# **Contamination of Urban Soils in an Area of Northern France Polluted by Dust Emissions of Two Smelters**

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Abstract The contamination of 27 urban topsoils has been assessed around two lead and zinc smelters (Metaleurop Nord and Umicore) in the North of France. Eighteen trace elements have been analysed (Ag, As, Bi, Cd, Co, Cr, Cu, Hg, In, Ni, Pb, Sb, Se, Sn, Tl, Th, U and Zn). The investigation included the study of the vertical distribution of Cd, Pb and Zn as indicators of pollution. It was shown that Cd, In, Pb, Sb and Zn were major pollutants followed in lesser quantities by Ag, Bi, Cu and Hg. In addition, As, Ni, Se, Sn and Tl were present at levels slightly higher than regional agricultural values. The other elements (Co, Cr, Th and U) were at endogenous levels. The observations have highlighted the strong heterogeneity of the physico-chemical parameters of urban soils and the existence of heavy contamination of the under layers by Cd, Pb and Zn. A potential transfer of metals from the topsoil to the deeper layers and

H. Ciesielski · N. Proix Laboratoire d'Analyses des Sols, Institut National de la Recherche Agronomique, 273, rue de Cambrai, 62000 Arras, France especially Cd and Zn, is not excluded. Indeed the soil rework is not the only factor explaining contamination level of the deeper layers of the studied soils. The comparison of the studied element concentrations in urban soils with nearby local agricultural values shows that the dust emission originating from the Metaleurop and Umicore smelters were not the only source of contamination. Thus a large contamination of the studied urban soils by Sb and In could be explained by domestic combustion of coal for heating.

$$\label{eq:contamination} \begin{split} & \textbf{Keywords} \ \ Contamination \cdot Smelter \cdot Trace \ elements \cdot \\ & \textbf{Urban soil} \cdot \textit{Vertical distribution} \end{split}$$

# **1** Introduction

Previous works have revealed a metal contamination of agricultural soils in Northern France nearby the zinc and lead smelters of Auby and Noyelles-Godault (Frangi and Richard 1997; Godin et al. 1985; Luttringer and de Cormis 1979). Contamination has been shown to reach levels in agricultural topsoils as high as 1,132 mg kg<sup>-1</sup> of Pb, 21 mg kg<sup>-1</sup> of Cd and 2,167 mg kg<sup>-1</sup> of Zn. Moreover, contamination to a lesser degree has been revealed for Ag, As, Bi, Cu, Hg, In, Sb, Se, Sn and Tl (Sterckeman et al. 2002b). Although for agricultural soils the main contamination is restricted to the ploughed layer, traces of non indigenous metal were also found in some cases at a depth of around 2 m (Sterckeman et al. 2000).

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The zinc smelter, called Umicore and located in Auby, is one of the largest zinc production plants in Europe. Created in 1869, it is now producing about 220,000 t of zinc per year. Until 1975, the smelter was using a pyrometallurgic process which generated significant quantities of dust, contributing to the surrounding soil contamination. After this date, its process changed to become an electrolytic one, reducing considerably atmospheric emissions (DRIRE 2003). Located less than 4 km from Umicore, the Metaleurop Nord smelter in Noyelles-Godault was the only producer of primary lead in France and one of the largest in Europe. After more than a century of pyrometallurgic process generating large quantities of dust, it closed in 2003 owing to economic problems. The dust emission of the two smelters has affected an area of around 120 km<sup>2</sup> where more than 55,000 inhabitants live.

Some studies published recently on urban topsoils in this area have shown concentrations up to 33.5 mg kg<sup>-1</sup> of Cd, 5,280 mg kg<sup>-1</sup> of Pb and 7,570 mg kg<sup>-1</sup> of Zn (Douay et al. 2005; Pruvot et al. 2006). In comparison with local agricultural values cited previously, those values are much higher. Urban soils present peculiar characteristics resulting from a high anthropogenic pressure. They are known to be compacted, to have a low biodiversity, and high concentrations of pollutants. They present an unpredictable layering due especially to the mixing and the incorporation of slag, ashes, waste, building rubble, tar, sludge, coal burning waste, etc. (Chirenje et al. 2002; Kabata Pendias and Pendias 1992; Norra and Stüben 2003; Peltola and Astrom 2003). These various anthropogenic actions induce difficulties for the characterisation of contamination in urban soils (de Kimpe and Morel 2000). Urban soils have been poorly studied and in comparison with agricultural and forestry soils the recognition of the function of urban soils is much more recent (Purves 1967). Only the soils of few cities in the world have been investigated, for example Hong Kong (Chen et al. 1997), Tallinn (Bityukova et al. 2000), Berlin (Birke and Rauch 2000), Stockholm (Linde et al. 2001), Palermo (Manta et al. 2002) and Naples (Imperato et al. 2003). In general the investigations on urban soils are performed on sites suspected to have been impacted by the massive use of leaded paint, car emissions or industrial activities (smelters, cement industries, incinerators, etc).

The aim of this study was (1) to evaluate the degree of contamination of urban topsoils in 18

elements (Ag, As, Bi, Cd, Co, Cr, Cu, Hg, In, Ni, Pb, Sb, Se, Sn, Th, Tl, U and Zn) around Umicore and Metaleurop smelters, (2) to compare the urban topsoil contamination level with regional agricultural values and with local agricultural ones, (3) to seek the specificity of the contamination induced by the two smelters and (4) to examine the degree of Cd, Pb and Zn contamination in deeper layers. In our approach, those three last elements were used as indicators of soil contamination.

