (MOM, $<50\ \mu\text{m}$) 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 clay-

358 organic matter (Kalathoor et al. 2015). The binding mechanism may include hydrogen and
359 ionic bonds between the oxygen-rich metalaxyl residues and the soil humic surface. In
360 addition, nonionic pesticides can sorb onto soil oxides, especially on clay minerals (Clausen et
361 al., 2001; Cornejo et al., 2008; Moyo et al., 2014; Remucal and Ginder-Vogel, 2014). This
362 may explain the slight increase in MTY and SMET in the clay fraction of the crop soil after
363 200 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,
366 respectively. Sterilization by autoclaving affected the distribution of MTY and SMET among
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
369 and increasing the clay fraction (Berns et al., 2008). The lysis of microorganisms and
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*

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

383 experiments (Table 1). Overall, soil type, sterilization and ageing did not significantly ($p>0.1$)
 384 affect MTY and SMET dissipation in soil. For all experiments and based on concentration
 385 decrease, more than 90% of MTY and SMET dissipated within 200 days (Table 1). The large
 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
 388 contribution of MTY and SMT volatilization, dilution, plant uptake, export or
 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

395 **Table 1.** Dissipated fractions of pesticides in nonsterile ($D_{biotic,t}$) and sterile soils ($D_{abiotic,t}$),
 396 along with the extent of biodegradation (B_{diss}) at 200 days.

	Crop			Vineyard		
	D_{biotic} [%] \pm SE	$D_{abiotic}$ [%] \pm SE	B_{diss} [%] \pm SE	D_{biotic} [%] \pm SE	$D_{abiotic}$ [%] \pm SE	B_{diss} [%] \pm SE
MTY	92 \pm 68	96 \pm 23	<72	97 \pm 7	96 \pm 7	<10
SMET	94 \pm 23	95 \pm 4	<23	99 \pm 4	93 \pm 7	<8

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
 400 soils limited sorption-desorption, MTY and SMET bioavailability and microbial activity, thus
 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
 403 dissipation of MTY and SMET (Rodríguez-Liébana and Peña, 2020). It can be hypothesized
 404 that a lower water content enhanced intraparticle diffusion over time through inner soil pores
 405 of more soluble and less hydrophobic pesticides, such as MTY and SMET (solubility >400

