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Environmental bioavailability of arsenic, nickel and chromium in soils impacted by high geogenic and anthropogenic background contents

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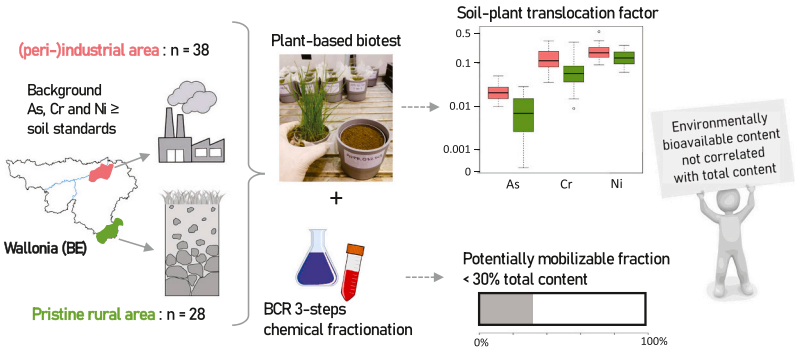
HIGHLIGHTS

- Total As, Cr and Ni soil content frequently surpass normative values in Belgium.
- Total As, Cr and Ni contents generally do not predict environmental bioavailability.
- The potentially mobile or mobilizable fraction of soil As, Cr and Ni is <30 %.
- Environmental bioavailability testing informs better soil management.

GRAPHICAL ABSTRACT



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ABSTRACT

High arsenic, chromium and nickel in soils can pose a hazard to the ecosystem and/or human health. Large areas can be affected by elevated potentially toxic elements (PTE) background contents, entailing a significant effort for managing the potential risk. Assessing the environmental hazard associated to PTE-contaminated soils requires the determination of soil PTE environmental bioavailability, which reflects the capacity of these elements to be transferred to living organisms. Here we assess the environmental bioavailability of As, Cr and Ni in topsoils from the Liège basin and Belgian Lorraine, two areas in Wallonia, Belgium, affected by elevated As, Cr and Ni background contents. The source of soil As, Cr and Ni differs in Liège and Lorraine: anthropogenic in the former location and geogenic in the latter. The environmental bioavailability of PTE was determined using two complementary approaches: (1) by chemical fractionation with the Community Bureau of Reference (BCR) three-step sequential extraction protocol and (2) by estimating the phytoavailability using a plant-based biotest (*Lolium multiflorum* as plant model). The results show that total As (6–130 mg·kg^{-1}), Cr (15–268 mg·kg^{-1}), and Ni (8–140 mg·kg^{-1}) contents in the Liège and Lorraine soils frequently exceed the soil clean-up standards. However, no positive correlation was found between the total contents and BCR extraction results or rye-grass contents, except for As in Liège soils. Total As, Cr or Ni contents surpassing soil standards do not necessarily result in elevated mobile, potentially mobilizable and phytoavailable contents. In general, environmental bioavailability of As, Cr and Ni is higher in soils from Liège basin compared to those sampled in Belgian Lorraine. The mobile and potentially mobilizable fractions of As, Cr and Ni account for <30 % of their total contents following the BCR

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extractions. Our study provides valuable information for sustainable management at the regional scale of soils containing high PTE contents.

1. Introduction

Potentially toxic elements (PTEs) such as As, Cr and Ni in soils represent an environmental and health issue as they can be transferred through living organisms such as via plant uptake (Zwolak et al., 2019). When transferred into living organisms, these substances pose a threat to human health and have detrimental effects on ecosystems (Tchounwou et al., 2012; Rehman et al., 2018; Billmann et al., 2023). PTEs in soils may originate from natural processes like rock weathering, wind erosion and volcanism, or from anthropogenic activities, including agricultural activities, pesticide and herbicide manufacturing, coal burning, wood treatment, tanning operations, cement manufacturing, waste incineration and mining or smelting (Adriano, 2001; Kabata-Pendias, 2010; Alloway, 2013; He et al., 2015; Zwolak et al., 2019).

Soil contamination by PTE can arise from either point source pollution, which is a single identifiable and confined source of pollution introducing locally massive amounts of contaminants (Carré et al., 2017), or pollution from widespread activities with no discrete source. The latter type of inputs contributes to elevate the background contents of PTEs in soils. The background content is the content of an element or a substance characteristic of a soil type in an area or region arising from both natural sources and anthropogenic diffuse sources such as atmospheric deposition (ISO 19258:2011). Diffuse anthropogenic inputs and natural sources of PTEs have led to high soil background contents over areas ranging from several municipalities to the regional scale (Pereira et al., 2012; Reimann et al., 2014; Boente et al., 2018; Zuzolo et al., 2020), resulting in significant soil management challenges. Numerous instances of areas affected by elevated PTEs background content are documented in the scientific literature, such as the soils of European cities affected by diffuse anthropogenic inputs (Davidson et al., 2006; Biasioli and Ajmone-Marsan, 2007; Boente et al., 2018; Zuzolo et al., 2020), the regional soil elevated Cr and Ni contents in New Caledonia due to ultramafic rocks parent materials (Becquer et al., 2003) or the elevated PTEs contents in soils due to carbonated rocks in southwest China (Liu et al., 2023).

Typically, the management of health risks associated with PTE-contaminated soils relies on quality standards that are based on total soil contents (Kim et al., 2015). These standards are utilized to determine whether the soils should be considered polluted or not. The use of total PTE content, however, does not adequately assess the potential risk to human health and ecosystems, as suggested by numerous authors (Kördel et al., 2013; Kim et al., 2015; Waterlot and Douay, 2015; Claes et al., 2021). To effectively manage soils with high background contents of PTEs and prevent costly remediation effort, it is essential to understand their environmental bioavailability, i.e. the fraction of contaminant potentially available to organisms (ISO 17402:2008). This knowledge can also help anticipate potential exposure risks to individuals residing in affected areas (Kim et al., 2015). The source (anthropogenic or geogenic) of the PTEs influences their environmental bioavailability. Referring to Rauret (1998), PTEs in unpolluted soils are mainly bound to silicates and primary minerals forming relatively immobile species, whereas they are generally more mobile and bound to other phases in anthropogenically polluted soils. The assessment of PTE bioavailability in soils is important, particularly in the context of remediating contaminated sites. The reduction of PTE bioavailability through soil amendments has been explored in many studies, as reviewed by (Palansooriya et al., 2020). For example, the immobilization of As has been investigated through the incorporation of magnetite, goethite, and zero-valent iron nanoparticles (Gil-Díaz et al., 2014; Baragaño et al., 2020; Ganie et al., 2021; Chen et al., 2022). Another well-known approach is phytoremediation, an innovative technique that utilises plants to remove bioavailable contents of PTEs from the soil (Oladoye et al., 2022).

The environmental bioavailability of PTEs can be assessed through either chemical or biological methods. Although biological methods are more complex, they produce results that can better address transfer of metal in organisms (ISO 16198:2015). In particular, the plant-based rhizotest has been developed specifically to assess PTEs environmental bioavailability, allowing comparison of the results between different soils. This biotest however does not inform about the distribution of PTEs among the different chemical pools which can be properly achieved by chemical sequential fractionation such as the Community Bureau of Reference (BCR) three-step sequential extraction protocol Quevauviller et al., 1997). The BCR protocol was originally designed for soil metals such as Cr and Ni occurring in cationic forms in acidic conditions. While there are inherent challenges associated with sequential extraction techniques (Gómez Ariza et al., 2000; Gleyzes et al., 2002), BCR provides practical advantages, as it offers a single method for analysing multiple PTEs (Gil-Díaz et al., 2021). The protocol is widely accepted and utilized worldwide for assessing the chemical fractionation of PTEs in soils (Sutherland, 2010; Cuvier et al., 2021). The BCR protocol has also been successfully applied for studying As in soils and sediments (Sahuquillo et al., 2003; Vázquez et al., 2008; Baig et al., 2009; Waterlot and Douay, 2015; Rosas-Castor et al., 2015; Gil-Díaz et al., 2021), although As is usually present as an oxyanion in these media (Wenzel et al., 2001).

The main objective of this study is to determine the environmental bioavailability of As, Cr and Ni in soils from two areas with high background contents of contrasting origin: (1) anthropogenic contamination (the Liège basin) and (2) geogenic contamination (the Belgian Lorraine). To achieve this, the relationship between environmental bioavailability and the origin of the soil PTEs is investigated, as well as the relationship between the environmental bioavailability with the soil PTEs chemical pools. This study also looks at the approximation of PTEs environmental bioavailability by considering the total content, the content in the different chemical pools, and soil parameters.