# 2 Materials and Methods

### 2.1 Sampling Sites

Twenty-seven sites were chosen between 2003 and 2006, including 15 kitchen gardens and 12 lawns in order to consider various contexts and uses of urban soils. The kitchen gardens have been used to produce food while the lawns are more associated with public or private recreational activities. The sites were chosen in the vicinity of the smelters at less than 2 km away (Fig. 1). From the 27 sampled sites, two groups were formed depending on the contamination source. The first group was composed of seven sites close to Umicore (UM) and the second one of 20 sites close to Metaleurop (ME). The number of sites for each group was related to the extent of the zone affected in the past by the smelter dust emissions.

### 2.2 Soil Sampling

First, both kitchen garden and lawn soils were sampled up to a depth of 25 cm. Depending on the site surface, 5 to 13 elementary samples were taken, homogenized and subsampled to constitute a representative sample. Care was taken to avoid the proximity of pathways, vehicle tracks or roads. For the lawns, roots were gently removed during soil sampling.

Subsequently, soils were described and sampled with a hand auger. Sampling was undertaken at different depths: 30–50, 50–70 (or 70–90), 100–120 and 130–150 cm. Care was taken to avoid contamination between layers. This was done by using hand auger of different diameters to avoid any lateral scrubbing in the drill hole. The sampling and description of soils using a pedological pit was not possible due to the use of the urban soils.



Fig. 1 Map of the studied area

### 2.3 Soil Analysis

The soil samples were dried at room temperature, crushed and sieved to pass through a 2 mm mesh. The element concentrations were quantified by the Laboratory of Soil Analysis of INRA (Arras, France) following protocols detailed in Sterckeman et al. (2002b).

The particle size determination was carried out according to the NF X 31-107 standard, after destruction of organic matter by hydrogen peroxide and the separation of the different classes of particles using sedimentation (particles  $<50 \mu$ m) and sieving (particles  $>50 \mu$ m) (Gee and Bauder 1986). The organic carbon was determined by dry combustion according to the NF ISO 10694 standard. The pH (suspension in water) and the total carbonate concentration (measurement of the CO<sub>2</sub> volume released through reaction with HCl) were measured according to the NF ISO 10390 and NF ISO 10693 standards respectively. The cation exchange capacity (CEC) was

measured after percolation of a 1 mol  $l^{-1}$  ammonium acetate solution at pH 7 (Lefevre 1961) according to the NF X 31-130 standard.

Moreover a representative subsample was then ground and passed through a 0.250 mm sieve for the measure of the studied element concentrations. Ashing at 450°C and a mixture of hydrofluoric (HF) and perchloric (HClO<sub>4</sub>) acids, as described by the NF X 31-147 standard (1996), were used for the total dissolution of Ag, Cd, Co, Cr, Cu, In, Mo, Ni, Pb, Sb, Sn, Th, Tl, U, Zn. Atomic absorption spectrometry with electro-thermal atomisation was used for the determination of Ag. Zinc and high concentrations of Cd and Pb were measured by inductively coupled plasma atomic emission spectrometry (ICPAES). Concentrations of the other elements and low concentrations of Cd and Pb were determined by inductively coupled plasma mass spectrometry (ICPMS).

Arsenic and Se were dissolved using a sulfonitric mixture containing  $V_2O_5$  and their concentrations

were measured by cold vapour atomic absorption spectrometry after hydride generation (HGAAS). Mercury was determined by atomic absorption spectrometry using dry ashing followed by gold amalgamation (CVAAS).

On the deeper layer samples, only the total concentrations of Cd, Pb and Zn were measured.

All precautions were taken with respect to the protocol application and the calibration. Quality control was based on the use of certified samples (BCR 141 and 142; GBW 07401, 07402, 07404, 07405 and 07406), samples from inter-laboratory comparisons, internal control samples and duplicates of the analysis.

# 2.4 Diagnosis of the Contamination

Usually the diagnosis of soil contamination requires knowledge of the pedo-geochemical background concentrations of the studied elements in regional soils. This may be sought either by analysing the corresponding horizons of non-contaminated soils of the same type, or by analysing the deep horizons of surface-contaminated soils (Baize 1994; Burt et al. 2003). The use of this last method is however complex in soils affected by anthropogenic shakeout such as urban soils. Nevertheless, our diagnosis of the contamination integrated those two approaches. For each case, a reflexion was carried out on the soil profile to better evaluate the contamination level of deeper layers.

For urban topsoils, the studied element concentrations were compared with two different reference values: regional and local agricultural values (Sterckeman et al. 2002b). Local values were determined in the area affected by the dust emission of the two smelters. Regional agricultural values are the most frequently observed concentrations in the ploughed layer of agricultural soils, without any major pollution source or industrial and mining activities (Baize 2001).

Moreover to assess the difference between smelter sites for urban topsoil element concentrations, a non-parametric Mann–Whitney U test was used. All analyses were performed with Statistica 6.0 for Windows.

For the profiles of soil, the element concentrations of each layer or horizon were compared with those of the underlying horizon. The pedo-geochemical background concentrations were considered to have been reached when the concentrations no longer decrease to a significant extent or when the value obtained was similar to that of the reference soil.

