ASSESSMENT OF A SMELTER IMPACT AREA USING SURFACE SOILS AND PLANTS

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Abstract. The concentrations of 37 trace elements (Ag, Ba, Be, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Ga, Gd, Ge, La, Li, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr, Tb, Th, Tl, U, V, W, Y, Yb, Zn and Zr) were determined by ICP-MS in surface soils and plants (*Sida rhombifolia*) sampled around a lead smelter in Lastenia, Province of Tucuman, NW Argentina. Soil and plant patterns of Pb, Cd, Ag, Zn and Cu demonstrate the effects of pollutant dispersion plumes following the prevalent wind directions. The high element concentrations observed, especially Pb ($>$ 5,000 mg/kg), could cause serious environmental problems in areas of close proximity to the smelter. Consequently, measures to assess potential consequences for the local population should be considered to determine if measures to protect the environment are necessary.

Key words: Argentina, contamination, lead, plant, smelter, soil, trace element

1. Introduction

Heavy metals are naturally occurring elements that are dispersed in the environment by natural processes such as weathering of the earth's surface, volcanic activity and forest fires. Man has also used some of them for thousands of years, but especially since the industrial revolution. Some elements like Pb, Zn, Cu or Cd, resulting from various industrial processes and domestic uses, can accumulate in dust, soil and water (AIHW, 1996). Due to the potential health risks such elements pose to humans, considerable interest and concern has focused on the impact of trace elements associated with smelter activities upon residential and agricultural soils. High levels of trace elements, such as Pb, Zn, Cu, or Cd are usually found in soils in the vicinity of smelters (Thornton *et al.*, 1980; Kabata-Pendias and Pendias, 1989; Angeloni and Bini, 1992; Gzyl, 1995; Rieuwerts and Farago, 1996; Verner *et al.*, 1996).

A significant proportion of these trace elements can be passed on to humans, with varying effects on human health. Lead, for example, is poisonous and cumulative in all forms. Lead ingestion by way of its inorganic or organic compounds may lead to many and severe toxic effects (Needleman *et al.*, 1990; Steenland

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et al., 1992). Although acute exposure to Cd can produce adverse health effects (Nogawa *et al.*, 1986; USEPA, 1989), no indication of these effects has been found in some places with high Cd levels (Morgan, 1988; Chaney, 1997). Although Zn and Cu are less toxic trace elements, especially Zn, they may lead to diarrhoea, nausea, vomiting and lesions in the gastrointestinal tract when found in significant quantities (Carlson *et al.*, 1987). As a consequence, it is important to determine the extent of the contaminated area and the concentration of these elements that might be potential hazards.

In this setting, surface soils and widespread plants have been used to establish the extent of the contaminated area around the lead smelter in Lastenia (Province of Tucuman, northwest Argentina), as well as to assess the current level of metal contamination.

2. Study area

The smelter lies in a flat residential area (430 m a.s.l.) in Lastenia, Province of Tucuman, northwest Argentina (Figure 1). The area is characterised by a mild and humid climate (19.2°C and 932 mm average temperature and rainfall, respectively). The summer is hot and humid (25.3°C and 179 mm in January) and the winter is mild and dry (11.9°C and 8 mm in July). This climate is classified as *Cwa* according to the Koppen classification. The prevalent winds in the area are N–S, and SW–NE (Figure 2), fluctuating from W–E to S–N (SMN, 1992).

The study area is rectangular in shape, 3.5 km in a N–S direction and 2.4 km in a W–E direction, and is mainly characterised by residential and industrial zones.

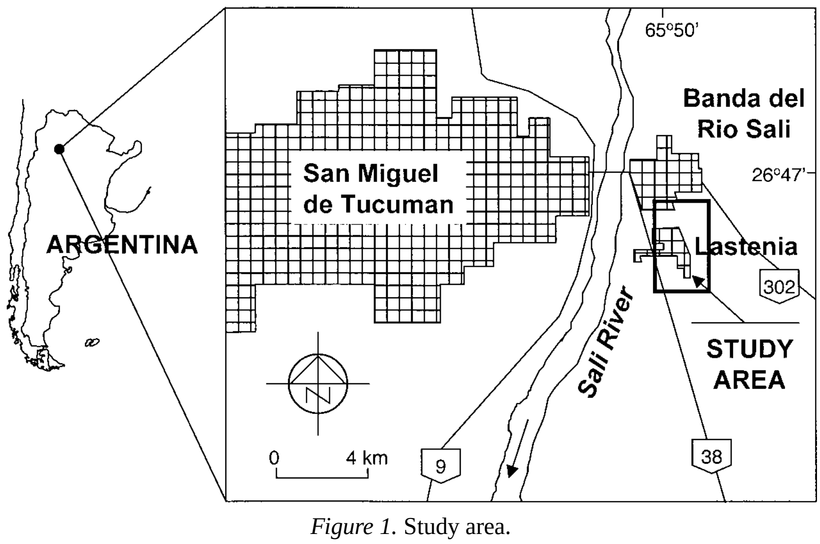

Figure 1. Study area.

