Biogeochemistry (2022) 161:373–387
https://doi.org/10.1007/s10533-022-00989-7

Rare earth elements in an intercropping cover crop to evaluate the trace element transfer from soil to plant

Bryan Arbalestrie · Julie Falys · Nathan Bemelmans · Adil Thami · Laurence Monin · Elodie Devos · Yannick Agnan

Received: 9 August 2022 / Accepted: 23 October 2022 / Published online: 3 November 2022

Abstract Transfer of trace elements, such as toxic metals, from soil to plant is a corner stone for risk assessment. Rare earth elements (REE) are frequently used as environmental tracers to understand biogeochemical processes in the soil–plant system. In this study, we combined trace element and REE measurements in the soil–plant continuum to evaluate the element transfer between different compartments. We specifically aimed at: (1) assessing the geochemical relevance and representativeness of intermediate compartments (soil solution and soil water-extract as a proxy of the bioavailable soil fraction) by comparing the REE normalized patterns; and (2) characterizing the environmental conditions that control the trace element transfer by quantifying the REE indices. For that purpose, we compared geochemical signatures in an intercropping cover crop (bean, Persian clover, and spelt) in Belgium, including soil, root, shoot, soil solution, soil water-extract, earthworm, and snow samples. Evaluation of the element mobility was performed using both soil extractability and transfer factors. The main result showed dissimilar REE patterns between soil/plant samples and soil solution/soil water-extract samples, indicating that the intermediate compartments (i.e., soil solutions or soil water-extracts) do not chemically represent the bioavailable fraction of elements without obvious propensity to biological accumulation (unlike Cd, Cu, or Zn). Compared to light REE, heavy REE were more extractable and thus transferred to plants unlike what is observed in the literature. According to their different extractabilities, Ce and Eu allowed to highlight distinct transfer from soil to plant due to possible adsorption or organic matter complexation that should be further confirmed by studying contrasted soils.

Keywords Rare earth elements · Trace elements · Soil · Plant · Soil solution · Transfer

Responsible Editor: Dale Johnson

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10533-022-00989-7.

B. Arbalestrie · J. Falys · N. Bemelmans · A. Thami · L. Monin · E. Devos · Y. Agnan (✉)
Earth and Life Institute, Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium
e-mail: yannick.agnan@biogeoscience.eu

Introduction

Trace elements, whose concentration is below 0.1% in the continental crust, include metals (Cd, Cu, Mn, Ti, V, Zn…) and metalloids (As, Sb…) that may induce potentially harmful effects on human and ecosystem health. The environmental cycling of trace elements depends on both element sources and compartment conditions (Rauch and Pacyna 2009; Kabata-Pendias 2010). In agricultural soils, they are originated from (He et al. 2005): (1) natural sources, mainly resulting

from parent material alteration according to the mineral composition; and (2) anthropogenic sources, such as organic amendments, fertilizers, and pesticides. Transfer of trace elements from soil to plant, and their recycling by vegetation, involve multiple processes that depend on pedological, biological, or climatic factors, all of them resulting in changes of element speciation. For instance, the main soil-associated factors affecting the trace element availability in soils are soil pH, redox potential, constituent content (both clays and organic matter control the cation exchange capacity), and "aging" of added elements promoting the element scavenging over time (Antoniadis et al. 2017). Moreover, the chemical speciation (cationic vs. anionic) and biological role (essential vs. non-essential) of the element also control their transfer from soil to plant (Kabata-Pendias 2010). Yet, environmental and human health concerns depend on the mobility and phytoavailability of these trace elements in the soil–plant system. Soil solution and soil extract are frequently used as proxies for evaluating this available fraction (Kabata-Pendias 2004; Chojnacka et al. 2005; Antoniadis et al. 2017), in parallel with element concentrations directly accumulated in plants or concentration ratios between compartments called transfer factors. The choice of the protocol used to collect such solutions, however, highly constrains the interpretation of transfer processes (Di Bonito et al. 2018). Also, concentrations in these compartments alone cannot directly confirm the representativeness of the available fraction. Predicting the actual transfer of trace elements and the related risk assessment still remains complex, encouraging the use of geochemical tracers to identify processes (e.g., adsorption or leaching) that influence the chemical dynamics of elements at the soil–plant interface.

Rare earth elements (REE), also called lanthanides, include 14 natural trace elements divided into light REE (LREE, from La to Eu) and heavy REE (HREE, from Gd to Lu). Sometimes, medium REE (MREE, from Pr or Nd to Dy or Ho) can be considered as an intermediate class. They are characterized by a similar electronic configuration, including a large ionic radius, a trivalent oxidation state, and a lower electronegativity than those of the transition elements (Henderson 1984; Laveuf and Cornu 2009). However, REE behave differently according to their atomic number: for example, LREE are estimated to be more soluble and less complexed than HREE (Cantrell and Byrne 1987), promoting LREE mobility and availability (Martinez et al. 2018; Monei et al. 2022). Then, root uptake largely depends on element speciation, as well as plant physiology (Tyler 2004): e.g., LREE seem to be preferentially translocated from roots to shoots, inducing a higher LREE/HREE ratio in shoots. Thus, the comparison of REE concentrations between compartments (soil, plant, solution, etc.) helps to describe the geochemical processes involved at the interfaces. The use of normalized REE patterns allows directly evaluation of relative LREE or HREE enrichment or depletion. Moreover, among REE, Ce and Eu present an extra valence (Ce^{4+} and Eu^{2+}, respectively) that generates positive or negative anomalies after fractionation processes. For example, reduction of Eu (Eu^{3+} to Eu^{2+}) with decreasing redox potential (e.g., in the rhizosphere) improves the Eu mobility in soils, resulting to a positive Eu anomaly in plants while soil presents a negative Eu anomaly (Krzciuk and Gałuszka 2020).

Thus, REE are helpful to trace biogeochemical processes (adsorption, leaching, redox and pH changes, etc.) in the soil–plant system (Liang et al. 2005; Laveuf and Cornu 2009). In this study, we aimed at: (1) assessing the geochemical relevance and representativeness of the intermediate compartments (soil solution and soil extract as a proxy of the bioavailable soil fraction) by comparing the REE normalized patterns along the soil–plant continuum; and (2) characterizing the environmental conditions that control the trace element transfer by quantifying the REE indices. For this purpose, we conjointly analyzed trace element and REE concentrations and compared geochemical signatures in the soil–plant continuum of an intercropping cover crop, including soil, root, shoot, soil solution, and soil water-extract samples, and evaluated the element mobility using both soil extractability and transfer factors. We hypothesize that, studying non-hyperaccumulator species in winter (i.e., wet period for soil solution sampling), we should better follow and understand trace element and REE transfers.

Materials and methods

Study area

The study was carried out from September 2020 to March 2021 in an intercropping cover crop of

ca. 24,000 m^2 (340 m × 70 m) located at the centre Alphonse de Marbaix, Corroy-le-Grand, Belgium (UCLouvain experimental farm, 135 m a.s.l). The field was covered by Persian clover (*Trifolium resupinatum*) and sorghum (*Sorghum bicolor* × *Sorghum sudanense*) sown at the end of August 2020, as well as bean (*Vicia faba*) and spelt (*Triticum spelta*) regrowth from the previous crop. The study area is characterized by a temperate oceanic climate with a mean annual air temperature of 10.6 °C and a mean annual precipitation of 820 mm (www.meteo.be). It is located on an aeolian loess deposit formation and characterized by silty and well-drained soils, typical agricultural soils found in northern Wallonia. Average soil pH_{KCl} reached 6.2 and 6.1 at 0–30 and 30–50 cm depth, respectively, and soil carbon content, 1.2 and 0.5%, respectively.

Sampling procedure

For representative purposes, soil, plant, and soil solution samples were collected within three distinct sub-areas (ca. 50 m away). In each sub-area that corresponds to a circle of 7 m in diameter, a composite soil sample (i.e. eight sub-samples) was considered at two depths (0–30 cm and 30–50 cm) using an auger. Soil solution samples were collected in each sub-area using 5 rhizons (10-cm long hydrophilic polyether sulphone membrane with a 0.15-µm porosity; 19.21.01 F, Rhizosphere, Wageningen, The Netherlands) installed vertically in the top 10 cm of the soil at the circle periphery. Sampling was performed using a 60-mL polypropylene syringe (BD Plastipak luer lock). The five collected samples were merged into a single composite soil solution sample per sub-area to obtain sufficient volume for chemical analysis. Five soil solutions were collected, approximately each month: 21 Oct. 2020, 16 Nov. 2020, 15 Dec. 2020, 14 Jan. 2021, and 4 Feb. 2021.

