

Combining spatial distribution with oral bioaccessibility of metals in smelter-impacted soils: implications for human health risk assessment

Aurélie Pelfrène · Sébastien Détriché · Francis Douay

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Abstract Geostatistical analysis and GIS-based spatial mapping have been widely used for risk assessment of environmental pollution. The objectives of this study were to: (1) investigate the spatial variability of pseudototal concentrations of Cd, Pb, and Zn; (2) estimate the degree of contamination on the basis of pollution indexes; and (3) combine geostatistical analysis with oral bioaccessibility to better assess the population's exposure to metals in smelter-impacted soils. Implications for human health risks were assessed by considering soil as a contaminant source, a release mechanism of contaminated soil to the hands, ingestion as an exposure route, and metal bioaccessibility. The bioaccessibility data in the gastric (G) and gastrointestinal (GI) phases were integrated into the standard hazard quotient-based risk assessment method. Using pollution indices showed that the entire area studied was highly polluted in terms of soil metal concentrations. However, the spatial pattern of health risk levels did not coincide with the spatial distribution of the degree of soil contamination. Introducing the bioaccessible fraction of metals from soils into the exposure calculations resulted in a substantial decrease in calculated risk (HI, hazard

index) and provided a more realistic estimate of exposure to the three metals. For the highly exposed population, 46 % of the soils studied provided an HI-G > 1.0 and 15 % provided an HI-GI > 1.0, suggesting probable adverse health effects in children. The present study highlights the importance of conducting studies taking into account metal bioaccessible values in risk assessment.

Keywords Bioaccessibility · Metals · Soil · Geostatistics · Risk assessment

Introduction

Mining and smelting activities are responsible for extensive metal contamination of soils. The accumulation of metals in soils can have adverse effects on environmental health, crop growth, and food quality and is of great concern because of the potential health risk to the local inhabitants if metals are directly ingested or transferred through food (Bermudez et al. 2011; Hough et al. 2004; Oliver 1997; Pruvot et al. 2006; Wang et al. 2005). Accidental ingestion of soil particles is considered an important pathway of metal exposure, especially for children through hand-to-mouth activities (Day et al. 1979; Duggan et al. 1985; Wixson and Davies 1994). Some children can ingest substantial amounts of soil particles on given days. The daily intake of soil via oral ingestion was

A. Pelfrène (✉) · S. Détriché · F. Douay
Groupe ISA, Laboratoire Génie Civil et
géo-Environnement (LGCgE), 48 boulevard Vauban,
59046 Lille Cedex, France
e-mail: aurelie.pelfrene@isa-lille.fr

estimated to range from 50 to 200 mg day⁻¹ (Doyle et al. 2012). However, it has been documented that some children can ingest up to 20 g of soil during a single day for pica behavior (deliberate ingestion of large amounts of non-nutritive substances; Calabrese et al. 1997), but the frequency with which children experience acute poisoning from ingestion of contaminated soils is unknown. The United States Environmental Protection Agency has recommended value of 100 mg day⁻¹ to represent the mean soil intake for children between 1 and 6 years of age (USEPA 2008). In sites with potential metal contamination of soil and children's exposure, quantifying metal levels and assessing potential metal intake and risk is of great concern. To pose a risk, ingested contaminants must become bioavailable, meaning they must dissolve during gastrointestinal (GI) digestion and be absorbed in the bloodstream (Oomen et al. 2002). Research on metal oral bioaccessibility (i.e., the fraction of a contaminant in soil that becomes soluble in the GI tract and is then available for absorption; Oomen et al. 2002) relating to contaminated-land management has attracted attention at an international level and has been ongoing for more than 10 years (Basta and Gradwohl 2000; Cave et al. 2011; Hamel et al. 1999; Juhasz et al. 2007; Pelfrêne et al. 2011a; Roussel et al. 2010; Ruby et al. 1996; Van de Wiele et al. 2007; Yang et al. 2003). A better understanding of the "bioavailable" or "bioaccessible" contaminant concentrations offers an opportunity to better refine contaminant exposure assessments and thus to more effectively target remedial efforts and health/welfare protection measures.

The present study is based on a previous screening soil survey discriminating the contaminant sources in the north of France (Douay et al. 2013; Pelfrêne et al. 2013a, b). Soil contamination is a major concern, especially in former mining areas, due to the past industrial context and strong demographic pressure. From the latter part of the nineteenth and through much of the twentieth century, considerable atmospheric emissions of dust were generated by two smelters (the former Metaleurop Nord smelter and the Nyrstar smelter), leading to high contamination of the surrounding soils. A large part of the area studied comprises agricultural fields, urban areas (kitchen gardens, lawns, recreational areas), and to a lesser extent woody habitats (e.g., groves, woods, wooded creations). The metal contamination of topsoils has

been shown to reach significantly higher concentrations in urbanized landscapes than in agricultural areas (Douay et al. 2009, 2013; Pelfrêne et al. 2013b). The contamination of agricultural soils was caused mainly by smelter fallout (Sterckeman et al. 2000, 2002), whereas contamination of urbanized landscapes was enhanced by other anthropogenic activities (removal and deposition of various contaminated materials, gardening practices, atmospheric fallout linked to motor vehicle traffic, urban heating, and industrial activities; Douay et al. 2009). The metal contamination observed in the soils of this area is of particular importance for human risk assessment since all these types of land use (1) constitute residential, recreational, or food production areas, (2) are intensively frequented by people, and (3) could contribute significantly to the population's exposure to metals. Previous studies in this area showed that attention should be given to the potential health risk to children, in particular through soil particle ingestion (Pelfrêne et al. 2011b, 2013a).