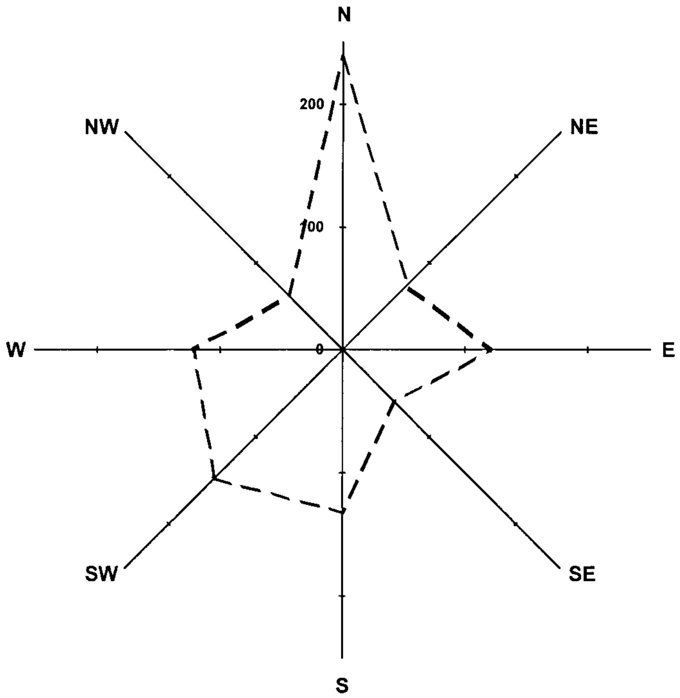

Figure 2. Frequencies ($^{o}/_{oo}$) of prevalent wind directions in the study area (after SMN, 1992). Time frequency in periods of 30 min.

In addition, there are sugar cane crops on the east side. The main industry in the area is a large sugar refinery. The smelter is in the centre of the study area and was in operation for more than 24 years, until the mid-nineties. It had a stack height of 45 m.

The soil is an argustoll (USDA, 1967). The parent materials are mainly loessic and alluvial sediments. The soil has a mollic epipedon of 25–65 cm in average thickness. It changes colour with depth. It is dark brown (10YR2/2) in the surface and dark grey-brown (10YR3/3-3/2) at the bottom. It has a moderately fine granular structure. The B-horizon has an average thickness of 85 cm varying between 45 and 140 cm. The argillic horizon has a strong, medium-coarse, angular blocky structure. The C-horizon consists of a brownish yellow argillaceous material, with very fine subangular blocky structures. The $CaCO_3$ content of this horizon is 0.6–5.0% (Zuccardi and Fadda, 1972).

The original vegetation in the zone was representative of a transitional forest region between the phytogeographic regions of the Yungas mountain rainforest in the west, and the dryer Chaco in the east (Cabrera, 1971). The typical tree species were *Tipuana tipu* (Fabaceae), *Enterolobium contortisiliquum* (Fabaceae), *Prosopis* spp. (Fabaceae), *Geofroea decorticans* (Fabaceae) and *Fagara coco* (Rutaceae). The common names of these species are tipa, pacar, algarrobo, chañar and cochucho, respectively. At present, these species are scattered throughout the study area due to agricultural and urban settlements. Tree species coexist with different shrub and grass species. *Sida rhombifolia* (Malvaceae), commonly known as afata, is one of the most common shrub species in the area. The agricultural activity is centred on sugar cane crops (*Saccharum officinale*, Poaceae) and, to a lesser extent, lemon crops (*Citrus* sp., Rutaceae). Allotments are also frequently found in the urban area. The most common allotment crops are lettuce (*Lactuca sativa*, Asteraceae), tomato (*Lycopersicon esculentum*, Solanaceae), parsley (*Petroselium crispum*, Apiaceae) and carrot (*Daucus carota*, Apiaceae).

3. Materials and methods

One hundred and twenty one soil samples were collected from the upper 5 cm of the soil profile round the smelter (Figure 3). The sampling was concentrated in the urban area closest to the factory. Samples were oven dried at 40°C for four days in the laboratory. The fraction obtained by sieving to less than 200 μm was used for the trace element analysis.