# **3 Results**

# 3.1 Physico-chemical Characteristics of Urban Topsoils

Texture was mainly loamy but showed a difference in clay concentrations between the soils of the two industrial sites (Table 1). Urban soils around Metaleurop had significantly higher clay concentrations than around Umicore (with a mean of 22.4% for 16.2%, respectively). Although it was not statistically

		$\begin{array}{c} Clay*\\ g \ kg^{-1} \end{array}$	Silt g kg <sup>-1</sup>	Sand g kg <sup><math>-1</math></sup>	Organic carbon g kg <sup><math>-1</math></sup>	$CaCO_3$ g kg <sup>-1</sup>	C/N*	pН	$CEC^*$ $cmol^+ kg^{-1}$
UM (n=7)	Mean	162	522	316	58.2	28	22.8	7.5	12.9
	Median	184	540	270	56.5	13	21.2	7.7	13.8
	Min	81	274	138	13.7	1	14.1	6.8	6.3
	Max	240	683	629	121.2	75	32.7	7.9	16.1
	SD	56	132	157	38.3	29	6.6	0.4	3.3
ME ( <i>n</i> =20)	Mean	224	534	242	56.0	30	17.5	7.4	18.7
	Median	237	537	203	51.0	15	15.1	7.5	19.3
	Min	147	424	130	15.7	1	10.7	6.7	12.2
	Max	288	699	416	123.0	102	31.8	8.2	30.8
	SD	43	82	94	28.8	36	6.0	0.4	4.9

Table 1 Mean, median, minimum, maximum and standard deviation (SD) of physico-chemical parameters of the urban topsoils around Metaleurop (ME) and Umicore (UM) smelters

Asterisks show significant differences amongst smelter sites (p < 0.05). *n* is the number of samples.

significant, the sandy fraction was more important in the soils around Umicore. The CEC was significantly higher in urban soils around Metaleurop. On the opposite, the C/N ratio was significantly higher in urban soils around Umicore than around Metaleurop. On the average, the topsoil pH was around 7.5, and the organic carbon concentration was around 56 g kg<sup>-1</sup>. Soil profiles of four gardens (two around Umicore and two around Metaleurop) showed an external addition of various materials within the 30 to 50 cm layer. One of those gardens situated near Umicore showed the presence of added slag in the underneath layer (30 to 60 cm).

# 3.2 Studied Element Concentrations in Urban Topsoils

As regards major pollutants, the lowest and highest Cd concentrations were measured in the urban soils around Umicore and were 3.1 and 31.4 mg kg<sup>-1</sup> respectively (Table 2). The lowest Pb concentration was measured around Umicore and was 95 mg kg<sup>-1</sup> while the highest concentration reached 3,711 mg kg<sup>-1</sup> around Metaleurop. However, the lowest Zn concentration was measured around Metaleurop (326 mg kg<sup>-1</sup>) and the highest one was measured around Umicore (6,908 mg kg<sup>-1</sup>).

The Mann–Whitney *U* test was used to investigate the difference in topsoil element concentrations between smelter sites. Only Zn and Tl showed significant differences between sites (p<0.05). Zn was more abundant in urban soils around Umicore (3,677 mg kg<sup>-1</sup> on average) compared to Metaleurop (1,341 mg kg<sup>-1</sup> on average). Tl was more abundant around Metaleurop (0.89 mg kg<sup>-1</sup> on average) compared to Umicore (0.61 mg kg<sup>-1</sup> on average).

3.3 Comparison with Regional Agricultural Topsoil Values

The comparison of the element mean concentrations in urban soils with the regional agricultural mean values taken from Sterckeman et al. (2002b) is shown in Fig. 2 using the ratio of the two values.

Around Umicore, Cr, Se and Tl had a ratio of the mean urban soil concentrations over the reference ones of between one and two. Arsenic, Bi, Co, Cu, Ni and Sn had a ratio between 2 and 10 and Cd, Hg, In, Pb, Sb and Zn over 10. The Sb concentration in urban soils was 24-fold higher than in reference soils while Cd and Zn were 30 and 47-fold higher, respectively.

Around Metaleurop, Th and U had a ratio slightly lower than one, Co, Cr and Ni between one and two and As, Bi, Cu, Hg, Se, Sn, Tl between 2 and 10. Six trace elements (Ag, Cd, In, Pb, Sb and Zn) sampled in sites around Metaleurop smelter had a ratio 10-fold higher than in reference soils. In those sites Cd was up to 37-fold higher and Pb 29-fold higher than in agricultural reference soils.

### 3.4 Comparison with Local Agricultural Soil Values

The comparison of the mean level of studied elements in urban topsoils with nearby agricultural soil concentrations is shown in Fig. 3. Only Th and U measured in urban soils close to Metaleurop and Se measured around Umicore are equivalent to the level of their counterpart agricultural soils. Ag, As, Cd, Co, Cr, Hg, Ni, Se and Tl in urban topsoils around Metaleurop and Co, Cr, Ni, Th, Tl and U around Umicore are between one and twofold higher than in agricultural soils of those areas. Ag, Cu, Hg, and Zn in the Umicore area showed a three to fivefold increase in urban soils. Around Metaleurop, Bi, Cu, In, Sn showed an increase of two to threefold. The highest ratios were measured around Umicore with six and sevenfold higher concentrations in urban than in agricultural soils for Pb and Sb respectively. For 13 elements out of 18, the ratios of urban/local agricultural soil concentrations in the area of Umicore were higher than the ones in the area of Metaleurop. The ratios of Ag, Cu, Hg, Pb, Sb, and Zn contents were much higher around Umicore compared to the ones around Metaleurop.