2. Materials and methods

2.1. Soil sampling

The study was conducted in Wallonia, Belgium. Soil sampling took place in 2010 and 2018 as part of the POLLUSOL 2 (Pereira et al., 2012) and SANISOL (Pereira et al., 2019) projects. The soil samples (Fig. 1, part A) were obtained from the industrial basin in Liège ($n = 38$) and Belgian Lorraine ($n = 28$). The Liège soils are known to have been affected during the last century by atmospheric fallout from non-ferrous metal smelting plants, iron blast and steelmaking blast furnace and coal industry, resulting in elevated contents of PTEs such as Pb or Zn (Pereira et al., 2012). Although disturbed horizon successions and occasional presence of technogenic materials were observed in some soil profiles (non-vegetable and vegetable gardens), these factors are not the primary source of contamination in the topsoils. In contrast, the soils sampled in this part of Belgian Lorraine are located far from any contamination sources and have not been exposed to significant anthropogenic inputs of PTEs. An undisturbed sequence of soil horizons was observed at all the Lorraine sites. The soils in Liège are Luvisols and Cambisols (WRB, IUSS Working Group, 2015), which formed from loess and Paleozoic sandstone and shales from Devonian deposits, respectively. The Lorraine soils are also Luvisols and Cambisols, but their parent material corresponds to Jurassic iron-rich calcareous sandstones and marls. All soil samples exhibited predominantly loamy texture, with Lorraine soils

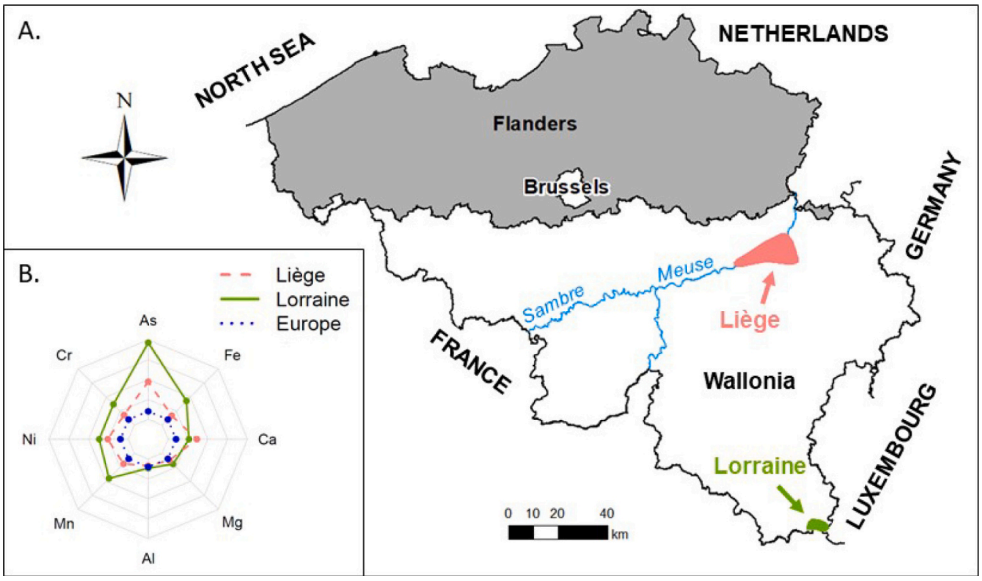

Fig. 1. A. Location of the Liège industrial basin (38 surface soils sampled) and the study area surveyed in Belgian Lorraine (28 surface soils sampled). B. Radarchart of the median aqua regia contents in Lorraine, Liège and Europe (GEMAS agricultural soils). The axes range from 0 to 10 times the European median value (in $mg \cdot kg^{-1}$: As = 5.5, Cr = 20, Ni = 15, Mn = 445, Mg = 2860, Ca = 3030; in %: Al = 11.0, Fe = 17.2).

having a comparatively higher clay content compared to Liège soils. Land use consisted in urban parks and gardens (Liège: $n = 12$), vegetable gardens (Liège: $n = 16$ and Lorraine: $n = 13$) and agricultural soils (Liège: $n = 10$ and Lorraine: $n = 15$). At each site, we collected the soil surface horizon using hand auger and to a maximum depth of 0–20 cm, depending on land use type. Individual soil samples (0.5 to 1 kg) were taken in the center of the plot to avoid border effects. Most topsoils from Liège are fine-grained (<2 mm fraction), whereas those from Lorraine have a stone content >15 %. Note that the number of samples collected in Liège soils enables an assessment of the general environmental bioavailability of soil As, Cr, and Ni content, but does not aims at providing an exhaustive description within the complex and spatially variable context of urban soils.

2.2. Soil sample characterization

The soil samples were air-dried at room temperature. Once the roots and leaves were removed, a glass bottle was gently rolled over the samples to crush the macroaggregates. The soil material was then sieved at 2 mm. Soil pH was measured using a glass electrode in a 1:5 (*V*/V) suspension of soil in water (ISO 10390:2005). Clay content was obtained by gravitational liquid sedimentation (ISO 13317-2:2001), and residual humidity after 105 °C drying on a separate subsample.

Elemental contents (As, Cr, Ni, Mn, Mg, Al, Ca and Fe) were obtained by aqua regia digestion under reflux heating of the soil material (ISO 11466:1995) and inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific™ iCAP™ 6500) measurements, and will be referred to as As_{AR}, Cr_{AR}, Ni_{AR}, Mn_{AR}, Mg_{AR}, Al_{AR}, Ca_{AR} and Fe_{AR} in what follows, respectively. Triplicates and analyses of internal standard reference materials were performed to ensure precision and trueness of the measurements. The detection limit in solution was 3 $\mu g \cdot L^{-1}$ for As and 0.3 $\mu g \cdot L^{-1}$ for both Cr and Ni. The Walkley-Black method was used for determination of soil organic carbon (OrgC) content after dissolving carbonates with hydrochloric acid (ISO 10694:1995). All element contents are given on a dry matter basis (i.e., dried at 105 °C).

2.3. BCR sequential extraction

The BCR three-step sequential extraction scheme, an analytical procedure recommended by the Reference Materials Directorate (F.6) of the European Commission's Joint Research Centre (JRC), formerly named BCR (Community Bureau of Reference; Quevauviller et al., 1997) was applied to assess the chemical fractionation of As, Cr and Ni. The BCR protocol allows quantification of three operationally-defined fractions corresponding to different chemical forms. Step 1 (0.11 $mol \cdot L^{-1}$ acetic acid) is aimed at extracting the exchangeable fraction (F1), including cations and anions weakly bound to surfaces or functional groups with either a negative or a positive charge. Step 2 (0.1 $mol \cdot L^{-1}$ hydroxylammonium chloride) targets the fraction associated to reducible compounds (F2), including elements/compounds bound to iron and manganese oxy-hydroxides. Step 3 (8.8 $mol \cdot L^{-1}$ H_2O_2 followed by 1.0 $mol \cdot L^{-1}$ ammonium acetate at pH 2) extracts the fraction associated to oxydizable compounds (F3), representing the fraction complexed to organic matter or associated to sulphides. Sample extraction was performed using a mechanical horizontal shaker during 16 h. After separation by centrifugation, the supernatant was filtered (0.45 μm), and the As, Cr and Ni concentrations in the solution were measured by ICP-Mass spectrometry (ICP-MS). Step 1-, Step 2- and Step 3-extractable contents ($mg \cdot kg^{-1}$) were expressed on a soil dry mass basis. For individual samples, the fractions F1, F2 and F3 (%) are the ratios of Step 1-, Step 2- and Step 3-extractable contents to the corresponding aqua regia-extractable contents. For simplification purposes, the notations As_{BCR}, Cr_{BCR} and Ni_{BCR} are used in the following sections to refer to BCR contents for As, Cr and Ni, respectively.

The interpretation of the extractions and fractions of the three steps of the BCR protocol depend on the authors. Here, the contents extracted in Steps 1, 2 and 3 are considered as the content potentially mobilizable under environmental changes (such as decomposition of organic matter, change in redox potential or pH), and the sum of the three fractions as the potentially mobilizable fraction (in %, as e.g. in Sutherland, 2002 or Hernández-Moreno et al., 2007). Step 1 will be considered as the mobile and bioavailable content of the element in the soil, and the proportion

extracted in Step 1 reported to the total content in soil, as the mobility factor (in %, Gusiatin and Klimiuk, 2012; Waterlot et al., 2013; Waterlot and Douay, 2015)[1]. As pointed out in Section 1, the BCR protocol was not originally designed for elements such as As, which normally occur predominantly as oxyanions in the environment. Some authors (e.g., Javed et al., 2013) have developed specific methods for investigating the chemical fractionation of As in soils. While this protocol may provide high selectivity, it is very difficult to perform on a large number of samples as it involves ten extraction steps. The complexity of the extraction also increases the chances of introducing errors during the manipulations. In comparison, the BCR protocol requires only three steps (Quevauviller et al., 1997), which simplifies its application significantly. Similar to PTE behaving as cationic species, the interpretation of the BCR results for As will be considered as the potentially mobilizable content under environmental changes, even if they may not truly reflect the actual As chemical fractionation.

2.4. Plant-based test (biotest)

Plant-based tests (or hereafter, biotest) were performed to assess the environmental bioavailability of trace elements (As, Cr and Ni) to plants. The biotests were conducted with *Lolium multiflorum* (Italian rye-grass) following the protocol detailed in (ISO 16198:2015). Rye-grass was used to assess soil metal environmental bioavailability in previous studies (Lambrechts et al., 2011; Waterlot and Douay, 2015; Waterlot et al., 2016; Di Carlo et al., 2020). The experiment includes two phases: (i) a growing phase during which the seeds are germinated and the seedlings are grown in an aerated nutrient solutions and (ii) an exposure (or contact) phase where the planar root mat (grown on a polyamide 30 μm mesh) are in contact with the tested soil (fresh equivalent of 10 g of dry soil) and fed with a nutrient solution. After a 21 days exposure phase in a growth chamber, the shoots of *Lolium multiflorum* were harvested, rinsed with deionized water and dried for 96 h at 45 °C in porous nylon bags. The samples were then weighed and digested in nitric acid before elements analysis by ICP- MS. For simplification purpose, the terms As_{RG}, Cr_{RG} and Ni_{RG} will be used to refer to As, Cr and Ni shoot rye-grass contents in what follows.