Plant samples considered three different species grown together: bean (*Vicia faba*), Persian clover (*Trifolium resupinatum*), and spelt (*Triticum spelta*). Several specimens were collected in each sub-area (within 5 m around the circle center point), considering both roots and shoots, and stored in plastic bags. Plant sampling were performed three times following the plant growth stages: early (16 Oct. 2020), middle (15 Dec. 2020), and late (4 Feb. 2021). Finally, earthworms (including various ecological categories) were sampled on 4 Feb. 2021 by collecting on average 18 specimens per sub-area in the first 10-cm soil depth. To complete the data set, a single sample of unfiltered fresh deposited snow was directly collected on plant leaves on 14 Jan. 2021.

Sample preparation

Collected soil samples were dried (25 °C in a drying room for seven days), sieved (< 2 mm), and ground using a soil grinder (Vibratory Disc Mill RS 200, Retsch, Haan, Germany). For plant material, samples were gently cleaned with distilled water to remove as much soil residue as possible and dried in a ventilated oven at room temperature. Shoots were separated from roots before grinding (Cyclotec 1093 Sample Mill, Foss A/S, Hillerød, Denmark). Earthworm samples were washed with distilled water and left on wet paper in Petri dishes for 12 days to evacuate their digestive tract content before being frozen in a freezer at − 18 °C, dried in an oven at 40 °C, and ground in a mortar with liquid nitrogen.

Approximately 100 mg of ground soil, plant, and earthworm samples were digested in a Savillex (Teflon bottle) in an ISO 6 cleanroom (Earth and Life Institute, UCLouvain, Belgium) using a mixture of suprapure acids (HNO_3, HCl, and HF) and H_2O_2 in a four-step procedure (Agnan et al. 2013). Heating plate temperature was fixed of 90 °C for heating steps (at least for 24 h) and 40 °C for evaporation steps. Finally, samples were preserved in 2% HNO_3 solutions before analysis. All cleaning and analytical procedures used high purity Milli-Q water (18.2 MΩ cm).

A water extraction was performed on 2 g of soil samples for each sub-area and depth by adding 20 mL of milli-Q water. The samples were stirred for 2 h and then centrifuged at 4000 rpm for 25 min. Then, samples were filtered, first with 20-µm Whatman filters, and then with 0.2-µm GHP Acrodisc (PSF and nylon, Pall). All liquid samples (soil solutions, soil water-extracts, and snow) were acidified to reach 2% HNO_3 before analysis.

Chemical analyses

A set of 11 trace elements (Ba, Cd, Co, Cr, Cu, Mn, Pb, Sr, Ti, V, and Zn) and 14 REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) was

quantified using an ICP–MS (iCAP Q ICP–MS, Thermo Fischer Scientific, Waltham, MA, USA) at the Earth and Life Institute analytical platform (MOCA, UCLouvain, Belgium). Common interferences were automatically corrected after analytical tests (e.g., Pourret et al. 2021). An internal standard (Ru, In, and Re) was used in each sample for drift instrumental correction. In order to evaluate the performance of the procedure for organic and mineral matrices, two certified materials well characterized for REE concentrations (lichen IAEA-336 and basalt BHVO-2, respectively) were added for each series. The average recovery ($C_{measured}$ / $C_{certified}$ × 100) calculated for each analyte was approximately: (1) 90 ± 5% for the lichen IAEA-336, except for Ti (110 ± 5%), for Cd, Cr, Gd, Mn, Pr, V, and Zn (100 ± 5%), for Er, Ho, Pb, and Tm (80 ± 5%), and for Lu (70 ± 5%); and (2) 90 ± 5% for the basalt BHVO-2, except for Cr, and V (110 ± 5%), for Ba, Co, Cu, La, Ti, and Zn (100 ± 5%), and for Ho (80 ± 5%). The blank samples were on average 0.005–252 ng L^{-1} according to the element (Er to Ti, respectively), which represented < 1% of the sample concentration analyzed (except for Cd and Ti with 2%). Limits of detection were estimated to < 1 ng kg^{-1}, except for Cr, Cu, Mn, Pb, Sr, and V (< 0.01 µg kg^{-1}), for Ba and Zn (< 0.1 µg kg^{-1}), and for Ti (< 1 µg kg^{-1}).

Data processing and statistical analyses

To evaluate the transfer of elements between compartments, two indices were considered (Adriano 2001; Marchiol et al. 2004; Antoniadis et al. 2017): the transfer factor from soil to plant ($TF_{soil-plant}$) and the transfer factor from root to shoot ($TF_{root-shoot}$), calculated as follows:

$$TF_{soil\text{-}plant} = \frac{C_{shoot}}{C_{soil}}$$

$$TF_{root\text{-}shoot} = \frac{C_{shoot}}{C_{root}}$$

with C_{shoot}, C_{root}, and C_{soil}, the element concentrations in shoot, root, and soil, respectively.

Rare earth elements were presented as normalized profiles as done in the literature using: (1) UCC (upper continental crust; Rudnick and Gao 2014) reference material for soil samples (Cidu et al. 2013); (2) soil (0–30 cm depth) for soil water-extract (except for soil water-extract samples from 30 to 50 cm depth normalized by 30–50 cm soil depth), plant, soil solution, and earthworm samples (Brioschi et al. 2013) for a better comparison; and (3) snow samples for soil solution samples to evaluate the potential atmospheric input. To facilitate comparisons, all graphs were performed using the same log scale. Several REE indices frequently used in the literature were calculated based on measured concentrations (Wyttenbach et al. 1998; Miao et al. 2008; Agnan et al. 2014): Ce, Eu, Tb, and Yb anomalies calculated by dividing the normalized value by the expected value (obtained by averaging the values of the elements immediately prior and after), and LREE/HREE ratio using the following normalized concentration ratio:

$$\frac{LREE}{HREE} = \frac{(La + Ce + Pr + Nd + Sm + Eu)/6}{(Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu)/8}$$

Statistical tests were performed using R 4.0.4 (R Core Team 2021). Statistically significant differences were tested using the non-parametric Kruskal-Wallis test (α = 0.05) and the post-hoc Dunn test (α = 0.05) with the *dunn.test* package (Dinno 2017). Principal component analyses (PCA) were performed to identify the relationships between elements using *FactoMineR* and *factoextra* packages (Lê et al. 2008) on element concentrations after centered log-ratio transformation (*clr* function) using *rgr* package (Garrett 2013). Scatter plots were performed using the *ggplot2* package (Wickham 2016).

Results

Trace elements

Trace element concentrations

Trace element concentrations (Table 1 and Online Resource) showed higher values in soil samples compared to other compartments, ranging from Cd (on average, 0.33 and 0.18 mg kg^{-1} at 0–30 and 30–50 cm soil depth, respectively) to Ti (2030 and 2606 mg kg^{-1}, respectively). In plant samples, trace elements were, on average, 3-times more concentrated in roots compared to shoots and still ranged from Cd (0.41 and 0.08 mg kg^{-1} in roots and shoots, respectively) to

Table 1 Summary table (means, standard deviations in italics) of trace element and sum of rare earth element (ΣREE) concentrations for each compartment sampled at the centre de Marbaix