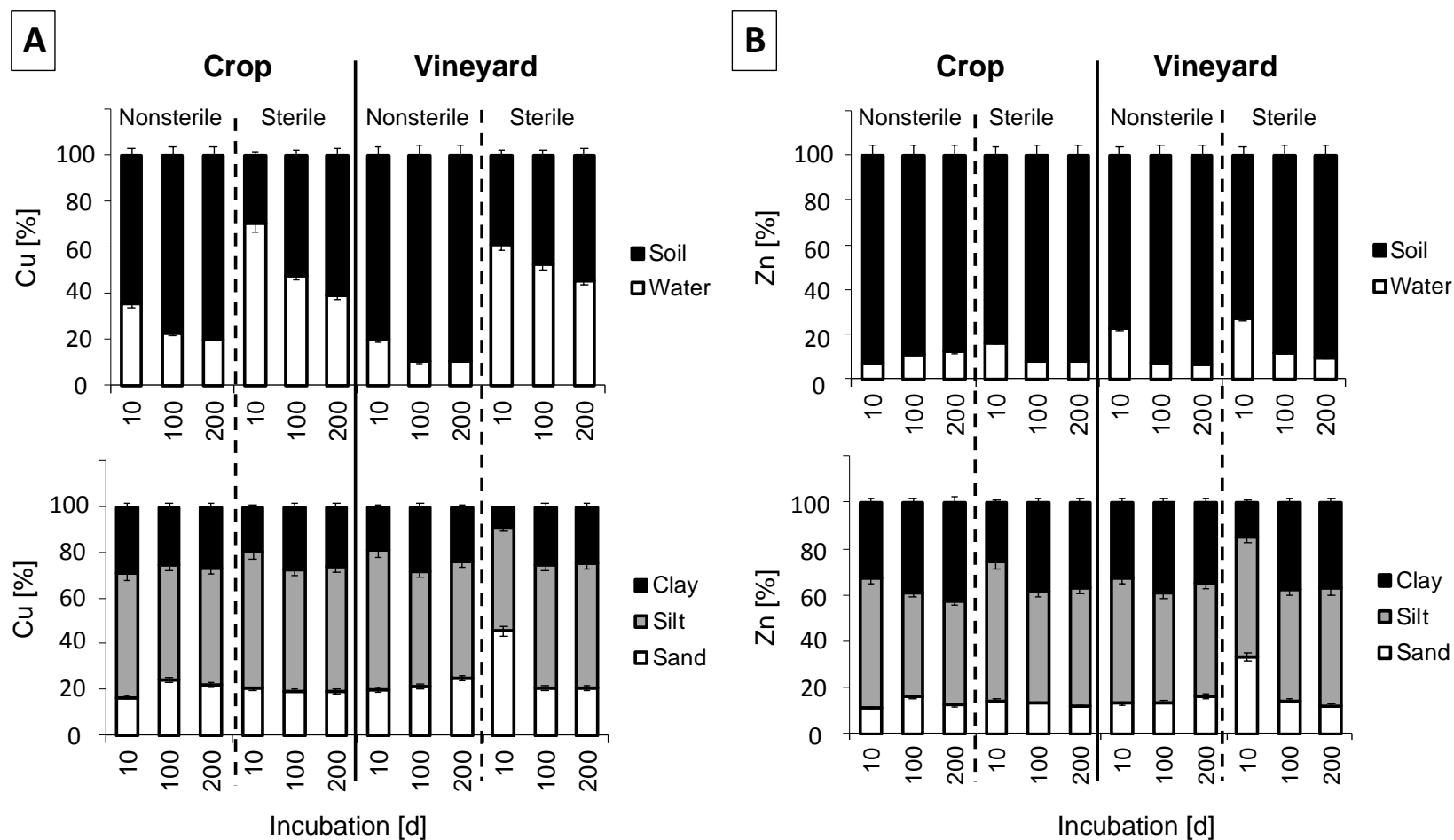
406 mg L⁻¹ and K_{dsoil}<2.5 mL g⁻¹; Table S1). In turn, this reduced MTY and SMET bioavailability
407 and biodegradation while increasing their half-lives in the soil. Sorption was thus the main
408 dissipation process controlling MTY and SMET extraction and dissipation during ageing in
409 soils with 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.

412

413 *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 ± 2%) was three times higher than that of Zn (12 ± 1%) in
417 nonsterile experiments (Figure 2). Partitioning of both Cu and Zn into water only slightly
418 decreased between 10 and 200 days of ageing. Overall, this emphasizes the potential release
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
426 autoclaving, favouring DOM release. In addition, the quality of DOM has profound and
427 different effects on Cu and Zn binding (e.g., Baken et al., 2011). Different DOM qualities
428 among experiments may have resulted in preferential Cu-DOM binding and release compared
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
433 distribution in both crop and vineyard soils followed a silt ($54 \pm 3\%$ of Cu and $51 \pm 3\%$ of Zn)
434 > clay ($24 \pm 1\%$ of Cu and $34 \pm 2\%$ of Zn) > sand pattern ($23 \pm 1\%$ of Cu and $15 \pm 1\%$ of Zn)
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

