



Soil contamination near a former Zn–Pb ore-treatment plant: Evaluation of deterministic factors and spatial structures at the landscape scale



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ARTICLE INFO

Article history:

Received 1 March 2014

Received in revised form 10 July 2014

Accepted 22 July 2014

Available online 28 July 2014

Keywords:

Trace elements

Soil contamination

Enrichment factor

Geochemical mapping

ABSTRACT

Historical soil contamination within a 3 km radius of a former ore treatment plant was evaluated. A total of 247 topsoil samples were collected in a stratified random sampling design taking into account three factors: land use (LU), soil type (ST) and wind direction (WD). Concentrations of trace elements (Cd, Co, Cr, Cu, Ni, Pb and Zn) and major elements (Ca, Mg, K, Fe, Al, Mn) as well as various soil properties (pH_{water}, pH_{KCl}, TOC and N) were measured. Total Cd, Pb and Zn concentrations were higher than typical background values. Enrichment factors for these three metals were, respectively, 260, 77.4 and 35.5. Principal component analysis (PCA) and factor analysis segregated anthropogenic contamination as a premier factor in influencing concentrations, followed by a second lithogenic factor. The anthropogenic origin of substantial contamination was confirmed through mapping of sample locations relative to contaminant sources. Factor 1 (26.5% of the variance) impacts a large area around the contaminated site and is also indicative of WD influence. Factor 2 (23.9% of the variance) is naturally linked to the local lithology and geology. LU and soil fertility are, respectively, represented by factor 3 (16.5% of the variance), which is linked to pH, and factor 4 (9.3% of the variance), related to organic content. The significance of landscape factors in the spatial distribution of metallic trace elements (MTE) was assessed with an ANCOVA using “distance to the source” as a covariate. Results of the analysis support the hypothesis that Cd, Cu, Pb and Zn concentrations are mainly driven by anthropogenic factors, specifically historical industrial activity at the former ore treatment plant. The ANCOVA also provides a means to quantify the impact of LU and ST as well, particularly on MTE availability in soils. The presence of MTE in soil poses known, and potentially significant, risks to both human health and the environment.

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1. Introduction

Processing of metal-bearing ore has occurred along the main rivers of the Wallonia region of Belgium (Sambre, Meuse, Vesdre, Gueule, from west to east) for at least 200 years, beginning with locally-mined product and then increasingly with imported material. Substantial air emissions rich in oxides (SO₂, SO₃, NO₂) and metal-bearing particulates laden with Cd, Pb and Zn (Graitson, 2005) have spread throughout the vicinity and have led to significant contamination. The combination of high acidity and enrichment by metallic trace elements (MTE) has resulted in environmental toxicity which has caused significant adverse effects to many species, communities and ecosystems (Graitson, 2005; Graitson et al., 2005; Rosengarten, 2010). The famous so-called calaminary sites,¹ which are now protected under the Natura 2000 regulation, present the clearest evidence of the impacts of former

industrial activity within the actual landscape. However, calaminary sites are usually of limited area (maximum of 75 ha) located close to the former plants. Nevertheless, there is no compelling evidence or arguments that the atmospheric fallout of contaminants was confined to these sites.

It is important to note that at some locations the stacks/chimneys were re-located from the valley floor to the surrounding plateaus. This placement allowed for better dispersion of emissions that previously had been concentrated in the low-lying valleys, resulting in very high levels of toxic contaminants. As with many mining and milling areas throughout the world, there was little concern over environmental degradation and contamination in the first century or more of operation. Not surprisingly, very few soil contamination data were reported in the literature (Denaeyer-De Smet and Duvigneaud, 1974; Ramaut, 1964; Tordoff et al., 2000). There are numerous examples, however, of surface contamination arising from metal extraction operations at a variety of locations, thus giving rise to concerns about risk to the environment and ecosystem sustainability (Dudka and Adriano, 1997), agricultural production (Zhuang et al., 2009), vegetable gardening (Sipter et al., 2008; Zu et al., 2011), groundwater (Critto et al., 2003) and human health (Cambier et al., 2009).

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¹ The origin of calaminary sites appellation comes from “Calamine” a mining expression to describe zinc-ores such as zinc-silicate, zinc-carbonate or the assemblage of hemimorphite, smithsonite, hydrozincite and willemite (Dejonghe, 1998).

Unlike slag and waste deposits, evidence of ancient atmospheric contamination is difficult to detect. This is especially true when the environment is rich in nutrients (Cambier et al., 2009; Hermanns and Duvigneaud, 1996). Typically, soil concentrations of MTE rapidly decline with increasing distance from the source (Denaeyer-De Smet and Duvigneaud, 1974; Ramaut, 1964). However, distance is only one factor that affects dispersion of metal particulate and aerosol contaminants, other factors include wind direction and strength, precipitation, topography and land use (Denaeyer-De Smet and Duvigneaud, 1974). Additionally, once deposited on soils, directly or having been washed from plant surfaces, metallic particulates are subject to biogeochemical processes and can be physically redistributed in the soil and the landscape.

Geostatistical and multivariate analyses have often been used to study the spatial structure of soil contaminant concentrations, to partition between lithogenic and anthropogenic origins and to identify contaminant sources (Facchinelli et al., 2001; Khalil et al., 2013; Liang et al., 2013; Micó et al., 2006; Mrvić et al., 2011; Yuan et al., 2014).

The goal of the present study was to evaluate and prioritize the apparent factors explaining the current soil levels of trace elements in the vicinity of a former ore-treatment plant. We studied contamination within 3 km of a former plant situated near the Sclaigheaux calaminary site (Andenne in Namur Province). This site is located on the left bank (looking downstream) of Meuse Valley where obvious and cryptic examples of historical human activity are well-represented. The lead–zinc deposits in the area were already being exploited during the Middle Ages. Those near the Sclaigheaux calaminary site (Haies Monet deposit, Landenne deposit) were mined beginning at least in the fourteenth century (De Nul, 2010; Dejonghe, 2010). The “Haies Monet” deposit is one of the six most important deposits located in Dinantian carbonate rocks (see Fig. 1) of the Namur-Verviers Synclinoria (Dejonghe, 1998). This Pb–Zn deposit consists of veins which are associated with clusters of Contact Type or mineralized Karstic Type. The veins are particularly well developed in carbonate rocks. Clusters of Contact Type are formed above the vein and called “gossan”, a mass of limonite resulting from the oxidation of sulfide ores (Dejonghe, 2010). Mineralized Karstic Type clusters are filled with detrital material (sand and clay) in which are found the oxidized ores of zinc (calamine) and lead (cerussite, PbCO_3) (Dejonghe, 2010). The walls of these pockets are covered with sulfide (galena = PbS and sphalerite = ZnS) and sulfide mineral oxidation products (calamine and cerussite) (Dejonghe, 2010). In addition to the extraction of Zn–Pb ore and its treatment in zinc kilns present in the lower portion of the Sclaigheaux calaminary site, waste slag from smelting operations was stored in the same area (De Nul, 2010).

To understand the impact of Zn–Pb mining and smelting around the Sclaigheaux calaminary site, a hierarchical spatial sampling design was developed in order to (i) study the spatial structure of the contamination, and (ii) test the significance of distance, wind direction, soil type, and land use as deterministic factors of trace element concentrations and related soil properties.