The biotest was carried out on 28 soils samples from Liège and 26 soils samples from Lorraine ($n = 54$). Three replicates were prepared for ten soil samples to assess the experimental reproducibility of the protocol. Pooled variation coefficients for As_{RG}, Cr_{RG} and Ni_{RG} were 22 %, 35 % and 16 %, respectively, which corresponds to the range of the variation coefficients (23 %, 18.5 % and 17.5 %) obtained with the ring-test conducted in (ISO 16198:2015) on *Festuca arundinaceum*. In addition to the As_{RG}, Cr_{RG} and Ni_{RG} contents obtained at the end of the exposure period, the translocation factor (TF) was calculated as the ratio of the element content in the plant (expressed in dry matter: mg·kg dm^{-1}) over the element content in soil (TF = shoot content/soil content). In this study, the term phytoavailability is used to represent the amount of the soil PTE that is taken up by the rye-grass shoot during the phytotron experiment.

2.5. Statistical data analysis

Statistical data analyses were performed using the R software (R Core Team, 2020). Pearson correlation coefficients, linear regression modeling and Principal Component Analysis (PCA) were computed after log transformation of the dataset in order to correct for distribution asymmetry. Robust statistical methods enabled the treatment of outlier values, which almost inevitably occur when working with environmental datasets (Reimann et al., 2008). Pearson correlation coefficients and PCA were computed based on a robust estimate (95 % of the data) of the covariance matrix using the MCD (Minimum Covariance Determinant) method of Rousseeuw (Rousseeuw and Driessen, 1999, implemented in the *robustbase* R package Maechler et al., 2019). Principal component analysis was performed using *prcomp* function (package *stats*, R Core Team, 2020) after data centering and scaling. For regression analysis, best predictor variables were first identified using the leaps-and-bounds algorithm (Furnival and Wilson, 1974; R package *leaps*, Lumley, 2020). Linear regression models were then computed using a MM-type regression estimator (Yohai, 1987; Koller and Stahel, 2011), which is available as the *lmrob* function in the *robustbase* R package (Maechler et al., 2019).

3. Results

3.1. General soil properties and aqua regia contents

The soil pH in H_2O in Liège ranges from 5.16 (slightly acidic) to 7.56 (neutral), and in Lorraine from 6.43 (neutral) to 7.87 (close to alkaline; Table 1). The soils in Liège have a higher OrgC content than those in Lorraine (46 g·kg^{-1} vs. 26 g·kg^{-1}, median). Both areas have loamy soil textures, but Lorraine soils have a higher clay content (22 % median vs. 15 % in Liège). This difference is likely due to chemical weathering of the parent material's Jurassic marls, which increases the clay content in the soil (Steffens, 1960). The As_{AR}, Cr_{AR} and Ni_{AR} are lower in Liège soils compared to Lorraine soils. Median As_{AR} and Cr_{AR} contents are indeed twice lower in Liège soils compare Lorraine soils (26 vs. 53 mg·kg^{-1} and 36 vs. 74 mg·kg^{-1}, respectively), while the median Ni_{AR} content in Liège soils is about 1.5 times lower than in Lorraine soils (55 mg·kg^{-1}). Finally, the median Fe_{AR} and Mn_{AR} contents in the soil is two to three times higher in Lorraine compared to Liège. The Mg_{AR} and Al_{AR} contents are also 1.5 times higher in Lorraine.

3.2. BCR-extractable contents and fractions

The As_{BCR}, Cr_{BCR} and Ni_{BCR} contents in Liège and Lorraine soils are shown in Table 1, and the distributions of fractions F1, F2, and F3 are depicted as boxplots in Fig. 2 (part A). In Liège, the median As_{BCR} content for each extraction step, i.e. Steps 1, 2, and 3, are 1.8 mg·kg^{-1} (F1 = 6.1 %), 2.8 mg·kg^{-1} (F2 = 10.8 %), and 3.4 mg·kg^{-1} (F3 = 13.1 %), respectively. For Cr_{BCR}, the median contents for Steps 1 and 2 (0.13 and 0.42 mg·kg^{-1}, respectively) are an order of magnitude lower than Step 3 (6.7 mg·kg^{-1}). The same observation holds for median Cr_{BCR} fractions: F1 = 0.38 %, F2 = 1.3 %, and F3 = 18.2 %. The median Ni_{BCR} content and fraction for Step 1 (1.9 mg·kg^{-1}; F1 = 4.8 %) are about two times lower than for Steps 2 (3.1 mg·kg^{-1}; F2 = 8.8 %) and 3 (3.9 mg·kg^{-1}; F3 = 9.1 %).

For the Lorraine soils, median As_{BCR} contents in Steps 1, 2, and 3 (0.5, 0.4, and 1.5 mg·kg^{-1}, respectively) are two to four times lower than in the Liège soils, accounting for <2 % of the aqua regia values. As for Liège soils, median Cr_{BCR} contents in Steps 1 and 2 in Lorraine soils are an order of magnitude lower than in Step 3 (0.1 and 0.3 mg·kg^{-1} compared to 7.3 mg·kg^{-1}), equivalent to 0.14 (F1), 0.33 (F2) and 10.5 % (F3) of the aqua regia content, respectively. Again, as for Liège soils, Cr_{BCR} F3 observations are far more dispersed than Cr_{BCR} F1 and F2, suggesting that Cr_{BCR} content in Step 3 varies strongly depending on the soil sample. Median Ni_{BCR} content in Step 1 of the Lorraine soils (1.5 mg·kg^{-1}) is four times lower than in Steps 2 and 3 (5.6 and 4.8 mg·kg^{-1}, respectively), with median Ni_{BCR} F1, F2 and F3 being roughly comparable to those in Liège soils (2.6, 7.4 and 10.2 %, respectively). Despite comparable medians in Liège and Lorraine soils, median Ni_{BCR} F2 and F3 vary much more in the latter soils.

The sum of the BCR-extractable contents for As, Cr, and Ni in both Liège and Lorraine soils account for <30 % of the aqua regia contents (Fig. 2, part B). In accordance with the BCR protocol definition (Karczewska, 1996; Sutherland, 2002), this indicates that the majority of these elements in the soils are in forms which are not potentially

[1] In this study, the aqua regia content is considered as the total content, and thus F1 as the mobility factor.

Table 1
Analysis results for soil and rye-grass samples in Liège (Lg; n = 38 soils, n = 28 rye-grass) and in Lorraine (Lor; n = 28 soils, n = 26 rye-grass). BCR-extractable contents: As, Cr and Ni contents extracted at each of the three steps of the BCR protocol - Step 1: acetic acid 0.11 mol·L^{-1}, Step 2: hydroxylamine 0.1 mol·L^{-1}, Step 3: 8.8 mol·L^{-1} H_2O_2 followed by 1.0 mol·L^{-1}. Rye-grass shoot contents: biotest for the determination of environmental bioavailability following ISO 16198:2015.

Mean			sd		5%ile		25%ile		Median		75%ile		95%ile	
Lg		*Lor*	*Lg*	*Lor*	*Lg*	*Lor*	*Lg*	*Lor*	*Lg*	*Lor*	*Lg*	*Lor*	*Lg*	*Lor*
Soil general properties (pH in H_2O; OrgC: g·kg^{-1}; Clay: %)														
pH	6.50	7.35	0.68	0.53	5.16	6.43	6.20	7.15	6.52	7.50	6.88	7.75	7.56	7.87
OrgC	46.66	29.66	26.59	15.15	9.83	14.93	23.02	18.50	46.43	26.00	64.57	38.05	89.98	61.13
Clay	14.24	22.58	4.86	10.21	2.19	10.74	13.93	16.14	15.04	22.00	17.04	25.41	18.76	43.35
Aqua regia-extractable contents (mg·kg^{-1}, except Al, Ca and Fe in %)														
As	29	63	15	38	12	17	22	29	26	53	35	96	50	121
Cr	39	90	12	56	26	34	31	55	36	74	44	103	58	202
Ni	38	65	10	30	26	33	34	44	39	55	42	90	52	121
Al	1.48	2.37	0.472	0.791	1.08	1.51	1.30	1.96	1.40	2.21	1.60	2.50	2.67	4.17
Ca	1.58	1.80	1.80	1.76	0.329	0.201	0.580	0.465	1.10	0.798	1.67	3.10	6.36	4.68
Fe	2.95	8.05	0.626	3.58	2.07	3.44	2.60	4.72	2.90	7.41	3.29	10.7	4.01	13.6
Mg	2581	3368	915	816	1668	2335	1925	2850	2400	3300	2775	3725	4280	4803
Mn	841	2467	223	1537	534	699	692	1285	841	1995	968	2959	1140	5650
BCR-extractable contents (mg·kg^{-1})														
As_{BCR}														
Step 1	1.94	0.71	1.18	0.50	0.43	0.19	1.00	0.50	1.77	0.50	2.69	0.64	3.89	1.72
Step 2	3.11	0.67	2.06	0.55	0.48	0.13	1.43	0.44	2.77	0.92	3.91	0.92	6.55	1.68
Step 3	3.83	1.66	2.05	0.78	1.57	0.63	2.56	1.11	3.38	1.54	4.64	2.06	6.85	3.20
Cr_{BCR}														
Step 1	0.15	0.12	0.06	0.05	0.08	0.07	0.11	0.09	0.13	0.10	0.18	0.14	0.27	0.22
Step 2	0.46	0.29	0.23	0.14	0.16	0.10	0.35	0.20	0.42	0.26	0.51	0.37	0.83	0.53
Step 3	7.85	9.61	4.17	6.63	3.27	4.12	4.58	6.18	6.66	7.32	10.47	10.06	14.42	25.48
Ni_{BCR}														
Step 1	1.75	1.57	0.68	0.94	0.70	0.51	1.20	0.82	1.87	1.46	2.22	1.88	2.70	3.49
Step 2	3.27	8.01	1.39	6.25	0.69	1.72	2.41	2.90	3.10	5.60	4.26	13.34	5.25	18.64
Step 3	3.83	5.15	1.26	2.23	1.90	2.14	3.00	3.70	3.85	4.77	4.59	6.22	5.38	9.25
Rye-grass shoot contents (mg·kg dm^{-1})														
As	0.60	0.38	0.25	0.24	0.29	0.09	0.42	0.21	0.57	0.32	0.68	0.54	1.09	0.81
Cr	4.76	5.44	2.03	3.29	2.04	1.54	3.68	2.90	4.40	4.43	5.77	7.50	8.62	11.05
Ni	6.52	7.91	1.52	2.38	4.73	5.13	5.45	6.18	6.27	7.42	7.33	8.98	10.01	12.63