Matrix	n	Ba	Cd	Co	Cr	Cu	Mn	Pb	Sr	Ti	V	Zn	ΣREE
		mg kg^{-1}											
Soil													
0–30 cm	3	230 *(10.3)*	0.33 *(0.03)*	9.01 *(0.64)*	58.0 *(3.65)*	13.7 *(1.33)*	315 *(21.3)*	21.4 *(1.20)*	37.7 *(2.15)*	2030 *(399)*	64.3 *(5.28)*	45.8 *(0.94)*	111 *(14.2)*
30–50 cm	3	226 *(9.29)*	0.18 *(0.03)*	9.31 *(1.57)*	62.8 *(2.83)*	12.2 *(1.49)*	263 *(87.5)*	15.1 *(1.18)*	32.0 *(6.07)*	2610 *(419)*	64.5 *(7.41)*	36.0 *(2.71)*	106 *(10.4)*
Plant													
Shoot	27	20.4 *(12.0)*	0.08 *(0.09)*	0.51 *(0.39)*	6.70 *(4.80)*	8.25 *(2.38)*	44.5 *(21.2)*	1.36 *(1.16)*	18.0 *(7.47)*	114 *(108)*	3.74 *(4.02)*	40.1 *(12.8)*	7.93 *(6.84)*
Root	27	61.2 *(25.2)*	0.41 *(0.18)*	1.83 *(0.75)*	26.1 *(27.5)*	15.8 *(5.64)*	101 *(39.5)*	4.99 *(3.40)*	27.4 *(7.26)*	301 *(227)*	15.6 *(6.26)*	56.5 *(36.6)*	28.9 *(12.4)*
Earthworm	3	2.61 *(0.56)*	6.47 *(0.78)*	3.50 *(0.79)*	0.68 *(0.08)*	7.16 *(0.17)*	19.7 *(11.0)*	0.47 *(0.20)*	8.46 *(3.06)*	13.7 *(1.04)*	0.71 *(0.01)*	335 *(9.15)*	1.07 *(0.19)*
		µg kg^{-1}											
Soil water-extract													
0–30 cm	3	136 *(109)*	0.08 *(0.03)*	0.28 *(0.17)*	1.82 *(1.04)*	8.31 *(1.11)*	13.0 *(10.3)*	1.21 *(1.52)*	11.8 *(1.34)*	20.8 *(12.0)*	9.44 *(2.08)*	87.2 *(79.7)*	4.95 *(3.86)*
30–50 cm	3	62.3 *(67.2)*	0.04 *(0.02)*	0.46 *(0.21)*	3.49 *(1.34)*	4.11 *(1.12)*	16.8 *(14.2)*	1.21 *(0.97)*	9.62 *(1.97)*	59.8 *(18.2)*	5.49 *(3.35)*	26.9 *(32.7)*	13.2 *(10.3)*
		µg L^{-1}											
Soil solution	15	22.6 *(7.05)*	0.02 *(0.00)*	0.16 *(0.04)*	0.47 *(0.12)*	5.00 *(2.04)*	2.46 *(2.13)*	0.08 *(0.13)*	79.4 *(9.48)*	0.82 *(0.85)*	2.90 *(0.55)*	160 *(85.5)*	0.40 *(0.32)*
Snow	1	1.69	0.03	0.10	0.66	2.75	9.73	1.24	1.48	1.84	0.43	33.7	0.86

Ti (301 and 114 mg kg^{-1}, respectively). Soil water-extract samples showed increasing concentrations from Cd (0.08 and 0.04 µg kg^{-1} at 0–30 and 30–50 cm depth, respectively) to Ba (136 and 62.3 µg kg^{-1}, respectively). They represented 0.01–1.9‰ of the soil element concentrations. Concentrations in soil solutions ranged from Cd (0.02 µg L^{-1}) to Zn (160 µg L^{-1}) with noticeable heterogeneity between sampling dates (average relative standard deviation of 47%). The soil solution/soil ratios had the same element order as observed for soil extractability. In general, soil solutions were more concentrated than snow sample, except for Cd, Cr, Mn, Pb, and Ti. Finally, earthworm samples showed lower concentrations than shoots, except for Cd, Co, and Zn.

Trace element transfer factors

Transfer factors ($TF_{soil-plant}$ and $TF_{root-shoot}$) were calculated for each trace element and each sampling date in *Trifolium resupinatum*, *Vicia faba*, and *Triticum spelta* (Fig. 1). The transfer from soil to *Trifolium resupinatum* showed significant differences between elements, including Ti, V, Pb, Co, and Cr with the minimum values ($TF_{soil-plant} < 0.05$) and Zn, Sr, and Cu with the maximum values ($TF_{soil-plant} > 0.5$) for the first sampling date (Fig. 1A). Statistically significant differences were observed with increasing $TF_{soil-plant}$ over time (> 2 times for half of the elements, and up to > 20 times for Ti), except for Cd and Sr where no evolution was evidenced. Zinc showed a singular pattern with higher $TF_{soil-plant}$ during the early season. The transfer from root to shoot showed more consistent pattern, both between trace elements and sampling dates (Fig. 1B). Cadmium, however, appeared as the lowest translocated element. $TF_{root-shoot}$ were generally higher than $TF_{soil-plant}$, except for Cd, Cu, and Zn. The two other plant species showed similar patterns for both factors, with higher heterogeneity for *Triticum spelta* (Fig. 1C–F).

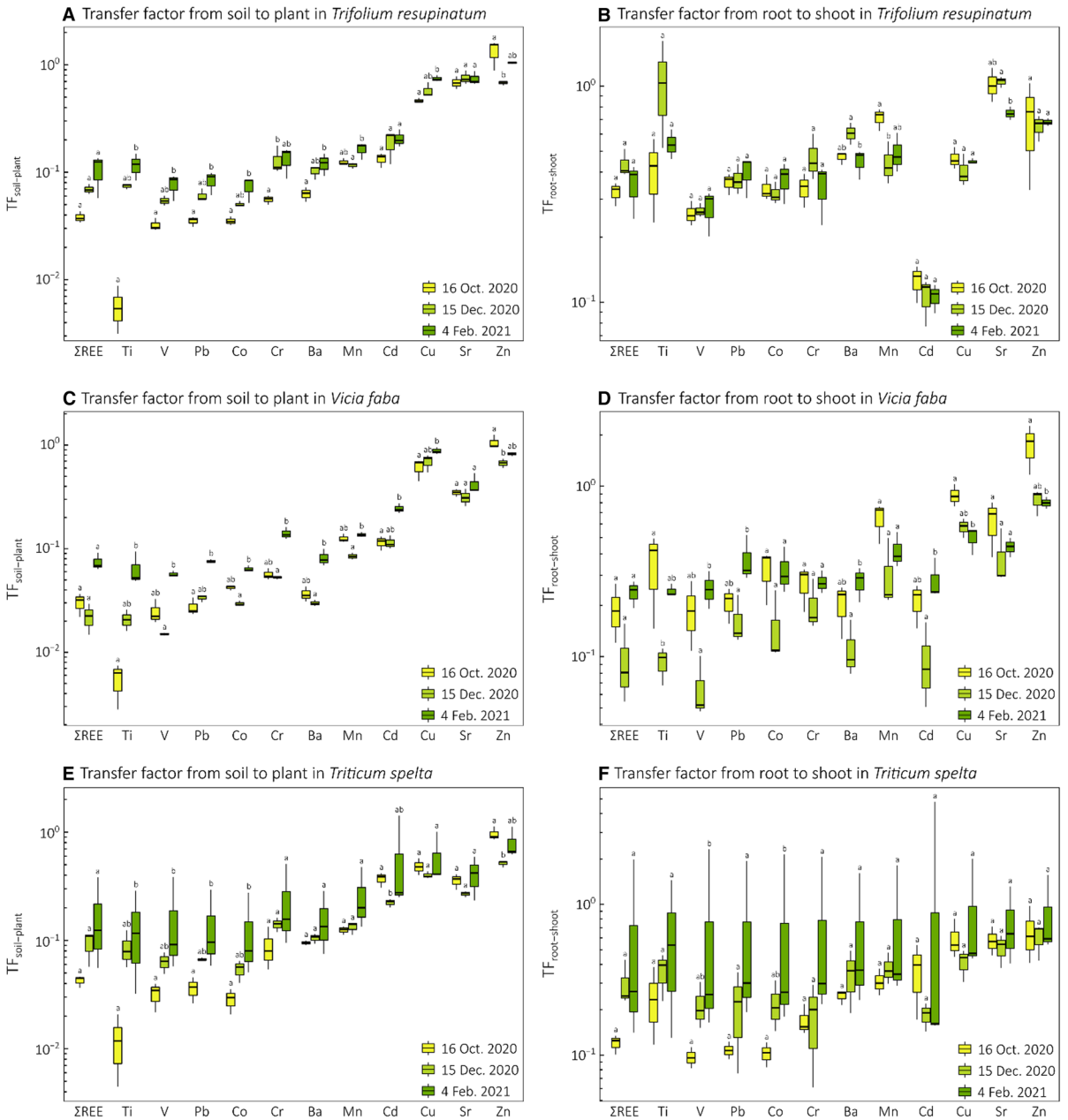

Fig. 1 Transfer factors from soil to plant ($TF_{soil\text{-}plant}$; **A**, **C**, and **E**) and from root to shoot ($TF_{root\text{-}shoot}$; **B**, **D**, and **F**) of trace elements and sum of rare earth elements (ΣREE) in Persian clover (*Trifolium resupinatum*; **A** and **B**), bean (*Vicia faba*; **C** and **D**), and spelt (*Triticum spelta*; E and F) collected at three sampling dates at the centre de Marbaix. Letters indicate statistically significant differences between sampling dates

Trace element relationships

The first component of the PCA (54% of data variance; Fig. 2A) was influenced by Sr, Zn, Cu, and Ba (positive scores) and Ti, Pb, Mn, and Cr (negative scores). This dimension opposed soil solutions and, to a lesser extent, soil water extracts (0–30 cm depth) with positive scores and soil samples with negative scores. Also, plant samples have essentially negative scores. The second component (22% of data variance)

grouped V and Ba (positive scores) in opposition to Cd and, to a lesser extent, Co (negative scores). Earthworm samples mostly drove this dimension with negative scores, mainly influenced by Cd concentrations.