2. Material and methods

2.1. Study area and sampling strategy

The Sclaigheaux calaminary site consists of forest, agricultural (crops and grasslands) and residential areas (Liénard et al., 2011). The study area is delineated within a 3 km radius circle surrounding stacks of the former zinc-ore treatment plant (Fig. 1). Sampling points were located according to (i) distance from contamination source, (ii) direction of dominant winds (WD1, WD2, WD3, WD4), (iii) soil types (ST1 – loamy soil with good drainage, ST2 – loamy soil with poor drainage and ST3 – loamy–stony soils with gravel) and (iv) land use (LU1 – crop, LU2 – grassland and LU3 – forest). In the center of

soil polygons located within each of the three land uses, sample points were evenly distributed along each wind direction vector and in each distance range (<500 m, 500–1000 m, 1000–1500 m, 1500–2000 m, 2000–2500 m and >2500 m) using ArcGIS. Once sampling points had been identified following these criteria, 247 locations were randomly selected from which topsoil (0–20 cm) samples were collected and analyzed. Details of the sampling design are provided in Liénard et al. (2011).

2.2. Analytical methods

Air-dried samples were sieved at 2.0 mm and a subsample was crushed to 200 μm . Soil pH was measured by creating a slurry in distilled water (pH_{water}) and 1N KCl (pH_{KCl}) (w:v 2:5 ratio). Total organic carbon (TOC) was determined following the Springer–Klee method and total nitrogen (N) was estimated by modified Kjeldahl method (Nelson and Sommers, 1996). Major (Ca, Mg, K, Fe, Al, Mn) and trace (Cd, Co, Cr, Cu, Ni, Pb, Zn) element concentrations were determined after (i) aqua regia digestion following ISO 11466 (referred to as AR metal concentration, also considered “total” metal concentration) and (ii) after extraction with $\text{CH}_3\text{COONH}_4$ (0.5 M) and EDTA (0.02 M) at pH 4.65 (w:v 1:5 ratio) and agitation for 30 min (referred to as available metal concentration) (Lakanen and Erviö, 1971). Co, Cr and Ni were not measured in this extract solution. The concentrations in the solution were measured by flame atomic absorption spectrometry (VARIAN 220, Agilent Technologies, Santa Clara, CA, USA). The detection limits for AR/available metals were, respectively, 0.66/0.10 $\text{mg}\cdot\text{kg}^{-1}$ (Cd), 0.99/0.15 $\text{mg}\cdot\text{kg}^{-1}$ (Cu), 3.33/0.50 $\text{mg}\cdot\text{kg}^{-1}$ (Pb) and 0.33/0.05 $\text{mg}\cdot\text{kg}^{-1}$ (Zn). As part of the quality control program for the study, a standard reference material was used and analyzed with each set of samples.

2.3. Statistical methods

A log transformation was applied to every variable, excepted $\text{pH}_{\text{H}_2\text{O}}$ and pH_{KCl} , in order to meet the normality of distribution for analysis. Homogeneity of variances within stratified sub-populations was verified with Levene's test which is more robust for small populations. The effects of WD, ST and LU on various parameters were evaluated using a three-way ANCOVA, with distance from source as the covariate within a general limited model in Minitab 16 (Minitab Inc., State College, PA, USA). Differences were considered significant at $p \leq 0.05$.

A multivariate factor analysis was performed in Minitab 16 after principal component analysis (PCA) and varimax rotation in order to identify the main factors underlying the variability of the soil chemical properties.

The spatial structure of the variables was analyzed first on the basis of their variograms, followed by the use of the interpolated maps. Specifically, the isotropy/anisotropy nature of variation, the ranges and the “partial sill”/“total sill” ($C/C + C_0$) variance ratio were compared between soil properties and including the potential structuration factors (LU, ST) studied by Liénard et al. (2011). The ($C/C + C_0$) ratio expresses the proportion of the variance which presents spatial continuity. This information was generated with ArcGIS 10.0 (ESRI, Redlands, CA, USA) and ISATIS (Geovariances Avon, France) softwares.

2.4. Geochemical approach and enrichment factor

Mineralogy and soil properties dictate the natural trace element concentrations of soil. These should therefore be predictable in the absence of anthropogenic impacts based on their natural proportion to other elements (Myers and Thorbjørnsen, 2004). Fe or Al concentrations have frequently been used as indicators of natural occurrence of trace elements such as Ni, Cr, Zn, Pb or Cd (Baize, 1997; Colinet et al.,

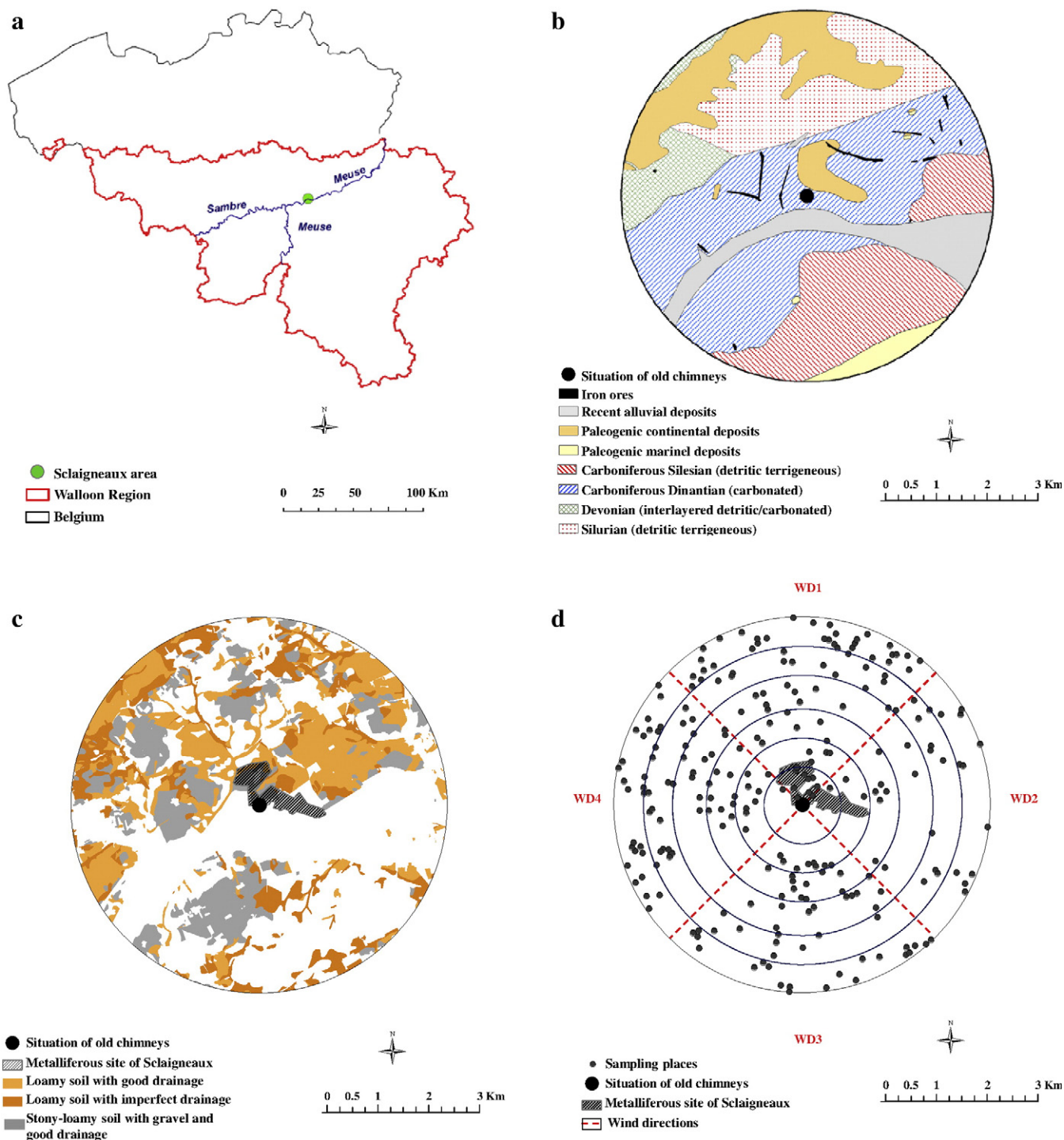


Fig. 1. (a) Location of the study area in Belgium, (b) Presentation of geologic formations (c) Three soil types that were sampled and the Sclaigheaux calaminary site, (d) Sampling locations, concentric indicators of distance from the contaminant source and the four wind directions (WD).