mobilizable, as they are not affected by organic matter decomposition, and/or any variation in redox potential or pH.

3.3. Rye-grass As, Cr and Ni contents and soil-shoot translocation factors

Table 1 displays As, Cr and Ni contents in rye-grass grown on soils from Liège and Lorraine. Nickel is the most abundant element, with a median content of 6.27 mg·kg dm^{-1} (Liège) and 7.42 mg·kg dm^{-1} (Lorraine). Median As_{RG} content in Liège soils is nearly double that of Lorraine soils (0.57 vs. 0.32 mg·kg dm^{-1}). The median Cr_{RG} content is similar for both soil groups (4.40 and 4.43 mg·kg dm^{-1} for Liège and Lorraine, respectively).

Fig. 3 presents the soil-to-shoot transfer factor (TF) of As, Cr, and Ni as boxplots. For each element, TF is significantly higher in Liège soils than in Lorraine soils. The median As TF for Liège soils (0.021) is three times lower than that of Lorraine soils (0.007), which show variations of two orders of magnitude (TF: 0.00039–0.029). Median Cr TF is twice as high for rye-grass grown in Liège soils (0.12) as in Lorraine soils (0.058). The median Ni TF is about 1.5 times higher for Liège soils (0.18) compared to Lorraine soils (0.13).

3.4. Relationships between BCR and aqua regia contents and soil properties

In general, the relationship between As_{BCR}, Cr_{BCR} and Ni_{BCR} contents and aqua regia contents in Liège soils is stronger than in Lorraine soils (Table 2, scatter plots are presented in Supplementary Fig. 1). There is no correlation between As_{BCR} and aqua regia content in Lorraine soils. Cr_{BCR} content in Step 3 is strongly correlated with Cr_{AR} in both Liège and Lorraine soils. Ni_{BCR} is always significantly correlated with Ni_{AR} in Liège soils (r = 0.55, 0.94, and 0.82 for Steps 1, 2, and 3, respectively). In Lorraine soils, significant correlation is found for Steps 1 and 2 only (r = 0.65 and 0.71, respectively).

In Liège, As_{BCR}, Cr_{BCR} and Ni_{BCR} contents in soils are not significantly correlated with OrgC or clay content ($p > 0.01$). Ni_{BCR} content in Step 3 is positively correlated with soil pH. As_{BCR} in Step 1 positively correlates with Fe_{AR} and Ca_{AR} (r = 0.76 and 0.77, respectively), and slightly positively with Fe_{AR}, Mn_{AR} and Ca_{AR} in Step 2. As_{BCR} in Steps 2 and 3 negatively correlates with Mg_{AR}. Cr_{BCR} in each step positively correlates with Ca_{AR}, and Cr_{BCR} in Step 3 also positively correlates with Mn_{AR} and Fe_{AR}. No significant correlation was found for Ni_{BCR} content in Step 1 with major elements aqua regia content, while Ni_{BCR} contents in Steps 2 and 3 strongly correlate with Ca_{AR} and Fe_{AR}, and correlate less with Mn_{AR}.

For Lorraine soils, As_{BCR} in Steps 2 and 3 and Cr_{BCR} in Step 3 slightly positively correlate with OrgC content ($0.55 < r < 0.6$). Ni_{BCR} in Step 2 negatively correlates with OrgC, and Ni_{BCR} in Step 3 slightly positively correlates with clay content (r = 0.52). As_{BCR} in steps 1, 2, and 3 positively correlate with Ca_{AR}, while As_{BCR} in Steps 2 and 3 negatively correlate with Fe_{AR}. Cr_{BCR} in Step 1 slightly positively correlates with Fe_{AR}, and Cr_{BCR} in Steps 2 and 3 positively correlate with Al_{AR} and Ca_{AR}, respectively. Ni_{BCR} in Steps 1 and 2 positively correlate with Fe_{AR} and Mn_{AR}, and negatively with Ca_{AR}, while Ni_{BCR} in Step 3 positively correlates with Ca_{AR}.

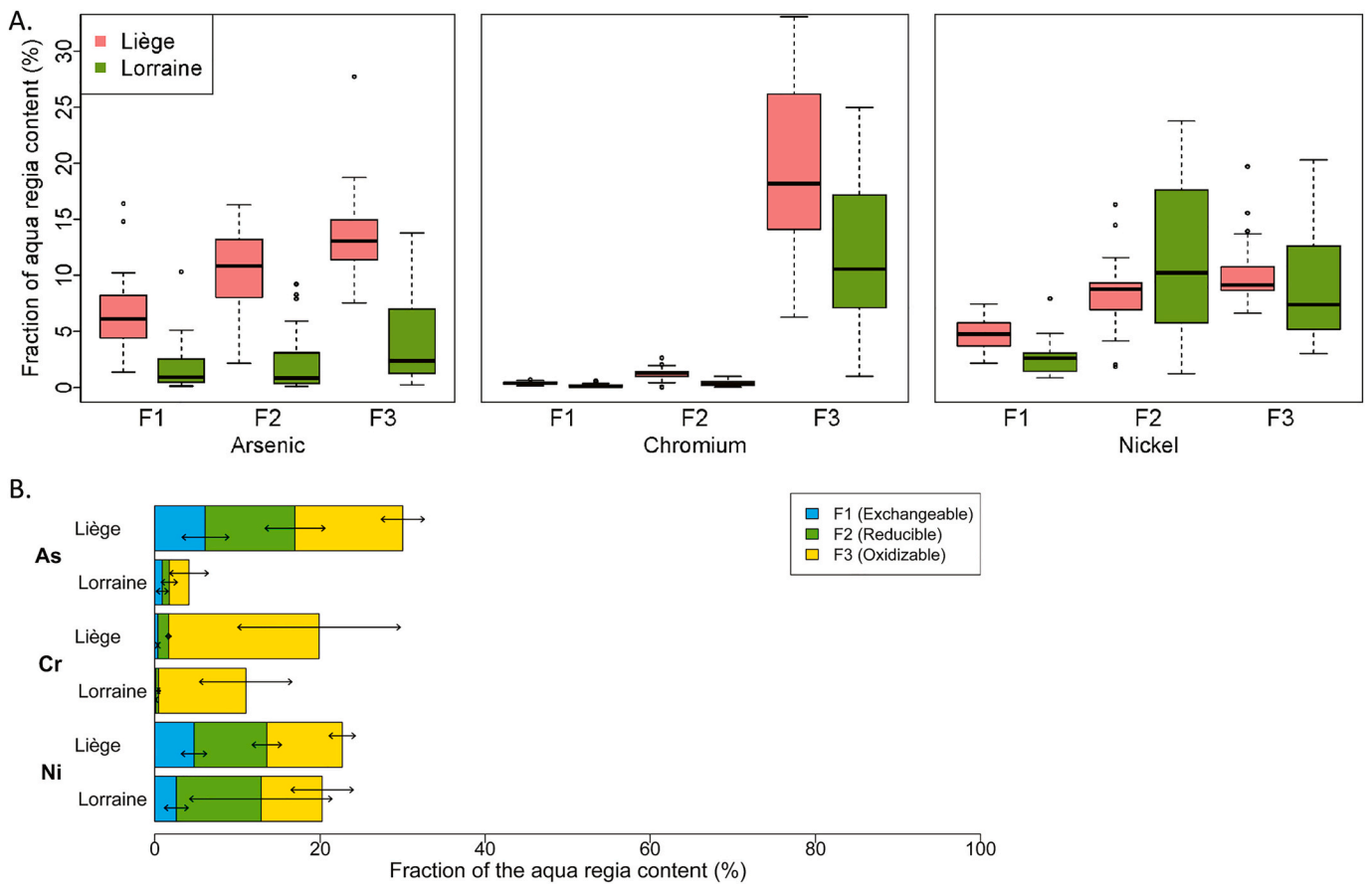

Fig. 2. A. As, Cr and Ni fractions for each of the three steps of the BCR protocol (expressed in % of aqua regia-extractable content) in Liège (n = 38) and Lorraine (n = 28). F1: exchangeable/weakly bound (0.11 mol·L^{-1} acetic acid), F2: bound to reducible compounds (0.1 mol·L^{-1} hydroxylammonium chloride), F3: bound to oxidizable compounds (8.8 mol·L^{-1} H_2O_2 followed by 1.0 mol·L^{-1}). B. BCR As, Cr and Ni cumulated mean fractions for each of the three steps of the BCR protocol (expressed in % of aqua regia-extractable content) in Liège and Lorraine. The error arrows represent the standard deviation.