A sample of the shrub *S. rhombifolia* was also collected of the sampling sites shown in Figure 3. One hundred and twelve plant samples were collected. Although the shrub was widely distributed in the area studied, *S. rhombifolia* was absent in nine sampling points. At least 200 g of twigs were collected from each plant using stainless steel garden clippers or by hand, washed with deionised water, and oven dried at 40°C for four days. The stem and leaf portions of dried plants were cut in small pieces by hand, and ashed in a muffle furnace at 450°C for 48 h. The ash content ranged between 7 and 23% by weight, with a mean of 12%. Ashing helps to homogenise the plant samples, and to increase the limits of detection and precision by preconcentration (Hall *et al.*, 1990). The disadvantages are related to the potential volatility of some trace elements.

Trace element concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS). A split (0.1 g) of soils and ashed plants was digested with $HF+HClO_4+HNO_3$ (5.0 + 2.5 + 2.5, v/v), evaporated twice to incipient dryness with the addition of HNO_3, and finally made up to 100 ml with 1% (v/v) HNO_3. Thirty seven trace elements (Ag, Ba, Be, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Ga, Gd, Ge, La, Li, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr, Tb, Th, Tl, U, V, W, Y, Yb, Zn and Zr) were simultaneously determined by ICP-MS using a PlasmaQuad 2+ instrument (VG Elemental Ltd., Thermo Group,, Manchester, UK). Sample input was via conventional nebulization (V-groove nebuliser) using a Gilson Minipuls2 peristaltic pump and a Gilson Autosampler (Gilson Medical Electronics, WI, USA) in order to ensure the controlled uptake of solution. The operating conditions were: RF power, 1350 W; plasma argon flow rate, 14.0 l min^{-1}; auxiliary argon flow rate, 2.0 l min^{-1}; nebuliser argon flow rate, 0.95 l min^{-1}; solution uptake rate, 1.0 ml min^{-1}. The acquisition time was 60 s per sample.

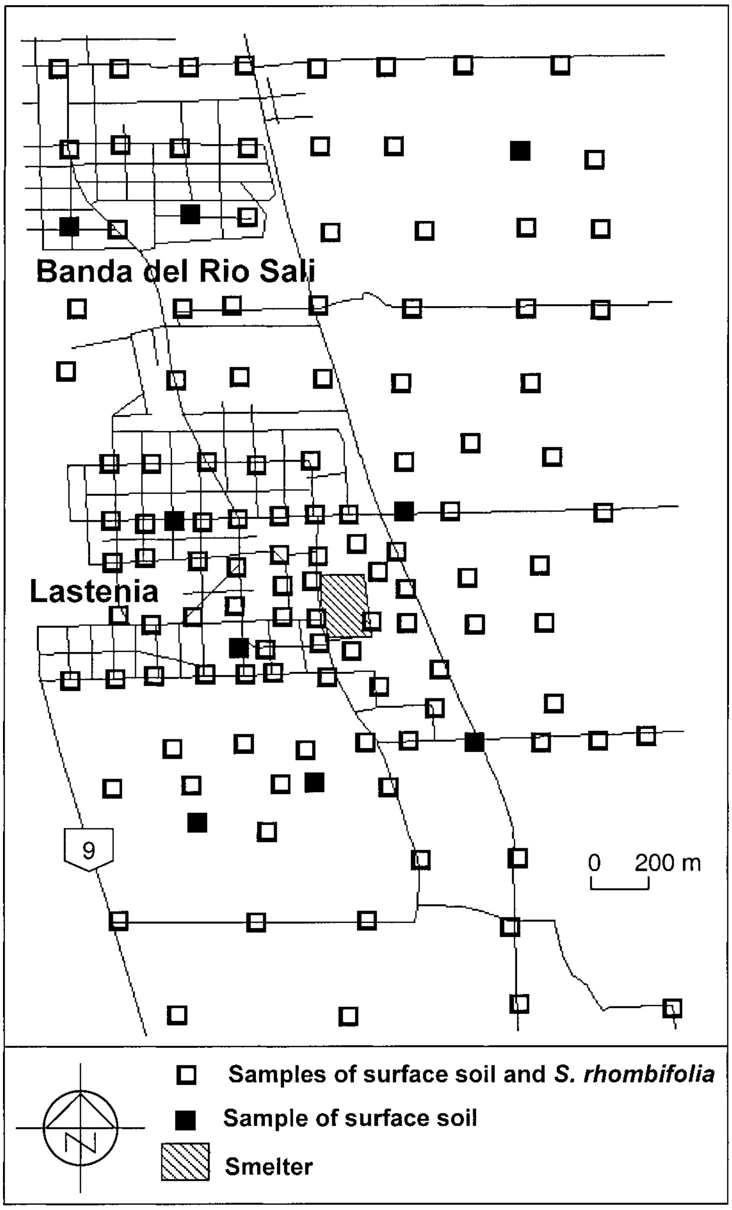

Figure 3. Distribution of sampling points.