2004; Myers and Thorbjørnsen, 2004). The Pearson correlation matrix and graphical analysis of relationships between the soil composition and Fe and Al concentrations were used in order to discriminate between natural and anthropogenic sources of elements.

Element enrichment factors are widely used in environmental science to identify the origin of elements in air, atmospheric dust or precipitation (Reimann and De Caritat, 2000, 2005). They have been used, for example, to detect the level of trace elements that are due to anthropogenic sources (Bourennane et al., 2010). The formula used

to calculate an EF is (Bourennane et al., 2010; Khalil et al., 2013; Reimann and De Caritat, 2000):

$$EF = \frac{\frac{[El]_{sample}}{[X]_{sample}}}{\frac{[El]_{crust}}{[X]_{crust}}}$$

where “El” is the element under consideration and “X” is the chosen reference element (e.g. Al). Reference elements most widely used are

Al, Li, Sc, Ti or Zr (Bourennane et al., 2010; Reimann and De Caritat, 2000). In this study, Al was selected as the reference element.

The value of the EF is used as an indicator of contamination. Researchers have generally defined enrichment as occurring when $EF > 2$, the cause of this enrichment being given as anthropogenic contributions (Hernandez et al., 2003; Khalil et al., 2013; Soubrand-Colin et al., 2007). Some authors subdivide EF categories to produce a more detailed indication of the level of contamination (Lu et al., 2009a; Lu et al., 2009b; Sutherland, 2000; Yongming et al., 2006): 1) $EF < 2$ indicates deficiency to minimal enrichment; 2) $2 \leq EF < 5$ indicates moderate enrichment; 3) $5 \leq EF < 20$ indicates significant enrichment; 4) $20 \leq EF \leq 40$ indicates very high enrichment; and 5) $EF > 40$ indicates extremely high enrichment.

3. Results

3.1. Statistical analysis

Descriptive statistics of major elements, trace elements, pH, TOC and N are summarized in Table 1.

Reference values are given for AR metal concentrations: Clarke's values (McLennan, 2001), enrichment factors and background values. Unlike Clarke's values, the latter are derived from a regional survey conducted in Wallonia and based on empirical data obtained using the aqua-regia mineralization method. In general, these data show that (i) variability is low (coefficient of variation [CV] about 20–30%) for pH, Al, Fe, Co and Cr, medium (CV ~ 40–100%) for TOC, N, major elements, Mn and Ni, and high for other trace elements (Cu, Cd, Zn and Pb), (ii) the relative variability is higher for available concentrations than it is for AR concentrations, (iii) most distributions are skewed and peaked, (iv) data sets remain non-normal even after \log_{10} transformation (except Al, Fe, Ni and K).

The variability in TOC concentrations, 0.83 to 6.99 g/100 g, may be associated with the different land uses (crop 43%, grassland 36%, forest

21%) from which samples were collected. Differences in sample pH values (water and KCl) also reflect land uses (very acidic in forests, circumneutral or basic in cultivated soils) and geology.

The mean EF for topsoil elements was the lowest for K and the highest for Cd. The sequence of increasing EF was $K < Ca < Mg < Cr < Ni < Co < Fe < Cu < Mn < Zn < Pb < Cd$. All of the elements could be distributed into five different classes based on the calculated EF. The first class ($EF < 2$) includes elements that are minimally enriched, such as Cr, K, Ca and Mg. In the second class ($2 \leq EF \leq 5$), Cu, Co, Ni and Fe show moderate contaminant enrichment. Only Mn (EF of 6.49) fell into the third class ($5 \leq EF \leq 20$). With an EF of 35.3, Zn in the topsoil was highly enriched, placing it in the fourth class. Finally, in the fifth class are Pb and Cd with EFs of 77.4 and 260, respectively. Because these EFs exceed 40, they are considered extremely highly enriched elements.

In addition to the descriptive statistics, visual presentations such as histograms and box-plots are convenient for comparisons (Mrvić et al., 2011; Yuan et al., 2014). For Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, histograms and box-plots are shown in Figs. 2 and 3, respectively. The sample concentration distribution patterns exhibited by Cd, Cu, Pb and Zn were similar. They appear clearly left-skewed with a long tail over very highly contaminated points. This observation is supported by Skewness and Kurtosis values (see Table 1). The most symmetrical distributions are those of Co, Cr and Al AR concentrations and pH (water and KCl) because their Skewness index is between 0 and 1. The Kurtosis index shows that the only distribution with a particularly flat peak is the pH data set. The other soil properties demonstrate sharply peaked distributions with a positive Kurtosis value (see Table 1 and Fig. 2).

3.2. Geochemical approach

Pearson correlation coefficients indicate a high degree of correlation between Fe, Al, and Ca (indicators of natural levels versus anthropogenic input) and some trace elements (Table 2). There were high degrees of

Table 1
Descriptive statistics ($\text{mg} \cdot \text{kg}^{-1}$), Clarke's values (McLennan, 2001), enrichment factors derived from topsoil samples and local background values (Ministère de la Région wallonne, 2008; Pereira and Sonnet, 2007). (N = 247).

