



# Influence of glyphosate and aminomethylphosphonic acid on the mobility of trace elements in uncontaminated and contaminated agricultural soils

Nathan Bemelmans<sup>1</sup> · Bryan Arbalestrie<sup>1</sup> · Hélène Dailly<sup>1</sup> · Etienne Bodart<sup>1</sup> · Yannick Agnan<sup>1</sup>

Received: 7 June 2023 / Accepted: 29 August 2023

© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2023

## Abstract

Glyphosate is one of the most widely used herbicides in the world. In addition to its herbicidal effect, glyphosate is a chelating agent that can form complexes with trace elements. Yet, agricultural soils can be contaminated with both organic and mineral substances, questioning the possible influence of glyphosate application on the trace element mobility. In this context, we specifically studied the extractability of trace elements in uncontaminated and metal-contaminated agricultural soils by adding glyphosate, formulated glyphosate, and aminomethylphosphonic acid (AMPA, a degradation product of glyphosate) in batch experiments from 0 to 100 mg L<sup>-1</sup>. Results showed that, on average, glyphosate enhanced the extractability of the elements considered (e.g., As, Cd, Cu, Pb, and Zn) at 20 and 100 mg L<sup>-1</sup>. Surprisingly, the uncontaminated soil highlighted the highest influence of glyphosate compared to the contaminated ones, likely resulting from a higher natural element extractability in the contaminated soils. Although formulated glyphosate presented an overall higher impact than unformulated glyphosate, it was evidenced that AMPA showed lower influence meaning that glyphosate degradation is beneficial to limit deleterious effects.

**Keywords** Glyphosate · AMPA · Trace elements · Mobility · Agricultural soil · Contamination

## Introduction

Glyphosate (N-(phosphonomethyl)glycine), a non-selective post-emergence organophosphorus herbicide that inhibits the biosynthesis of the aromatic amino acids (Plé et al. 2002), is widely used in agriculture. The commercial glyphosate-based products include additional molecules (also called co-formulants) to enhance the herbicide role of the active substance (e.g., by facilitating penetration through the cuticle; Leaper and Holloway 2000). Unfortunately, the composition of these glyphosate co-formulants are usually unknown due to commercial confidentiality (Mesnage et al. 2019). The common glyphosate concentration in the commercial formulated products is 360 g L<sup>-1</sup>, then diluted by the farmer for field application. The maximum authorized application of glyphosate

depends on both culture and country: for example, in Belgium, it reaches up to 6 L ha<sup>-1</sup> of 360 g L<sup>-1</sup> glyphosate solution (i.e., 2160 g ha<sup>-1</sup>; Phytoweb 2015).

With a theoretical half-life of 16 days (Lewis et al. 2016), glyphosate is considered to be non-persistent in soil. The degradation rate, however, varies according to environmental conditions, such as climate (moisture and temperature), soil microbial activity, soil organic matter (Alletto et al. 2010; Bento et al. 2016), or even formulation (Wilms et al. 2023). Its main degradation product is aminomethylphosphonic acid (AMPA) with a similar chemical structure. AMPA, however, is more persistent in soil with a typical half-life that is ranging widely from 23 to 958 days (Bento et al. 2016; Lewis et al. 2016; Bergström et al. 2011). Due to the widespread use of glyphosate, both glyphosate and AMPA are largely present as pesticide residues in agricultural soils (Silva et al. 2019). In soil, these molecules can interact with soil constituents. Indeed, with its three acid functions (phosphonate, carboxylic, and amino; pKa of 2.6, 5.6, and 10.6, respectively; Sprankle et al. 1975), glyphosate has three negative and one positive charges in most

Responsible Editor: Kitae Baek

✉ Yannick Agnan  
yannick.agnan@biogeoscience.eu

<sup>1</sup> Earth and Life Institute, Université catholique de Louvain, Louvain-La-Neuve 1348, Belgium

agricultural soils. This allows binding with ions, such as metals, and form complexes.

Trace elements are mineral elements present in low concentrations in the Earth's crust ( $< 1\%$ ), including various metals (e.g., Cd, Cu, Zn) and metalloids (e.g., As, Sb) with specific behaviours in the environment (i.e., volatility, solubility, interaction with organic compounds). The occurrence and chemical forms of trace elements in soil depend on the parent material, pedogenesis, and anthropogenic inputs (Adriano 2001). Indeed, trace elements may be brought to soils by fertilizers, exogenous organic matter (e.g., manure, compost, sludge), metal-based pesticides (e.g., Bordeaux mixture), and atmospheric deposition (Belon et al. 2012; He et al. 2005). Despite the metabolic roles played by some elements, all trace elements are toxic for human and environmental health at concentrations exceeding the threshold value. Leaching to the hydrosystem and uptake by plants constitute the two major pathways for human exposure through water and food consumption, respectively (Adriano 2001; Barati et al. 2010; El-Kady and Abdel-Wahhab 2018). Understanding the trace element fate and parameters that control their transfer is thus required for health assessment.

As a chelating agent, glyphosate applied in agricultural soils can modify the trace element mobility, as already observed for major elements, such as Mg, impacting the soil fertility and the crop nutrition (Cakmak et al. 2009; Kaur et al. 2017). Consequently, there is a concern about the potential environmental impact of glyphosate application, particularly in metal-contaminated agricultural soils. Increasing mobility from soil (or mineral surfaces) to solution have already been evidenced for As, Cd, Cu, Ni, Pb, and Zn after adding glyphosate (Barrett and McBride 2006; Divisekara et al. 2018; Morillo et al. 2002; Si et al. 2013) and could promote either the transfer to the plant by increasing the trace element availability (and thus a potential plant contamination), or the transfer to the hydrosystem (and thus a potential groundwater contamination). However different methodologies were used, especially with unrealistic high glyphosate concentration, making comparison difficult. Moreover, no information is available for some exclusively toxic elements (e.g., Sb and Cr). While glyphosate can enhance the mobility of trace elements, those elements also influence the glyphosate adsorption on soil by the formation of cationic bridges (Dousset et al. 2007; Morillo et al. 2000).

In this study, we aimed to assess the influence of glyphosate concentration (0, 20, and 100 mg L<sup>-1</sup> of glyphosate) and substance (unformulated glyphosate, formulated glyphosate, and AMPA at 100 mg L<sup>-1</sup>) on the mobility of trace elements from contrasted soils to soil solution in batch experiment. For that purpose, we measured a set of 15 trace element concentrations after an extraction experiment and considering one uncontaminated and three distinct metal-contaminated agricultural soils collected in Wallonia, Belgium.

## Materials and methods

### Study area

Four agricultural soils were collected in Wallonia, Belgium: an uncontaminated soil from Vieuxart, Walloon Brabant, two anthropogenically metal-contaminated soils from Sainte-Walburge and Bressoux (moderately and highly contaminated, respectively) in the province of Liège, and a naturally enriched soil from Aubange in Belgian Luxembourg. The Vieuxart soil (50.6799°N; 4.6357°E) is a silty soil developed on Quaternary loess characterized by slightly acidic conditions (pH<sub>H2O</sub> = 6.5), low total carbon content (1.25%), and a CEC of 11.1 cmol<sub>c</sub> kg<sup>-1</sup> (Table 1). The Sainte-Walburge soil (50.6644°N; 5.5887°E) is a silty soil developed on flint and chalk from the Mastrichtian (Gulpen formation). The soil was collected at the slag heap foothill and contained a non-neglectable load of coal extraction debris resulting in a higher total carbon content (11.1%) and soil pH (pH<sub>H2O</sub> = 7.8; Table 1). The CEC, however, was slightly higher than at Vieuxart (15.2 cmol<sub>c</sub> kg<sup>-1</sup>). The Bressoux soil (50.6374°N; 5.6109°E) is a silty with a slight stony load formed of Miocene alluvium. The soil was characterized by inputs of faience debris and industrial residues and presented a total carbon content of 15.8%, a soil pH<sub>H2O</sub> of 7.0, and a CEC of 26.9 cmol<sub>c</sub> kg<sup>-1</sup> (Table 1). Due to the industrial history of this region of the city of Liège (mostly steel industry and coal extraction), both Sainte-Walburge and Bressoux were influenced by atmospheric deposition of metal contaminants impacting their total trace element content from Sainte-Walburge (moderately contaminated soil) to Bressoux (highly contaminated soil; Table 1). Finally, the Aubange soil (49.5765°N; 5.7684°E) is a silty soil with moderate stony load developed on the Aubange formation, a complex of sandstone, siltstone, and argillite dating from the Toarcien with high naturally enriched trace element content, such as As, Ni, and Cr (Table 1; Vandeuren et al. 2023). The soil was characterized by a pH<sub>H2O</sub> of 7.3, a total carbon content of 2.43%, and a CEC of 20.8 cmol<sub>c</sub> kg<sup>-1</sup> (Table 1).