Based on the PCA, we considered contrasting elements (Cd, Cu, and Mn) to plot relationships between trace elements for all compartments: Cd/Mn vs. Cu/Mn (Fig. 2B). Two main end-members emerged: soils (with low Cd/Mn and Cu/Mn ratios) and soil solutions (with higher ratios and higher heterogeneity). Soil water extract samples showed an intermediate signature with lower ratios in the 30–50 cm depth. Despite that plant samples fell in-between the two end-members, they presented a fractionation with higher relative Cd/Mn ratios for roots and higher relative Cu/Mn ratios for shoots. Distribution of plant samples discriminated plant species, particularly for root samples with *Triticum spelta* closer to the soil end-member and *Trifolium resupinatum* closer to the soil solution end-member. Finally, earthworm samples had higher Cd/Mn ratios than all other compartments (from 40 to 500 times for soil solutions and soils, respectively) and the snow sample was located between the two previously mentioned end-members.

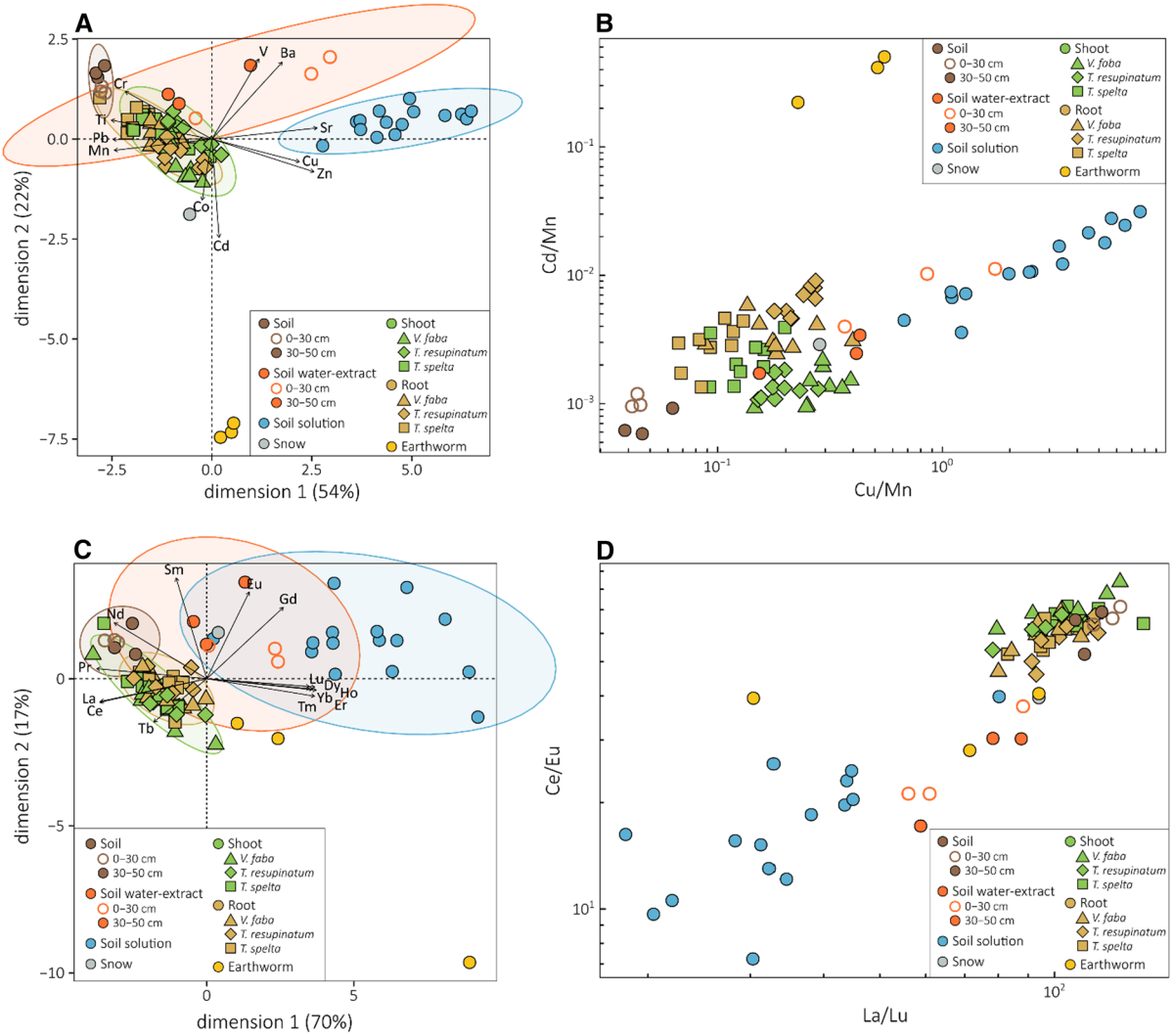

Fig. 2 Principal component analysis of log-ratio transformed trace element (**A**) and rare earth element (**C**) concentrations and element ratios Cd/Mn vs. Cu/Mn (**B**) and Ce/Eu vs. La/Lu (**D**) in samples collected at the centre de Marbaix

Rare earth elements

Rare earth element concentrations and transfer factors

Total REE (ΣREE) showed decreasing concentrations in the following order (Table 1 and Online Resource): soil (111 mg kg^{-1} at 0–30 cm soil depth) > root > shoot > earthworm (1.07 mg kg^{-1}). Soil water-extract samples represented 0.04 and 0.12‰ of soil ΣREE concentrations at 0–30 and 30–50 cm depths, respectively (soil ΣREE concentrations about 2.7-times higher at 30–50 cm depth). Heavy REE were 42 and 36% more extractable than LREE at 0–30 and 30–50 cm depths, respectively. Moreover, REE extractability was in the same range as Ti, Co, Cr, Mn, and Pb. Soil solutions had ΣREE concentrations of 0.40 µg L^{-1}, corresponding to half of the snow sample ΣREE concentrations. The soil solution/soil REE concentration ratios showed similar trends as observed for soil water-extract/soil, with increasing ratios of 90% from LREE to HREE. However, it is noteworthy that Ce was relatively less extractable (16 and 38% at 0–30 and 30–50 cm depth, respectively) and Eu relatively more extractable (30 and 18%, respectively) compared to their neighboring elements in the periodic table.

The REE transfer from soil to *Trifolium resupinatum* showed similar pattern as observed for trace elements with increasing $TF_{soil-plant}$ over time, despite no statistically significant difference (Fig. 1A). The $TF_{soil-plant}$ measured for REE (from 0.04 to 0.14 according to the element and sampling date) were close to those of Ti, V, Pb, Co, Cr, or Ba. However, distinct behaviors appeared with increasing $TF_{soil-plant}$ of 20% from LREE to HREE. The REE $TF_{root-shoot}$ in *Trifolium resupinatum* showed consistent pattern between sampling dates as for the trace elements (Fig. 1B). Similar trends were observed for *Vicia faba* and *Triticum spelta* (Fig. 1C–F).

REE normalized patterns of soil and soil water-extract samples

UCC-normalized REE patterns were studied at both 0–30 and 30–50 cm depths (Fig. 3A). Results showed similar patterns for the three sub-areas. We thus averaged sub-areas in the following results. The comparison between the two soil depths also showed similar patterns, despite statistically significant higher ($p < 0.05$) LREE/HREE ratios in the topsoil (on average, 1.24) than in the subsoil (1.18). Both REE patterns, however, showed a negative Eu anomaly (on average, 0.80 and 0.82 at 0–30 and 30–50 cm depth, respectively).

The soil water-extract samples, normalized by the corresponding soil horizon (0–30 and 30–50 cm depth), showed distinct REE behaviors than soil samples (Fig. 3B): relative MREE enrichment, LREE/HREE ratios < 1, negative Ce anomaly, and positive Eu anomaly. Although soil water-extract REE patterns were similar between both soil depths, the negative Ce anomaly was more pronounced at 30–50 cm depth (on average, 0.63) compared to 0–30 cm depth (0.85).

REE normalized patterns of soil solution and snow samples

All soil solution samples showed similar soil-normalized REE patterns (Fig. 3C), including negative Ce anomaly (on average, 0.61), negative Tb anomaly (0.64), and low LREE/HREE ratios (0.51). These characteristics were not fully observed in soils (Fig. 3A) nor soil water-extracts (Fig. 3B). Only the soil solutions collected on 15 Dec. 2020 was slightly different from the other samples, with 2.7-times higher ΣREE concentrations and 1.5-times less pronounced negative Ce anomaly.