Elements	Min	Max	Mean	Median	SD	CV (%)	Skewness	Kurtosis	A–D test	A–D test (log I)	Crust Clarke values	Enrichment factor	Background values
AR													
Cd	<DL	82.6	4.50	2.42	8.21	182	5.71	41.45	<0.005	<0.005	0.1	260	0.2
Co	1.38	25.8	10.2	9.89	3.22	31.5	0.95	3.33	<0.005	<0.005	17	3.07	10
Cr	9.66	58.2	28.5	27.9	6.71	23.6	0.65	1.75	<0.005	0.007	83	1.75	34
Cu	7.41	290	21.8	17.5	24.1	111	7.84	74.65	<0.005	<0.005	25	4.98	14
Mn	106	6386	763	692	478	62.6	7.14	78.46	<0.005	<0.005	600	6.49	*
Ni	3.47	77.2	21.4	20.5	9.73	45.4	1.83	6.44	<0.005	0.144	44	2.41	24
Pb	25.2	3286	212	86.1	413	194	4.91	27.39	<0.005	<0.005	17	77.4	25
Zn	63.4	8222	426	221	782	183	6.31	50.36	<0.005	<0.005	71	35.3	67
Ca ($\text{mg } 100 \text{ g}^{-1}$)	66.8	3726	456	343	451	99.0	4.19	21.15	<0.005	<0.005	3000	0.780	*
Mg ($\text{mg } 100 \text{ g}^{-1}$)	88.5	1564	320	280	205	63.9	3.52	16.05	<0.005	<0.005	1330	1.18	*
K ($\text{mg } 100 \text{ g}^{-1}$)	64.1	1073	330	302	145	43.9	1.59	5.22	<0.005	0.052	2800	0.576	*
Fe (%)	0.91	5.74	2.28	2.21	0.69	30.1	1.09	0.73	<0.005	0.055	3.5	3.27	*
Al (%)	0.62	3.05	1.62	1.58	0.40	24.5	0.43	78.46	0.098	0.036	8.04	1.00	*
Available													
Cd	0.37	39.2	3.03	1.41	5.8	190	5.17	31.9	<0.005	<0.005	*	*	*
Cu	1.49	82.5	5.69	3.81	9.7	171	6.79	51.9	<0.005	<0.005	*	*	*
Pb	10.4	1561	124	40.6	273.7	221	4.21	19.2	<0.005	<0.005	*	*	*
Zn	7.90	1705	101	36.2	259.8	257	7.16	65.6	<0.005	<0.005	*	*	*
Mn	143	413	227	220	53.9	23.7	2.47	11.3	<0.005	<0.005	*	*	*
Ca ($\text{mg } 100 \text{ g}^{-1}$)	48.2	1865	277	236	214	77.5	4.04	22.6	<0.005	<0.005	*	*	*
Mg ($\text{mg } 100 \text{ g}^{-1}$)	7.79	99.0	32.0	25.1	19.8	62.1	2.42	7.46	<0.005	0.091	*	*	*
K ($\text{mg } 100 \text{ g}^{-1}$)	3.43	93.5	18.3	15.6	13.5	73.6	2.70	10.8	<0.005	0.170	*	*	*
P ($\text{mg } 100 \text{ g}^{-1}$)	1.66	29.8	8.03	6.69	5.68	70.8	1.65	3.99	<0.005	0.257	*	*	*
pHwater	3.92	8.13	6.52	6.67	0.97	14.9	−0.61	−0.15	<0.005	*	*	*	*
pHKCl	3.28	7.70	5.97	6.18	1.12	18.7	−0.52	−0.50	<0.005	*	*	*	*
TOC (%)	0.83	6.99	2.53	2.23	1.21	47.7	1.13	1.16	<0.005	<0.005	*	*	*
N (‰)	0.07	0.51	0.22	0.19	0.09	41.5	1.01	0.47	<0.005	<0.005	*	*	*

Asterisk means there is no values.

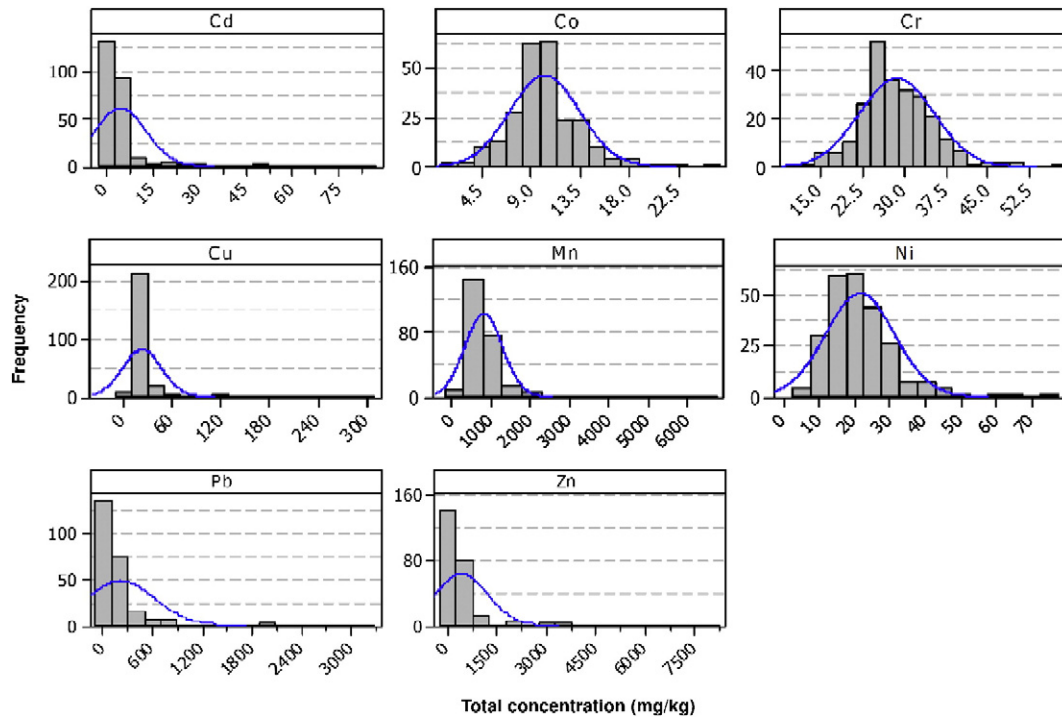


Fig. 2. Cumulative frequency curves for selected elements in the topsoil (N = 247).

correlation between Al, Fe and Co, Cr, Mn and Ni on the one side and between Cd, Cu, Pb, and Zn on the other side. Relationships between (AR) Fe and (AR) Al, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn are illustrated in Fig. 4, with distinct markers indicating distance from source intervals (0: 0 to 500 m; 1: 501 to 1500 m; 2: 1501 to 2500 m; 3: >2500 m). These relationship assessments show that the soil concentrations of Co, Cr, Mn and Ni appear to reflect natural geochemical trends and are tracked by the Fe concentration without showing spatial patterns related to the distance from the contamination source. In contrast, Cd, Pb, and

Zn showed no distinct trend, and only a weak trend was indicated for Cu, with evidence of contamination near the center of the study area.

3.3. PCA and factor analysis

The goal of principal component analysis is to reduce the number of variables that are found to be significant in affecting the dependent factor(s) being studied. The purpose of factor analysis is to identify the explanatory factors that drive variance across the dataset. In this study

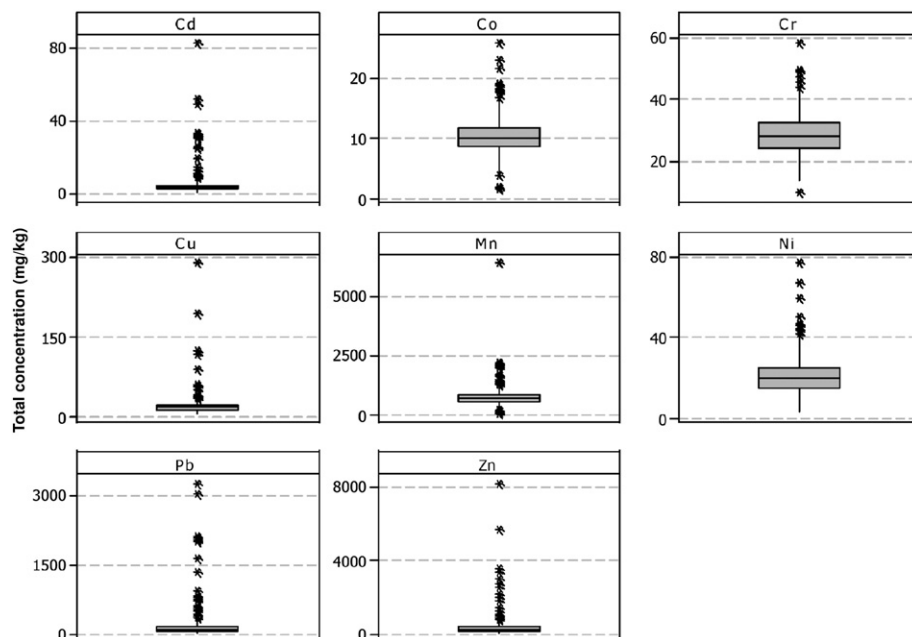


Fig. 3. Box-plots of the AR concentration (mg/kg) of selected elements (N = 247).