### Soil sampling and characterization

#### Soil sampling and sample preparation

On each study site, we collected the top 30 cm soil using a shovel to perform a homogeneous composite sample. The soil samples were then air-dried at 25 °C temperature for 15 days and sieved through a 2-mm mesh. An aliquot was crushed for trace element analyses using a soil grinder

**Table 1** Summary table of the soil properties and total trace element content of the four study agricultural soils in Wallonia, Belgium

	Vieusart	Sainte-Walburge	Bressoux	Aubange
Soil properties				
pH <sub>H2O</sub>	6.4	7.8	7	7.3
Total carbon content (%)	1.25	11.1	15.8	2.43
CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	11.1	15.2	26.9	20.8
Trace element content (mg kg <sup>-1</sup> )				
As	7.59	14.9	35.6	147
Ba	261	346	422	197
Cd	0.269	1.87	6.92	0.433
Co	7.75	23.4	42.7	63.9
Cr	48.4	66.0	79.9	129
Cu	11.9	72.7	263	15.2
Mn	283	462	1080	9080
Mo	0.710	2.12	4.40	6.34
Ni	14.8	41.9	73.1	124
Pb	20.1	142	623	67.7
Sb	0.622	3.35	12.5	1.01
Sn	1.14	12.8	59.9	1.68
Ti	1680	2540	996	259
V	52.2	84.5	115	403
Zn	44.1	353	1350	237

(Vibratory Disc Mill RS 200, Retsch, Haan, Germany). Basic soil characterization included soil pH<sub>H2O</sub> (using a 1:5 ratio), total carbon content (Elementar vario EL cube, Langensfeld, Germany), and CEC (Metson method with ammonium acetate at pH 7). Due to the absence of carbonates, total carbon content can be assumed as organic carbon content.

#### Trace element concentration quantification

Before quantification of trace element concentrations, 100 mg of ground soil samples were digested in an ISO 6 cleanroom (Earth and Life Institute, UCLouvain) in a Teflon bottle (Savillex). We applied a four-step procedure (HNO<sub>3</sub>/HF, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>/HCl, and HNO<sub>3</sub>) using suprapure chemicals and high purity Milli-Q water (Arbalestrie et al. 2022). Heating steps were fixed at 90 °C and evaporation steps at 40 °C. The samples were preserved in 2% HNO<sub>3</sub> solutions before analysis.

For all samples, a set of 15 trace elements (As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Sn, Ti, V, and Zn) was quantified in the MOCA platform (Mineral and Organic Chemical Analysis, Earth and Life Institute, UCLouvain) using an ICP–MS (iCAP Q ICP–MS, Thermo Fischer Scientific, Waltham, MA, USA). An internal standard (Ru, In, and Re) was used in each sample for drift instrumental correction. The performance of the procedure was evaluated using two certified soil material (GSS1 and GSS4; Xuejing et al. 1985) in each series. The average recovery

( $C_{\text{measured}}/C_{\text{certified}} \times 100$ ) was estimated to  $100 \pm 15\%$  for all analytes, except for Cd (117%), Sb (121%), Mn (78%), Ti (75%), and Ba (70%). Limits of detection were estimated to  $< 0.01 \mu\text{g kg}^{-1}$ , except for Ti, Ni, and Zn ( $< 0.1 \mu\text{g kg}^{-1}$ ) and for Mo ( $< 1 \mu\text{g kg}^{-1}$ ).

#### Experimental procedure

##### Trace element extraction procedure

To test the influence of both glyphosate concentrations and substances on the soil trace element mobility, four extraction solutions were considered: Milli-Q water (control), glyphosate (*Sigma Aldrich*) at 20 and 100 mg L<sup>-1</sup> (corresponding to 0.12 and 0.59 mmol L<sup>-1</sup>, respectively), formulated glyphosate (*Glyfall plus*) 100 mg L<sup>-1</sup> (corresponding to 0.59 mmol L<sup>-1</sup>), and AMPA (*Sigma Aldrich*) at 100 mg L<sup>-1</sup> (corresponding to 0.90 mmol L<sup>-1</sup>). These concentrations were in the range of concentrations tested in the literature (Wang et al. 2008; Si et al. 2013). Trace element concentrations in the extraction solutions were negligible. Extractions were performed in triplicate in a 50-mL centrifuge polypropylene tubes with 5 g of sieved soil and 25 mL of extraction solution, i.e., 1:5 ratio, adapted from Divisekara et al. (2018). The mixture was then agitated in the dark for 2 h at 150 bpm. After agitation, the tubes were centrifuged for 25 min at 4000 rpm and filtrated using a 0.45- $\mu\text{m}$  pore size Nylon *Acrodisc*®. All extraction solutions have been prepared using Milli-Q water. An aliquot of 1 mL of the

filtered solution was diluted 10 times and acidified (2%  $\text{HNO}_3$ ) for trace element analysis, while another aliquot of 10 mL was used for pH measurement and glyphosate and AMPA analysis.

## Chemical analyses

Trace element concentrations were measured by ICP-MS as described for soil sample analysis. In each series, the quality was checked using the river water SLRS 6 reference material that presented an average recovery of  $100 \pm 15\%$ , except for Zn (83%), Cd (60%), and Pb (133%). The concentration of all considered elements were always above the quantification limit.

For glyphosate and AMPA analysis, the solution samples were diluted to reach the range of the analytical method (1 to  $20 \mu\text{g L}^{-1}$ ) adapted from ISO 21458 and ISO 116308. Glyphosate and AMPA were derivatized at pH 9 (borate buffer) by an excess of FMOC-Cl. Glyphosate and AMPA were measured by HPLC (1200 series, Agilent Technologies Santa Clara, CA, USA) with a Merck Lichrocart C18  $150 \times 4.6 \text{ mm} - 5 \mu\text{m}$  column kept at  $35^\circ\text{C}$ . Elutants were pH 7 10 mM phosphate buffer (A) and 45:45:10 acetonitrile:methanol:Milli-Q water solution (B). Elution was performed at a flow rate of  $1 \text{ mL min}^{-1}$  using the following gradient (expressed as solvent B): from 0 to 1 min, 25% B (initial composition); from 10 to 15 min, 100% B; from 17 to 22 min, 25% B. The detection was performed by a fluorescent detector with an excitation at 260 nm and an emission at 310 nm.

## Data processing and statistical analyses

Measured trace element concentrations in the extraction solution were expressed as soil extractability (i.e., masse of extracted element by mass of soil) and soil extractability potential (i.e., mass of extracted element by mass of element in soil). Statistical analyses were performed using R 4.0.2 and RStudio 2023.06.1. Statistical comparisons between glyphosate concentrations (0, 20, and  $100 \text{ mg L}^{-1}$ ) or tested substances (unformulated glyphosate, formulated glyphosate, and AMPA at  $100 \text{ mg L}^{-1}$ ) were performed using a Kruskal–Wallis test and a post-hoc Dunn tests including the Bonferroni adjustment (*rstatix* library).