The agricultural soils were tested for differences in element concentrations amongst the sites (Metaleurop or Umicore smelter) with a Mann–Whitney U test. Ag, As, Bi, Co, Hg, In, Pb, Sb, Th and U showed significantly lower concentrations in agricultural soils around Umicore than around Metaleurop (p<0.05). Only Zn had a significantly higher concentration in the agricultural soils around Umicore than the ones around Metaleurop. However, the urban soils showed fewer differences between the smelter sites. Only Tl and Zn showed significantly differences between the smelters (Table 2). However results have to be carefully considered due to the lower number of samples compared to the study of Sterckeman et al. (2002b).

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Site	Reference	Ag	As	Bi	Cd	Co	Cr	Cu	Hg	In	Ni	Рb	Sb	Se	Sn	Th	TI*	U	Zn*
ΝM	04-175	1.32	8.55	2.05	21.50	12.9	53.6	79.0	0.40	0.407	27.2	623.0	9.21	0.27	7.36	7.6	0.56	2.17	2,970.0
ΝN	$04-178^{r}$	4.79	21.00	0.92	21.80	21.4	57.1	230.0	1.74	0.908	38.1	1,670.0	83.40	0.11	13.30	7.9	0.74	2.34	5,610.0
Ν	04-179	1.07	16.40	0.68	10.30	11.5	53.1	57.5	0.38	0.262	24.6	515.0	11.30	0.50	5.57	15.5	0.53	3.24	1,280.0
ΠM	06-1032	0.34	5.80	0.16	3.15	6.7	33.8	19.7	0.12	0.106	17.2	95.1	2.48	0.20	2.56	6.8	0.38	1.56	450.6
Ν	$06-1033^{r}$	0.94	20.26	0.44	22.20	27.8	91.2	149.7	0.54	0.615	67.1	568.2	8.87	1.18	10.49	8.2	0.78	2.46	3,686.4
ΝN	06-1034	2.59	42.55	0.60	21.22	23.7	73.6	181.6	0.40	0.448	61.3	2,867.3	18.78	0.70	10.31	8.9	0.70	2.55	6,908.2
ΝN	06-1092	1.07	18.51	0.36	31.43	10.3	47.3	63.8	0.48	0.516	24.0	824.0	11.90	0.54	11.90	7.0	0.56	1.60	4,832.1
ΝN	Mean	1.73	19.0	0.75	18.80	16.3	58.5	111.6	0.58	0.466	37.1	1,023.2	20.85	0.50	8.78	8.9	0.61	2.28	3,676.8
ΠM	Median	1.07	18.5	0.60	21.50	12.9	53.6	79.0	0.40	0.448	27.2	623.0	11.30	0.50	10.31	7.9	0.56	2.34	3,686.4
ΠM	Minimum	0.34	5.8	0.16	3.15	6.7	33.8	19.7	0.12	0.106	17.2	95.1	2.48	0.11	2.56	6.8	0.38	1.56	450.6
ΝN	Maximum	4.79	42.6	2.05	31.43	27.8	91.2	230.0	1.74	0.908	67.1	2,867.3	83.40	1.18	13.30	15.5	0.78	3.24	6,908.2
ΝN	SD	1.51	11.9	0.62	9.23	7.9	18.7	76.5	0.53	0.257	19.6	943.9	28.00	0.37	3.80	3.0	0.14	0.58	2,315.4
ME	03-159	1.87	44.20	1.89	29.90	14.4	64.3	78.4	1.14	1.200	37.7	1,830.2	175.00	1.09	15.70	8.6	1.17	2.55	1,050.0
ME	03-161	7.83	65.13	2.70	30.21	9.1	70.1	189.0	0.95	1.250	39.6	3,710.6	80.40	0.05	18.60	8.1	1.15	2.37	5,830.0
ME	03-163	0.78	17.90	0.85	11.50	10.2	63.0	38.3	0.53	0.492	24.7	816.0	11.80	0.75	4.55	8.7	0.84	2.15	825.0
ME	03-164	2.05	30.21	2.07	27.32	13.1	58.1	113.0	1.15	1.540	43.7	1,812.6	21.20	1.93	12.60	8.5	1.13	2.97	1,990.0
ME	03-165	2.08	54.37	1.52	30.40	12.7	51.8	90.8	1.29	1.040	67.7	1,954.6	31.90	2.00	13.10	7.9	1.33	2.98	2,260.0
ME	04-170	0.46	13.20	0.60	7.31	10.2	68.1	37.1	0.29	0.443	22.6	475.0	6.59	0.40	3.91	7.5	0.62	1.77	568.0
ME	04-171	0.79	25.24	1.00	15.29	11.6	62.3	52.8	0.47	0.439	31.1	893.4	15.80	1.20	7.63	8.7	0.80	2.67	765.0
ME	04-172	1.09	15.42	1.56	15.11	13.4	65.1	89.8	0.50	0.626	31.7	918.3	12.40	0.56	6.37	8.3	0.83	2.46	931.0
ME	04-173	1.09	51.93	1.67	16.73	20.1	77.3	90.4	0.56	0.595	50.6	1,032.5	15.90	0.05	8.71	10.1	1.01	3.69	1,030.0
ME	04-174	1.79	15.10	1.75	22.10	11.7	54.9	73.3	1.35	1.110	34.8	1,460.0	22.90	0.54	10.40	8.0	1.10	2.48	1,540.0
ME	04-176	0.35	12.60	0.59	4.29	11.9	54.6	32.9	0.17	0.139	29.1	297.0	4.30	0.57	3.86	9.1	0.59	2.10	526.0
ME	04-177	1.16	4.40	0.75	8.81	13.1	46.7	76.3	0.41	0.349	34.0	956.0	8.85	0.64	6.82	6.2	0.56	1.80	1,530.0
ME	06-1026	1.01	44.39	1.71	10.41	19.8	78.4	93.3	0.50	0.499	50.0	694.9	15.31	0.61	15.10	10.1	0.89	2.66	1,183.7
ME	06-1027	0.50	19.86	0.91	5.01	14.9	60.1	50.6	0.31	0.253	37.7	313.6	7.30	0.73	10.79	9.3	0.75	2.13	524.4
ME	$06-1028^{r}$	0.40	12.30	0.32	3.32	9.6	47.3	26.1	0.16	0.297	22.4	217.5	5.06	0.42	4.34	9.4	0.54	2.09	395.3
ME	06-1029 <sup>r</sup>	0.74	13.66	0.58	8.61	10.9	51.8	30.4	0.37	0.525	28.7	456.9	5.89	0.86	4.66	7.7	0.70	1.71	587.3
ME	06-1030	1.97	24.20	1.08	16.68	15.0	62.6	95.6	0.83	1.164	38.4	1,462.4	90.22	0.81	16.89	7.1	0.89	1.84	2,193.6
ME	06-1031	0.96	13.24	0.98	13.76	10.1	46.9	50.7	0.64	0.890	33.5	778.2	10.68	0.94	7.55	6.7	0.83	1.58	960.0
ME	06-1035	2.42	29.26	4.78	26.80	16.2	67.1	100.0	1.15	1.540	42.3	2,043.1	26.18	1.39	12.83	8.7	1.66	2.31	1,796.7
ME	06-1093	0.40	9.36	0.36	3.99	9.3	59.7	26.0	0.15	0.21	20.3	239.3	2.16	0.33	2.79	6.2	0.51	1.34	325.9
ME	Mean	1.49	25.8	1.38	15.38	12.9	60.5	71.7	0.65	0.730	36.0	1,118.1	28.49	0.79	9.36	8.2	0.89	2.28	1,340.6
ME	Median	1.05	18.9	1.04	14.43	12.3	61.2	74.8	0.52	0.560	34.4	905.9	13.85	0.68	8.17	8.4	0.84	2.23	995.0
ME	Minimum	0.35	4.4	0.32	3.32	9.1	46.7	26.0	0.15	0.139	20.3	217.5	2.16	0.05	2.79	6.2	0.51	1.34	325.9
ME	Maximum	7.83	65.1	4.78	30.40	20.1	78.4	189.0	1.35	1.540	67.7	3,710.6	175.00	2.00	18.60	10.1	1.66	3.69	5,830.0
ME	SD	1.63	17.2	1.02	9.40	3.2	9.2	39.3	0.40	0.447	11.3	851.2	41.72	0.52	4.87	1.1	0.30	0.56	1,213.2
Total (	soncentrations	are expi	essed in 1	ng kg <sup>-1</sup>	of soil dr	v weight	t. Asteris	ks indica	e signifi	icant diffe	erences b	etween sm	elters. <sup>r</sup> in	the refer	ence colu	mn indi	cates a re	worked	soil.