The main objective of this study was to collect data obtained in this highly contaminated area in order to better assess the population's exposure to metals. Geostatistical analysis and GIS-based spatial mapping have been used to study spatial distribution patterns and possible hot spots of elevated concentrations of metal contamination. This approach has been widely used in the literature for modeling spatial variability of soil properties and mapping spatial distribution (Bourennane et al. 2003; Goovaerts 1999; Lin 2002) as well as for assessing the level of soil pollution (Davis et al. 2009; Guagliardi et al. 2012; Gong et al. 2010; Li and Feng 2012; Maas et al. 2010; Zhao et al. 2010) and human health risk (Hough et al. 2004; Meza-Montenegro et al. 2012; Sun et al. 2010; Zhang et al. 2009a, b; Zhao et al. 2012). However, spatial analysis has rarely been carried out in human health risk assessment by taking into account the oral bioaccessibility of metals (Barsby et al. 2012; Ettler et al. 2012).

In this paper, the specific objectives were to: (1) investigate the spatial variability of pseudototal concentrations of Cd, Pb, and Zn, (2) estimate the degree of contamination on the basis of pollution indexes, and (3) use the bioaccessibility data to assess human health risk using the standard hazard quotient (HQ)-based risk assessment method. The spatial distribution of the pollution indexes and the HQ values are also discussed.

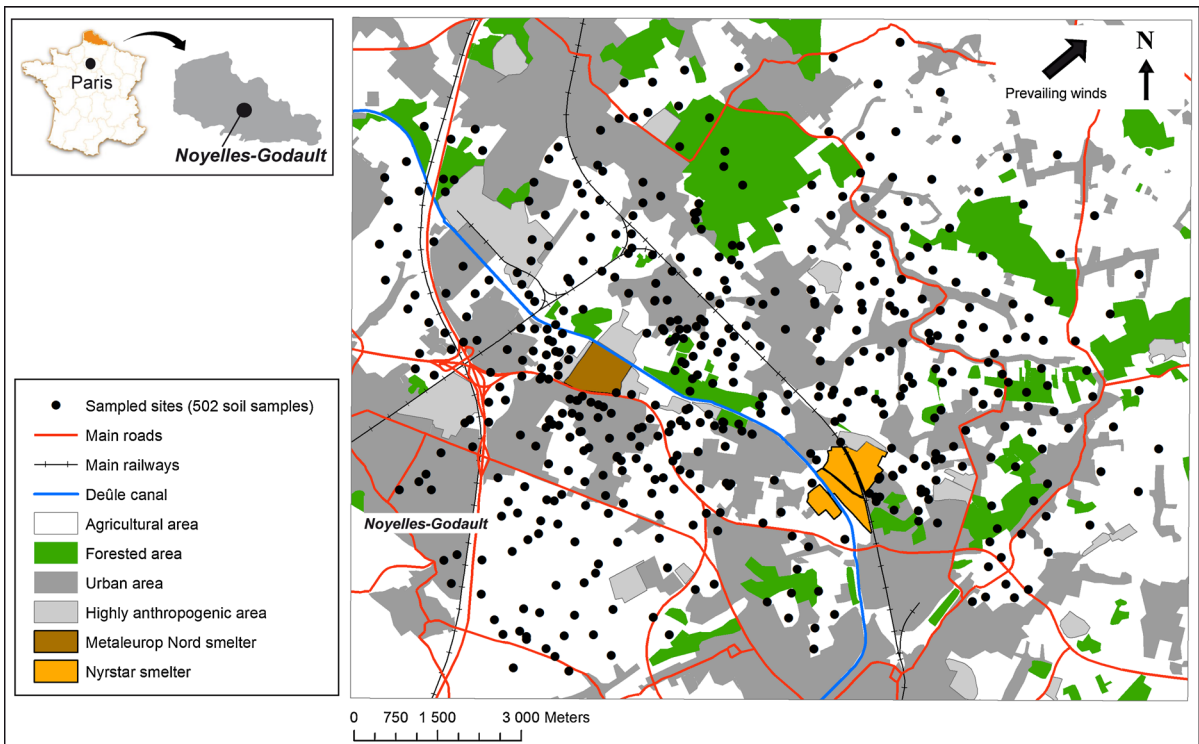


Fig. 1 Location of the study area (northern France), distribution of sampling sites, and land cover (2012 data)

Materials and methods

Study area

The study area is located in the former coal-mining area in northern France where considerable atmospheric emissions of dust were generated by two smelters. The Metaleurop Nord smelter (Noyelles-Godault, 50°25'42N 3°00'55E), which was the largest producer of primary lead in Europe from 1894 to 2003, used a pyrometallurgic process. Until 1975, the Nyrstar zinc smelter (Auby, 50°24'26N 3°04'36E), located 4 km to the east of Metaleurop Nord, also used a similar process. After this date, it changed to an electrolytic process, which considerably reduced its atmospheric emissions. The atmospheric fallout generated by former Metaleurop Nord smelter and Nyrstar smelter led to high contamination of the surrounding topsoils in an area that extends over 120 km² and where 55,000 inhabitants live (Sterckeman et al. 2002; Douay et al. 2008, 2009).

A 180-km² surface was defined as the study area (Fig. 1), which comprises agricultural (50 %), urban

(35 %), and woody habitat (10 %) soils (Pelfrêne et al. 2013b). Woody habitats were natural forests, tree plantations (poplar groves), or copses and hedgerows in natural or cultivated lands and urban parks. A total of 502 sites were chosen surrounding two neighboring smelters in order to represent large-scale metal contamination of soil (Fig. 1).

Soil sampling and analysis

Five hundred and two soil samples were collected from the upper soil layer (0–25 cm) at sites with various land uses included: agricultural (*n* = 390), urban (*n* = 50), and woody habitat (*n* = 62) soils (Pelfrêne et al. 2012, 2013b). The risk assessment calculations and geostatistical data analysis were carried out for all the data without differentiating land uses.

The soil samples were prepared according to the ISO 11464 standard. The samples were air-dried at a temperature below 40 °C and crushed to pass through a 2-mm stainless steel sieve. For each of the soil samples, a representative subsample was obtained

with an automatic sieve used with an ultracentrifugal mill <250 μm (Retsch type ZM 200, Germany).