## Results

### Trace element extractability in uncontaminated agricultural soil

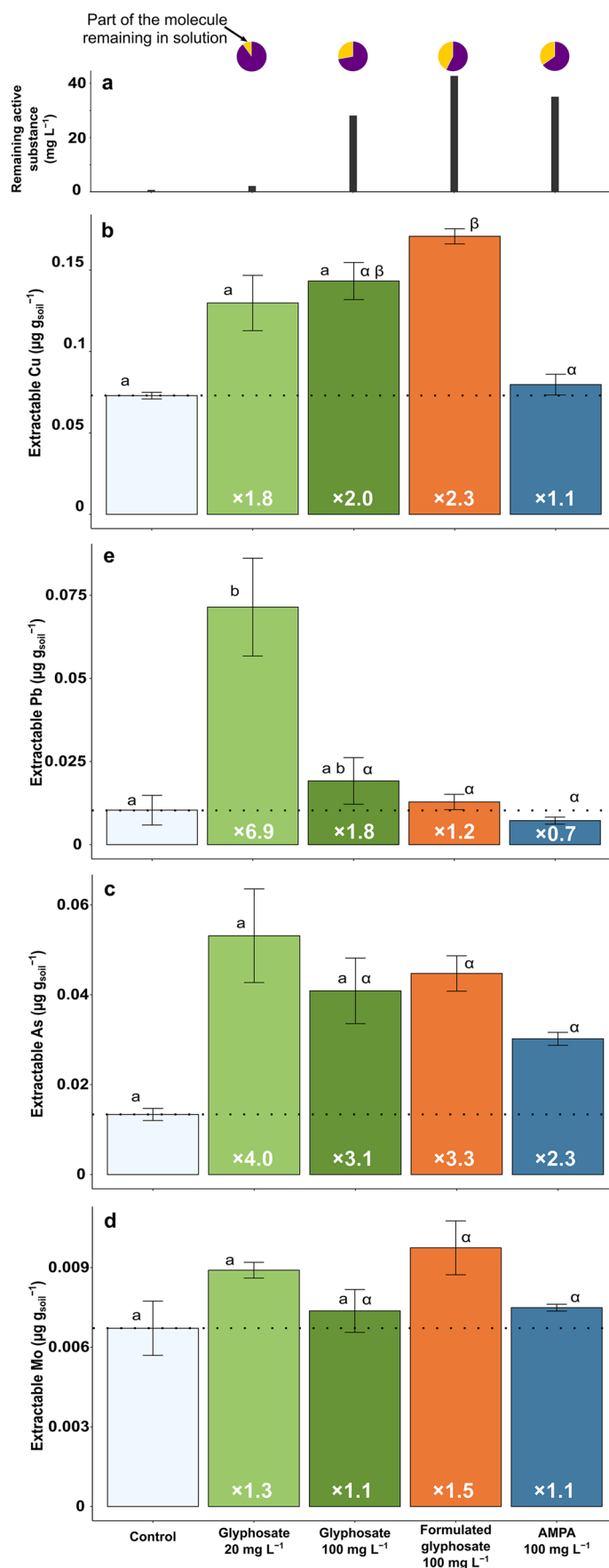
Trace element content in the uncontaminated soil (i.e., Vieuxart) was in the range of the European agricultural soils

(Table 1; Baize 2000). We first investigated the extractability of four trace elements as contrasted examples: Cu, As, Mo, and Pb (Fig. 1B–E). The element water-extractability (i.e., control modality) was ranged in the following order: Mo ( $0.007 \mu\text{g g}_{\text{soil}}^{-1}$ ) < As  $\leq$  Pb < Cu ( $0.75 \mu\text{g g}_{\text{soil}}^{-1}$ ). Results showed an overall increase of element extractability with both concentrations of glyphosate (20 and  $100 \text{ mg L}^{-1}$ ) compared to the control, on average 3.5 and 2.0 times higher, respectively, and up to 6.9 times for Pb with  $20 \text{ mg L}^{-1}$  of glyphosate. We highlighted an increase from  $0.0014$  to  $0.22 \mu\text{mol L}^{-1}$  for Mo and Cu, respectively, with an addition of  $0.59 \text{ mmol L}^{-1}$  of glyphosate (i.e.,  $100 \text{ mg L}^{-1}$ ), representing an elements/glyphosate molar ratio of 0.05% (considering the four trace elements: Cu, As, Mo, and Pb). Note that only Pb with  $20 \text{ mg L}^{-1}$  of glyphosate showed a statistically significantly higher concentration than the control ( $p < 0.05$ ). Interestingly, the intermediate glyphosate concentration (i.e.,  $20 \text{ mg L}^{-1}$ ) sometimes reached higher tested modality/control extractability ratio than for  $100 \text{ mg L}^{-1}$  (e.g., for As, Mo, and Pb). Only Mo showed low or a lack of effect, with 1.1 to 1.3 times higher extractability than the control according to the glyphosate concentration. For formulated glyphosate, the results were similar to unformulated glyphosate with only positive effect compared to the control in the following order: Pb ( $\times 1.2$ ) < Mo < Cu < As ( $\times 3.3$ ). The tested modality/control extractability ratios were either higher (for Cu and Mo) or lower (for Pb) compared to glyphosate (Fig. 1). Finally, the influence of AMPA on the extractability of trace elements was more heterogeneous depending on the element considered, including positive effect for As ( $\times 2.3$ ), negative effect for Pb ( $\times 0.7$ ), and no effect for Cu and Mo ( $\times 1.1$ ).

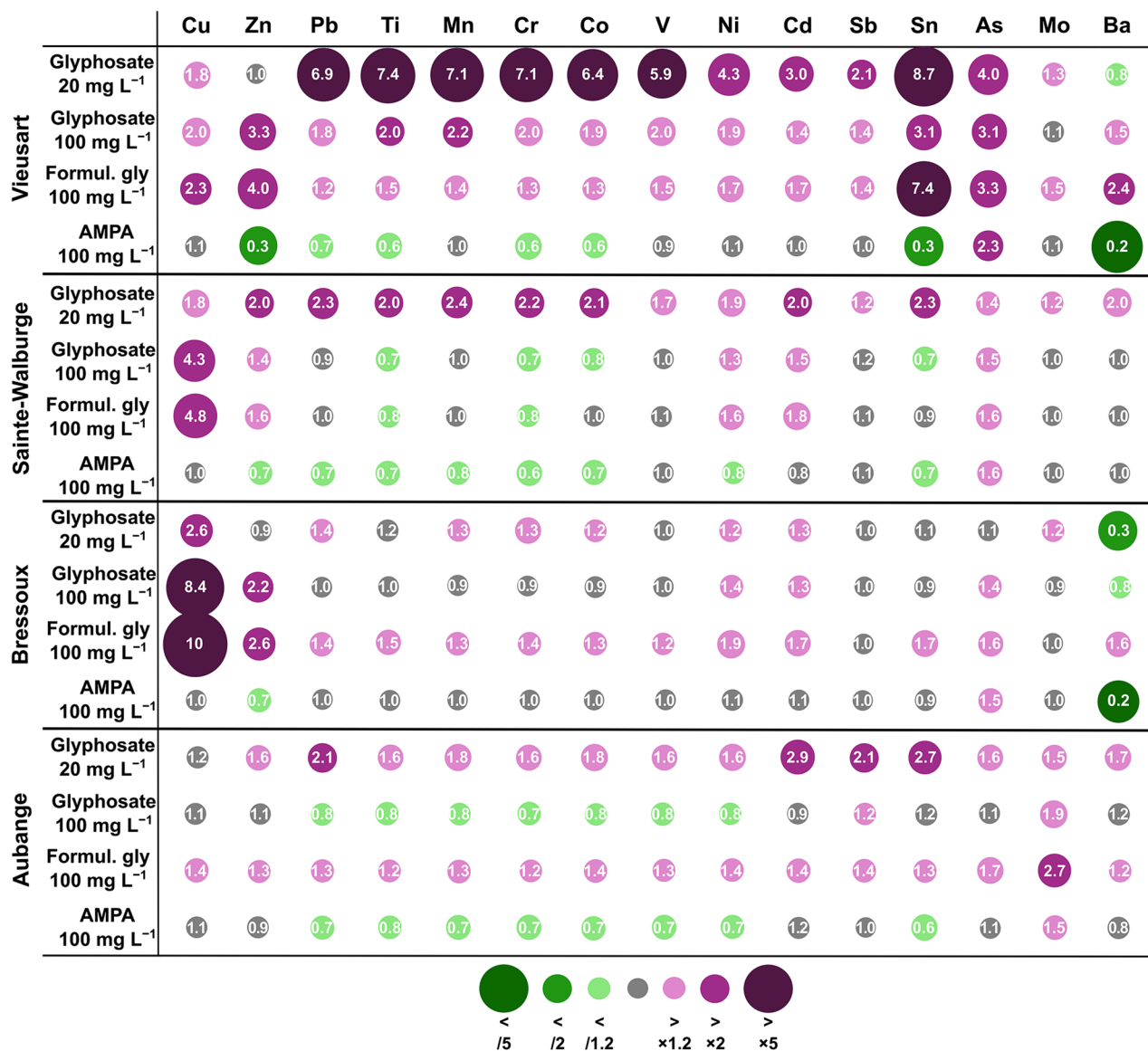
For > 70% of the considered element-modality combination, the extractability was also enhanced (i.e., modality/control extractability ratio > 1.2, and up to 8.7 for Sn; Fig. 2). Titanium, V, Cr, Mn, Co, and Ni also presented a similar behaviour as Pb with higher extractability with  $20 \text{ mg L}^{-1}$  of glyphosate than with  $100 \text{ mg L}^{-1}$ . Comparing the tested substances with the unformulated glyphosate, results were similar as the four previously mentioned elements: formulated glyphosate with slightly lower extractability and AMPA with almost no extractability effect, despite no statistically significant differences. Copper and Zn, however, showed higher extractability with: (1)  $100 \text{ mg L}^{-1}$  of glyphosate compared to  $20 \text{ mg L}^{-1}$ , and (2) formulated glyphosate compared to unformulated one at  $100 \text{ mg L}^{-1}$ . Finally, with  $100 \text{ mg L}^{-1}$  of AMPA, Zn, Sn, and Ba presented the maximum extractability decrease compared to the control (at least 3 times).