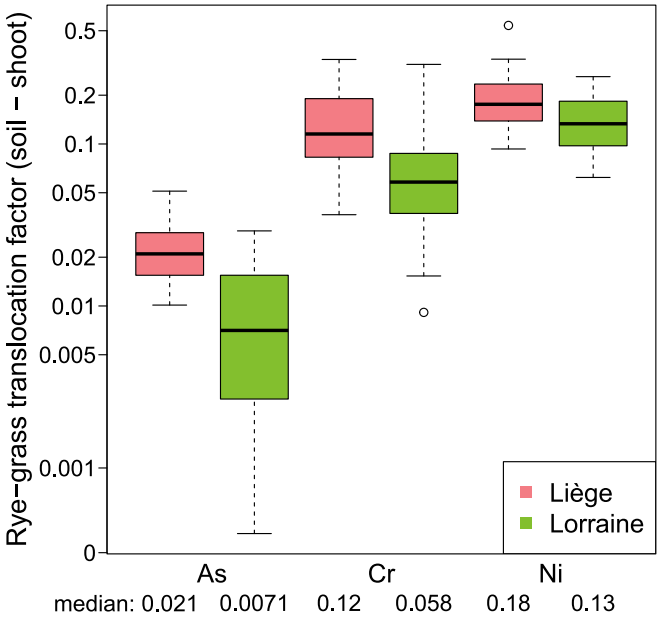

Fig. 3. Rye-grass soil-shoot translocation factors (rye-grass content/soil aqua regia-extractable content) in logarithmic scale for As, Cr and Ni for Liège soils (n = 28) and Lorraine soils (n = 26). Median values reported below the x-axis are significantly different for Liège and Lorraine (P-values resulting from Wilcoxon rank sum test are <0.01).

3.5. *Rye-grass As, Cr and Ni contents relationship with aqua regia contents, BCR extracts and soil properties*

No significant correlation p > 0.01) is found between As_{RG}, Cr_{RG}, Ni_{RG} and clay fraction (Clay), organic carbon (OrgC) and pH. The correlation coefficients between element shoot rye-grass, BCR-extractable and aqua regia contents are shown in Table 2 (scatter plots of shoot rye-grass contents versus aqua regia and BCR contents in Step 1 are presented in Supplementary Fig. 2). In Liège soils, As_{RG} is positively correlated with As_{AR} (r = 0.7) and with As_{BCR} in each of the three steps (r = 0.83 for Step 1). As_{RG} also positively correlates with Ca_{AR} content (r = 0.81). However, Cr_{RG} and Ni_{RG} contents do not have significant correlation with corresponding aqua regia contents or Step 1 contents. Cr_{RG} is negatively correlated with Cr_{BCR} in Steps 2 and 3 (r = −0.54 and −0.59, respectively) and with Fe_{AR} (r = −0.61). Ni_{RG} negatively correlates with Mn_{AR} (r = −0.63). In Lorraine soils, there is no significant correlation between As_{RG}, Cr_{RG} and Ni_{RG} contents, and corresponding aqua regia contents. As_{RG} is slightly positively correlated with As_{BCR} in Steps 1, 2, and with Ca_{AR} (r = 0.54, 0.57, and 0.53, respectively). Cr_{RG} never has a significant correlation with Cr_{BCR} and major elements aqua regia contents. Ni_{RG} is positively correlated with Ni_{BCR} in Steps 1 and 2 (r = 0.51 and 0.63, respectively) and slightly negatively with Ni_{BCR} in Step 3 (r = −0.42). With major elements aqua regia contents, Ni_{RG} negatively correlates with Ca_{AR} (r = −0.65) and positively with Fe_{AR} (r = 0.53).

Table 2
Robust Pearson correlation coefficients between BCR-extractable or rye-grass contents and corresponding aqua regia content (AR), soil properties (pH, OrgC and Clay), major elements (Al, Ca, Fe, Mg, Mn) and corresponding BCR-extractable contents (3 last columns, only for rye-grass shoot contents)."/": non-significant correlation ($p > 0.01$).

	AR	pH	OrgC	Clay	Al	Ca	Fe	Mg	Mn	Step 1	Step 2	Step 3
BCR-extractable contents												
Liège												
As_{BCR}												
Step 1	0.84	/	/	/	/	0.76	0.77	/	/			
Step 2	0.93	/	/	/	/	0.59	0.59	−0.58	0.57			
Step 3	0.83	/	/	/	/	/	/	−0.66	/			
Cr_{BCR}												
Step 1	/	/	/	/	/	0.57	/	/	/			
Step 2	/	/	/	/	/	0.57	/	/	/			
Step 3	0.61	/	/	/	/	0.86	0.71	/	0.58			
Ni_{BCR}												
Step 1	0.55	/	/	/	/	/	/	/	/			
Step 2	0.94	/	/	/	/	0.83	0.91	/	0.78			
Step 3	0.82	0.7	/	/	/	0.85	0.82	0.55	0.61			
Lorraine												
As_{BCR}												
Step 1	/	/	/	/	/	0.57	/	/	/			
Step 2	−0.58	/	0.6	/	/	0.8	−0.68	/	−0.64			
Step 3	/	/	0.56	/	/	0.57	−0.59	/	/			
Cr_{BCR}												
Step 1	/	/	0.71	/	/	/	−0.52	/	/			
Step 2	/	/	/	/	0.56	/	/	/	/			
Step 3	0.62	/	0.55	/	/	0.54	/	/	/			
Ni_{BCR}												
Step 1	0.65	/	/	/	/	−0.77	0.69	/	0.54			
Step 2	0.71	/	−0.53	/	/	−0.68	0.8	/	0.79			
Step 3	/	/	/	0.52	/	0.67	/	/	/			
Rye-grass shoot contents												
Liège												
As	0.7	/	/	/	/	0.81	/	/	/	0.83	0.61	0.46
Cr	/	/	/	/	/	/	−0.61	/	/	/	−0.54	−0.59
Ni	/	/	/	/	/	/	/	/	−0.63	/	/	/
Lorraine												
As	/	/	/	/	/	0.53	/	/	/	0.51	0.57	/
Cr	/	/	/	/	/	/	/	/	/	/	/	/
Ni	/	/	/	/	/	−0.65	0.53	/	/	0.51	0.63	−0.42

3.6. Principal component analysis

Soil pH, Clay, and OrgC content showed no significant correlation with shoot rye-grass content, therefore these soil properties were removed from the PCA. To reduce the number of variables tested, only As_{BCR}, Cr_{BCR}, and Ni_{BCR} contents from Step 1 were included in the analysis. These parameters showed better correlation with rye-grass contents compared to the BCR-extractable contents from Steps 2 and 3 (Fig. 4). In Liège soils, Component 1 explains 46.8 % of the dataset variability and is strongly positively correlated with As_{RG}, Fe_{AR}, Cr_{AR}, Mn_{AR}, As_{AR}, Ni_{AR}, and to a lesser extent, Cr_{BCR} and As_{BCR} from Step 1. Component 2 explains 17.7 % of the variability and is negatively correlated with Ni_{RG}, Cr_{RG}, Al_{AR} and Mg_{AR}. Component 3 explains 12.5 % of the variability and is positively correlated with Ni_{BCR} from Step 1 and Ca_{AR}. In Lorraine soils, Component 1 explains 41.2 % of the variability and is very negatively correlated with Fe_{AR}, Mn_{AR}, Cr_{AR}, Ni_{AR} and As_{AR}. Components 2 and 3 account for only 15.6 and 11.6 % of the variability, respectively. Component 2 is related to As_{RG}, As_{BCR} in Step 1 and Ca_{AR}. Component 3 only shows moderate negative relationships with Cr_{RG}, Cr_{BCR} from Step 1, Mg_{AR} and Al_{AR}. Since the studied variables are not always entirely independent from one another, the result need cautious interpretation. Specifically, the bioavailable contents represent subsets of the total contents, and the total contents are constrained by data closure. We could have applied compositional data analysis (CoDA; Filzmoser et al., 2018; Kynčlová et al., 2016) to represent our data, but this approach does not fully address the issue of interdependence between variables and it complexifies interpretation.