Table 2

Pearson correlation matrix between AR concentrations of trace elements, Fe, Al, and Ca (N = 247).

	Al	Fe	Ca
Fe	0.746***		
Ca	0.126*	0.296***	
Cd	−0.152*	−0.029	0.129*
Co	0.426***	0.720***	0.206**
Cr	0.657***	0.694***	0.285***
Cu	−0.150*	0.156*	0.149*
Mn	0.225***	0.485***	0.104
Ni	0.580***	0.764***	0.118
Pb	−0.240***	0.053	0.221***
Zn	−0.171**	0.121	0.221***

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

PCA was employed prior to factor analysis to identify potential clusters of soil properties and summarize them in a reduced number of meaningful dimensions (see Fig. 5). The correlation matrix was used to standardize the variables as they were not measured on the same scale. A varimax orthogonal rotation was applied on initial loading.

Four factors were retained during factor analysis, resulting in a cumulative accounting of 76% of the total variance (Table 3). The amount of variability explained by each factor progressively decreased but remained significant. Factor 1 explained 26.5% of the total variance and included both AR and available Zn, Pb, Cd and Cu. Factor 2 explained 23.9% and encompassed AR concentrations of Ni, Co, Cr, Fe, Al, K, Mg and Mn, as well as available Mn. The remaining two factors explained 16.5% and 9.3%, respectively, of the total variance. Factor 3 included pH_{water}, pH_{KCl}, AR Ca and available Ca, K and P. Factor 4 consisted mainly of TOC, N and available Mg.

3.4. Spatial distribution

The spatial distribution of every measured soil characteristic was analyzed with ArcGIS. A variographic analysis was performed and the information is summarized in Table 4 and Fig. 6.

A spherical model was applied to all experimental variograms (Fig. 7). Both AR and available Cd, Cu, Pb and Zn appeared to be anisotropic, as did AR Ni. However, the spatial dimensions of the variograms were dissimilar. We found that Cd, Pb and Zn were present in two distinct ranges, one minor around 2000 m and another one major around 4000 m. These results are likely linked to dominant wind direction. For Cu there was a peak at 3000 m which is different relative to all of the other metals; the cause of this apparent deviation is not known. All four of these elements, however, demonstrated high levels of spatial continuity with the $C/(C + C_0)$ ratio above 75%. This suggests that a large proportion of the variability is linked to a common spatial phenomenon driven by wind dispersion. The major vector for elevated concentrations corresponds to the dominant wind direction while the minor vector range is perpendicular to the dominant.

Elements contributing to second factor of variation, Al, Fe, Ni, Cr, K, Mg, Co present quite lower ranges of variation between 500 and 1000 m and $C/(C + C_0)$ ratio between 30% (Al) and 87% (Fe). This significant difference between Al and Fe could be linked to their differences of extractability by aqua-regia. Previous unpublished studies comparing performances of aqua-regia and triacid digestions showed that less than 60% of Al was extracted by aqua-regia compared to more than 90% for Fe. Properties linked to acidity/basicity levels present similar spatial characteristics, while TOC and N contents present less spatial continuity but over a longer range (2000 m).

3.5. Landscape factors

An ANCOVA using “distance to source of contamination” as the covariate was developed to assess the significance of the impact of landscape factors on the MTE concentration in topsoil. The results of statistical analysis with at least one significant p-value are compiled in Table 5.

AR and available Cd, Cu, Pb and Zn in topsoil are highly influenced by distance from the source ($p < 0.001$ in all cases). Distance to contamination source is therefore the main factor that accounts for the topsoil concentrations of these four MTEs.

The second most significant factor is land use (LU), which is a major driver behind AR Pb and Cr concentrations and available Cu, Pb and Zn

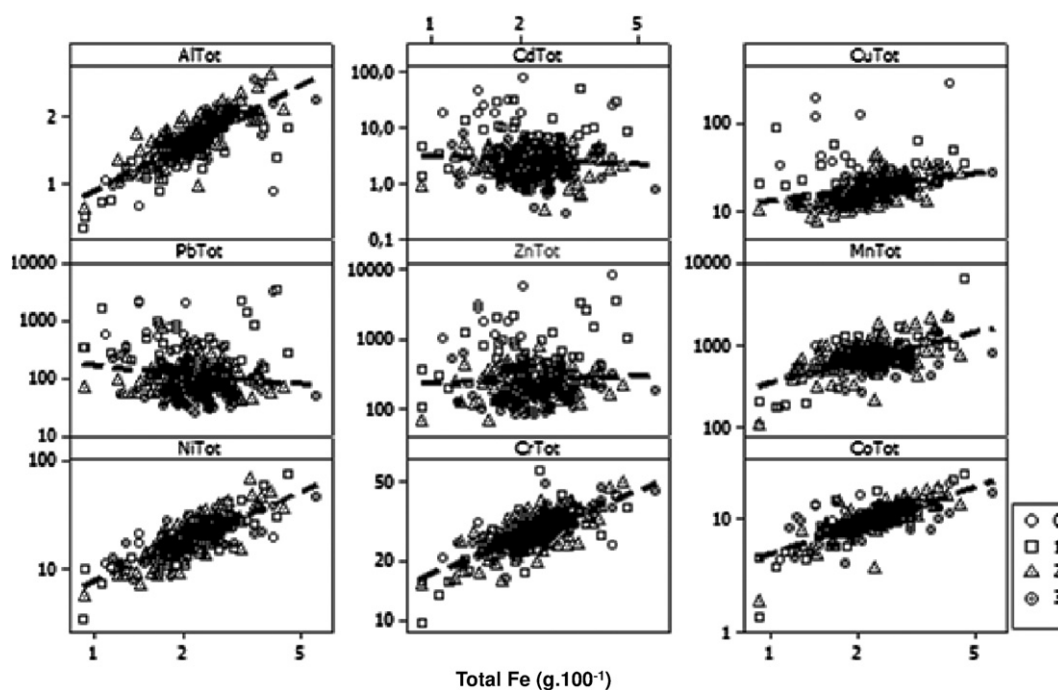


Fig. 4. Relationships between nine elements (Al plus eight trace elements) and Fe concentrations. The distance index refers to the distance to the center of the study area (0: 0 to 500 m; 1: 501 to 1500 m; 2: 1501 to 2500 m; 3: >2500 m).