Table 2 Studied elements in the urban topsoils sampled around Metaleurop (ME) or Umicore (UM)

Fig. 2 Ratio of the mean studied element levels in urban topsoils over regional agricultural values (Sterckeman et al. 2002b) for the sites around Umicore and Metaleurop smelters



3.5 Influence of the Distance to the Smelters

Sterckeman et al. (2002b) and Douay et al. (2006) showed a non-linear relationship between Pb concentrations in agricultural topsoils and the distance to Metaleurop. The same relationship (power model) performed with urban soils did not give significant results (Fig. 4). There was a very poor determination coefficient ( $r^2=0.2$ ), indicating no clear decrease of the contamination with the distance from the smelter. Similarly there was a poor relationship between Pb contents in urban soils around Umicore and the distance from the smelter ( $r^2=0.3$ ).

The data obtained on the urban soils showed that, as for the agricultural ones, the Pb and Zn concentrations were not correlated to those of Co, Cr, Ni, Sb, Se, Th and U (Table 3). However, for the urban soils around Metaleurop, there were some correlations between the Cd, Pb and Zn and Ag, As, Cu and Sn. In addition, there was a correlation between Pb and Bi, Hg, In and Tl.

For the urban soils around Umicore, there were some correlations between the Pb and Zn concentrations and As. Moreover, there were correlations between Zn and Cd, Cu, and Sn. With regard to the agricultural soils around Umicore, some correlations have been previously observed between Zn concentrations and Ag, Cd, Cu, Hg, In and Pb.

3.6 Deeper Layer Contamination in Cadmium, Lead and Zinc

The soil profile descriptions demonstrated a high anthropogenic action on the soils. This was confirmed by the thicker organo-mineral layer than usually observed in the agricultural soils of the area. Moreover, added material like slag, bricks or pebbles of various origins were frequently observed. In these urban gardens the organization of the upper layers does not always conform to the regional soil development. In addition, unlike agricultural soils, the transition between the organo-mineral layer and the underneath one was often more gradual. The median Cd, Pb and Zn concentrations of the regional pedo-geochemical background (without distinction of the kind of parental materials) were equal to 0.11, 15.7 and 46.5 mg kg<sup>-1</sup>, respectively (Sterckeman et al. 2002a).