The only snow sample collected on 14 Jan. 2021 showed distinct REE pattern to soil solutions: no obvious negative Ce and Tb anomalies and no relative HREE enrichment (Fig. 3C). We thus normalized soil solution samples to the snow concentrations to highlight differences between these two compartments (Fig. 3D). Therefore, snow-normalized REE profiles still showed negative Ce (on average, 0.59) and Tb (0.72) anomalies and presented a low negative Yb anomaly (0.81). Beside theses anomalies, the REE profiles were relatively flat with the exception of the last HREE (Tm to Lu): LREE/HREE of 0.68.

REE normalized patterns of plant and earthworm samples

Soil-normalized REE patterns of plant samples showed similar trends between considered species and parts of plant without noticeable anomaly

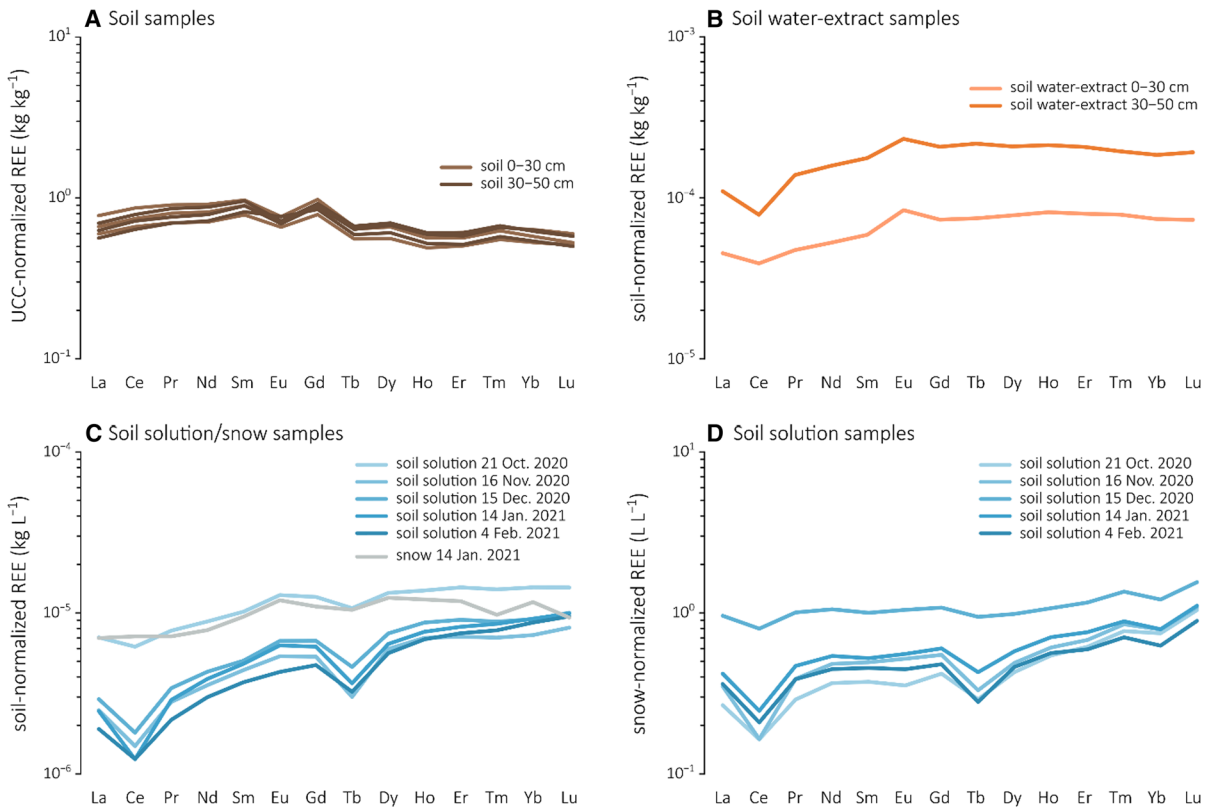

Fig. 3 Normalized profiles of rare earth elements (REE) from samples collected at the centre de Marbaix: UCC-normalized soil profiles (**A**), soil-normalized soil water-extract profiles (**B**), soil-normalized soil solution and snow profiles (**C**), and snow-normalized soil solution profiles (**D**)

(Fig. 4A–C). Despite relatively flat profiles, all REE patterns showed a relative MREE depletion, modifying the LREE/HREE ratio (on average, 0.86 for shoots and 0.83 for roots). However, REE concentrations highlighted systematic higher values in roots compared to shoots (on average, 6.0 times for *Vicia faba*, 2.7 times for *Trifolium resupinatum*, and 3.4 times for *Triticum spelta*). Also, REE concentrations increased over time in shoots (except for *Vicia faba*) and roots (except for *Triticum spelta*). The increasing ratios from the first sampling date to the last one were between 2.5 and 4.1 for shoots according to the species. The respective ratios for roots were either lower (from 1.8 to 2.4) or showed no evolution over time (*Triticum spelta*).

Earthworms collected in each sub-area indicated different soil-normalized REE patterns than the other compartments considered (Fig. 4D): low LREE/HREE ratios (0.49) and negative Ce anomaly (0.69) as observed in soil solution samples, but no pronounced negative Tb anomaly. One composite sample (i.e., a sub-area) showed singular REE pattern with higher relative HREE concentrations and more pronounced negative Eu anomaly (0.76).

Rare earth element relationships

As for trace elements, a PCA was performed on REE concentrations (Fig. 2C). The first component (70% of data variance) was influenced by Dy, Er, Ho, Yb, Lu, and Tm (positive scores) and Pr, La, Ce, and Nd (negative scores). As observed on the first PCA (Fig. 2A), soil solutions and, to a lesser extent, 0–30 cm soil water-extracts (positive scores), were opposed to soil samples (negative scores). Also, the REE signatures of plants and soils were closer compared to the trace elements. The second component

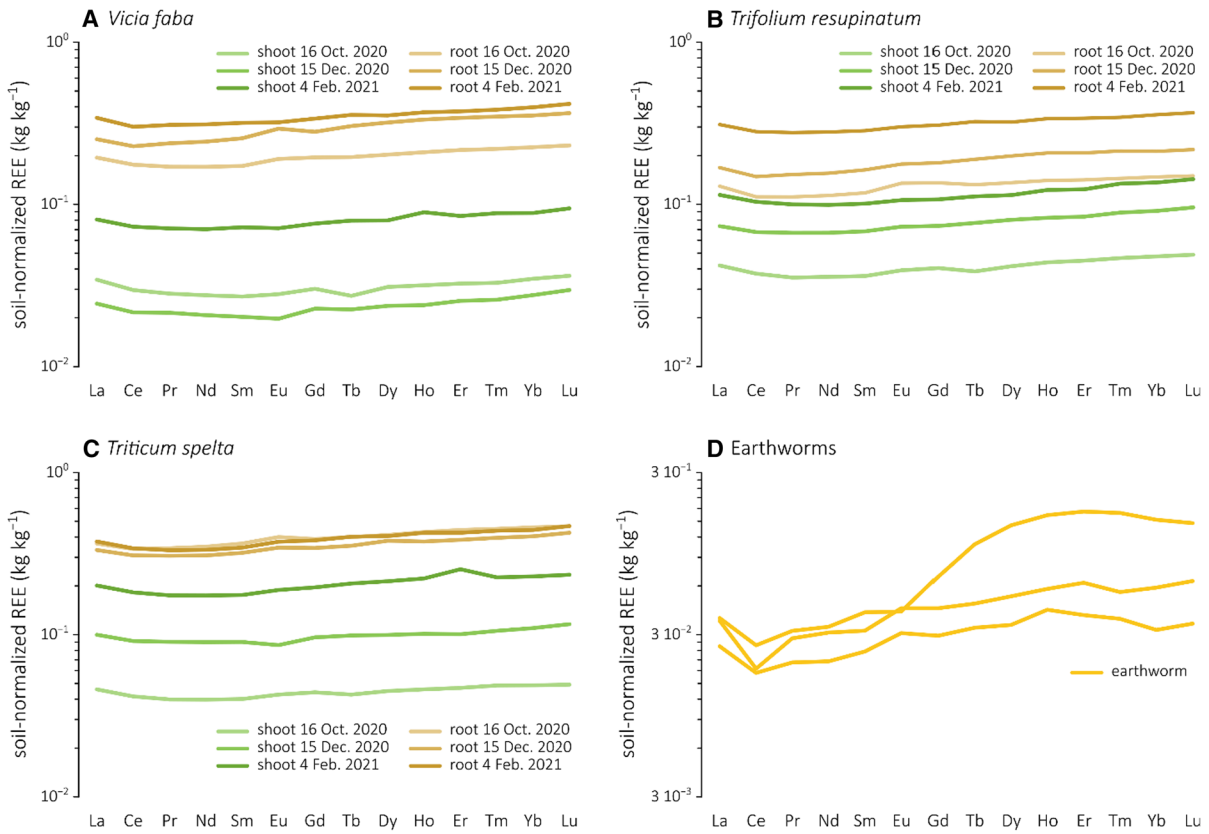

Fig. 4 Soil-normalized profiles of rare earth elements (REE) from plant (shoot and root) and earthworm samples collected at the centre de Marbaix: bean (*Vicia faba*; **A**), Persian clover (*Trifolium resupinatum*; **B**), spelt (*Triticum spelta*; **C**), and earthworms (**D**)

(17% of data variance) grouped Sm, Eu, Gd, and, to a lesser extent, Nd (positive scores).