The pseudototal element concentrations (Cd, Pb, and Zn) in the soil subsamples were obtained by a Hot Block system-assisted digestion (Environmental Express[®] SC100, Charleston, SC, USA). For this, 300 mg of soil subsamples was digested in a mixture of 1.5 mL nitric acid (70 %) and 4.5 mL hydrochloric acid (37 %) (aqua regia). The quality of the analytical data was checked by including a certified reference material (BCR CRM 701) and a blank (Pelfrène et al. 2013b).

The bioaccessibility test was performed according to the unified bioaccessibility method (UBM; Wragg et al. 2011) previously described in full by Roussel et al. (2010) and Pelfrène et al. (2011a, b, 2012). The UBM test consisted in two parallel sequential extractions and provided samples for analysis from both the gastric (G) and GI phases. For every ten soil samples analyzed from the study set, a triplicate soil, a standard control soil (NIST 2710; Pelfrène et al. 2013b), and a blank were included in the tested sample batch.

The pseudototal and bioaccessible concentrations were measured by flame atomic absorption spectrometry (FAAS, AA-6800, Shimadzu, Japan).

Potential risk of topsoil contamination

To assess the degree of soil contamination, an accumulation factor (pollution index, PI) and an integrated pollution index (IPI) were quantified (Chen et al. 2005; Meza-Montenegro et al. 2012; Sun et al. 2010; Wei and Yang 2010). The PI is defined as the ratio of metal concentration in the area studied to the regional agricultural soil concentration of the corresponding metal:

$$\text{PI} = \frac{C_i}{B_i} \quad (1)$$

where PI is the evaluation score corresponding to each sample, C_i is the measured pseudototal concentration of the metals in the soils studied, and B_i is the mean regional topsoil values of the metals, which are 0.44 mg kg⁻¹ for Cd, 32 mg kg⁻¹ for Pb, and 68 mg kg⁻¹ for Zn (Sterckeman et al. 2002; Table 1). The PI value of each metal was calculated and classified as either low contamination (PI \leq 1.0), moderate contamination (1 < PI \leq 3.0), or high contamination (PI > 3.0). The IPI is defined as the mean

Table 1 Summary statistics of metal concentrations (mg kg⁻¹) in topsoils

	Cd	Pb	Zn
Studied area ($n = 502$)			
Range	0.44–62.7	42–6,002	50–7,263
Mean	5.29	273	515
Median	3.30	140	298
SD	6.24	447	779
Regional values ^a ($n = 232$)			
Range	0.03–1.36	13–198	24–206
Mean	0.44	32	68
Median	0.41	29	67
SD	0.21	17	25

SD standard deviation

^a Sterckeman et al. (2002)

of all the PIs of all of the metals considered and was classified as a low level of pollution where IPI \leq 1, a moderate level where 1 < IPI \leq 2, a high level where 2 < IPI \leq 5, or an extremely high level of pollution where IPI > 5 (Chen et al. 2005; Wei et al. 2009).

Human health risk assessment

The risk associated with chronic exposure to metals in the soils was assessed using the standard HQ-based risk assessment method (USEPA 2007). In this method, the potential noncarcinogenic risk for Cd, Pb, and Zn was expressed as the HQ. Index doses (to assess cancer risk) for metals were not determined due to lack of slope factor information for oral exposure. Although the HQ-based risk assessment method does not provide a quantitative estimate of the probability of an exposed population experiencing a reverse health effect, it does provide an indication of the risk level due to pollutant exposure.

For the contaminated soils studied, a previous study showed that particle or dust ingestion was usually by far the greatest exposure route for small children (Pelfrène et al. 2013a). For the purpose of this assessment: (1) only the uptake of metals by soil ingestion was considered, and (2) because children aged 2–6 years were identified as the most sensitive population due to their behavioral and physiological parameters, only children were considered as the exposed population. An HQ is defined as the ratio of the estimated contaminant exposure (the estimated

daily intake, EDI) to the tolerable daily intake (TDI). If the ratio is <1.0 , the exposed population is unlikely to experience obvious adverse effects. However, if the HQ is higher than 1.0 , the contaminant may produce an adverse effect, and an HQ >10.0 is considered to be a high chronic risk. TDI is the oral reference dose, which is an estimation of maximum permissible risk on a human population through daily exposure over a lifetime. For Cd and Zn, TDIs were based on $1\text{E}-03$ and $3\text{E}-01$ mg kg body weight $^{-1}$ day $^{-1}$, respectively (USEPA 2007). For Pb, for children, we chose a TDI of $3\text{E}-04$ mg kg body weight $^{-1}$ day $^{-1}$, which provides a more conservative assessment (JECFA 2010; Pelfrène et al. 2013a). For exposure assessment, the HQ and EDI of Cd, Pb, and Zn from incidental soil ingestion were calculated with the following equations:

$$\text{HQ} = \frac{\text{EDI}}{\text{TDI}} \quad (2)$$

$$\text{EDI} = \frac{C_s \times \text{IR} \times \text{EF} \times \text{ED} \times \text{BAF}}{\text{BW} \times \text{AT}} \times 10^{-6} \quad (3)$$

where EDI is the estimated daily intake through soil particle ingestion (mg kg $^{-1}$ day $^{-1}$), C_s is metal concentration in soil (mg kg $^{-1}$), IR is the time-averaged soil and dust ingestion rate (100 mg day $^{-1}$), EF is the exposure frequency (180 days year $^{-1}$), ED is the exposure duration (5 years from age 2 to 6), BAF is the bioaccessible fraction for soil (unitless; BAF-G in the G phase and BAF-GI in the GI phase), BW is the average body weight (15 kg; USEPA 1989), and AT is the averaging time (1,825 days).