Four urban soil profiles showed particularly high concentrations of Cd, particularly between 70 and 90 cm depth (Table 4). This remark concerns the sample references 04-179, 04-178, 06-1032 and 06-1033 with concentrations of 4.1, 9.5, 4.8 and 2 mg kg<sup>-1</sup>,







Fig. 4 Relationships between Pb soil concentrations and distance to Metaleurop for agricultural soils (Sterckeman et al. 2002b) and for urban soils. Note that scales for Pb concentration in soils are different and that distance to the smelter is expressed in meter

respectively. For the other profiles, except 06-1027, the enrichment in Cd at this same depth was between 2 to 11-fold the background value. For at least five profiles, concentrations between 130–

150 cm did not reach the Cd background value. It should be noticed that the highest Cd concentrations measured in deep layers were from the Umicore area.

	Soils aro	und the Umic	ore smel	ter			Soils arou	nd the Metal	europ sn	nelter		
	Correlati	ons with Pb c	ontent	Correlati	ons with Zn	content	Correlatio	ns with Pb c	ontent	Correlatio	ns with Zn o	content
у	a	b	$r^2$	a	b	$r^2$	a	b	$r^2$	a	b	$r^2$
Ag	nc	nc	nc	nc	nc	nc	0.002	-0.5	0.86	0.001	-0.271	0.95
As	0.012	7.14	0.85	0.004	3.51	0.67	0.015	9.42	0.52	0.009	13.3	0.43
Bi	nc	nc	nc	nc	nc	nc	0.001	0.43	0.51	nc	nc	nc
Cd	nc	nc	nc	0.003	7.69	0.576	0.01	4.35	0.80	0.005	8.41	0.45
Со	nc	nc	nc	nc	nc	nc	nc <sup>a</sup>	nc	nc	nc	nc	nc
Cr	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
Cu	nc	nc	nc	0.026	14.49	0.64	0.042	25.08	0.82	0.029	32.47	0.82
Hg	nc	nc	nc	nc	nc	nc	0.0004	0.24	0.60	nc	nc	nc
In	nc	nc	nc	nc	nc	nc	0.0004	0.26	0.66	nc	nc	nc
Ni	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
Pb	-	_	-	0.356	-287.87	0.77	-	-	-	0.646	252.47	0.85
Sb	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
Se	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
Sn	nc	nc	nc	0.001	3.52	0.76	0.004	4.38	0.61	0.003	5.52	0.51
Zn	2.145	1,481.22	0.77	-	-	-	1.312	-126.03	0.85	-	-	-
Th	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
Tl	nc	nc	nc	nc	nc	nc	0.0003	0.6	0.57	nc	nc	nc
U	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc

**Table 3** Parameters for linear correlations (y=ax+b) between the total lead or zinc concentrations (x) and the total concentrations of the other elements in the urban topsoils around the two smelters;  $r^2$ : the determination coefficients

<sup>a</sup> Non correlated

All given correlations are statistically significant (p < 0.05).

Table	4 Vertical	distrib	ution of	total Cd	, Pb and	Zn concen	ntrations in	the urb	an soils	around 1	Metaleur	op and Um	iicore smel	ters					
		Cd						Pb						Zn					
		0-25	30-50	50-70	70-90	100-120	130-150	0-25	30-50	50-70	06-02	100-120	130-150	0-25	30-50	50-70	70-90	100-120	130-150
ΝM	04-175	21.5	3.8	1.1	0.3			623	41	21	16			2,970	706	230	77		
ΝM	04-179	10.3	21.0		4.1			515	970		67			1,280	2,640		1,180		
ΠM	04-178	21.8	72.8		9.5	3.5	2.4	1,670	5,258		142	69	47	5,610	14,559		2,335	946	473
ME	03-164	27.3	4.1	1.4	0.6	0.2		1,813	245	71	26	18		1,990	364	134	93	60	
ME	03-163	11.5	0.6		0.4			816	31		27			825	87		74		
ME	04-170	7.3	5.2		0.3			475	331		27			568	440		60		
ME	04-176	4.3	3.9		0.3			297	144		21			526	409		58		
ME	04-171	15.3	1.5		0.5			893	51		21			765	178		88		
ME	03-165	30.4	0.6	0.6	1.0			1,955	34	29	75			2,260	101	102	186		
ME	04-177	8.8	4.6	1.3	0.4			956	986	358	41			1,530	1,270	416	85		
ME	03-159	29.9	0.5		0.6			1,830	31		27			1,050	73		58		
ME	03-161	30.2	0.4		0.2			3,711	36		24			5,830	89		66		
ME	04-172	15.1	12.4		0.5			918	760		17			931	886		68		
ME	04-174	22.1	0.8	0.2	0.2			1,460	49	23	23			1,540	106	64	99		
ME	04-173	16.7	5.8		0.3			1,033	354		18			1,030	627		71		
ΠM	06-1032	3.2	13.0		4.8		0.5	95	929		45		24	451	2,330		1,210		104
ΠM	06-1033	22.2	13.5		2.0		0.2	568	770		21		10	3,686	2,500		564		59
ΠM	06-1034	21.2	10.2		1.0	0.2		2,867	1,090		34	21		6,908	2,640		171	69	
ΠM	06-1092	31.4	14.8		1.1		0.3	824	54		17		19	4,832	2,300		319		65
ME	06-1035	26.8	1.8		0.4		0.2	2,043	88		30		19	1,797	225		90		50
ME	06-1026	10.4	1.7		0.3			695	143		19			1,184	315		58		
ME	06-1027	5.0	1.0		0.1	0.1	0.1	314	63		17	20	19	524	175		53	58	51
ME	06-1028	3.3	3.9		0.2		0.1	218	216		22		19	395	291		49		51
ME	06-1031	13.8	0.9		0.5			778	45		19			960	95		53		
MOE	06-1093	4.0	6.7		0.6		0.1	239	391		37		16	326	543		79		42
ME	06-1029	8.6	5.4					457	277					587	425				
ME	06-1030	16.7	4.5		0.6		0.1	1,462	271		35		24	2,194	564		106		65
The co	ncentratior	1s are a	given in	mg kg <sup>-1</sup>	and the	depths in	cm.												