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

444

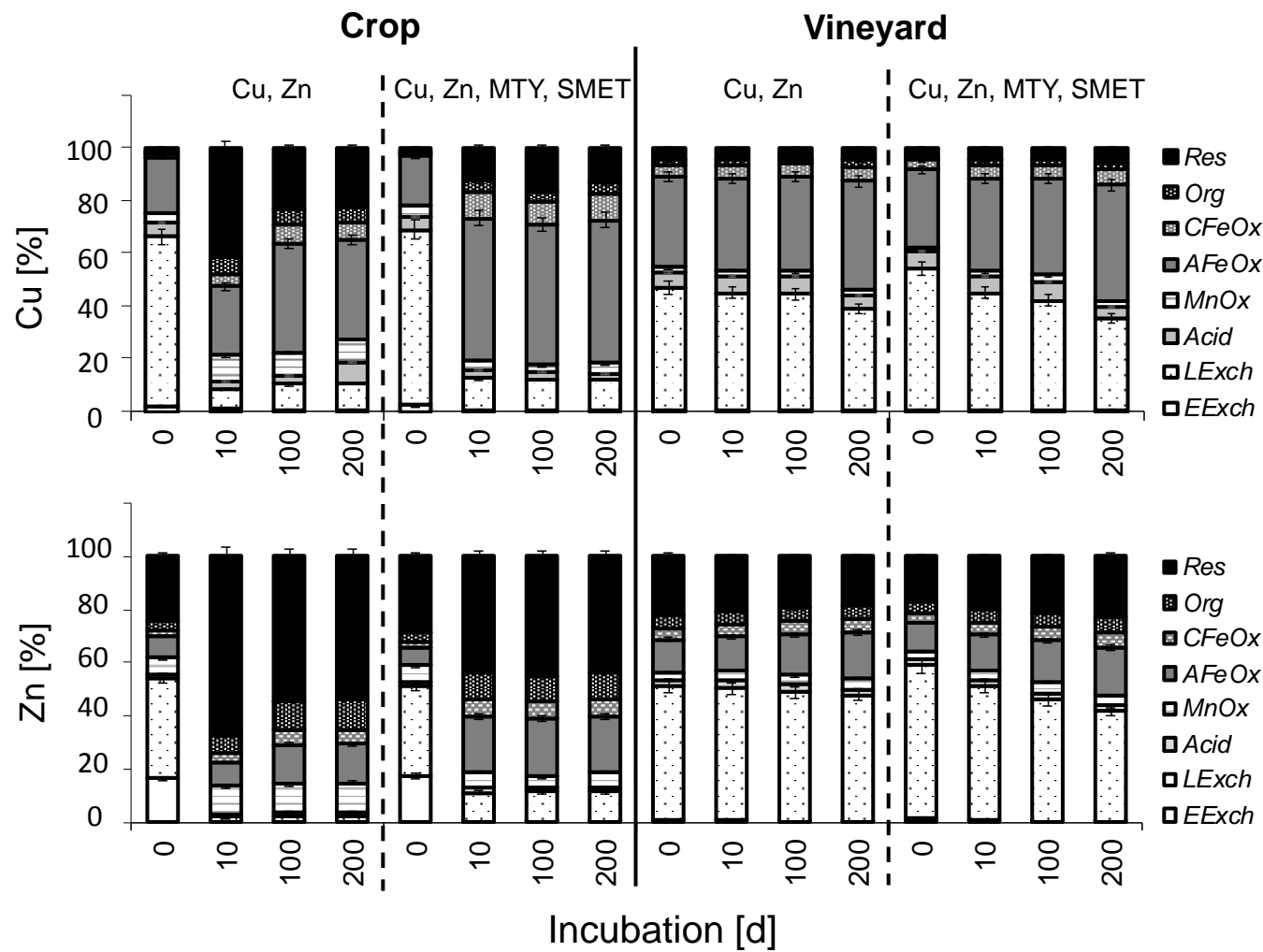
445 3.4. Distribution of Cu and Zn among chemical fractions