The bioaccessibility of metal in the soil ingestion process was incorporated into risk calculations by modifying the BAF in equation (3). Two different scenarios were considered. The first scenario assumed that 100 % of metals in soil ingested by children was bioaccessible (i.e., the BAF was equal to one). This is a conservative assumption and one that is commonly used when bioaccessibility data are not available during risk assessment. The second scenario assumed that only a fraction of metals in soil ingested by children was bioaccessible (i.e., the BAF corresponds to %bioaccessibility/100). The metal's BAF in the GI phase is more physiologically relevant. However, for human health risk assessment, the metal's BAF in the G phase would provide a more conservative assessment. For the purposes of the discussion in this paper, the results in both phases were presented. HQs can be added and can generate a hazard index (HI) to estimate

the risk of mixing contaminants. Therefore, the HQ for each metal at a location was summed to generate the HI. The potentially harmful metals (Cd, Pb, and Zn) were considered for HI calculations.

Geostatistical treatment

Geostatistical mapping of metal concentrations and risk indices was conducted using ordinary kriging (Matheron 1970; Chilès and Delfiner 1999). The geostatistical procedure follows the classical steps clearly explained and detailed in Oliver and Webster (2014).

Exploratory spatial data analysis was conducted to characterize the distribution of the data. The distribution appears to be heavily skewed so data were log-transformed before variogram analysis. Data distribution and semivariogram cloud analysis show the presence of extreme values (outliers), mainly located near the smelters, which nonetheless were considered as reliable measurements. Outliers were removed for the estimation of the semivariogram model but incorporated back during the kriging estimation process.

The spatial dependence of topsoil contamination was first studied by calculating directional empirical semivariograms. Since no anisotropy was detected, omnidirectional empirical semivariograms were used to fit isotropic models. The omnidirectional variograms were modeled testing spherical, circular, Gaussian, and exponential models together with modeling the nugget effect. Models were then cross-validated, and the best model was chosen according to cross-validation statistics (Krivoruchko 2011; Oliver and Webster 2014). A circular-searching neighborhood composed of eight sectors with a minimum two neighbors and a maximum number of four per sector was used.

The GIS and geostatistical procedures were conducted on ArcMap and Geostatistical Analyst from ArcGIS 10 (©ESRI).

Results and discussion

Spatial distribution of metal concentrations

The concentration ranges, means, and medians of Cd, Pb, and Zn for the topsoil data set are given in Table 1. The results showed a wide range of concentrations, which varied for Cd from 0.44 to 62.7 mg kg $^{-1}$, for Pb

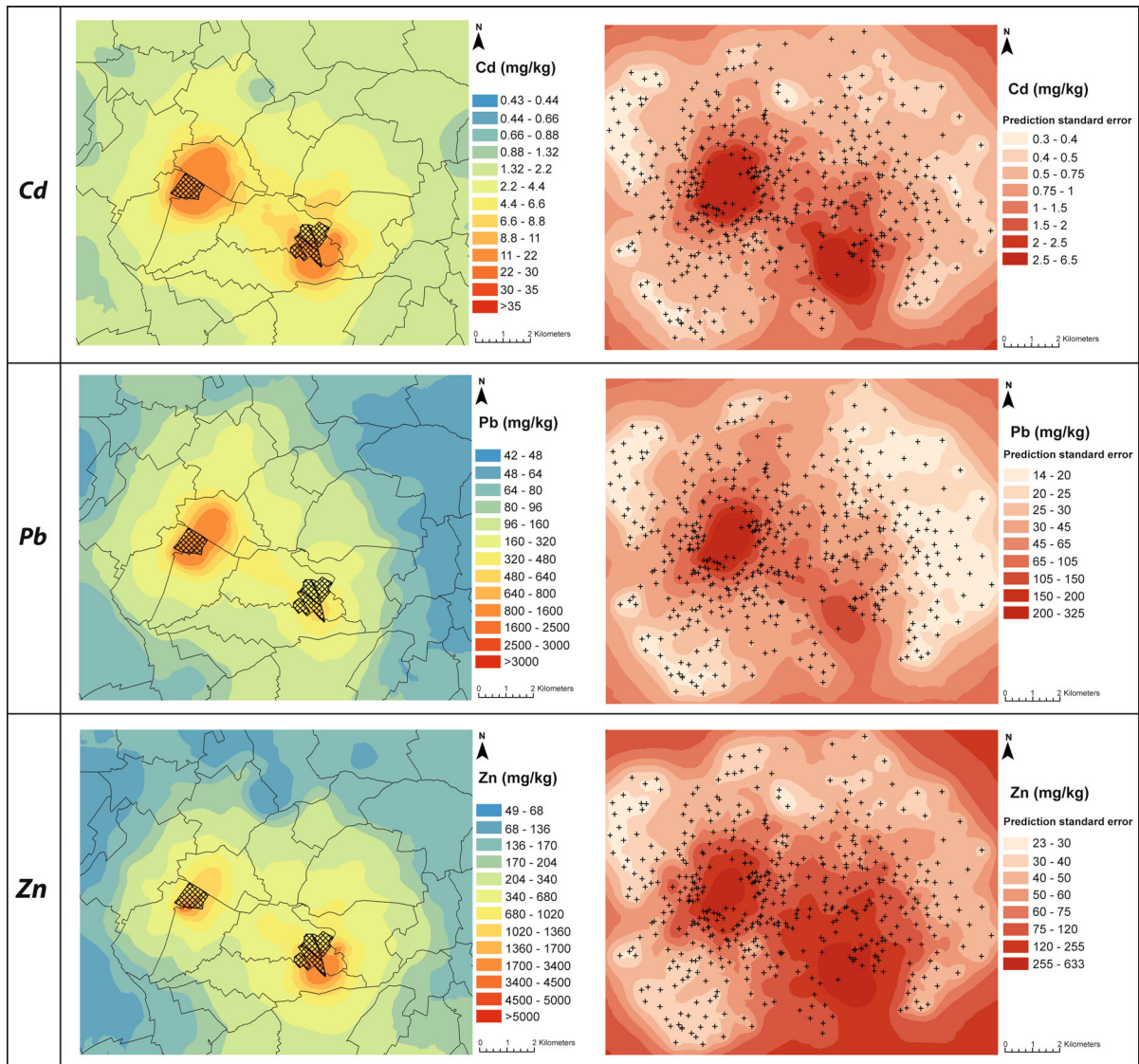


Fig. 2 Prediction maps of pseudototal Cd, Pb, and Zn concentrations in topsoils (mg kg^{-1}) estimated by ordinary kriging and corresponding prediction standard error maps (the standard error corresponds to the square root of the kriging variance). For prediction maps, symbology classes were defined according to regional values of metal concentrations in topsoils