Based on these results, we plotted the relationship between Ce/Eu (proxy of both Ce and Eu anomalies) and La/Lu (proxy of LREE/HREE fractionation) for all samples collected in this study (Fig. 2D). Once again, soil solutions (relatively low Ce/Eu and La/Lu) and soils (relatively high Ce/Eu and La/Lu) were the two main end-members. Plant signatures were close to soil ones (despite lower Ce/Eu and La/Lu), and their distribution was neither related to sampling dates nor plant species unlike for trace elements. Yet, shoots showed higher relative Ce/Eu ratio than roots, resulting in a discrepancy from the linear relationship between the two main end-members. Soil water-extract samples showed an intermediate signature despite lower relative Ce/Eu ratio. Finally, earthworm samples presented a high heterogeneity and the snow sample had a signature between soil and soil water-extract samples.

Discussions

Transfer of trace elements from soil to plant

Trace elements concentrations measured in soil and plant samples (Table 1) were in the same order of magnitude as observed in the literature (He et al. 2005; Kabata-Pendias 2010; Antoniadis et al. 2017). Their transfer from soil to plant was investigated using two transfer factors ($TF_{soil–plant}$ and $TF_{root–shoot}$; Fig. 1) that were in the same range as those found in Senesil et al. (1999). Although these transfers depended on sampling date, we distinguished, as expected, weakly transferred elements (including elements without or with low physiological role, such as Ti, V, Pb, and Co) from highly transferred ones

(including plant nutrients, such as Zn and Cu, or Sr following the metabolic pathway of Ca). The physicochemical behavior of the considered element also influenced its transfer: for example, Cd had $TF_{soil-plant}$ 3-times greater than Pb due to its higher soil mobility and phytoavailability (Angelova et al. 2004). The uptake of essential elements followed the nutritional requirement, as observed for Zn with higher transfer from soil to roots and/or stem at the beginning of the growth (Nan et al. 2002; Wu et al. 2010), unlike continuous transfer over time for the other elements. The influence of plant species was observed in the trace element ratios where root samples of *Triticum spelta* were closer to the soil end-member than *Trifolium resupinatum* (Fig. 1B). Differences between species (lower relative Cu and Cd accumulation in *Triticum spelta* compared to Mn) could be explained by low acquisition efficiency for some elements in monocotyledon compared to dicotyledon (Wiche et al. 2016b). Note that intercropping cover crop promotes the accumulation of trace elements and REE in plants.

The soil–plant transferability coincided with the soil extractability assessed using soil water-extract/soil concentration ratios (except for Mn and V; Table 1). Similar patterns were evidenced for soil solution/soil concentration ratios, indicating geochemical commonalities between soil water-extracts and soil solutions: the more extractable an element is, the more it is present in the soil solution. The transfer from root to shoot, however, highlighted a lower heterogeneity among trace elements (mean $TF_{root-shoot}$ between 0.15 and 1.06 for *Trifolium resupinatum*) compared to $TF_{soil-plant}$ (except for Cd with $TF_{root-shoot}$ <0.13 due to high root accumulation; Green et al. 2006). Note that we cannot exclude any soil particle contamination in root samples (Han et al. 2005), which could explain high concentrations for lithogenic elements (e.g., Ti), but this does not prevent species differences observed in roots for both essential and non-essential elements (Fig. 1B).

The PCA and element relationships (Fig. 2 A–B) indicate that the compartments considered behaved differently: (1) soils and soil solutions were the two end-members of this system in which both plants and soil water-extracts were located somewhere in between; (2) the different signatures of roots and shoots highlight distinct soil–root–shoot transfer processes (high Cu uptake by plant and transfer to shoot vs. Cd accumulation in roots; Fig. 1), resulting in a discrepancy from the soil–soil solution linear relationship; and (3) soil solutions and soil water-extracts were highly heterogeneous according to the sampling date, sub-area, or soil depth.

Rare earth elements: implications for the soil–plant transfer understanding

Soil ΣREE concentrations measured in this study (111 mg kg^{-1}; Table 1) were in the same range as observed in European soils (about 126 mg kg^{-1}; Fedele et al. 2008; Mihajlovic and Rinklebe 2018). We also notice low spatial heterogeneity across the study area with similar soil ΣREE concentrations and REE patterns (Fig. 3A). However, all parts of plants showed an obvious concentration increase over time (up to 4 times; Fig. 4A–C), which reveals the element accumulation with time, as observed for trace elements (Fig. 1). The $TF_{soil-plant}$ of REE (on average, 0.07, close to data reported by Tyler 2004) were comparable to values calculated for V, Pb, or Co, although REE did not correctly represent elements largely accumulated in roots (e.g., Cd) nor transferred to shoot (e.g., Cu or Zn). However, no species influence was observed for REE distribution unlike trace elements. Note that the mixing ratio of plant species in an intercropping cover crop do not significantly influence the REE accumulation (Wiche et al. 2016a). Due to higher soil–root transfer than root–shoot transfer, however, root REE concentrations were higher than shoot ones, as frequently reported in various crop species (Li et al. 1998; Lihong et al. 1999; Xu et al. 2002).

Despite similar trends between soil solutions and soil water-extracts, resulting to a linear relationship between soil extractability (i.e., soil water-extract/soil concentration ratio) and soil solution/soil concentration ratios (Fig. 5A), soil extractability does not appear as a 'universal' proxy of element bioavailability and effective transfer from soil to plant (heterogeneous distribution of elements; Fig. 5B). Indeed, even if the most extractable elements were generally the most transferred from soil to plant, some exceptions occurred: relatively lower transfer for Ba, Cd, and V and higher transfer for Ti and Sr compared to their extractability. This was also evidenced by dissimilar REE patterns between soil/plant samples and soil solution/soil water-extract samples (Figs. 3 and

4), including distinct REE indices (Fig. 2C–D). This highlights that the plant REE composition is largely determined by the soil REE composition, while the intermediate compartments (i.e., soil solutions and soil water-extracts) do not represent the bioavailable chemical fraction. The large heterogeneity of these signatures with space (soil solutions and soil water-extracts) and time (soil solutions) may result from different soil chemistry or a sampling protocol bias (pF 3.46 using a 60 mL syringe with rhizons, likely including both capillary and gravitational water; Di Bonito et al. 2018), respectively. Indeed, the latter might be influenced by atmospheric deposition that would modify the chemical composition (e.g., the strong negative Tb anomaly in soil solution samples also present in the snow sample; Fig. 3C–D).

Distinct behaviors between LREE and HREE throughout the soil–plant system indicate higher HREE extractability (+42% for the topsoil), occurrence in soil solution (+90% after soil-normalization), and soil–plant transfer (+20% from the topsoil) compared to LREE. Despite lower HREE solubility reported in the literature (Tyler 2004; Stille et al. 2006; Martinez et al. 2018), we suggest a higher relative HREE mobility (from soil to soil solution; Cidu et al. 2013), and thus plant bioavailability (Fig. 5B), instead of HREE leaching due to complexation during weathering, as suggested by Laveuf and Cornu (2009). We hypothesize that: (1) REE fractionation is limited in the plant species studied (cover crop species); and/or (2) the relative non-enrichment of HREE in the soils studied limits this fractionation. As for LREE and HREE, Ce and Eu depicted diametrically opposed soil extractability (Ce << Eu), despite no $TF_{soil–plant}$ difference (Fig. 5). The difference of negative Ce anomaly between 0 and 30 and 30–50 cm soil water-extracts (Fig. 3B) may be explained by: (1) higher mineral content in the deeper soil horizon, such as Fe and Mn oxyhydroxides, promoting the Ce adsorption (Brioschi et al. 2013); or (2) higher soil organic matter content in topsoil (Leleyter et al. 1999; Cidu et al. 2013). Indeed, Ce has a less organic matter affinity than the other LREE, explaining the lowest relative Ce content in topsoil (Davranche et al. 2005). This is supported by a strongest negative Ce anomaly in earthworms feeding on soil organic matter (Fig. 4D), as well as the relative HREE enrichment (Cidu et al. 2013). Negative Ce anomaly also appeared in soil solutions due to either Ce adsorption on soil minerals particularly significant as Ce^{4+} in oxidized waters (Leybourne et al. 2000) or influence of dissolved organic matter (Fig. 3). These hypotheses are supported by the relative HREE enrichment in soil solutions that were also influenced by adsorption and/or dissolved organic matter (Laveuf and Cornu 2009; Cidu et al. 2013).