3.7. Predicting phytoavailability

Table 3 summarizes the best regression models obtained for As_{RG} (a complete list of the regression models obtained for predicting As_{RG} with $R^2 > 0.30$ are presented in Supplementary Table 2). For Cr_{RG} and Ni_{RG}, no satisfactory models were found. In Liège soils, As_{RG} can be accurately predicted by As_{BCR} in Step 1 ($R^2 = 0.62$) and slightly better predicted with the addition of Mn_{AR} ($R^2 = 0.67$). Excluding As_{BCR}, As_{AR} is the best variable for predicting As_{RG} ($R^2 = 0.47$) and the prediction is slightly improved with the inclusion of Ca_{AR} ($R^2 = 0.54$). In Lorraine soils, As_{RG} is best predicted by As_{BCR} in Step 2 ($R^2 = 0.62$) and the model can be improved with the inclusion of Mg_{AR} ($R^2 = 0.73$). Excluding As_{BCR} contents, As_{RG} is predicted by As_{AR}, Ca_{AR}, and a negative contribution from Fe_{AR} ($R^2 = 0.63$). For both study zones combined, As_{RG} can be predicted by As_{BCR} in Step 1 ($R^2 = 0.62$) and the model can be improved with the inclusion of As_{BCR} in Step 2 ($R^2 = 0.68$). Excluding As_{BCR} contents, a good prediction model for As_{RG} ($R^2 = 0.60$) emerges by incorporating As_{AR}, Ca_{AR}, and a negative contribution from Fe_{AR}.

4. Discussion

4.1. As, Cr and Ni aqua regia contents

The median As_{AR}, Cr_{AR} and Ni_{AR} contents in soils from Liège and Lorraine are two to ten times higher than European background levels Fig. 1, part B). Thirty-four percent of Liège soils and 72 % of Lorraine soils have As_{AR} levels above the Walloon soil standards for agriculture (30 $mg \cdot kg^{-1}$; Parlement Wallon, 2018). Five percent of Liège soils and

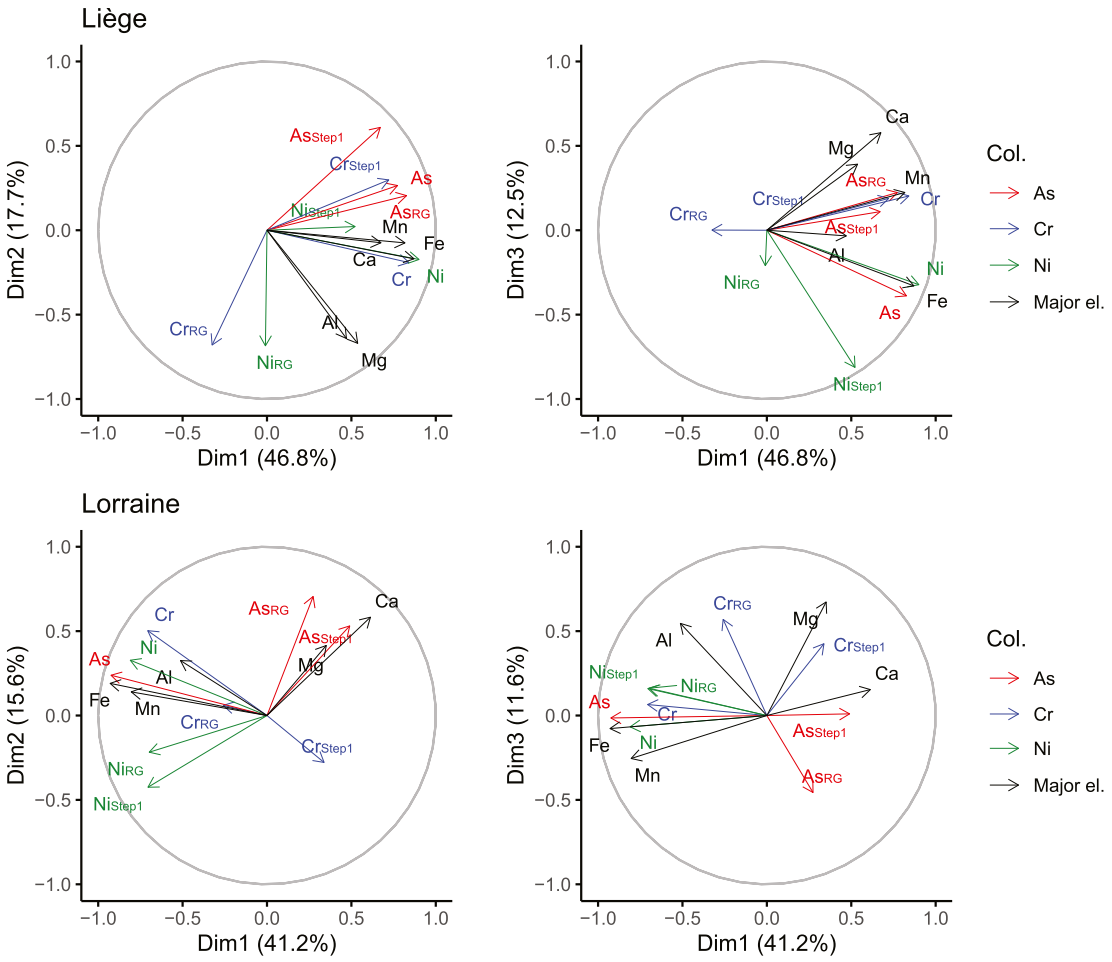

Fig. 4. Robust PCA of the Liège soils samples (topline) and the Lorraine soils samples (bottomline): components 1 vs. 2 (left) and components 1 vs. 3 (right). Vectors related to As, Cr and Ni are colored in red, blue and green, respectively.

Table 3
Robust regression models predicting As shoot rye-grass content (As_{RG}) basing on aqua regia and BCR (Step1, 2 and 3) extractable content. R^2: adjusted coefficient of determination. For the last models (two in Liège, one for Lorraine and one for the combined dataset), BCR extracts were excluded. The best model with one or two variables is reported if $R^2 > 0.30$, and a second model up to maximum three variables is presented. All variables are in logarithmic scale.

Model	R^2
Liège	
Rye-grass = − 0.736 + 0.434 Step 1	0.65
Rye-grass = − 4.25 + 0.361 Step 1 + 0.524 Mn	0.69
Rye-grass = − 2.75 + 0.663 As	0.46
Rye-grass = − 4.00 + 0.559 As +0.172 Ca	0.56
Lorraine	
Rye-grass = − 0.846 + 0.617 Step 2	0.66
Rye-grass = − 8.43 + 0.579 Step 2 + 0.931 Mg	0.74
Rye-grass = 0.0713 + 0.398 Ca + 0.558 As - 0.641 Fe	0.58
Lorraine and Liège combined	
Rye-grass = − 0.853 + 0.553 Step 1	0.62
Rye-grass = − 0.902 + 0.301 Step 1 + 0.239 Step 2	0.70
Rye-grass = 5.68 + 0.880 As +0.355 Ca - 1.21 Fe	0.59

72 % of Lorraine soils exceed the Cr_{AR} threshold (57 mg·kg^{-1}). No Liège soil surpasses the Ni_{AR} threshold (87 mg·kg^{-1}) in the Walloon decree, while 29 % of Lorraine soils have higher Ni_{AR} levels.

In a previous study, Pereira et al. (2007) found that past non-ferrous smelting activities caused Cd, Pb, and Zn enrichment in the surface soils of Liège. The presence of As, Cr, and Ni in the topsoils may also be related to this past industry. Some authors suggest As contamination near non-ferrous smelting plants (Kim et al., 2014; Waterlot and Douay, 2015; Chai, 2019; Baragaño et al., 2022), indicating a possible anthropogenic origin for As in Liège soils. Migoni et al. (2021) and Shalini Gupta et al. (2022) also reported As contamination related to coal burning activities. Chromium deposition in surface soils may be from smelting fumes (Rowbotham and Levy, 2000), but Pereira et al. (2012) concluded that Cr and Ni in Liège soils are mostly geogenic, originating from the shale and sandstone parent materials. Similarly, Yang et al. (2023) documented As enrichment in soils affected by a zinc smelting plant in China, but neither Cr nor Ni contents were significantly affected.

Soils in Lorraine are distant from industrial sources, but yet the topsoils contain elevated contents of As, Cr, and Ni. These probably reflect a geogenic origin and presence of Jurassic iron-rich calcareous sandstones and marls in the parent material (Fe_{AR} median content = 7.4 %, Table 1). The PCA biplots show a positive correlation between As_{AR}, Cr_{AR}, Ni_{AR} and Fe_{AR} contents. This is similar to findings in other regions with iron-rich soils, such as in Northamptonshire and Lincolnshire, England, or in the south of the Grand Duchy of Luxembourg (Palumbo-Roe et al., 2005; Breward, 2007; Claes et al., 2021).

4.2. As mobility and potentially mobilizable fractions

Arsenic in Liège soils is significantly more mobile and potentially mobilizable than in Lorraine soils. Liège soils have a median mobile As

content (As_{BCR} in Step 1) of 1.8 mg·kg^{-1}, more than three times higher than Lorraine soils (0.5 mg·kg^{-1}), although the soil As_{AR} content in Liège is half that in Lorraine. The median As mobility factor (F1) is consequently seven times higher in Liège (6.1 %) than in Lorraine (0.92 %). The median potentially mobilizable soil As content (As_{BCR} in Step 1 + 2 + 3) is three times higher in Liège (8.2 mg·kg^{-1}) than in Lorraine (2.6 mg·kg^{-1}), resulting in a potentially mobilizable fraction (F1 + F2 + F3) that is more than six times higher in Liège soils (32 %) than in Lorraine soils (4.6 %, Fig. 2, part B). Van Herreweghe et al. (2003), Fernández et al. (2004), Ko et al. (2005), Baig et al. (2009) and Waterlot and Douay (2015) studied As mobility in soils and sediments of various contexts with similar As contents to our samples. They report As mobility factors varying from 2 % (mine tailings) to 37 % (anthropogenically contaminated soils), with higher values than those in Lorraine soils and mostly higher than those in Liège soils. The potentially mobilizable fraction also showed a wide range, from 30 % (mine tailings) to 76 % (canal sediments). The As content extracted in Step 2 and 3 may underestimate the pools targeted by the BCR protocol. Upon acidic conditions, oxyanions such as arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) released during reductive dissolution of the amorphous iron oxide may then readsorb onto remaining iron (hydr)oxydes phases (Gruebel et al., 1988; Sadiq, 1997).