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
450 Zn fractions were significantly higher ($p<0.001$), whereas the *Res*-Cu and Zn fractions were
451 lower ($p<0.001$) in the vineyard than in the crop soil. In both soils, Cu and Zn were mainly
452 associated with *LExch* ($\bar{X} \pm SD$ across conditions: $34 \pm 2\%$ for Cu and $32 \pm 2\%$ for Zn),
453 *AFeOx* ($37 \pm 2\%$ for Cu and $15 \pm 1\%$ for Zn) and *Res* fractions ($11 \pm 1\%$ for Cu and $33 \pm 2\%$
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
458 $\text{cmol}^+ \text{kg}^{-1}$, Table S2) compared with crop soil (CEC= $9.1 \text{ cmol}^+ \text{kg}^{-1}$). In the *AFeOx* fraction,
459 Cu and Zn were generally associated with amorphous Fe oxides following coprecipitation,
460 adsorption, surface complex formation, ion exchange and/or penetration into the mineral. In
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-
463 Vogel, 2014; Ruggiero et al., 2002). Higher proportions of both Al_2O_3 and Fe_2O_3 in the crop
464 soil (Table S2) may explain the higher *Res*-Cu and Zn in the crop than in the vineyard soil.

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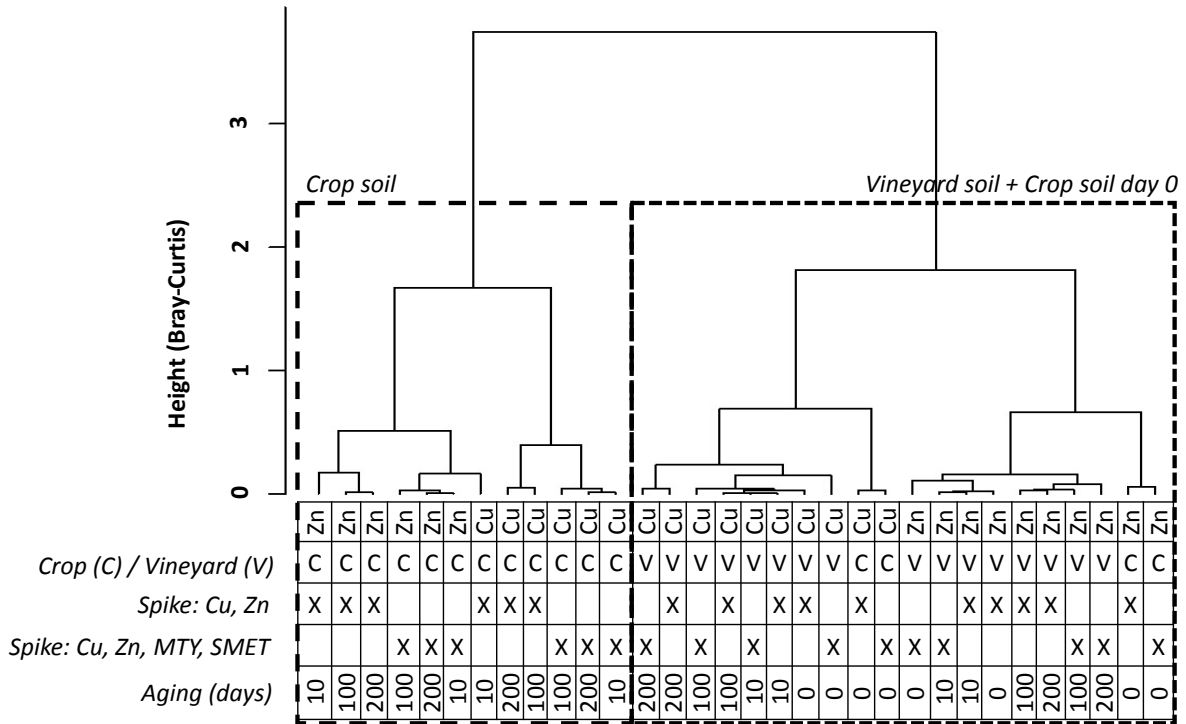
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468

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.



471

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.