The molecule concentrations were measured in the post-extraction solution (Fig. 1A). Results indicated a minor part of glyphosate used for the experiment that remained in solution, from 10 (with  $20 \text{ mg L}^{-1}$  of glyphosate) to 28% (with  $100 \text{ mg L}^{-1}$  of glyphosate). This part, however, increased

**Fig. 1** Concentrations (lines) and proportion (pie charts) of molecule remaining in solution after extraction ( $n=3$ ; **a**) and extractability ( $n=3$ ) of Cu (**b**), As (**c**), Mo (**d**), and Pb (**e**) in the uncontaminated soil (Vieusart) following four extraction modalities: control (Milli-Q water), glyphosate (20 and 100 mg L<sup>-1</sup>), formulated glyphosate (100 mg L<sup>-1</sup>), and AMPA (100 mg L<sup>-1</sup>). Numbers indicate the tested modality/control extractability ratios (the dashed line represents the control value). The Latin and Greek letters on the top of the bars represent the statistically significant differences (Kruskal–Wallis test and Dunn test with Bonferroni adjustment) for concentrations and substances, respectively







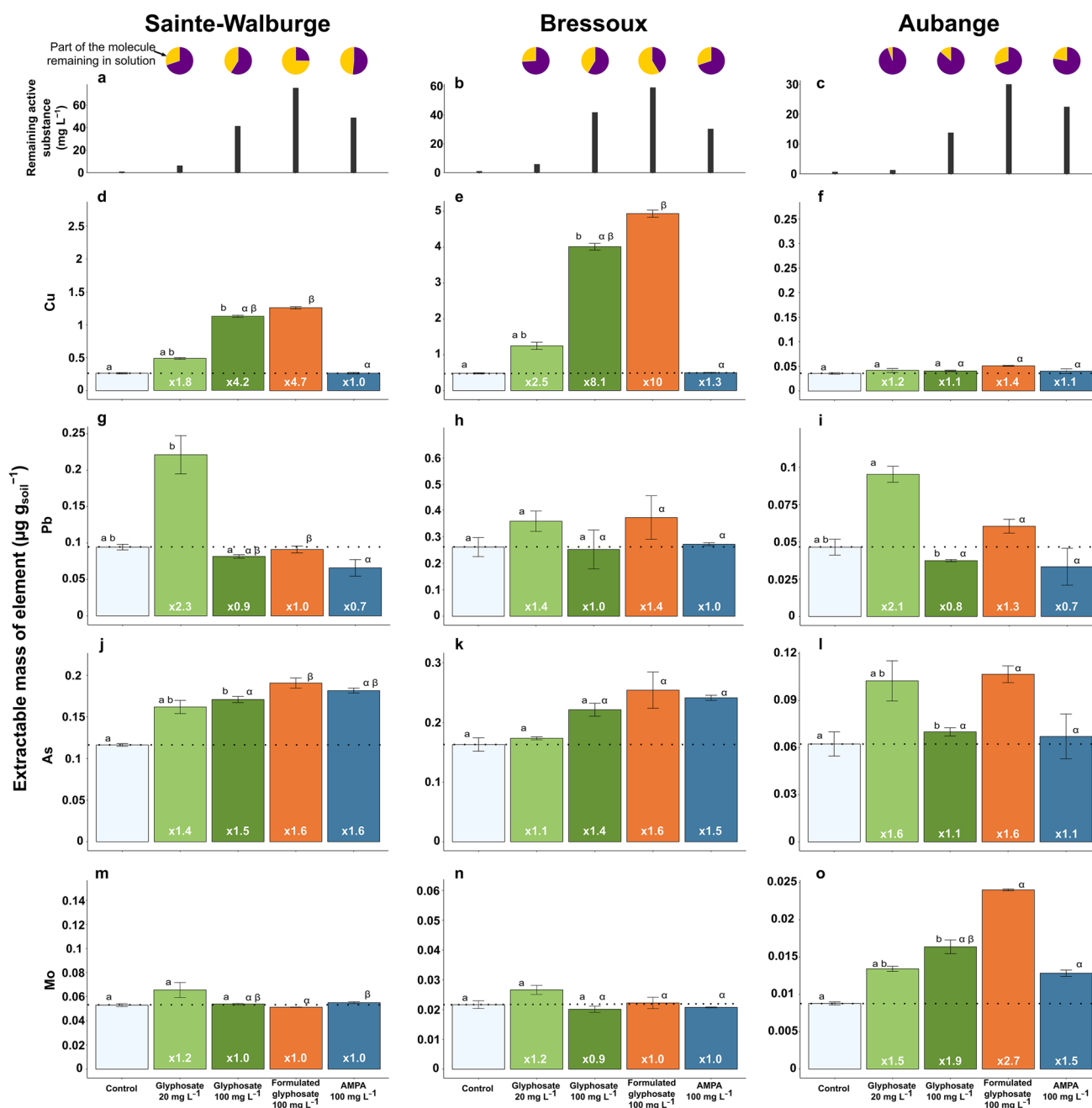
**Fig. 2** Summary of tested modality/control extractability ratios ( $n=3$ ) for each studied element in the uncontaminated (Vieusart) and the three contaminated (Sainte-Walburge, Bressoux, and Aubange) soils.

Colours represent the range of positive (purple) or negative (green) influence compared to the control

to 42% when 100 mg L<sup>-1</sup> of formulated glyphosate was added. For the same mass concentration of AMPA (i.e., 100 mg L<sup>-1</sup>), the molecule remaining in solution reached 35%, in-between glyphosate and formulated glyphosate. Note that AMPA in the post-extraction solutions was below detection limit for all unformulated and formulated glyphosate modalities. The average pH values in the post-extraction solutions were ranged from 6.4 to 7.0, representing a decrease from the pH of the control ranging between 0 (for 20 mg L<sup>-1</sup> of glyphosate) and 0.57 (for 100 mg L<sup>-1</sup> of formulated glyphosate) pH unit.

### Trace element extractability in contaminated agricultural soils

A similar experiment was performed for the two anthropogenically contaminated (Sainte-Walburge and Bressoux) and one naturally enriched (Aubange) soils (Fig. 3). These three soils indicated elevated trace element content compared to European agricultural soils (Table 1; Baize 2000). The element water-extractability was ranged from Cd in Aubange (0.22 ng g<sub>soil</sub><sup>-1</sup>) to Mn in Aubange (3.8 µg g<sub>soil</sub><sup>-1</sup>), i.e., on average 5.5 times higher than for the uncontaminated



**Fig. 3** Concentrations (lines) and proportion (pie charts) of molecule remaining in solution after extraction ( $n=3$ ; a) and extractability ( $n=3$ ) of Cu (d, e, f), Pb (g, h, i), As (j, k, l), and Mo (m, n, o) in the three contaminated soils (Sainte-Walburge, Bressoux, and Aubange) following four extraction modalities: control (Milli-Q water), glyphosate (20 and 100 mg L<sup>-1</sup>), formulated glyphosate

(100 mg L<sup>-1</sup>), and AMPA (100 mg L<sup>-1</sup>). Numbers indicate the tested modality/control extractability ratios (the dashed line represents the control value). The Latin and Greek letters on the top of the bars represent the statistically significant differences (Kruskal–Wallis test and Dunn test with Bonferroni adjustment) for concentrations and substances, respectively

soil. Overall, the tested modality/control extractability ratios for the four selected trace elements were between 0.7 (for Pb with 100 mg L<sup>-1</sup> of AMPA at Sainte-Walburge and Aubange) and 10 (for Cu with 100 mg L<sup>-1</sup> of formulated glyphosate at Bressoux). This highlighted a higher heterogeneity compared to the uncontaminated soil. We