(1.5 \times , 2 \times , 2.5 \times , 3 \times , 5 \times , 10 \times , 15 \times , 20 \times , 25 \times , 50 \times , and more). The localization of the smelters is indicated with *dashed lines*. Municipality boundaries are shown on the prediction maps (*lines*), while sample location is displayed on prediction error maps (*crosses*)

from 42 to 6,002 mg kg^{-1} , and for Zn from 50 to 7,263 mg kg^{-1} . This high heterogeneity and variability was explained by the soil uses and the past or present anthropogenic activities (Douay et al. 2009, 2013; Fritsch et al. 2010; Pelfrène et al. 2013b). The degree of contamination of urban and woody habitat soils was significantly higher than that of agricultural

soils, and previous studies have provided the evidence for the substantial anthropogenic reworking of these soils. The metal concentrations in soils were compared with the regional values (Table 1), which confirmed the high level of metal contamination. The mean Cd, Pb, and Zn concentrations were 12-, 9-, and 8-fold, respectively, greater than the regional values, whereas

Table 2 Summary of the main parameters corresponding to the variogram models retained for metals (Cd, Pb, Zn), hazard indices (IPI, HI, HI-G, HI-GI), and the cross-validation results (Values in mg kg⁻¹)

	Variogram model parameters				Cross-validation parameters				
	Correlation function	Nugget	Partial sill	Major range (m)	ME	MS	RMSS	RMS	ASE
Metals									
Zn	Spherical	0.077	0.46	5,500	-0.039	0.027	1.057	199.955	165.870
Pb	Circular	0.128	0.64	5,600	-0.047	0.067	1.004	135.294	130.943
Cd	Spherical	0.099	0.582	5,395	-0.041	0.048	1.035	3.214	2.486
Indices									
IPI	Spherical	0.093	0.566	5,579	-0.059	0.058	0.960	5.158	4.065
HI	Circular	0.134	0.691	5,173	-0.044	0.062	1.048	2.267	1.640
HI-G	Spherical	0.172	0.796	6,275	-0.021	0.075	0.960	1.488	1.173
HI-GI	Spherical	0.351	0.782	5,158	-0.027	0.067	0.989	0.989	0.625

ME mean error, MS mean standardized error, RMSS root-mean-square-standardized error, RMS root-mean-square error, ASE average standard error

the median concentrations were 8-, 5-, and 4-fold, respectively, greater than the regional values.

The spatial distribution of pseudototal Cd, Pb, and Zn concentrations in the area topsoils studied are plotted in Fig. 2. The variograms demonstrated clear spatial structures for the three metal pseudototal concentrations, and the cross-validation statistics showed that model parameters were accurate. More precisely, the mean prediction errors and the standardized mean of the prediction errors were close to zero, the root-mean-square-standardized errors were close to one, and the average standard errors were close to the root-mean-squared prediction errors (Table 2).

The spatial patterns of the three metals were globally similar with elevated concentrations focused around the two smelters, indicating that the elevated metal concentrations were related to the former smelting activities. The dispersal of contaminants in the vicinity of the Metaleurop Nord smelter was different from that of the Nyrstar smelter: (1) the highest concentrations of Cd and Pb were recorded in the soils around the Metaleurop Nord smelter and (2) the soils around the Nyrstar smelter showed the highest concentrations of Zn and high concentrations of Cd. These results can be explained by the atmospheric fallout generated by the two smelters (Sterckeman et al. 2002). The Metaleurop Nord smelter was a producer of primary lead, which generated large quantities of dust contaminated by

Pb, but also by Cd and Zn. Despite strong environmental regulations set up in the 1970s, dust emissions from the smokestacks were still 17 t of Pb, 1 t of Cd, and 32 t of Zn in 2002 (DRIRE 2003). In addition to the smokestack emissions, the slag created by the pyrometallurgic process was piled in an outdoor heap and was subjected to dispersion by wind, contributing to the dispersal of pollutants in the environment. The Nyrstar smelter is one of the largest zinc production plants in Europe. Because of a change in industrial processes in 1975, the Nyrstar smelter has ceased emitting to the atmosphere (DRIRE 2003); however, large quantities of dust contaminated by Zn as well as Cd and Pb were generated.

Assessment of the degree of soil contamination

To further assess the contamination levels of the metals in the area studied, the PIs of Cd, Pb, and Zn were calculated according to the regional soil values of metals. The results show that the PIs varied considerably across the different metals (Table 3): (1) the PI value of Cd varied from 1.0 to 116.0, and more than 93 % of soil samples had a high-level PI, (2) the PI value of Pb ranged from 1.3 to 106.0, and all soil samples had a moderate (31 %) or high (69 %) PI, and (3) the PI value of Zn varied from 0.7 to 101.6, and all soil samples (except one) were moderately (30 %) or heavily (70 %) contaminated by Zn. The mean PI values for Cd, Pb, and Zn were 11.9, 8.2, and 7.4,

Table 3 Pollution index (PI) and integrated pollution index (IPI) of Cd, Pb, and Zn in soils ($n = 502$)

	PI			Number of samples			IPI		
	Min	Max	Mean	Low	Moderate	High	Min	Max	Mean
Cd	1.0	116.0	11.9	1	32	469			
Pb	1.3	106.0	8.2	0	154	348	1.3	90.1	9.2
Zn	0.7	101.6	7.4	1	152	349			

PI \leq 1.0: low pollution; 1.0 < PI \leq 3.0: moderate pollution; PI > 3.0: high pollution

Table 4 The evaluation standard and results of soil metals

Grade level	IPI	Pollution grade	Percent (%)
1	IPI < 1	Low	0
2	1 < IPI < 2	Moderate	2
3	2 < IPI < 5	High	43
4	IPI > 5	Extreme high	55

respectively, indicating that the soils studied were seriously contaminated by the three metals. Overall, all soils in urban, agricultural, or woody habitat areas had moderate or high PIs. Comparison of the three PIs shows that Cd was on average the heaviest contamination in this area.