We attribute the different fractions of mobile and potentially more mobilizable As in the two soil groups to a difference in speciation, likely in relation to different origins of As in the soils from Liège and Lorraine. Our findings suggest that anthropogenic As in Liège soils is more mobile and potentially mobilizable than geogenic As in Lorraine soils, as suggested by the low median mobility factor (0.92 %) and low potentially mobilizable fraction (4.2 %) in the latter. Only a small fraction (0.86 %) is extracted in Step 2 of the BCR protocol in Lorraine soils, compared to 20 % to 70 % in other studies in various contexts (Van Herreweghe et al., 2003; Fernández et al., 2004; Ko et al., 2005; Baig et al., 2009; Waterlot and Douay, 2015). In soils, the mobility and toxicity of inorganic As^{III} species are higher compared to inorganic As^{V} species (Van Herreweghe et al., 2003). The assessment of the redox status of As during BCR extraction is challenging due to changes in redox conditions occurring during the analysis (Huang and Kretzschmar, 2010). Although we anticipate that AsO_4^{3-} predominates in our soils due to the neutral pH and aerobic conditions (Cullen and Reimer, 1989; Waterlot and Douay, 2015), our results do not allow for a conclusive determination of the preferential chemical form of the As extracted.

Based on the high iron (hydr)oxides content (Table 1) and the significant correlation between Fe_{AR} and As_{AR} (Table 2) observed in the Lorraine soils, and considering the capacity of the BCR Step 2 to dissolve the reducible fraction (specifically Mn/Fe (hydr)oxides), we anticipated that the As extraction during the BCR Step 2 should have produced the maximum As content. A supplementary analysis on six soil samples showed that As extractable with aqua regia is equal to that obtained by chemical extraction to selectively dissolve crystalline and amorphous Fe oxides (Supplementary Table 1). This indicates that As in Lorraine soils is likely associated with Fe (hydr)oxides (probably coprecipitated) such as goethite or ferrihydrite, which cannot be dissolved using Step 2 of the BCR protocol. This means that Step 2 of BCR protocol may largely underestimate the amounts of elements bound to iron (hydr)oxides in soils derived from iron rich substrates. Considering that the dissolution of As is dictated by the complete dissolution of iron (hydr)oxides, we expect that the use of other sequential extraction procedures would lead to similar findings, i.e. a significant proportion of the soil As would be extracted in the residual fraction. A significant fraction of total As could be relased during an extraction aiming at the dissolution of crystalline iron (hydr)oxides, as for Step 4 of Wenzel et al. (2001).

For As in soils affected by a lead smelting plant in Lille (France), Waterlot and Douay (2015) found higher As mobility factor (15–37 %) and potentially mobilizable content (58–68 %) compared to those in Liège soils, despite a similar origin of soil contamination. The lower As mobility in Liège soils, reflecting stronger binding with the solid phase, may be explained by the diverse industrial activities Liège has experienced, whereas the contamination in Lille is attributed to a sole industry, or by different importance of aging processes (inclusion of As in the structure of Al and Fe oxides; Wang et al., 2015). The higher potentially mobilizable As fraction in Lille soils may also be partly due to the use a more concentrated hydroxylamine solution in Step 2 by Waterlot and Douay (2015) of, as specified in the revised BCR protocol (Rauret et al., 1999), possibly resulting in more efficient As extraction.

4.3. Cr and Ni mobility and potentially mobilizable fractions

With a median mobile content of 0.10 mg·kg^{-1} (Table 1) and a mobility factor of <1 % (Fig. 2, part A), Cr mobility and availability in soils from this study are negligible. Mobility of Cr in the environment is highly dependent on its oxidation state, the hexavalent form being more mobile than the trivalent one (Salem et al., 1989). Thus, in accordance with Pereira et al. (2012), we suggest that Cr in our soils occurs mostly as reduced Cr^{III} inherited from the shales and sandstones in Liège and from Fe/Mn (hydr)oxides in Lorraine. The low mobility of geogenic Cr in soils has been documented elsewhere (Davidson et al., 1998; Fernández et al., 2004; Bielicka-Giełdoń et al., 2013; Pavlović et al., 2021).

The potentially mobilizable Cr content (7.1 and 7.9 mg·kg^{-1}, medians) is higher than the mobile content in both soils and is mostly extracted in Step 3 of the BCR protocol (Fig. 2, part A). Chromium has a strong affinity for oxidizable phases such as organic matter and sulfides, and the hydrogen peroxide in Step 3 can oxidize chromium hydroxides in chromate, more soluble than Cr^{3+} (Coetzee et al., 1995). Davidson et al. (1998), Bielicka-Giełdoń et al. (2013) and Pavlović et al. (2021) made a similar observation for geogenic Cr in industrially-contaminated, garden and urban soils, respectively. The median potentially mobilizable Cr fraction in Liège soils is almost twice as high as that in Lorraine soils (20 % vs. 11 %), demonstrating the presence of different Cr-bearing phases, those of Liège being less stable under environmental changes.

The Ni mobility and availability in our soils are lower compared to values in other studies, such as Fernández et al. (2004) and Lu et al. (2007), who estimated mobility factors of Ni in unpolluted and urban soils to be 4.8–20.9 %. Our results match better those of Sungur and İşler (2021), Pavlović et al. (2021) and Lu et al. (2017) for agricultural soils close to a city center (mobility factor of 10 %), unpolluted and urban soils (mobility factor of <7 %) and soils in the vicinity of a coal mine (mobility factor of <2 %), respectively. Nickel in Liège soils is slightly more mobile and available than the Lorraine soils (Table 1 and Fig. 2, part A). However, Liège soils have lower potentially mobilizable Ni content (median = 8.5 vs. 13 mg·kg^{-1}, p-value = 0.0007), although the potentially mobilizable fractions of the two soil groups are close (median = 23 vs. 24 %). In both soil groups, Step 2 extracts the most amount. This is because hydroxylamine can easily extract Ni adsorbed on manganese oxides (Tessier et al., 1979; Umoren et al., 2007), potentially mobilizable upon reductive conditions. The potentially mobilizable Ni fraction in our soils varies widely (Fig. 2, part A), as also seen in Fernández et al. (2004), where the fraction ranged from 27 to 81 %. Based on our median fraction values (23 % and 24 %), we conclude that Ni in our soils is mainly present in the immobile and non-mobilizable fractions. A similar conclusion was reached by Fernández et al. (2004) for non-polluted soils and Davidson et al. (2006) for urban soils.

4.4. As phytoavailability

The As_{RG} contents in Liège and Lorraine soils (Table 1) are higher than values reported by Kabata-Pendias (2010) for grass grown on uncontaminated soils (0.28–0.33 mg·kg dm^{-1}), but they match Hartley and Lepp (2008) and Waterlot et al. (2016)'s rye-grass measurements for soils exposed to non-ferrous smelting emissions. As_{AR} contents in our soils fall within the same range as theirs (10–79 mg·kg dm^{-1}). However, Hartley and Lepp (2008) report higher soil-shoot TF values (0.03–0.09),

suggesting more phytoavailable site-specific contamination in their soils compared to Liège soils, where contamination probably originated from multiple sources.

Despite a lower median As_{AR} content, the soils in Liège have As_{RG} and relative phytoavailability values that are about two and three times higher than those found in Lorraine soils (Table 1 and Fig. 3). As a result, soil As is more available to plants in Liège, in line with the greater mobility and potentially mobilizable content and fraction of As in these soils (refer to Section 4.2). The binding of As with Fe hydr(oxides) is likely to explain the lower mobility and phytoavailability of As in Lorraine soils. We also observed that the distribution of As TF in Fig. 3 is highly dispersed for Lorraine soils. These soils are formed on two main different rock types: iron-rich calcareous sandstones and marls (Section 2.1). Arsenic's relative mobility and phytoavailability were compared in soils developed on marls and in soils developed on iron-rich calcareous sandstones (Fig. 5). It appears that As in soils developed on marls is three to four times relatively more mobile and phytoavailable than in the latter soils, emphasizing the limitation of As mobility and phytoavailability by Fe (hydr)oxides-bearing phases. Additionally, the higher clay content in marl soils may impact As sorption, as adsorption of the arsenate anion (AsO_4^{3-}) on clay minerals decreases when pH exceeds 5, compared to adsorption on iron oxides, which peaks at pH = 7 (Brookins, 1988).