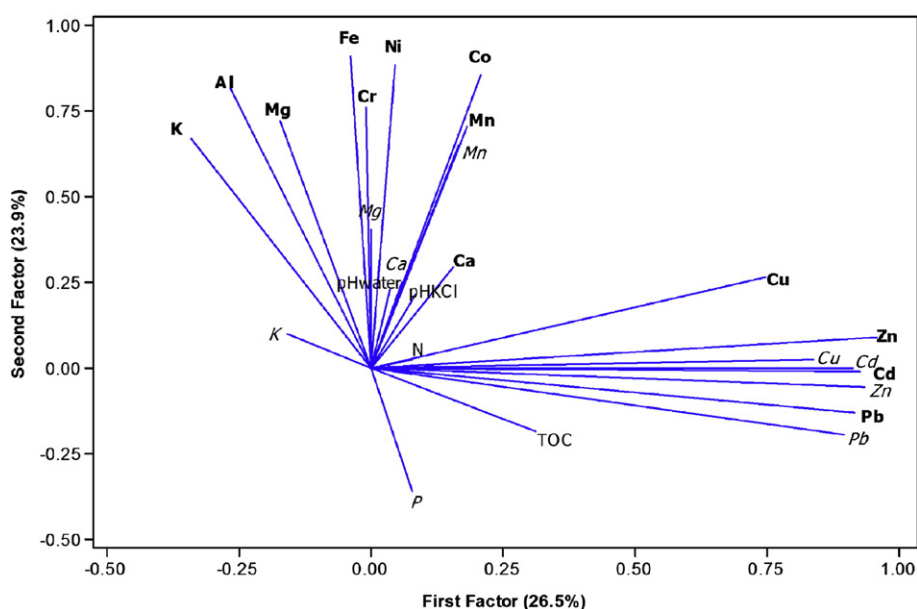


Fig. 5. Factor analysis for various elements (available concentrations in *italics*; AR concentrations in **bold**) and soil properties. In parentheses after the axes titles are the percentage of the total variance accounted for by each principal component in percentage.

concentrations ($p < 0.001$). Except for AR Cr, a post hoc means comparison test (Tukey HSD method) found that LU3 (forest) yielded greater MTE concentrations than the two other LUs. The metals influenced by land use were available Cd and AR Cu, both being significant at $p < 0.01$, and AR Cd and Zn ($p < 0.05$). For these four metals, Tukey's test once again showed that LU3 had higher MTE concentrations than LU1 and LU2.

The third and fourth factors are soil type (ST) and wind direction (WD). The ST factor strongly impacts AR Ni concentration and available Pb and Zn concentration ($p < 0.01$). AR Cd, Pb, Zn and available Cd are

also influenced by ST ($p < 0.05$). The Ni concentration was higher for ST1 and ST2 compared to ST3 while for the other elements ST3, a loamy-stony soil rich in clay, was richer. Only available and AR Cu appear to be impacted by WD ($p < 0.001$).

4. Discussion

4.1. Evidence of contamination

Based on the data obtained from measured AR concentrations of Cd, Cr, Co, Cu, Ni, Zn and Pb, two different scenarios present themselves in

Table 3

Results of factor analysis for various elements (available concentrations are listed separately in *italics*) and soil properties. Proportional variance explained by each of the four factors is given.

Variables	Factor1	Factor2	Factor3	Factor4	Communality
Zn	0.959	0.088	0.089	−0.039	0.938
Zn	0.938	−0.055	0.177	0.079	0.920
Cd	0.927	−0.012	0.107	0.014	0.871
Pb	0.917	−0.131	−0.169	0.062	0.891
Cd	0.913	0.000	0.141	0.035	0.854
Pb	0.897	−0.197	−0.130	0.024	0.861
Cu	0.840	0.022	0.022	0.137	0.725
Cu	0.748	0.266	−0.094	0.124	0.654
Fe	−0.039	0.909	0.101	0.015	0.839
Ni	0.045	0.886	−0.049	0.077	0.795
Co	0.208	0.856	−0.020	−0.055	0.779
Al	−0.265	0.815	0.156	−0.054	0.762
Cr	−0.010	0.762	0.293	0.153	0.690
Mg	−0.172	0.721	0.208	0.112	0.605
Mn	0.183	0.707	0.081	−0.109	0.552
K	−0.340	0.669	0.369	−0.046	0.702
Mn	0.168	0.648	0.358	−0.212	0.621
pHKCl	0.086	0.213	0.865	−0.331	0.910
Ca	0.060	0.249	0.862	0.087	0.815
pHwater	0.037	0.232	0.847	−0.388	0.922
Ca	0.156	0.296	0.813	0.170	0.803
K	−0.158	0.098	0.685	0.009	0.504
P	0.078	−0.362	0.493	0.215	0.427
N	0.079	0.025	−0.032	0.956	0.923
TOC	0.312	−0.184	−0.217	0.863	0.924
Mg	0.000	0.405	0.305	0.511	0.517
Variance	6.896	6.203	4.285	2.418	19.802
Variance %	26.5	23.9	16.5	9.3	76.2

In bold : the variables explained by factors.

Table 4

Variographic analysis of various elements (available concentrations are listed separately in *italics*) and soil properties.

Variables	Model	Isotropy	C/(C0 + C)	Range (m)	
				Minor	Major
pHwater	Spheric	Y	0.51	946	–
pHKCl	Spheric	Y	0.53	947	–
TOC	Spheric	Y	0.20	2259	–
N	Spheric	Y	0.13	2115	–
Ca	Spheric	Y	0.50	1206	–
Mg	Spheric	Y	0.56	3874	–
K	Spheric	Y	0.36	851	–
P	Spheric	Y	0.19	922	–
Mn	Spheric	Y	0.44	627	–
Ca	Spheric	Y	0.39	1240	–
Mg	Spheric	Y	0.54	1046	–
K	Spheric	Y	0.57	635	–
Fe	Spheric	Y	0.87	402	–
Al	Spheric	Y	0.32	1185	–
Mn	Spheric	Y	0.54	475	–
Cr	Spheric	Y	0.49	931	–
Co	Spheric	Y	0.68	429	–
Cd	Spheric	N	0.86	2081	3920
Cu	Spheric	N	0.90	2115	3017
Pb	Spheric	N	0.83	2033	4855
Zn	Spheric	N	0.86	2069	3937
Cd	Spheric	N	0.89	2068	4125
Cu	Spheric	N	0.79	2000	2572
Pb	Spheric	N	0.84	2032	4347
Zn	Spheric	N	0.88	2096	4037
Ni	Spheric	N	0.71	496	985

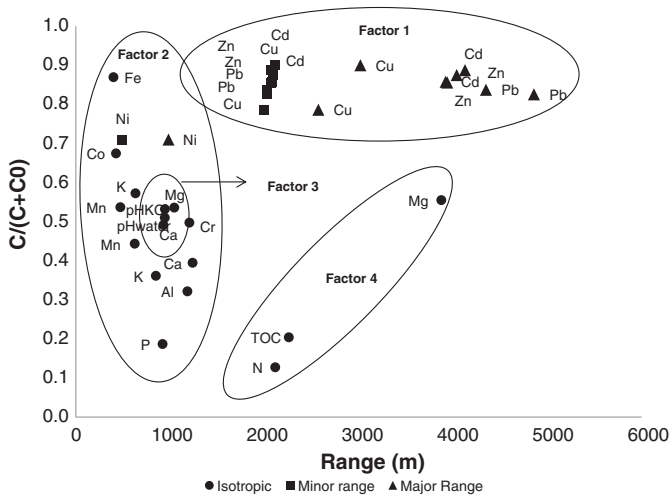


Fig. 6. Relationship between $C/(C + C_0)$ ratio and distance (m) from contaminant source. Ovals enclose variables along with the factors to which they contribute (C = spatially structured semi-variance, C_0 = semi-variance for distances between the points equal to "0", $C + C_0$ = maximum semi-variance).

this area of Wallonia. First, levels of Co, Cr and Ni in the studied soils are similar to the background values of 10, 34 and 24 ppm, respectively. Measured means (10.2, 28.5 and 21.4 ppm, respectively) were less than or equal to background. However, there were examples of extreme values which, while they might be considered unrepresentative outliers, actually demonstrate that relatively isolated 'hot spots' of local contamination do exist and should not be excluded, whatever their origin. Conversely, while mean concentrations of Cu, Zn, Pb and Cd are clearly higher than background, much lower measured values from certain locations suggest that contamination is not generalized over the entire area. When considering human health risk, Zn, Pb, and Cd are of concern as their concentrations exceed the legal thresholds that can trigger remedial action.