476

477 The distribution of Cu and Zn among chemical fractions also varied over time,
 478 especially in the crop soil. For both Cu and Zn, *EExch* and *LExch* fractions and, to a lesser
 479 extent, *Org*- and *CFeOx* fractions significantly differed ($p < 0.05$) between Days 0 and 10 in
 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

486

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

488 The distribution of Cu and Zn among chemical fractions slightly differed in
489 experiments spiked with MTY, MET, Cu and Zn and with Cu and Zn only (Figure 3),
490 particularly in the crop soil between Days 10 and 200 (Figure 4). Concomitant ageing of
491 MTY, MET, Cu and Zn significantly ($p < 0.01$) increased the *LExch* fraction and decreased the
492 *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,
509 thereby modifying the sorption rates. For instance, reductive dissolution of oxides by
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.

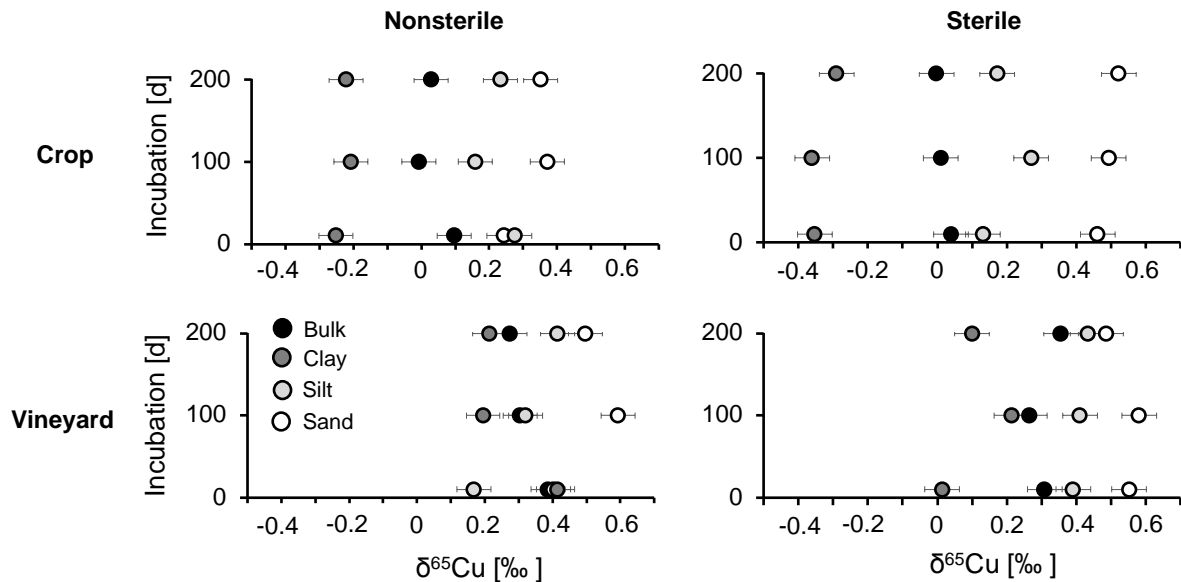
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521 *3.6. Cu and Zn stable isotope fractionation during Cu and Zn ageing in agricultural soils*

522 Stable isotope signatures of Cu ($\delta^{65}\text{Cu}$) and Zn ($\delta^{66}\text{Zn}$) were analysed from Day 10
523 onwards to evaluate the isotope fractionation and associated processes during long-term
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
528 spikes represented >90% and >70% of the initial Cu and Zn mass in soil, respectively. As
529 expected, $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ values of bulk soils on Day 0 (data not shown) did not change
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 $\delta^{65}\text{Cu}$ values differed mainly among soil fractions, particularly in the crop soil
534 experiments ($\Delta\delta^{65}\text{Cu}$ up to 1 ‰), and slightly over time in the clay fraction of the vineyard
535 soil (Figure 5). In contrast, $\delta^{66}\text{Zn}$ values did not vary significantly among soil types,
536 granulometric fractions or over time ($\Delta\delta^{66}\text{Zn}$ <0.4 ‰) (Figure S1). Both binding to organic