The IPI of the metals considered, another criterion to evaluate the metal pollution in soils, was calculated (Table 3) and classified as various pollution grades (Table 4). The IPI value of soils varied from 1.3 to 90.1 with an average of 9.2. There were no samples with IPI \leq 1, 2 % of the samples had an IPI between 1 and 2, 43 % of the samples had an IPI between 2 and 5, and 55 % of the samples had an IPI > 5. Thus, most of the soils are highly or extremely highly polluted with the three metals studied. The spatial distribution of IPIs in agricultural, urban, and woody habitat soils is presented in Fig. 3. From the evaluation map, it is clear that: (1) the entire area studied was contaminated by Cd, Pb, and Zn and (2) severe pollution areas were mainly distributed in areas close to the point sources of pollution. Taking into account the results for Cd, Pb, and Zn, measures must be applied to protect human health. To confirm or invalidate these results, human health risks were assessed.

Implications for human health risk assessment

To better refine contaminant exposure assessments, the *in vitro* GI extraction procedure was applied to all

soil samples ($n = 502$) from the site to assess oral bioaccessibility (Pelfrène et al. 2013b). A summary of the data is shown in Table 5, indicating the BAF values of Cd, Pb, and Zn in the G and GI phases. The results showed a wide range of BAF for the three metals and for both phases, which could be mainly explained by the soil uses and by different metal–ligand ratios in digestive juices (Pelfrène et al. 2013b). The BAF ranged as follows: Cd (25.4–99.8 and 7.7–99.0 % in G and GI phases, respectively), Pb (5.2–87.5 and 2.2–63.2 % in G and GI phases, respectively), and Zn (3.1–84.6 and 0.2–46.6 % in G and GI phases, respectively). It is apparent that the G phase always exhibited the highest BAF, as reported by several authors (Appleton et al. 2012; Barsby et al. 2012; Gbafa et al. 2011; Oomen et al. 2006; Poggio et al. 2009). On average, Cd demonstrated the highest bioaccessibility in soil samples. The order for mean values of BAF in both phases was as follows: Cd > Pb > Zn, suggesting that there were great differences in terms of bioaccessibility among these metals. In a previous study, Pelfrène et al. (2013b) reported that the soil feature, the incorporation of extraneous materials, or cultural practices influenced the physicochemical parameters of soils, the pseudo-total metal concentration, and metal bioaccessibility. Comparing the calculated BAF for each metal with other studies such as Barsby et al. (2012), Okorie et al. (2011), Poggio et al. (2009), and Gbafa et al. (2011) investigating human bioaccessibility of anthropogenic soil pollution showed that higher BAF values were generally observed for Cd, Pb, and Zn.

To assess the health risk associated with metal contamination in soils, the HQs of Cd, Pb, and Zn for children were calculated by considering soil as a contaminant source, the release mechanism as the adherence of contaminated soil particles to hands, and ingestion as the exposure route. The HQ values of metals in soils are listed in Table 6. Two different

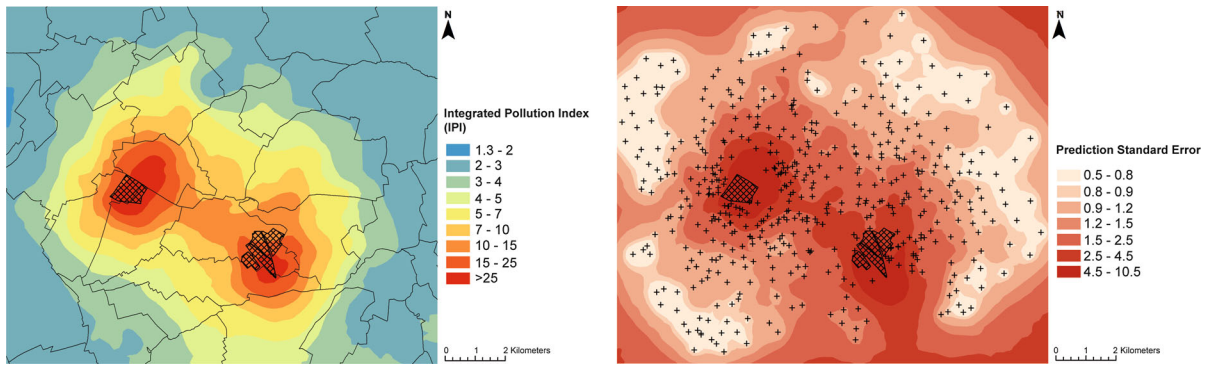


Fig. 3 Prediction map of the integrated pollution index (IPI) estimated by ordinary kriging and corresponding prediction standard error map (the standard error corresponds to the square root of the kriging variance). The location of the smelters is

indicated with *dashed lines*. Municipality boundaries are shown on the prediction map (*lines*), while sample location is displayed on the prediction error map (*crosses*)

Table 5 Bioaccessible fraction (BAF) of Cd, Pb, and Zn in the gastric (G) and gastrointestinal (GI) phases expressed as a percentage of pseudototal concentrations in soils ($n = 502$)

	Cd		Pb		Zn	
	BAF-G	BAF-GI	BAF-G	BAF-GI	BAF-G	BAF-GI
Min	25.4	7.7	5.2	2.2	3.1	0.2
Max	99.8	99.0	87.5	63.2	84.6	46.6
Mean	76.1	42.9	58.7	21.6	34.9	10.2
Q1	69.0	29.5	52.4	14.6	27.3	5.9
Median	76.7	40.1	60.0	20.3	33.1	9.4
Q3	85.7	55.0	65.7	27.0	41.2	12.6