All geochemical behaviors of REE between compartments in the soil–plant continuum studied and gaps identified were summarized in the Fig. 6, including comparison between UCC-normalized patterns.

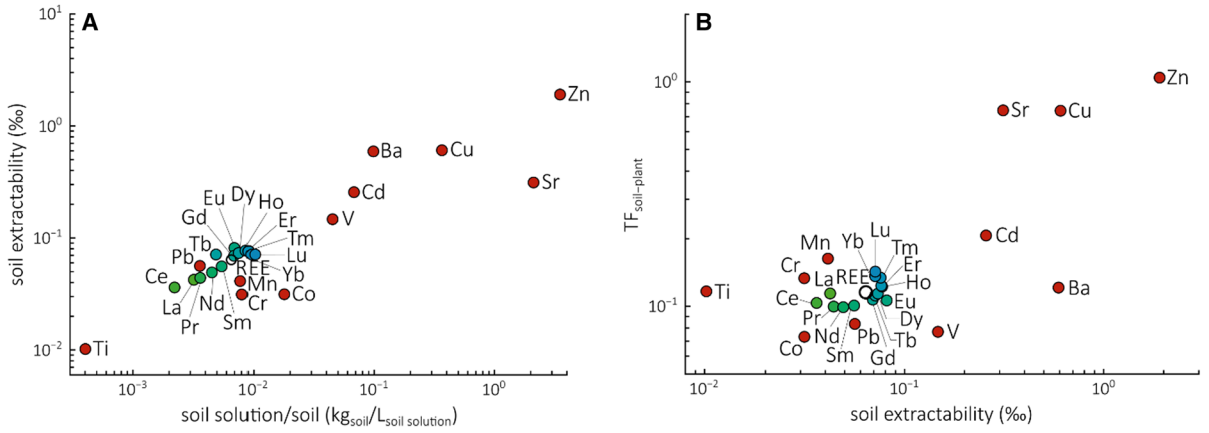

Fig. 5 Relationship between soil extractability (soil water-extract/soil concentration ratio, 0–30 cm soil depth) and soil solution/soil concentration ratio (**A**) and between soil–plant transfer ($TF_{soil–plant}$) and soil extractability (**B**) of trace elements (red) and rare earth elements (REE, from green for LREE to blue for HREE), as well as the average REE (open circle), in an intercropping cover crop soil–plant system

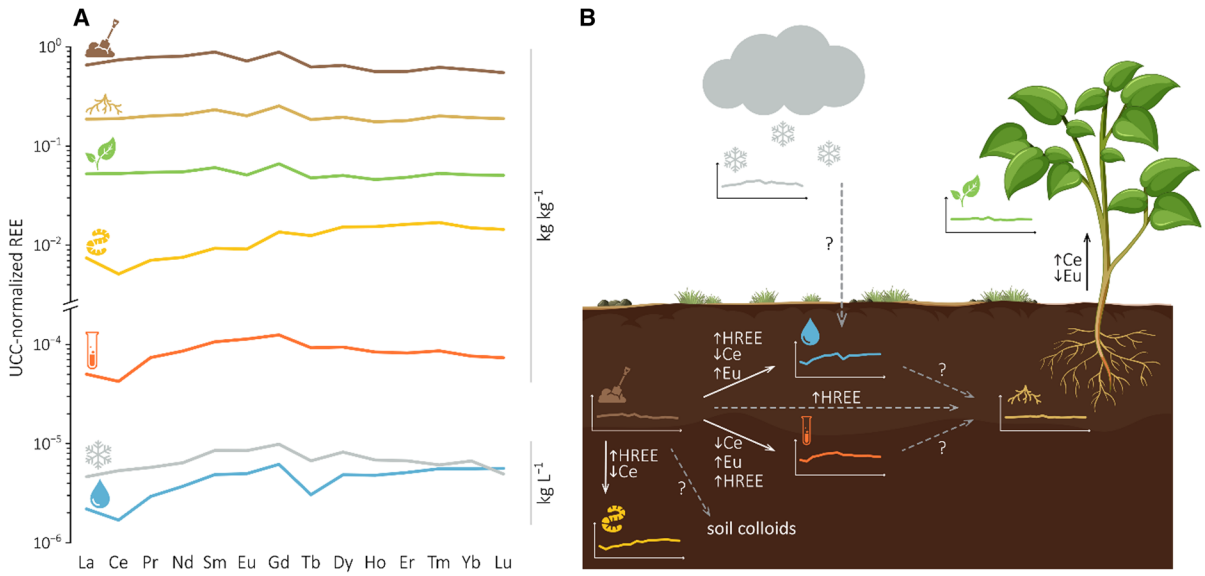

Fig. 6 Synthesis of rare earth element (REE) transfer in an intercropping cover crop soil–plant system: UCC-normalized REE patterns of the different compartments considered (**A**) and hypothetical chemical relationships between compartments (**B**)

Conclusion

This paper aimed at evaluating the geochemical relevance and representativeness of soil solution and soil water-extract as intermediate compartments in the transfer of trace element from soil to plant. For that purpose, we compared REE normalized patterns along the soil–plant continuum. The main result showed dissimilar REE patterns between soil/plant samples and soil solution/soil water-extract samples, meaning that these intermediate compartments in the soil–plant system do not appear as a 'universal' proxy for the element bioavailability. This confirms that is mentioned in the literature for trace elements, considering a set of elements without obvious propensity to biological accumulation (unlike Cd, Cu, or Zn). Moreover, REE distribution evidenced distinct extractability and transferability despite their similar chemical characteristics. We thus characterized the environmental conditions that may control trace element transfer by quantifying the REE indices. The distinct LREE and HREE behaviors highlight more or less mobile elements whose trends do not always seem in agreement with the literature. Coupled with LREE/HREE and due to their different extractabilities, Ce and Eu allowed to highlight distinct transfer from soil to plant thanks to possible adsorption or organic matter complexation that should be further confirmed by studying contrasted soils.

Acknowledgements Thanks to Hugues Falys and Rémi Desmet for the sampling site access to the centre de Marbaix (UCLouvain) and providing relevant advice. We also thank Claudine Givron for the carbon analysis. We thank two anonymous reviewers for their valuable comments.

Author contributions JF, BA, NB, and YA contributed to the study conception and design, material preparation, and data collection. Analyses were performed by JF, BA, NB, LM, and ED. The first draft of the manuscript was written by BA, JF, and YA and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript. Funding was acquired by YA.

Funding This work was financially supported by the Fonds spéciaux de recherche (FSR) from UCLouvain.

Data availability The data set generated during the current study are available in the electronic supplementary material (ESM_1.xlsx).

Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

References

Adriano DC (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals, 2nd edn. Springer, New York

Agnan Y, Séjalon-Delmas N, Probst A (2013) Comparing early twentieth century and present-day atmospheric pollution in SW France: a story of lichens. Environ Pollut 172:139–148. https://doi.org/10.1016/j.envpol.2012.09.008

Agnan Y, Séjalon-Delmas N, Probst A (2014) Origin and distribution of rare earth elements in various lichen and moss species over the last century in France. Sci Total Environ 487:1–12. https://doi.org/10.1016/j.scitotenv.2014.03.132

Angelova V, Ivanov K, Ivanova R (2004) Effect of chemical forms of lead, cadmium, and zinc in polluted soils on their uptake by tobacco. J Plant Nutr 27:757–773. https://doi.org/10.1081/PLN-120030609

Antoniadis V, Levizou E, Shaheen SM et al (2017) Trace elements in the soil-plant interface: Phytoavailability, translocation, and phytoremediation–A review. Earth-Sci Rev 171:621–645. https://doi.org/10.1016/j.earscirev.2017.06.005

Brioschi L, Steinmann M, Lucot E et al (2013) Transfer of rare earth elements (REE) from natural soil to plant systems: implications for the environmental availability of anthropogenic REE. Plant Soil 366:143–163. https://doi.org/10.1007/s11104-012-1407-0

Cantrell KJ, Byrne RH (1987) Rare earth element complexation by carbonate and oxalate ions. Geochim Cosmochim Acta 51:597–605. https://doi.org/10.1016/0016-7037(87)90072-X