Multiple lines of evidence (i.e., coefficients of variation, summary statistics, background values, enrichment factors, and distribution curves) indicate severe contamination by Cd, Zn and Pb, and less severe, although still significant, contamination by Cu. This conclusion is consistent with what is known about the mineralogy and composition of the Zn–Pb ores that were processed at the former plant. The pattern of spatial topsoil contamination seen for these MTE is apparently reflective of the Sclaigneaux industrial past and illustrates historical dissemination and aerial deposition of metal-contaminated particulates.

This observation is supported by PCA results. The first studied factor takes into account the variance surrounding Cd, Pb, Zn and Cu concentrations. As shown in Table 1, the mean total (AR) concentrations of these four metals were far higher than background values, especially for Zn, Pb and Cd. Elevation about background is strongly indicative of anthropogenic factors, in this case industrial activities. This PCA result supports the EF data which already showed high or extremely high enrichment of topsoil for Zn, Pb and Cd. For the several parameters that are driven by Factor 2, soil concentrations are most likely lithogenic without undo anthropogenic impacts. Factor 3 is reflective of the effects of land use and geology (Ca), while Factor 4 reflects only the influence of the land use factor (TOC and N). It is worth noting that land use (LU) does not appear to have any significant influence on contaminant distribution; only lithology and historical industrial activity are the major drivers.

4.2. Factors associated with spatial variation

In a previous study (Liénard et al., 2011), we evaluated the spatial structure of ST and LU. Only the nugget structure was identified as important for the three ST, while spherical models were relevant for

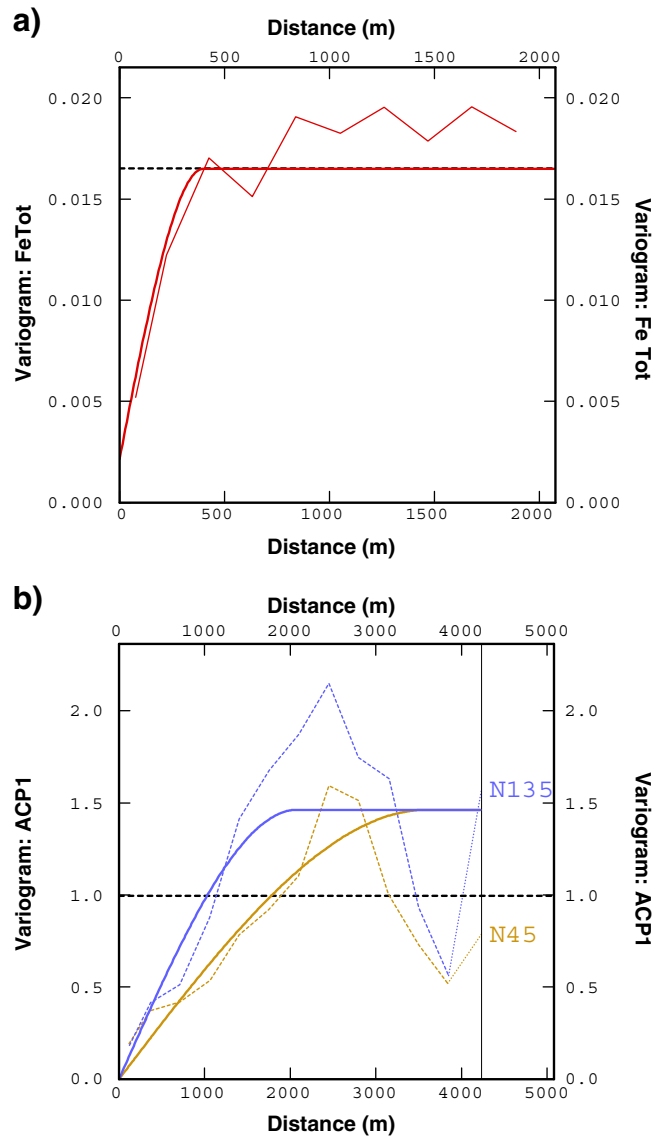


Fig. 7. Example of experimental and fitted variograms (spherical model) for variables with (a) isotropic spatial variation (Fe AR) and (b) anisotropic variation (Factor 1 of PCA).

LU. The distance ranges were modeled at 655, 780 and 1390 m, for crop, grassland and forest, respectively. The ranges identified for pH and the soil properties linked to Factor 3 are consistent with the LU ranges, in contrast to TOC and N concentrations. However, in the study area, the forest is bordered mostly by grassland, and the effective distance from forest (typified by high organic matter concentrations) to cropland (low organic matter concentrations) is nearly 2000 m. This is not the case for pH due to a stark contrast between forest and adjacent grassland.

Mapping of soil properties was completed using ordinary kriging from the reduced factors. A map of deciles is given in Fig. 8. The spatial distribution of Factor 1 clearly illustrates Cd, Pb, Zn and Cu contamination by atmospheric deposition originating from the center of the study area, that is, the historical industrial zone. The pattern closely reflects prevailing winds; distance to the source, while the dominant factor accounting for data variability, is not the only one. Distance is also the most important factor to emerge from the ANCOVA. These results imply that elevated Cd, Cu, Pb and Zn concentrations in topsoil (0–20 cm) have the same industrial origin. Data indicate that Co, Cr and Ni concentrations were not influenced by historical industrial activities and subsequent atmospheric deposition, which is reasonable

Table 5

Results of a three-way analysis of covariance (ANCOVA) using distance from the contaminant source as the covariate. Analyses were conducted using both AR and available concentrations.

Elements	Distance F _{1,207}	ST F _{2,207}	LU F _{2,207}	WD F _{3,207}	ST * WD F _{6,207}	LU * WD F _{6,207}	Dist. * WD F _{3,207}
AR							
Cd	160.36***	4.26*	4.48*	3.63*	2.50	3.39**	1.11
Co	0.15	0.34	1.59	1.24	0.14	1.47	1.23
Cr	2.25	0.20	15.15***	1.65	1.73	0.66	0.31
Cu	25.67***	1.30	7.45**	6.75***	1.70	0.41	5.84**
Ni	0.66	4.82**	1.94	1.69	0.23	1.69	1.54
Pb	144.39***	3.73*	25.63***	0.27	0.89	0.52	0.31
Zn	146.75***	3.14*	3.53*	1.53	1.51	1.95	0.28
Available							
Cd	139.36***	3.79*	4.95**	1.58	2.44*	4.82***	0.70
Cu	39.14***	1.07	9.80***	8.91***	1.75	0.30	6.94***
Pb	146.46***	5.67**	34.63***	2.04	1.10	0.41	1.14
Zn	121.67***	6.27**	9.10***	2.14	1.98	1.86	0.44

* p < 0.05.