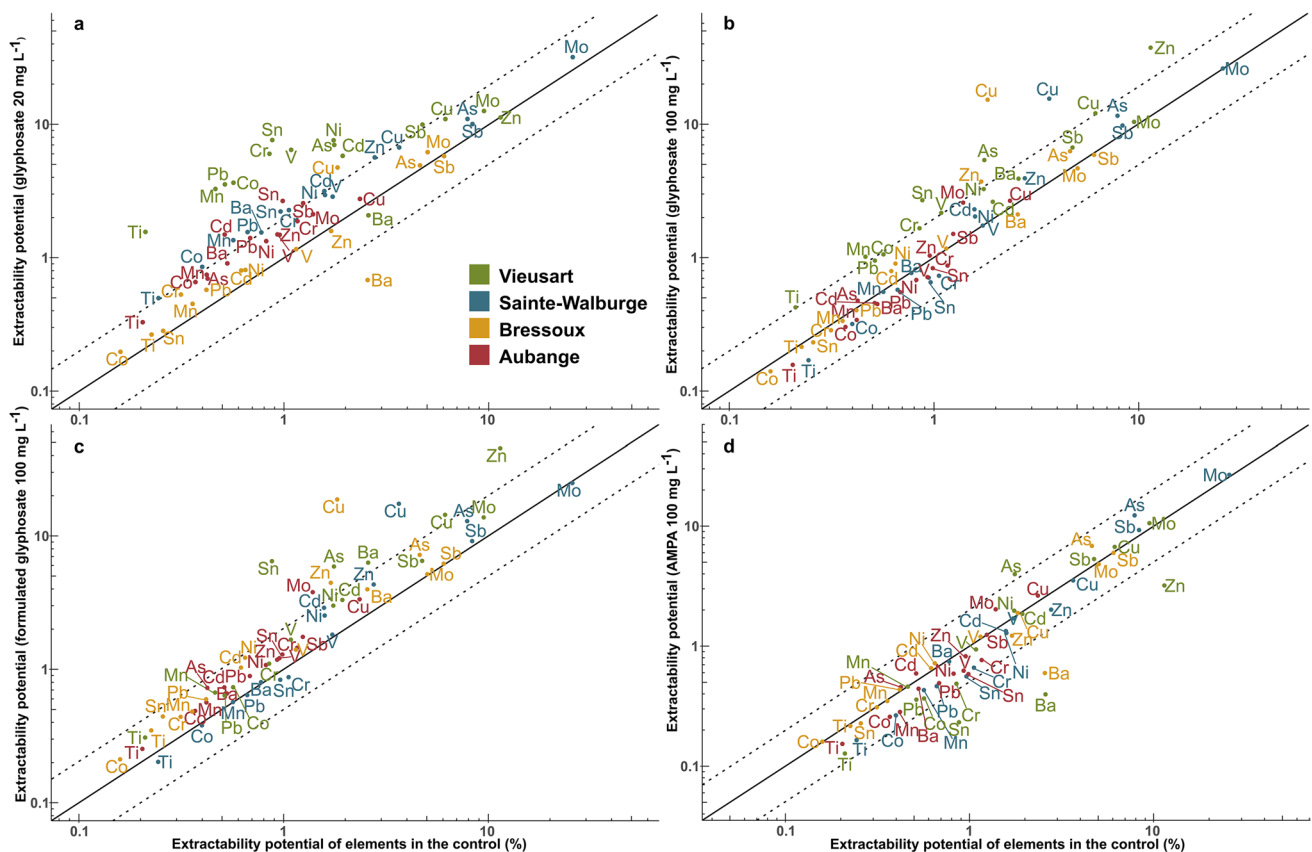
also compared these four trace elements with the glyphosate: according to the soil considered, molar concentration increased from 0.0019–0.0016 to 0.015–11.1  $\mu\text{mol L}^{-1}$  for Mo and Cu, respectively, with an addition of 0.59 mmol L<sup>-1</sup> of glyphosate (i.e., 100 mg L<sup>-1</sup>), representing an elements/glyphosate molar ratio of 0.5–1.9 for the anthropogenically

contaminated and 0.009% for the naturally enriched soils (considering Cu, As, Mo, and Pb). Except for Pb with 20 mg L<sup>-1</sup> of glyphosate, both anthropogenically contaminated soils presented similar patterns between modalities and elements (including comparable extractability ratios for Mo and As), and dissimilar to Aubange. For glyphosate, the extractability was either enhanced or similar compared to the control depending on the tested concentrations. The highest influence was observed for Cu with 100 mg L<sup>-1</sup> of glyphosate at Bressoux and, to a lesser extent, Sainte-Walburgue ( $p < 0.05$ ), while the naturally enriched soil generally showed lower effects ( $p > 0.05$ ). As for the uncontaminated soil, the effect can be evidenced from 100 mg L<sup>-1</sup> of glyphosate (e.g., Cu at Bressoux,  $p < 0.05$ ) or from 20 mg L<sup>-1</sup> of glyphosate (e.g., As at Aubange,  $p < 0.05$ ). Surprisingly, the extractability was increased for some trace elements with 20 mg L<sup>-1</sup> of glyphosate without effect observed with 100 mg L<sup>-1</sup> of glyphosate: case for Zn in Sainte-Walburgue or As in Aubange ( $p < 0.05$ ).

The four selected trace elements presented frequently a positive effect with 100 mg L<sup>-1</sup> of formulated glyphosate. The tested modality/control extractability ratios were similar

or higher than for unformulated glyphosate (statistically significant differences for As in Sainte-Walburgue and Cd in Aubange compared to the control,  $p < 0.05$ ). The influence of AMPA on trace element extractability was generally lower (on average, from  $\times 0.7$  to  $\times 1.6$  depending on the selected elements and the considered site), with no effect for half of the presented results ( $p > 0.05$ ). As for the uncontaminated soil, Pb also highlighted lower extractability than the control (with the exception of Bressoux).

Similar groups of elements defined in the uncontaminated soil were also observed in the contaminated ones (Fig. 2): e.g., Ti, V, Cr, Mn, and Co behaved like Pb, with higher extractability with 20 mg L<sup>-1</sup> of glyphosate than 100 mg L<sup>-1</sup>. The overall effect of glyphosate, however, was lower in contaminated soils and formulated glyphosate showed higher influence compared to glyphosate (except for Sainte-Walburgue). Also, Cu and Zn behave similarly in regard to glyphosate with some exceptions in Sainte-Walburgue (Zn more extracted with 20 mg L<sup>-1</sup> of glyphosate compared to 100 mg L<sup>-1</sup>, as observed for Cd). AMPA generally presented no effect (for 24 cases) or negative influence (for 17 cases) on element extractability compared to



**Fig. 4** Extractability potential of trace elements of each tested modalities compared to extractability potential in the control ( $n=3$ ): glyphosate 20 mg L<sup>-1</sup> (a), glyphosate 100 mg L<sup>-1</sup> (b), formulated

glyphosate 100 mg L<sup>-1</sup> (c), and AMPA 100 mg L<sup>-1</sup> (d). The solid line represents the 1:1 ratio, and the dashed lines represent the 2:1 ratio (upper line) and 1:2 ratio (lower line)



the control. However, differences appeared among contaminated soils: the negative influence was observed in Sainte-Walburge and Aubange, but not in Bressoux (except for Ba and to a lesser extent Zn).

Results of the molecule remaining in the post-extraction solution indicated the same trend in the three contaminated soils: increasing proportion of active substance with increasing glyphosate concentration (on average,  $\times 1.7$  from 20 to 100 mg L<sup>-1</sup>), higher proportion with formulated glyphosate than unformulated glyphosate, and intermediate proportion with AMPA (Fig. 3). The naturally enriched soil, however, showed on average 3.2 times less glyphosate remaining in solution with 100 mg L<sup>-1</sup> compared to both Sainte-Walburge and Bressoux. As observed for the uncontaminated soil, no AMPA was measured above the detection limit in the post-extraction solution in the unformulated and formulated glyphosate modalities.