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Concerning Pb, the concentrations in the 70–90 cm layers were equal or below two times the background value in more than 50% of the cases. The enrichment did not exceed fourfold the background value, except the profile 04-178 which showed, as for Cd, a ninefold higher Pb concentration.

The distribution of Zn with soil depth was similar to that of Cd. Five soil profiles were differentiated by high Zn concentrations in the 70–90 cm layer (04-179, 04-178, 06-1032, 06-1033 and 06-1092). The profile 04-178, between 130 and 150 cm depth, exhibited Zn concentrations nearly 10-fold higher than background values.

# **4** Discussion

# 4.1 Physico-chemical Characteristics of Urban Soils

The difference of soil clay concentrations between the two sites is explained by the origin of the parent materials. The soils around Metaleurop are developed on loessic materials while the ones around Umicore originate from alluvial deposits, which are characterised by a large textural variability in this area. This results in a difference in the CEC values between the two smelter sites.

Two hypotheses can be given to explain the C/N difference measured in soils amongst the two smelter sites. The slow down of the organic matter degradation in soils around Umicore can be induced by the higher contamination levels and/or by the more frequent waterlogging in this area. It was shown that high concentrations of Cd, Pb and Zn around the two smelters strongly affected the ecosystem functioning by reducing the biodiversity and especially the terrestrial macroinvertebrates (Grelle et al. 2000; Nahmani and Rossi 2003) and thus disturbing the carbon cycle. Waterlogging of the soils around Umicore is related to an alluvial characteristic and to the presence of the ground water rising at the soil surface during the wet season and especially in winter.

Observations showed that the studied urban soils were affected by important anthropogenic reworking (sometimes at more than 1.5 m depth). This results in a high material heterogeneity with sometimes the presence of gravels, slag, pieces of bricks, etc. and a high physico-chemical parameter variation. In kitchen gardens, local contaminated composts might have been added to improve soil fertility. The original soils were buried under added materials. This type of soil reworking is not specific to the studied area, and it is a major characteristic of the urban soils (Fetzer et al. 1998; Norra and Stüben 2003).

# 4.2 Comparison with Regional Agricultural Values

Urban soils showed much higher elemental concentrations than regional agricultural soils (Sterckeman et al. 2002b). The ratio shown in Fig. 2 revealed that Cd, In, Pb, Sb and Zn can be considered as major pollutants (ratio higher than 15) while for agricultural soils, only Cd, Pb and Zn are considered as major pollutants. Other elements such as Ag, Bi, Cu, Hg are present at high concentrations (ratio between 5 and 15). Arsenic, Co, Cr, Ni, Sn, Th, Tl and U are present at a moderate concentration (ratio below 5). Similarly Se is present in moderate concentration but this element is a particulate case. Although Se was present in the atmospheric emissions of Metaleurop, Sterckeman et al. (2002b) have shown the absence of a simple relation between Se concentrations in agricultural topsoil and the distance from the source. These authors explain this finding by the volatile properties of Se. This element encounters in the soil some rapid physico-chemical transformations under the effect of oxido-reduction and biological activity.

The high Sb and In contamination of urban soils could originate from the domestic burning of coal, either by dust fallout or by addition of coal ash residues (Zeng et al. 2001). Indeed the coal has been used for long time as domestic heating source, especially in this former mining area where those two smelters are located.

#### 4.3 Comparison with Local Agricultural Values

The comparison of elemental concentrations in urban soils with contaminated agricultural ones revealed a higher contamination of urban topsoils (Fig. 3). Different points draw attention to this finding. Firstly, the "urban/local agricultural values" ratio is always higher than one and can reach sevenfold for Sb, showing an increase of all elements in urban soils compare to their agricultural counterparts (Sterckeman et al. 2002b). Secondly, there is no relationship between the distance from the Metaleurop smelter and the urban soil Pb concentrations while a non-linear relationship has been previously shown in the case of agricultural soils (Douay et al. 2006; Sterckeman et al. 2002b). Thirdly, there were fewer linear correlations between the concentrations in the urban topsoils than in the agricultural ones (see Table 3 of this paper and Table 1 of Sterckeman et al. 2002b). Fourthly, although Ag, As, Bi, Co, Hg, In, Pb, Sb, Th and U showed significantly different concentrations amongst the smelter sites in agricultural soils, only Tl and Zn were significantly different amongst the sites in urban soils. This last point shows that the urban activities have flattened the contamination pattern of the smelters. Those points call attention to the effects of anthropogenic actions on the urban soils, which is adding up contamination over the industrial ones.