Q1 first quartile, Q3 third quartile

scenarios were considered: (1) the first assumed that 100 % of metals in soil ingested by children were bioaccessible (HQ) and (2) in the second, the metal’s BAF in the G and GI phases was incorporated into the method (HQ-G and HQ-GI, respectively). In considering the first scenario, the HQs for Cd and Zn were <1.0 (Table 6), suggesting that children will not experience any form of deleterious health effects from ingesting of these single elements in the soils studied. In considering the BAF values, HQs decreased and showed low values (<0.2 for Cd and <0.08 for Zn). For Pb, the results present a different behavior. In considering the first scenario, the majority (73 %) of the soils provided an HQ > 1.0 and only 27 % provided an HQ < 1.0. The average HQ for all the soil samples was 2.99 (Table 6). These results suggest that Pb levels in these topsoils are the main issue of concern and that children are exposed to a relatively high health risk. However, the BAF

data produced in the present study suggest that the ingested dose of metal is not equal to the actual absorbed pollutant dose. A high fraction of the ingested metal may be excreted, and only the remainder accumulated in body tissues may affect human health. Moreover, it has been demonstrated that the UBM test is a good analog of juvenile swine bioavailability measurements (Denys et al. 2012). In considering the BAF values, HQ-G greatly decreased, 55 % of the soils provided an HQ < 1.0, and 45 % provided an HQ > 1.0. The average HQ-G for all the soil samples was 1.83 (Table 6). When the GI phase was considered, HQs sharply decreased. Only 15 % of the soils studied provided an HQ-GI > 1.0, and the use of BAF-GI reduced HQs to <1.0 for 85 % of soils. Introduction of the BAF of Pb from soils into the exposure calculations resulted in a substantial decrease in the calculated risk (Fig. 4). By simulating the amount of contaminant mobilized into

Table 6 Calculated values of hazard quotient (HQ, unitless) for each metal and hazard index (HI, unitless) taking into account the gastric (G) and gastrointestinal (GI) phases

	Cd			Pb			Zn			HI	HI-G	HI-GI
	HQ	HQ-G	HQ-GI	HQ	HQ-G	HQ-GI	HQ	HQ-G	HQ-GI			
Min	0.001	0.001	0.0001	0.46	0.14	0.02	5.46E-04	6.48E-05	2.67E-06	0.46	0.15	0.03
Max	0.206	0.165	0.079	65.8	45.4	16.3	7.96E-02	5.75E-02	3.05E-02	66.10	45.7	16.4
Mean	0.017	0.013	0.007	2.99	1.83	0.70	5.64E-03	2.46E-03	9.55E-04	3.01	1.84	0.71
Q1	0.007	0.005	0.003	0.96	0.55	0.18	1.99E-03	5.83E-04	1.39E-04	0.96	0.55	0.19
Median	0.011	0.008	0.005	1.53	0.87	0.30	3.26E-03	1.06E-03	3.09E-04	1.56	0.88	0.31
Q3	0.019	0.015	0.007	3.13	1.77	0.66	5.58E-03	2.19E-03	5.89E-04	3.15	1.79	0.67

Q1 first quartile, Q3 third quartile

the digestive juices, bioaccessibility analyses provide a more realistic estimate of exposure than do total metal concentrations.

The HQs of Cd, Pb, and Zn were added to generate HI and to estimate the risk of mixing contaminants, but without taking into account interactions between pollutants (Table 6; Fig. 4). On average, the contribution of metals from soil ingestion to HQ, HQ-G, and HQ-GI was about 99, 1, and 0.1 % of HI values for Cd, Pb, and Zn, respectively. However, the proportion of HQs that was attributable to Cd, Pb, and Zn varied slightly with the two different scenarios. The transition from scenario 1 (HQ) to scenario 2 (HQ-G and HQ-GI) resulted in: (1) an increase in the contribution of Cd to the HI (from 0.7 % for HQ to 1.7 % for HQ-GI), (2) a decrease in the contribution of Pb to the HI (from 99.1 % to 98.1 %), and (3) a decrease in the contribution of Zn to the HI (from 0.2 % to 0.1 %). Because the largest contribution to the HI was from Pb, the HI results were similar to the HQ results for this element. The average HI for the entire population was 3.01 considering the first scenario and highly decreased when considering the BAF values (1.84 with BAF-G and 0.71 with BAF-GI; Table 6). The HI maps showed that the HI estimates varied considerably with and without consideration of the BAF values (Fig. 4). The highest HI values were located surrounding the two smelters. Moreover, the transition from scenario 1 to scenario 2 resulted in a substantial decrease in the HI depending on the surface area. When the HI exceeds 1.0, there is a chance that noncarcinogenic effects may occur with a probability that tends to increase as the HI value increases (Fig. 4).

Introduction of the BAF of metals from soils into the exposure calculations resulted in a considerable

decrease in the calculated risk. By simulating the amount of contaminant mobilized into the digestive juices, bioaccessibility analyses provide a more realistic estimate of exposure than do total TE concentrations. However, caution is required when interpreting the results of risk assessment. To provide a more conservative assessment, the HI-G values could be used compared to the HI-GI values. In this case, for the highly exposed population, 54 % of the soils studied provided an HI < 1.0, 31 % provided an HI between 1.0 and 3.0, and 15 % had an HI > 3.0. Only 7 % provided an HI > 5.0, with 2 % providing an HI > 10.0. To provide a more physiologically based estimate of exposure, the HI-GI values should be used, which here showed that 85 % of the soils studied provided an HI < 1.0, 11 % provided an HI between 1.0 and 3.0, and 5 % had an HI > 3.0.

The HI is a relative index, but it can be used to identify populations that potentially are at higher risk and indicates the relative severity of these risks. Thus, these maps highlight the importance of a site-specific approach to define the areas where risks are high related to topsoil ingestion. These results are in agreement with other studies of metal bioaccessibility (Ettler et al. 2012; Juhasz et al. 2011; Karadas and Kara 2011), indicating that a higher risk can be expected in smelter-impacted areas.