The correlation between As_{RG} and As_{AR} is only significant in Liège soils ($r = 0.7$). This means that As phytoavailability can be predicted from total content in Liège soils but not in Lorraine soils. The good correlation between As_{RG} and As_{BCR} content in Step 1 in both Liège ($r = 0.83$) and Lorraine ($r = 0.54$) soils enables the prediction of As phytoavailability from As_{BCR} content in Step 1 (Table 3). The results of the PCA (Fig. 4) support this, with As_{RG} in Liège soils related to the same component as As_{AR} and As_{BCR} content in Step 1, while in Lorraine, As_{AR} is only related to As_{BCR} content in Step 1. This confirms the findings of Waterlot et al. (2016), who suggested (based only on three soils) that protocols like water extractible As content are a better alternative method to determine As phytoavailability than total content. Soil parent material influences As phytoavailability in Lorraine soils. This is reflected in the models shown in Table 3, where the major elements contents (Fe_{AR}, Mg_{AR} and Ca_{AR}) have a strong impact on As_{RG} content. Marls have higher As_{RG} content compared to iron-rich calcareous sandstones due to higher Mg_{AR} and Ca_{AR}, and lower Fe_{AR} content.

4.5. Cr and Ni phytoavailability

The Cr_{RG} and Ni_{RG} contents found in our study (Table 1) exceed typical levels in grass (Cr: 0.5–3.4 mg·kg dm^{-1}, Ni: up to 4.8 mg·kg dm^{-1}) in Europe (Kabata-Pendias, 2010). This discrepancy may be due to higher Cr and Ni contents occurring in Liège and Lorraine soils compared to typical values in European soils. Median Cr_{RG} is similar in both soil groups (4.4 mg·kg dm^{-1}, p-val = 0.98). However, median Cr TF in Liège soils is twice higher than in Lorraine soils (0.12 vs. 0.058, p-val < 0.01) suggesting a difference in Cr mobility. The lower median Cr TF in Lorraine soils aligns with its lower potentially mobilizable Cr fraction (Section 4.3). Like As, this lower Cr TF in Lorraine soils is attributed to its association with Fe/Mn (hydr)oxides. The minimal mobile Cr content in both soil groups compared to the potentially mobilizable Cr suggests that the latter is the primary contributor to plant-available Cr, not the mobile content.

Although Liège soils have slightly lower median Ni_{RG} (6.3 vs. 7.4 mg·kg dm^{-1}, p-val = 0.018), Ni in Liège soils is more plant-available than in Lorraine soils (median Ni TF soil-shoot = 0.18 vs. 0.13, p-val < 0.01). Mobile Ni content is similar in both soil groups, but Lorraine soils have nearly twice the Ni potentially mobilizable content compared to Liège soils (Section 4.3). These results indicate that both mobile and potentially mobilizable Ni contribute to Ni_{RG} levels.

Plant-available Cr and Ni cannot be predicted from total or Step 1 BCR content in Lorraine or Liège soils. No significant correlation was found between Cr or Ni rye-grass content and corresponding aqua regia or BCR content in Step 1, except for Ni_{RG} with BCR content in Lorraine soils ($r = 0.51$, Table 2 or scatter plots in Supplementary Fig. 2). This correlation allows for a model predicting Ni_{RG} from Ni_{BCR} content in Step 1, but the model's accuracy is low ($R^2 < 0.3$). These relationships between rye-grass, aqua regia, and BCR content in Step 1 are supported by the PCA result (Fig. 4). The lack of a model for predicting Cr_{RG} and Ni_{RG} shows that these variables are not related to any other variables measured, including soil properties (pH, OrgC, Clay content) and major/trace elements aqua regia content. For example, Cr solubility in soil is pH-sensitive (minimum at pH 5.5–8, Bartlett and Kimble, 1976), but no relationship between Cr phytoavailability and pH was found in our study.

4.6. Implication for soil protection management

Soils in areas with high background contents present management challenges as they frequently exceed the normative values. In our case study, the As, Cr and Ni contents in the majority of the Liège and Lorraine soils do not comply with the soil clean-up standards laid down in the Walloon soil decree (Section 4.1). According to this regulation, detailed soil characterizations would be required to evaluate possible remediation measures. A such procedure entails substantial costs and resources. For As, Cr and Ni, we highlight that neither the potentially

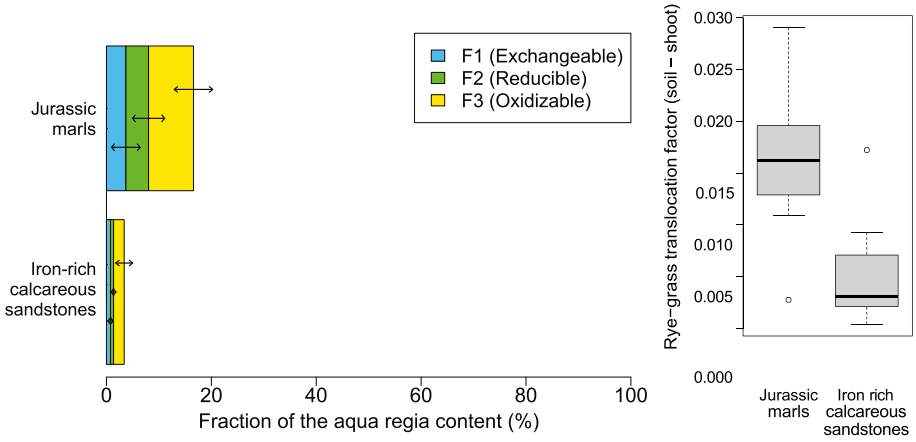

Fig. 5. Left: BCR As cumulated median fractions for each of the three steps of the BCR protocol (expressed in % of aqua regia-extractable content) in Lorraine soils developed on iron-rich calcareous sandstones and marls. The error arrows represent the median absolute deviation. Right: As translocation factors soil-shoot (rye-grass content/soil aqua regia-extractable content) in logarithmic scale for soils in Lorraine developed on iron rich calcareous sandstones and marls.

mobilizable contents (BCR protocol; Table 2 or scatter plots in Supplementary Fig. 1) nor the phytoavailable contents (except As in Liège soils; Table 2 or scatter plots in Supplementary Fig. 2) correlate positively with total content values. Accordingly, higher total As, Cr, or Ni contents will not necessarily result in higher mobile, potentially mobilizable and phytoavailable contents. Therefore, the use of normative values based on total contents (as in Wallonia or other regions/countries in Europe and North America, Kim et al., 2015) for assessing potential risks can be misleading. Our finding aligns with previous works (NRC, 2003; Kim et al., 2015; Kumpiene et al., 2017; Petruzzelli et al., 2020; Claes et al., 2021). Similar conclusions have also been reached in studies investigating the bioaccessibility of PTEs in soil for human health risk assessment. In these studies, there is a consensus that the use of total (or pseudo-total) PTE contents tends to result in an overestimation of the potential human health risk (Li et al., 2014; Izquierdo et al., 2015; Darko et al., 2017; Mehta et al., 2019; Monneron-Gyurits et al., 2020; Billmann et al., 2023).

Compared to total PTE contents in soils, we suggest that the measurement of environmental bioavailability, as carried out in this study, produces a more accurate information for implementing a sustainable management strategy for contaminated soils in high-background contexts. For the soils affected by high As, Cr and Ni background contents surveyed in this study, normative values based on total contents could be adapted considering that mobile and potentially mobilizable fractions of As, Cr, and Ni account for <30 % of the total contents. Moreover, the linear models developed in this study, which predict As in rye-grass based on total contents and/or on selective extraction (such as Step 1 of the BCR protocol), could be utilized to refine criteria in soil regulations pertaining to the management of PTE-contaminated soils. Finally, our data on potentially mobilizable and phytoavailable contents provide valuable insights for assessing the feasibility of implementing future phytoremediation treatments or alternative strategies aimed at immobilizing As, Cr and Ni occurring in soils.

5. Conclusions

The As, Cr and Ni contents in the 66 soils from the Liege basin and Belgian Lorraine frequently exceed the soil clean-up standards laid down in the regional soil protection regulation. As such, they would be regarded as “problematic” soils that need to be managed. Chemical fractionation and plant-based biotest analyses show that the environmental bioavailability of As, Cr and Ni is higher in soils from Liège basin compared to those sampled in Belgian Lorraine. For As, this probably reflects the impact on soils of anthropogenic emissions associated with the urban and industrial development of the Liège basin. In contrast, the environmental bioavailability of Cr and Ni in both areas is primarily controlled by the soil parent material. The lower environmental bioavailability of Cr and Ni in Lorraine soils is attributed to the iron-rich soil parent material, which results in a greater chemical immobilization of these elements. In both areas, about 70 % of the total As, Cr and Ni contents may be considered as immobile or unavailable. Translocation soil-plant factors estimated experimentally are higher for Liège soils compared to Lorraine soils, and Cr and Ni are better transferred to rye-grass than As. While normative values are generally applied across an entire region, our study highlights significant regional variations in environmental availability of As, Cr and Ni in soils. By providing new data on environmental bioavailability of As, Cr and Ni, our study can facilitate improved practices for sustainable soil management in areas with elevated contents of PTEs on a regional scale, and questions the use of normative values based on total contents in soil management.

CRediT authorship contribution statement

Aubry Vandeuren: Conceptualization, Methodology, Formal analysis, Data curation, Visualization, Writing – original draft. **Benoît Pereira:** Conceptualization, Methodology, Formal analysis, Data curation, Writing – review & editing. **Abdoulaye Julien Kaba:** Investigation. **Hugues Titeux:** Writing – review & editing. **Pierre Delmelle:** Supervision, Writing – review & editing.

Declaration of competing interest

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

Data availability

The data that has been used is confidential and could be made partially available on request after removing sensible information

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Appendix A. Supplementary data

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