Previous authors have reported similar findings, showing often higher contamination of urban soils (kitchen gardens, lawns, public gardens) than those of the neighbouring agricultural soils (Chen et al. 1997; Paterson et al. 1996). This specific enrichment is often combined with a high heterogeneity and variability of the physico-chemical parameters of the urban soils (Chirenje et al. 2002; de Kimpe and Morel 2000). In this study, a particularly high spatial variability in concentrations was observed. Urban soils are known to present an extremely high spatial variability due to the diversity of land use. As described by Zhai et al. (2003) not only are the concentrations of Sc, Cr, Co, Ni, Cu, Zn and Pb higher in the urban soils of Gaborone city (Botswana) compared to their rural counterparts, they also display a larger range, and have a larger standard deviation. They defined this phenomenon as characteristic of dotshaped contamination in soils. In fact, land use that may disturb contaminant concentrations include lawn mowing and maintenance, gardening, leisure activities, vehicular traffic, addition of coal burning waste or slag to improve soil texture and many other activities. The introduction of such materials is increasing pollutants over the global industrial contamination which mainly results from dust fallout. In addition, Machemer and Hosick (2004) cited the sizes, shapes, positions, densities and orientations of buildings and other structures which may significantly affect locally airborne contaminant distribution and thus enhance dotshaped contamination. Corrosion of zinc roofs can also lead to an increase in the concentrations of Zn and to a lesser extent of Cd in surface waters (Gromaire et al. 2002), and by extension in soils.

On the top of this, the contamination level of urban soils is highly affected by activities and residues of nearby industries. Zhai et al. (2003) revealed that urban soils of a residential area were more Cr, Co, Ni, Cu, and Zn contaminated than the soils in the city centre, although the population density was higher than in the residential area. The pollution of these elements in residential soils originated mainly from residential waste, especially liquid waste due to the presence in the neighbourhood of two abandoned sewage works. This point towards that the presence of pollutants is more related to the occurrence of industry providing waste material to the neighbourhood than to density of population. In a similar way, the common use of sludge waste originating from a zinc smelter as "herbicide" in kitchen gardens has been mentioned in Northern France (Cambier 2001). Moreover the slag from the smelters was used in the past by gardeners to improve soil permeability, and to stabilise pathways. All those urban management practices were probably one of the causes of the high metal concentrations in some soils and this was emphasized by the lack of a relationship between concentrations and distance from the smelters.

Moreover it was shown by Wagner et al. (2003) that the use of lead arsenate insecticide could lead to a soil enrichment of As and as well of Sb. It was known that, in the past, some local gardeners used to get lead arsenate from Metaleurop to limit the development of Colorado beetles on potatoes.

With regard to urban soil contamination of the studied areas, little significant difference has been shown between smelter sites and land uses. However, a difference has been proven for agricultural soils according to the sites with higher Cd/Pb and Zn/Pb ratio for field topsoils near Umicore than the ones near the Metaleurop smelter (Sterckeman et al. 2002b). These differences were explained by the different kind of ores used in the zinc and the lead smelters. This relationship was however not shown with the urban soils but a higher number of samples would be necessary to confirm this finding due to the high variability observed.

4.4 Deeper Layer Contamination Level in Cadmium, Lead and Zinc

The observations showed frequent Cd, Pb and Zn contamination of the urban soil deeper layers,

contrary to their agricultural counterpart. In the latter it was shown a contamination limited to the ploughed layer, i.e. up to 30 cm (Sterckeman et al. 2002b). The enrichment factor of the deeper layers compared to the pedo-geochemical background concentrations suggests that the anthropogenic reworking of the soil is not the only reason for the metal distribution with depth. A Cd and Zn transfer to the deeper layer is suspected, these elements being more mobile than Pb.

These transfers could be favoured by the redox potential fluctuation related to the temporal waterlogging of the soils. In addition a locally lower pH due to a less regular calcareous amendment compared to the agricultural soils could have favoured downward element migration.

Nevertheless, from this high Cd, Pb and Zn contamination of the urban soils there is not only sanitary risk for the inhabitants (Pruvot et al. 2006) but a risk for ground water contamination.

### **5** Conclusion

The urban topsoils around Metaleurop and Umicore smelters are known to be strongly contaminated by Cd, Pb and Zn, and this at a level largely over the agricultural topsoils situated in the same area. This contamination is explained by the atmospheric fallout discharged by the smelters and the various anthropogenic activities: traffic, addition of contaminated materials (slag, pesticides). The introduction of external materials and the anthropogenic reworking have led to a high variability of the urban soil physico-chemical parameters of this area. This results in a large spatial heterogeneity that makes more complex the study of the soils and the spatial distribution of the elements. This would necessitate a more detailed soil sampling strategy that would integrate the various contamination pathways of the soil (distance from the smelters, soil uses, concerned surface, history of the zone, etc.). Considering the complexity of such area, a large number of soil samples would be necessary to evaluate the contamination level of the urban soils.

The study revealed Sb and In contamination of urban topsoils to such an extent that they were considered as major pollutants, which was not the case in agricultural soils of this area. The source of those pollutants could be, in addition to the two smelter emissions, the fallout and the addition to the soil of the ash originating from the domestic combustion of coal.

To those five major contaminants (Cd, In, Pb, Sb and Zn), Ag, Bi, Cu, Hg have to be mentioned as being present at high levels. In addition, As, Ni, Se, Sn and Tl were slightly higher than regional agricultural values. Cobalt, Cr, Th and U were at concentrations close to regional agricultural values and were thus considered to be endogenous.

Investigations showed that soil reworking could have affected the deeper layers (even below 1.5 m depth). Its modification could go along with a high Cd, Pb and Zn contamination, considered in this study as pollution indicators. A transfer of the most mobile elements (Cd and Zn) to the deeper layers is suspected and suggests that it could be accompanied by other pollutants.

The high contamination of the urban soils around the Metaleurop and the Umicore smelters is raising questions owing to its multi-element pollution, its heterogeneity and its potential risk of transfer to the deeper layers and to the food chain. Nowadays, the consideration of those urban living areas in the environmental and sanitary risk assessments is lacking due to soil complexities, their use and their contamination.

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### Appendix

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