Conclusions

The present study integrated oral bioaccessibility to assess a population's exposure to metals in smelter-impacted soils. Using spatial analysis, high-concentration zones of Cd, Pb, and Zn were found at areas

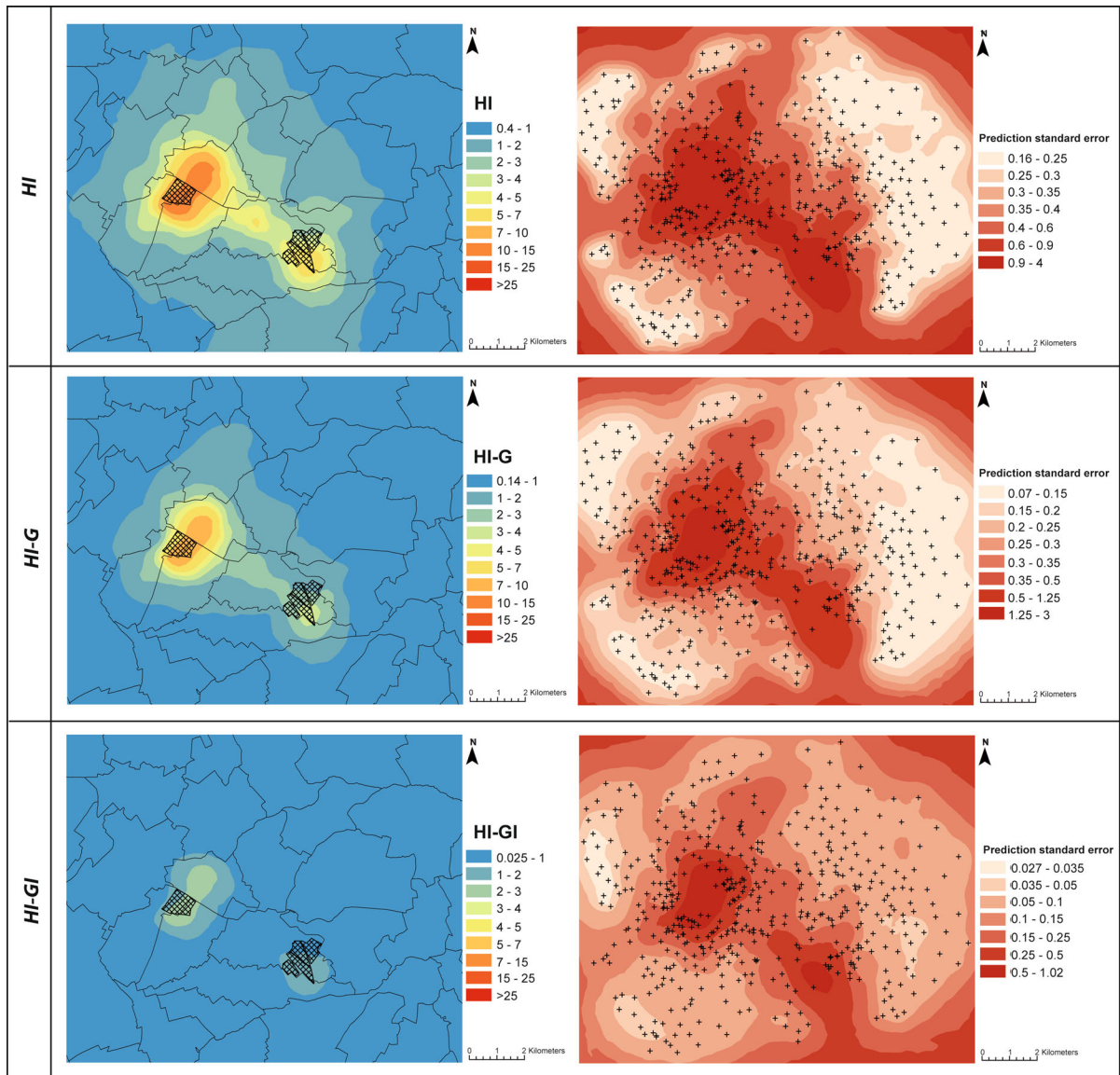


Fig. 4 Prediction maps of HI, HI-G, and HI-GI estimated by ordinary kriging with corresponding prediction standard error maps (the standard error corresponds to the square root of the kriging variance). The location of the smelters is indicated with

dashed lines. Municipality boundaries are shown on the prediction and probability maps (*lines*), while sample location is displayed on prediction error maps (*crosses*)

surrounding both smelters. Pollution indexes showed that the entire area studied was highly polluted in terms of metal concentrations in soils. However, the spatial pattern of human health risk levels did not coincide with the spatial distribution of the degree of soil contamination. Introduction of the BAF of metals from soils into the exposure calculations resulted in a substantial decrease in the calculated risk. For the highly exposed population, 46 % of the soils studied

provided an HI-G > 1.0 and 15 % provided an HI-GI > 1.0, suggesting that adverse health effects in children are probable. These results highlighted the importance of conducting studies taking into account BAF values in risk assessment.

Geostatistical analysis considered all the data without differentiating land use, which made it possible to define the main areas where risks are high related to topsoil ingestion, but introduced a significant

uncertainty into the spatial mapping, particularly as a consequence of the smoothing effect of ordinary kriging. The various land uses should be taken into account in the geostatistical treatment to (1) infer the spatial variability at finer scales and then potentially (2) contribute to the choice of strategies for reducing human exposure to high levels of metals in soils.

Regarding noncancer effects, Pb levels in the soils studied were the main issue of concern. The potential health risk from Cd was lower than the safe level. However, Cd exposure to soil particles cannot be overlooked and its health implications need further investigation. More detailed epidemiological studies should be conducted and other routes of exposure (dust ingestion and inhalation) and potential interactions between metals should also be taken into account.

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