### Extractability potential

We finally considered the extractability potential of trace elements (i.e., extractability normalized to soil element concentration) to compare the different soils by eliminating any concentration influence. We thus compared the extractability potential of each tested modality (20 mg L<sup>-1</sup> of glyphosate, 100 mg L<sup>-1</sup> of glyphosate, 100 mg L<sup>-1</sup> of formulated glyphosate, and 100 mg L<sup>-1</sup> of AMPA) to the extractability potential in the control (Fig. 4). Considering the glyphosate influence on the extractability potential of elements (Fig. 4a–b), Vieuxart depicted an overall higher positive effect compared to the contaminated soils, particularly with 20 mg L<sup>-1</sup> of glyphosate. For contaminated soils, Sainte-Walburge and Aubange generally presented higher extractability potential than Bressoux with 20 mg L<sup>-1</sup> of glyphosate, while negative effect was common with 100 mg L<sup>-1</sup> of glyphosate. Overall, Cu, Zn, Mo, and Sb were the most potentially extractable element in all uncontaminated and contaminated soils considered in this study, whereas Co, Ti, and Sn highlighted the lower extractability potential. Arsenic was the only element with a wide range of extractability potential according to the considered soil. Formulated glyphosate showed similar pattern as unformulated glyphosate with the same concentration (Fig. 4c), while AMPA decreased the influence on the extractability potential compared to glyphosate, reducing differences observed between the soils studied (Fig. 4d).

## Discussions

### Influence of glyphosate on trace element mobility in uncontaminated soil

The application of glyphosate in uncontaminated soil samples frequently highlighted a positive effect on trace element

mobility. Indeed, 67% of the tested trace elements showed a mean mobility  $> 1.2$  times higher than the control after adding 20 mg L<sup>-1</sup> of glyphosate, despite not always statistically significant differences due to the low number of replicates and the statistical tests used. Some of these observations have already been documented (e.g., As, Cd, Cu, Ni, and Pb; Barrett and McBride 2006; Divisekara et al. 2018; Morillo et al. 2000), while, to our knowledge, no information is available in the literature regarding other trace elements. Some trends (Cu  $>$  Zn) were in accordance with metal-glyphosate complexation coefficients found in the literature (Madsen et al. 1978). For some elements (e.g., Ba and Zn), an increasing mobility was only observed when the concentration of glyphosate reached 100 mg L<sup>-1</sup>. Although these two tested concentrations are not commonly found in soil solutions (glyphosate concentrations are generally below 1 mg L<sup>-1</sup> in soil solution samples and decrease dramatically with soil depth; Borggaard and Gimsing 2008; Veiga et al. 2001; Vereecken 2005), they are 100 to 500 times lower than the concentrations of the solution directly applied to the field. This suggests that trace elements should mostly be mobilized in the upper soil layers that are exposed to higher glyphosate concentrations after spraying than the commonly reported soil solution ones before dilution by consecutive rain event. We assume that along the vertical transport and the environmental changes with soil depth (such as glyphosate concentration), both trace elements and glyphosate could find new sorption sites. Despite the high heterogeneity of uncontaminated soils, Vieuxart soil can be representative of a large range of temperate agricultural soils because of its physical and chemical characteristics (i.e., silty soil with low organic carbon content).

Among the trace elements considered, we highlighted different groups with comparable masses following the same behaviours regarding their interaction with glyphosate (Fig. 2): e.g., Ti, Mn, Cr, Co, and V (light elements) or Cd, Sb, and Mo (heavy elements), despite that some elements did not fully fit with this grouping (e.g., Pb). For instance, both Cu and Zn (in between those light and heavy elements) showed frequent complexation to organic matter (Borggaard et al. 2019; Martínez and McBride 1999; Wong et al. 2007) that highlights their affinity for organic compounds, such as organic pollutants (including glyphosate), resulting in element mobility enhancement (Fig. 2; Barrett and McBride 2006). Note that although organic molecules can have an effect on the trace element extractability, the nature of these molecules may largely influence this mobility. However, water-extractable organic compounds being present in every modality (both in the control and in the pesticide treatments) from the same soil, it becomes possible to determine the role of glyphosate alone. Several other trace element chemical features, however, are pointed out as important factors controlling their sorption capacity, such as electronegativity, charge/radius ratios and related Goldschmidt categories, or hydrolysis constant (Covelo et al. 2004; Goldschmidt 1937;

McBride 1994). The element origin (e.g., lithogenic elements such as Co, Mn, Ni, and Ti; Rubio et al. 2000) or their complexation capacity may also contribute to this grouping.

Surprisingly, the effect of glyphosate on the element mobility was higher at 20 mg L<sup>-1</sup> compared to 100 mg L<sup>-1</sup> for 11 of the 15 elements considered (especially for Co, Cr, Mn, Pb, Sn, Ti, and V; Fig. 2). Note that the glyphosate concentration in the post-extraction solution was lower for the 20 mg L<sup>-1</sup> modality and, despite a higher relative sorption of glyphosate, the total mass of glyphosate that was sorbed on the soil was still lower than for the 100 mg L<sup>-1</sup> modality (Fig. 1). With three negative and one positive charges under common soil pH conditions (from 5.6 to 10.6; Sprankle et al. 1975), sorbed glyphosate could contribute to the soil CEC, and thus promote the cation binding. The antagonist processes between trace element mobilization by free glyphosate and trace element binding by sorbed glyphosate could explain the non-linear response between applied glyphosate concentration and trace element mobility. The absence of such trends in literature data (e.g., for Pb and Cd; Divisekara et al. 2018) may result from more contrasted glyphosate concentrations, from extremely low (up to 2 times lower concentrated compared to our lowest tested values) to high (up to 44 times higher) concentrations, preventing intermediate behaviours. Moreover, only formulated glyphosate was considered in Divisekara et al. (2018) which makes the comparison potentially difficult. Further investigations are thus required to confirm or refute this hypothesis, with particular focus on the structure of the soil-trace element-glyphosate complexes.

### Influence of glyphosate on trace element mobility in contaminated soils

Influence of glyphosate on trace element mobility in anthropogenically contaminated soils (i.e., Sainte-Walburge and Bressoux) highlighted similar groups as observed in the uncontaminated soil (Fig. 2), involving similar geochemical behaviours. The effect of glyphosate, however, was lower compared to Vieusart soil, particularly at 100 mg L<sup>-1</sup> of glyphosate where no influence was evidenced for 50% of the elements considered. This likely results from the higher extractability of anthropogenically derived trace elements even without glyphosate (up to 25 times more extracted in the control depending on the element considered; Figs. 1 and 3), frequently observed in human-induced contaminated soils (Rauret 1998; Sungur et al. 2014), making the influence of glyphosate negligible for many elements. Indeed, the overall influence of 20 mg L<sup>-1</sup> of glyphosate decreased with the contamination level, i.e., Vieusart > Sainte-Walburge > Bressoux. In an absolute point of view, however, the same molar concentration of glyphosate mobilizes a higher proportion of trace elements in anthropogenically-contaminated soils

(i.e., trace elements/glyphosate molar ratio of 0.5–1.9% vs 0.05% in Vieusart, considering Cu, As, Mo, and Pb). Conversely, Cu presented a higher mobility with glyphosate in anthropogenically contaminated soils compared to Vieusart soil. Again, this may result from the high affinity of Cu with organic compounds (Gao et al. 1997; Manceau and Matynia 2010; Sposito et al. 1979), including glyphosate. Note that Cu belongs to the most mobile elements (along with As, Mo, Sb, and Zn according to the control data; Fig. 4), we suspect potential environmental and health risks due to available toxic elements in glyphosate-treated soils, especially when Cu is applied as fungicide (Ballabio et al. 2018).

In contaminated soils, the sources of trace elements may largely control the element behaviour. For instance, similar trends between Cd and Zn in the modality/control extractability ratios (Fig. 2) likely results from a similar industrial source: both are frequently emitted from metallurgical and extractive industry along with Pb and Cu among others (Cox et al. 2002; Helios Rybicka 1996). The nature of soil contamination determines the trace element speciation, and thus the trace element-glyphosate interactions. The interaction between Cu and glyphosate has been extensively studied in regard to both the role of ionic bridge that Cu can form to enhance the glyphosate adsorption (Dousset et al. 2007; Maqueda et al. 2002; Morillo et al. 2000) and the chelating effect of glyphosate on the Cu extractability and sorbability (Barrett and McBride 2006; Glass 1984; Morillo et al. 2002). Yet, we have demonstrated that Cu, one of the most investigated elements in published glyphosate experiments, exhibits a unique biogeochemical behaviour that cannot be extrapolated to other elements.