537 complexes and sorption to secondary minerals, such as clays and Fe-Mn oxyhydroxides, may
 538 compete to control Cu and Zn behaviour in soils (Grybos et al., 2007) and is certainly key for
 539 isotope fractionation in soil. Nevertheless, different chemical distributions of Cu and Zn
 540 (Figures 3 and 4), and redox transitions in the case of Cu, and specific values of the stability
 541 constant for each complex (Ryan et al., 2014) resulted in distinct Cu and Zn isotope
 542 fractionation in soil. Similar patterns of $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ values in nonsterile and sterile
 543 experiments emphasize that slight differences in the physical and chemical distribution of Cu
 544 and Zn and biotic processes did not significantly affect Cu and Zn stable isotope fractionation.
 545



546
 547 **Figure 5.** $\delta^{65}\text{Cu}$ values in bulk soil and clay, silt and sand fractions of nonsterile and sterile
 548 crop and vineyard soils spiked with Cu, Zn, MTY and SMET. Error bars denote analytical
 549 uncertainty (± 0.05).

550
 551 The difference in $\delta^{65}\text{Cu}$ 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 ^{65}Cu , whereas the silt and sand fractions were enriched in ^{65}Cu 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
557 are in agreement with previous results insofar as Cu sorption to Fe oxides (Balistrieri et al.,
558 2008b) and SOM (Bigalke et al., 2010) is expected to enrich Cu in ^{65}Cu , whereas Cu sorption
559 to clay minerals may deplete Cu in ^{65}Cu (Li et al., 2015b). In particular, the formation of Cu-
560 SOM complexes at pH above 7 may affect $\delta^{65}\text{Cu}$ among soil fractions (Quenea et al., 2009).
561 However, the SOM quality varies in grain-size fractions, with more altered (oxidized) SOM
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
565 higher Cu enrichment in ^{65}Cu in the clay fraction of crop soil. In addition, Cu precipitation in
566 carbonates is also expected to deplete the clay fraction in ^{65}Cu (Maréchal and Sheppard, 2002)
567 in the vineyard soil since CaCO_3 contributed to 27.1% of the soil content (Table S2).
568 However, XRD data showed that carbonate phases prevailed in the silt fraction of the
569 vineyard soil that was enriched in ^{65}Cu , whereas only traces of calcite were found in clays
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
572 the clay fraction in ^{65}Cu .

573 The $\delta^{65}\text{Cu}$ 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 ^{65}Cu from Day 10 to 200 ($\Delta\delta^{65}\text{Cu} = 0.25$

580 ± 0.10 ‰) in nonsterile experiments with vineyard soil, whereas the clay fraction was
581 depleted in ^{65}Cu ($\Delta\delta^{65}\text{Cu} = -0.20 \pm 0.10$ ‰) (Figure 5). Interestingly, the enrichment in ^{65}Cu
582 of the silt fraction mirrored the increasing contribution of the *AFeOx* fraction of nonsterile
583 vineyard soil over time (Figure 3). Since the *AFeOx* fraction involved Cu association with
584 amorphous Fe oxides, it may be inferred that Cu sorption to Fe oxides gradually increased
585 during ageing in the silt fraction of vineyard soil to reach $\delta^{65}\text{Cu}$ typically ranging between
586 0.24 and 0.98 ‰ (Balistrieri et al., 2008a; Pokrovsky et al., 2008).

587

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
603 identify risks associated with pollutant distribution among soil fractions in multiple-
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
607 into Cu isotope fractionation during ageing in soils, emphasizing that $\delta^{65}\text{Cu}$ partly mirrored
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.

612
613

Credit authorship contribution statement

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

618

Declaration of competing interest

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

622

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628

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