Chojnacka K, Chojnacki A, Górecka H, Górecki H (2005) Bioavailability of heavy metals from polluted soils to plants. Sci Total Environ 337:175–182. https://doi.org/10.1016/j.scitotenv.2004.06.009

Cidu R, Vittori Antisari L, Biddau R et al (2013) Dynamics of rare earth elements in water–soil systems: The case study of the Pineta San Vitale (Ravenna, Italy). Geoderma 193–194:52–67. https://doi.org/10.1016/j.geoderma.2012.10.009

Davranche M, Pourret O, Gruau G et al (2005) Adsorption of REE(III)-humate complexes onto MnO_2: Experimental evidence for cerium anomaly and lanthanide tetrad effect suppression. Geochim Cosmochim Acta 69:4825–4835. https://doi.org/10.1016/j.gca.2005.06.005

Di Bonito M, Breward N, Crout N et al (2018) Extraction and characterization of pore water in contaminated soils. In: De Vivo B, Belkin HE, Lima A (eds) Environmental geochemistry. Site characterization, data analysis and case histories, 2nd edn. Elsevier, Amsterdam, pp 195–235

Dinno A (2017) dunn.test: Dunn's Test of Multiple Comparisons Using Rank Sums

Fedele L, Plant JA, Vivo BD, Lima A (2008) The rare earth element distribution over Europe: geogenic and anthropogenic sources. Geochem Explor Environ Anal 8:3–18. https://doi.org/10.1144/1467-7873/07-150

Garrett RG (2013) The 'rgr' package for the R Open Source statistical computing and graphics environment - a tool to support geochemical data interpretation. Geochem Explor Environ Anal 13:355–378. https://doi.org/10.1144/geochem2011-106

Green ID, Jeffries C, Diaz A, Tibbett M (2006) Contrasting behaviour of cadmium and zinc in a soil–plant–arthropod system. Chemosphere 64:1115–1121. https://doi.org/10.1016/j.chemosphere.2005.11.074

Han F, Shan X, Zhang J et al (2005) Organic acids promote the uptake of lanthanum by barley roots. New Phytol 165:481–492. https://doi.org/10.1111/j.1469-8137.2004.01256.x

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

Henderson P (1984) Rare earth element geochemistry. Elsevier, Amsterdam

Kabata-Pendias A (2004) Soil–plant transfer of trace elements—an environmental issue. Geoderma 122:143–149. https://doi.org/10.1016/j.geoderma.2004.01.004

Kabata-Pendias A (2010) Trace elements in soils and plants, 4th edn. CRC Press, Boca Raton

Krzciuk K, Gałuszka A (2020) Presence and possible origin of positive Eu anomaly in shoot samples of Juncus effusus L. J Trace Elem Med Biol 58:126432. https://doi.org/10.1016/j.jtemb.2019.126432

Laveuf C, Cornu S (2009) A review on the potentiality of rare earth elements to trace pedogenetic processes. Geoderma 154:1–12. https://doi.org/10.1016/j.geoderma.2009.10.002

Lê S, Josse J, Husson F (2008) FactoMineR: an R package for multivariate analysis. J Stat Softw. https://doi.org/10.18637/jss.v025.i01

Leleyter L, Probst J-L, Depetris P et al (1999) REE in river sediments: partitioning into residual and labile fractions. Comptes Rendus Acad Sci 329:45–52. https://doi.org/10.1016/S1251-8050(99)80226-2

Leybourne MI, Goodfellow WD, Boyle DR, Hall GM (2000) Rapid development of negative Ce anomalies in surface waters and contrasting REE patterns in groundwaters associated with Zn–Pb massive sulphide deposits. Appl Geochem 15:695–723. https://doi.org/10.1016/S0883-2927(99)00096-7

Li F, Shan X, Zhang T, Zhang S (1998) Evaluation of plant availability of rare earth elements in soils by chemical fractionation and multiple regression analysis. Environ Pollut 102:269–277. https://doi.org/10.1016/S0269-7491(98)00063-3

Liang T, Zhang S, Wang L et al (2005) Environmental biogeochemical behaviors of rare earth elements in soil–plant systems. Environ Geochem Health 27:301–311. https://doi.org/10.1007/s10653-004-5734-9

Lihong Y, Xiaorong W, Hao S, Haishi Z (1999) The effect of EDTA on rare earth elements bioavailability in soil ecosystem. Chemosphere 38:2825–2833. https://doi.org/10.1016/S0045-6535(98)00496-2

Marchiol L, Assolari S, Sacco P, Zerbi G (2004) Phytoextraction of heavy metals by canola (*Brassica napus*) and radish (*Raphanus sativus*) grown on multicontaminated soil. Environ Pollut 132:21–27. https://doi.org/10.1016/j.envpol.2004.04.001

Martinez RE, Pourret O, Faucon M-P, Dian C (2018) Effect of rare earth elements on rice plant growth. Chem Geol 489:28–37. https://doi.org/10.1016/j.chemgeo.2018.05.012

Miao L, Xu R, Ma Y et al (2008) Geochemistry and biogeochemistry of rare earth elements in a surface environment (soil and plant) in South China. Environ Geol 56:225–235. https://doi.org/10.1007/s00254-007-1157-0

Mihajlovic J, Rinklebe J (2018) Rare earth elements in German soils - A review. Chemosphere 205:514–523. https://doi.org/10.1016/j.chemosphere.2018.04.059

Monei N, Hitch M, Heim J et al (2022) Effect of substrate properties and phosphorus supply on facilitating the uptake of rare earth elements (REE) in mixed culture cropping systems of Hordeum vulgare, Lupinus albus and Lupinus angustifolius. Environ Sci Pollut Res 29:57172–57189. https://doi.org/10.1007/s11356-022-19775-x

Nan Z, Zhao C, Li J et al (2002) Relations between soil properties and selected heavy metal concentrations in spring wheat (*Triticum aestivum* L.) grown in contaminated soils. Water Air Soil Pollut 133:205–213. https://doi.org/10.1023/A:1012962604095

Pourret O, van der Ent A, Hursthouse A et al (2021) The 'europium anomaly' in plants: facts and fiction. Plant Soil. https://doi.org/10.1007/s11104-021-05210-6

Rauch JN, Pacyna JM (2009) Earth's global Ag, Al, Cr, Cu, Fe, Ni, Pb, and Zn cycles. Glob Biogeochem Cycles 23:16. https://doi.org/10.1029/2008GB003376

R Core Team (2021) R: A language and environment for statistical computing

Rudnick RL, Gao S (2014) Composition of the continental crust. In: Holland HD, Turekian KK (eds) Treatise on geochemistry, 2nd edn. Elsevier, Oxford, pp 1–51

Senesil GS, Baldassarre G, Senesi N, Radina B (1999) Trace element inputs into soils by anthropogenic activities and implications for human health. Chemosphere 39:343–377. https://doi.org/10.1016/S0045-6535(99)00115-0

Stille P, Steinmann M, Pierret M-C et al (2006) The impact of vegetation on REE fractionation in stream waters of a small forested catchment (the Strengbach case). Geochim Cosmochim Acta 70:3217–3230. https://doi.org/10.1016/j.gca.2006.04.028

Tyler G (2004) Rare earth elements in soil and plant systems - a review. Plant Soil 267:191–206. https://doi.org/10.1007/s11104-005-4888-2

Wiche O, Kummer N-A, Heilmeier H (2016a) Interspecific root interactions between white lupin and barley enhance the uptake of rare earth elements (REEs) and nutrients in shoots of barley. Plant Soil 402:235–245. https://doi.org/10.1007/s11104-016-2797-1

Wiche O, Székely B, Kummer N-A et al (2016b) Effects of intercropping of oat (*Avena sativa* L.) with white lupin (*Lupinus albus* L.) on the mobility of target elements for phytoremediation and phytomining in soil solution. Int J Phytoremediation 18:900–907. https://doi.org/10.1080/15226514.2016.1156635

Wickham H (2016) ggplot2: elegant graphics for data analysis, 2nd edn. Springer, New York

Wu C, Lu L, Yang X et al (2010) Uptake, translocation, and remobilization of zinc absorbed at different growth stages by rice genotypes of different Zn densities. J Agric Food Chem 58:6767–6773. https://doi.org/10.1021/jf100017e

Wyttenbach A, Furrer V, Schleppi P, Tobler L (1998) Rare earth elements in soil and in soil-grown plants. Plant Soil 199:267–273. https://doi.org/10.1023/A:1004331826160

Xu X, Zhu W, Wang Z, Witkamp G-J (2002) Distributions of rare earths and heavy metals in field-grown maize after application of rare earth-containing fertilizer. Sci Total Environ 293:97–105. https://doi.org/10.1016/S0048-9697(01)01150-0