In the naturally enriched soil (i.e., Aubange), the influence of glyphosate on the trace element mobility may be related to either the uncontaminated soil (e.g., Cu without drastic enhancement with glyphosate) or anthropogenically contaminated soils (e.g., low influence for the other elements; Fig. 2). Since the overall mobility of trace elements in Aubange was as low as in the uncontaminated soil (i.e., basically low extractability in the control), glyphosate did not contribute much to the trace element transfer from soil to water.

### Influence of formulated glyphosate and AMPA on trace element mobility

When glyphosate is formulated, its influence on trace element mobility depended on the elements considered: lower influence compared to the unformulated glyphosate for lower mass elements (< Ni) and Pb vs higher influence for the other elements (except for Sb with no significant difference; Fig. 2). We proposed several hypotheses for this contrasted result: (1) a complex formation between glyphosate and the co-formulant that would limit the availability

In comparison to unformulated and formulated glyphosate, AMPA showed a lower influence on trace element mobility. Here, distinct groups of elements were evidenced, suggesting other processes involved in the trace element AMPA interactions (Fig. 2). We hypothesize that (1) complexes between trace elements and AMPA might be easily sorbed to the soil (the lack of literature data about AMPA sorption on soil particles prevent any validation) or (2) AMPA plays a role of chelating agent for more mobile elements resulting in empty sites on the exchange complex for less mobile ones (Bloem and Vogler 2018). The concentrations of AMPA remaining in the solution being higher than those of glyphosate in the unformulated experiment (with the exception of Bressoux where there was no negative influence on the trace element mobility), this mainly leads to the second hypothesis. Note that we compared glyphosate and AMPA with the same mass concentration: considering the molar mass (i.e., 1.5 times lower than the glyphosate) and the fact that one mole of glyphosate is degraded to less than one mole of AMPA because of the multiple degradation pathways (Liu et al. 1991), we overestimate the concentration

à la Recherche dans l'Industrie et l'Agriculture (FRIA) from the Fonds de la Recherche Scientifique (F.R.S.-FNRS).

**Data availability** Enquiries about data availability should be directed to the authors.

## Declarations

**Ethics approval** This article does not contain any studies with human or animal subjects performed by any of the authors.

**Consent for publication** Not applicable.

**Consent to participate** Not applicable.

**Conflict of interest** The authors declare no competing interests.

## References

- Adriano DC (2001) Trace elements in terrestrial environments. Springer New York, New York. <https://doi.org/10.1007/978-0-387-21510-5>
- Alletto L, Coquet Y, Benoit P, Heddadj D, Barriuso E (2010) Tillage management effects on pesticide fate in soils. A Review. *Agron Sustain Dev* 30:367–400. <https://doi.org/10.1051/agro/2009018>
- Arbalestrie B, Falys J, Bemelmans N, Thami A, Monin L, Devos E, Agnan Y (2022) Rare earth elements in an intercropping cover crop to evaluate the trace element transfer from soil to plant. *Bio-geochemistry*. <https://doi.org/10.1007/s10533-022-00989-7>
- Baize D (2000) Teneurs totales en “métaux lourds” dans les sols français. *CourrEnviron INRA* 22:37–46
- Ballabio C, Panagos P, Lugato E, Huang J-H, Orgiazzi A, Jones A, Fernández-Ugalde O, Borrelli P, Montanarella L (2018) Copper distribution in European topsoils: an assessment based on LUCAS soil survey. *Sci Total Environ* 636:282–298. <https://doi.org/10.1016/j.scitotenv.2018.04.268>
- Barati AH, Maleki A, Alasvand M (2010) Multi-trace elements level in drinking water and the prevalence of multi-chronic arsenical poisoning in residents in the west area of Iran. *Sci Total Environ* 408:1523–1529. <https://doi.org/10.1016/j.scitotenv.2009.12.035>
- Barja BC, dos Santos Afonso M (2005) Aminomethylphosphonic acid and glyphosate adsorption onto goethite: a comparative study. *Environ Sci Technol* 39:585–592. <https://doi.org/10.1021/es035055q>
- Barrett KA, McBride MB (2006) Trace element mobilization in soils by glyphosate. *Soil Sci Soc Am J* 70:1882–1888. <https://doi.org/10.2136/sssaj2005.0415>
- Belon E, Boisson M, Deportes IZ, Eglin TK, Feix I, Bispo AO, Galsomies L, Leblond S, Guellier CR (2012) An inventory of trace elements inputs to French agricultural soils. *Sci Total Environ* 439:87–95. <https://doi.org/10.1016/j.scitotenv.2012.09.011>
- Bento CPM, Yang X, Gort G, Xue S, van Dam R, Zomer P, Mol HGI, Ritsema CJ, Geissen V (2016) Persistence of glyphosate and aminomethylphosphonic acid in loess soil under different combinations of temperature, soil moisture and light/darkness. *Sci Total Environ* 572:301–311. <https://doi.org/10.1016/j.scitotenv.2016.07.215>
- Bergström L, Börjesson E, Stenström J (2011) Laboratory and lysimeter studies of glyphosate and aminomethylphosphonic acid in a sand and a clay soil. *J Environ Qual* 40:98–108. <https://doi.org/10.2134/jeq2010.0179>
- Bloem E, Vogler I (2018) Influence of graded EDTA applications on mobilization and translocation of trace elements—a soil column experiment. *J Plant Nutr Soil Sci* 181:220–230. <https://doi.org/10.1002/jpln.201700353>
- Borggaard OK, Gimsing AL (2008) Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. *Pest Manag Sci* 64:441–456. <https://doi.org/10.1002/ps.1512>
- Borggaard OK, Holm PE, Strobel BW (2019) Potential of dissolved organic matter (DOM) to extract As, Cd Co, Cr, Cu, Ni, Pb and Zn from polluted soils: a review. *Geoderma* 343:235–246. <https://doi.org/10.1016/j.geoderma.2019.02.041>
- Cakmak I, Yazici A, Tutus Y, Ozturk L (2009) Glyphosate reduced seed and leaf concentrations of calcium, manganese, magnesium, and iron in non-glyphosate resistant soybean. *Eur J Agron* 31:114–119. <https://doi.org/10.1016/j.eja.2009.07.001>
- Chittleborough G (1980) A chemist's view of the analysis of human hair for trace elements. *Sci Total Environ* 14:53–75. [https://doi.org/10.1016/0048-9697\(80\)90126-6](https://doi.org/10.1016/0048-9697(80)90126-6)
- Covelo EF, Couce MLA, Vega FA (2004) Competitive adsorption and desorption of cadmium, chromium, copper, nickel, lead, and zinc by humic umbrilsols. *Commun Soil Sci Plant Anal* 35:2709–2729. <https://doi.org/10.1081/CSS-200036421>
- Cox SE, Bell PB, Lowther JS, VanMetre PC (2002) Vertical distribution of trace-element concentrations and occurrence of metallurgical slag particles in accumulated bed sediments of Lake Roosevelt (Technical report). U. S. Geological Survey, Washington
- Divisekara T, Navaratne AN, Abeysekara ASK (2018) Impact of a commercial glyphosate formulation on adsorption of Cd(II) and Pb(II) ions on paddy soil. *Chemosphere* 198:334–341. <https://doi.org/10.1016/j.chemosphere.2018.01.155>
- Doussot S, Jacobson AR, Dessogne J-B, Guichard N, Baveye PC, Andreux F (2007) Facilitated transport of diuron and glyphosate in high copper vineyard soils. *Environ Sci Technol* 41:8056–8061. <https://doi.org/10.1021/es071664c>
- El-Kady AA, Abdel-Wahhab MA (2018) Occurrence of trace metals in foodstuffs and their health impact. *Trends Food Sci Technol* 75:36–45. <https://doi.org/10.1016/j.tifs.2018.03.001>
- Gao S, Walker WJ, Dahlgren RA, Bold J (1997) Simultaneous sorption of Cd, Cu, Ni, Zn, Pb, and Cr on soils treated with sewage sludge supernatant. *Water Air Soil Pollut* 93:331–345. <https://doi.org/10.1007/BF02404765>
- Glass RL (1984) Metal complex formation by glyphosate. *J Agric Food Chem* 32:1249–1253. <https://doi.org/10.1021/jf00126a010>
- Goldschmidt VM (1937) The principles of distribution of chemical elements in minerals and rocks. The seventh Hugo Müller Lecture, delivered before the Chemical Society on March 17th, 1937. *J Chem. Soc.* 655–673. <https://doi.org/10.1039/JR9370000655>
- He ZL, Yang XE, Stoffella PJ (2005) Trace elements in agroecosystems and impacts on the environment. *J Trace Elem Med Biol* 19:125–140. <https://doi.org/10.1016/j.jtemb.2005.02.010>
- Helios Rybicka E (1996) Impact of mining and metallurgical industries on the environment in Poland. *Appl Geochem* 11:3–9. [https://doi.org/10.1016/0883-2927\(95\)00083-6](https://doi.org/10.1016/0883-2927(95)00083-6)
- Kaur S, Kumar V, Chawla M, Cavallo L, Poater A, Upadhyay N (2017) Pesticides curbing soil fertility: effect of complexation of free metal ions. *Front Chem* 5:43. <https://doi.org/10.3389/fchem.2017.00043>
- Leaper C, Holloway PJ (2000) Adjuvants and glyphosate activity. *Pest Manag Sci* 56:313–319. [https://doi.org/10.1002/\(SICI\)1526-4998\(200004\)56:4%3c313::AID-PS147%3e3.0.CO;2-3](https://doi.org/10.1002/(SICI)1526-4998(200004)56:4%3c313::AID-PS147%3e3.0.CO;2-3)
- Lewis KA, Tzivilakis J, Warner D, Gree A (2016) An international database for pesticide risk assessments and management. *Hum Ecol Risk Assess Int J* 22:1050–1064. <https://doi.org/10.1080/10807039.2015.1133242>