** p < 0.01.

*** p < 0.001.

given that these elements were generally not elevated or concentrated in the processed ore. Cu concentrations appeared to be influenced by wind direction. In the case of CU, WD2 is highly dissimilar relative to the three other WD factors, suggesting Cu contamination is not necessarily associated with a unique source.

The spatial distribution of Factor 2 is less continuous than Factor 1, with the presence of localized hotspots and coldspots. No clear pattern was found regarding a relationship with LU or ST. However, levels of ST3 under forest and cropland were slightly lower than other combinations, and higher on soils developed from Frasnian rocks.

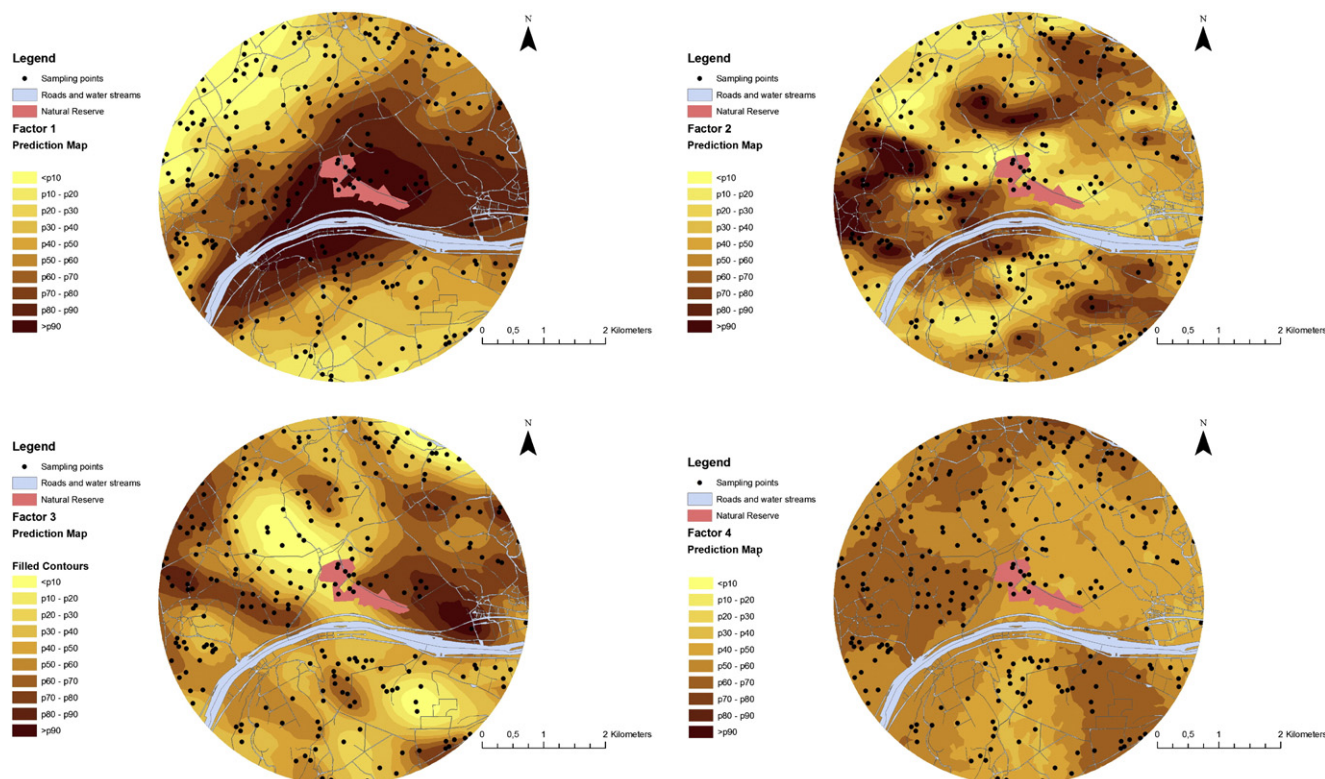
The Factor 3 map reflects the northwest to southeast orientation of rock outcrops modified by LU. Carbonate rocks tend to make substantial contributions to Factor 3, while forested areas and, to a lesser extent grasslands, yield lower pH soils. There is a dual influence of LU and ST on Factor 4. Forest and grassland soil is clearly higher in organic matter

than crop soil. Typical explanations for the results observed in forest soils include the high level of aerial particulate capture by vegetation that occurs in forests, and the higher mobility of TE due to elevated acidity. Regarding ST, the loamy-stony soils that developed on old Meuse terraces contained more organic matter than loess soils, perhaps in combination with a more clay-like texture.

5. Conclusion

We evaluated the level and extent of MTE contamination in soil collected from within 3 km of a former Zn–Pb ore treatment plant and used various statistical tools to investigate the potential factors influencing spatial distribution of the various metals.

As in many other places in Wallonia, and throughout the world, the lawns of nature reserves constitute the only visible sign of contamination

**Fig. 8.** Maps of soil properties identified by ordinary kriging from the reduced factors.

in the landscape. However, we found evidence of large-scale soil contamination from Cd, Pb, Zn and Cu which raises numerous questions about the potential short-term and long-term environmental impacts.

We analyzed our results according to various approaches that have been used by numerous researchers to investigate environmental contaminants. The use of an enrichment factor (EF) to quantify natural versus anthropogenic contributions should be used with caution since the extractability of some elements differ largely according to digestion method. The EF can be useful within a given dataset but comparing absolute values to other studies could be problematic. There are alternative techniques that might be employed, such as the local background or geochemical indices (Liang et al., 2013). Regardless of the technique used, some level of qualification should be applied to data analysis to take into account variability in analytical methods and provide a means of comparing to other studies.

Clarke and local references, histograms and box-plots, multivariate and geostatistical analyses yielded convergent clues of the prevailing anthropogenic source for Cd, Zn, Pb and Cu, and the lithogenic origin of other studied MTE. With these analytical data in hand, future study design can better account for geographical boundaries between anthropogenic and natural concentrations.

Analysis of variance using distance as a covariate was helpful in refining the model relative to spatial variation. Indeed, LU and ST appear to make significant contributions to the spatial distribution of soil MTE levels. In particular, LU impacts to the available metal concentration may be due to differences in soil acidity or ion exchange capacity. This is an interesting point to consider since, given the highly significant linear correlations, it is tempting to consider AR and available concentrations as essentially providing redundant information. However, there are key reasons for distinguishing between these two metal forms that are related to bioavailability and potential toxicity, which will be further elaborated in a separate paper.

A lithogenic effect is apparent as ST3, which presents a different parent material than loessic ST1 and ST2. The current research design places certain restrictions on the extent to which lithology/geology can be used to understand variations in metal concentrations. Since only the three dominant soils present in each quadrant were evaluated in the current investigation, it is important to consider the potential influence of other geochemical signatures in soils of the area.

The establishment of a soil contamination map is only a first step in this assessment as it does not fully answer the question of redistribution of contaminants within the landscape. It does, however, provide a firm basis for further comparisons and assessments. By developing a thorough understanding of the current assessment design and evaluation process, it may be possible to target future sampling efforts to reduce time and monetary expenditures. Regardless, there is little doubt that understanding metal mobility and bioavailability is crucial in determining the fate and effects of soil contaminants.

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