- Liu C-M, McLean PA, Sookdeo CC, Cannon FC (1991) Degradation of the herbicide glyphosate by members of the family *Rhizobiaceae*. *Appl Environ Microbiol* 57:1799–1804. <https://doi.org/10.1128/aem.57.6.1799-1804.1991>
- Madsen HE, Christensen HH, Gottlieb-Petersen C, Amrine-Madsen H (1978) Stability constants of copper(II), zinc, manganese(II), calcium, and magnesium complexes of N-(phosphonomethyl) glycine (glyphosate). *Acta Chem Scand A* 32:79–83
- Manceau A, Matynia A (2010) The nature of Cu bonding to natural organic matter. *Geochim Cosmochim Acta* 74:2556–2580. <https://doi.org/10.1016/j.gca.2010.01.027>
- Maqueda C, Morillo E, Undabeytia T (2002) Cosorption of glyphosate and copper (II) on goethite. *Soil Sci* 167:659–665. <https://doi.org/10.1097/00010694-200210000-00004>
- Martínez CE, McBride MB (1999) Dissolved and labile concentrations of Cd, Cu, Pb, and Zn in aged ferrihydrite–organic matter systems. *Environ Sci Technol* 33:745–750. <https://doi.org/10.1021/es980576c>
- McBride MB (1994) *Environmental chemistry of soils*. Oxford University Press, New York
- Mesnage R, Benbrook C, Antoniou MN (2019) Insight into the confusion over surfactant co-formulants in glyphosate-based herbicides. *Food Chem Toxicol* 128:137–145. <https://doi.org/10.1016/j.fct.2019.03.053>
- Morillo E, Undabeytia T, Maqueda C, Ramos A (2002) The effect of dissolved glyphosate upon the sorption of copper by three selected soils. *Chemosphere* 47:747–752. [https://doi.org/10.1016/S0045-6535\(01\)00338-1](https://doi.org/10.1016/S0045-6535(01)00338-1)
- Morillo E, Undabeytia T, Maqueda C, Ramos A (2000) Glyphosate adsorption on soils of different characteristics. Influence of copper addition. *Chemosphere* 40(1):103–107. [https://doi.org/10.1016/S0045-6535\(99\)00255-6](https://doi.org/10.1016/S0045-6535(99)00255-6)
- Phytoweb (2015) Consulter autorisations de produits phytopharmaceutiques. <https://fytoweb.be/fr/produits-phytopharmaceutiques/consulter-autorisations-de-produits-phytopharmaceutiques>. Accessed 10 Aug 2023
- Pline WA, Wilcut JW, Duke SO, Edmisten KL, Wells R (2002) Tolerance and accumulation of shikimic acid in response to glyphosate applications in glyphosate-resistant and nonglyphosate-resistant cotton (*Gossypium hirsutum* L.). *J Agric Food Chem* 50:506–512. <https://doi.org/10.1021/jf0110699>
- Rauret G (1998) Extraction procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta* 46:449–455. [https://doi.org/10.1016/S0039-9140\(97\)00406-2](https://doi.org/10.1016/S0039-9140(97)00406-2)
- Rubio B, Nombela MA, Vilas F (2000) Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. *Mar Pollut Bull* 40(11):968–980. [https://doi.org/10.1016/S0025-326X\(00\)00039-4](https://doi.org/10.1016/S0025-326X(00)00039-4)
- Si Y-B, Xiang Y, Tian C, Si X-Y, Zhou J, Zhou D-M (2013) Complex interaction and adsorption of glyphosate and lead in soil. *Soil Sediment Contam Int J* 22:72–84. <https://doi.org/10.1080/15320383.2012.714421>
- Silva V, Mol HGJ, Zomer P, Tienstra M, Ritsema CJ, Geissen V (2019) Pesticide residues in European agricultural soils — a hidden reality unfolded. *Sci Total Environ* 653:1532–1545. <https://doi.org/10.1016/j.scitotenv.2018.10.441>
- Sposito G, Holtzclaw KM, LeVesque-Madore CS (1979) Cupric ion complexation by fulvic acid extracted from sewage sludge-soil mixtures. *Soil Sci Soc Am J* 43:1148–1155. <https://doi.org/10.2136/sssaj1979.03615995004300060018x>
- Sprinkle P, Meggitt WF, Penner D (1975) Adsorption, mobility, and microbial degradation of glyphosate in the soil. *Weed Sci* 23:229–234. <https://doi.org/10.1017/S0043174500052929>
- Sungur A, Soylak M, Ozcan H (2014) Investigation of heavy metal mobility and availability by the BCR sequential extraction procedure: relationship between soil properties and heavy metals availability. *Chem Speciat Bioavailab* 26:219–230. <https://doi.org/10.3184/095422914X14147781158674>
- Veiga F, Zapata JM, Fernandez Marcos ML, Alvarez E (2001) Dynamics of glyphosate and aminomethylphosphonic acid in a forest soil in Galicia, north-west Spain. *Sci Total Environ* 271:135–144. [https://doi.org/10.1016/S0048-9697\(00\)00839-1](https://doi.org/10.1016/S0048-9697(00)00839-1)
- Vandeurén A, Pereira B, Kaba AJ, Titeux H, Delmelle P (2023) Environmental bioavailability of arsenic, nickel and chromium in soils impacted by high geogenic and anthropogenic background contents. *Sci Total Environ* 902:166073. <https://doi.org/10.1016/j.scitotenv.2023.166073>
- Vereecken H (2005) Mobility and leaching of glyphosate: a review. *Pest Manag Sci* 61:1139–1151. <https://doi.org/10.1002/ps.1122>
- Wang Y-J, Zhou D-M, Sun R-J, Jia D-A, Zhu H-W, Wang S-Q (2008) Zinc adsorption on goethite as affected by glyphosate. *J Hazard Mater* 151:179–184. <https://doi.org/10.1016/j.jhazmat.2007.05.060>
- Wilms W, Parus A, Homa J, Batycka M, Niemczak M, Woźniak-Karczewska M, Trzebný A, Zembruska, Dabert M, Táncsics A, Cajthaml T, Heipieper HJ, Chrzanowski Ł (2023) Glyphosate versus glyphosate based ionic liquids: Effect of cation on glyphosate biodegradation, soxA and phnJ genes abundance and microbial populations changes during soil bioaugmentation. *Chemosphere* 316:137717. <https://doi.org/10.1016/j.chemosphere.2022.137717>
- Wong JWC, Li KL, Zhou LX, Selvam A (2007) The sorption of Cd and Zn by different soils in the presence of dissolved organic matter from sludge. *Geoderma* 137:310–317. <https://doi.org/10.1016/j.geoderma.2006.08.026>
- Xuejing X, Mingcai Y, Lianzhong L, Huijun S (1985) Usable values for Chinese standard reference samples of stream sediments, soils, and rocks: GSD 9–12, GSS 1–8 and GSR 1–6. *Geostand Geo-analytical Res* 9:277–280. <https://doi.org/10.1111/j.1751-908X.1985.tb00458.x>

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.