All chemicals used were of analytical-reagent grade; purified water of 18.2 MO cm^{-1} MilliQ Plus type was employed throughout for dilutions and washing. Analytical quality assurance was performed using replicate samples, triplicate measurement of each analysed sample, internal calibration with ^{103}Rh, and reference materials for soils (SRM-4355, National Institute of Standards and Technology, USA; SO-2, SO-3 and SO-4, Canadian Certified Reference Materials Project) and plants (SRM-1575, National Institute of Standards and Technology, USA; NIES-3, NIES-9, NIES-10c, National Institute for Environment Studies, Japan).

The mineralogy of representative soil samples was determined by X-ray diffraction using a Siemens D-500 powder diffractometer with Cu K_a radiation fitted with a graphite monochromator and NaI(TI) scintillation detector. The spectra were obtained with a step scanning of 0.05° 2 theta and a counting time of 5 s $step^{-1}$.

4. Results and discussion

Univariate analysis indicated that the trace element data were distributed approximately log-normally. Table I shows the central tendency of the data, expressed as the geometric mean, and their range. The data were normalised accordingly by log-transformation for geostatistical analysis with the Geo-EAS (Geostatistical Environmental Assessment) Software (Englund and Sparks, 1988). The results of the geostatistical analysis are shown in contour maps (Figure 4–6).

The soil pH is neutral to alkaline. The pH ranges from 6.7 to 8.1 with a mean value of 7.4 (25 soil samples randomly distributed in the study area). The spatial variation of trace element concentrations on soils and plants is shown in Figure 4–6:

(1) Elements with a broad range of values but with two zones in particular (north-east of the smelter and also towards the south) where Pb, Cd, Ag, Zn, Cu, Sb and Sn soil and plant concentrations decrease with distance from the factory, and

(2) Elements showing the regional background concentrations and no spatial relationship with the lead smelter (Ba, Be, Ce, Co, Cr, Cs, Dy, Er, Ga, Gd, Ge, La, Li, Mo, Nb, Nd, Ni, Pr, Rb, Sm, Sr, Tb, Th, Tl, U, V, W, Y, Yb and Zr).

As expected, the highest Pb soil and plant concentrations were found at sites near the smelter, and in some samples Pb soil concentration exceeded 8,000 mg kg^{-1} and 6,000 mg kg^{-1} in ashed plants. The contour map of this element shows substantial Pb accumulation in two well-defined plumes of dispersion from the pollution source as well as decreasing metal content with increasing distance from the smelter in the northeasterly and southerly directions. The influence of both plumes is detectable to a distance of approximately 1,000 m. The northeastern area is more affected than the southern area.

The zones with high Pb, Cd and Ag contents in soils and plants are comparable. In contrast, there are some differences between the contour maps obtained for soils and those generated with the *S. rhombifolia* data for Zn, Cu, Sb and Sn. Thus, the soil contour map for Cu better reflects the two aforementioned dispersion zones (north-east and south of the smelter), whereas Sb and Sn plant contour maps are more comparable to those obtained for Pb, Cd and Ag.

TABLE I

Geometric mean and range of trace elements determined in soils (121 samples) and ashed plants (112 samples), expressed as mg kg^{-1}

	Soil samples			Ashed plant samples		
	Geometric mean	Minimum	Maximum	Geometric mean	Minimum	Maximum
Ag	1.18	0.54	14.92	1.14	0.14	6.12
Ba	371	225	646	355	174	669
Be	2.34	0.89	4.09	1.00	0.32	2.46
Cd	0.77	0.27	30.68	2.39	0.27	21.7
Ce	70.4	23.0	136.9	23.1	6.9	58.8
Co	10.0	5.8	17.0	7.0	2.6	14.5
Cr	38.1	17.5	94.1	41.0	6.9	713.2
Cs	12.2	4.8	36.4	5.0	1.6	14.7
Cu	43	20	241	102	44	209
Dy	3.75	1.41	6.65	1.38	0.09	3.84
Er	1.97	0.64	3.43	0.91	0.36	2.13
Ga	13.6	5.1	19.1	5.7	1.8	13.0
Gd	4.74	1.67	8.62	1.90	0.69	4.67
Ge	1.19	0.33	2.67	0.38	0.10	0.94
La	32.6	11.0	56.1	11.7	2.3	30.2
Li	30.2	11.3	71.0	15.8	5.8	41.7
Mo	1.3	0.5	4.8	7.9	1.8	53.3
Nb	9.0	1.0	26.7	1.8	0.4	8.2
Nd	27.8	8.3	58.8	9.4	0.4	24.8
Ni	17.8	10.9	63.0	31.3	9.3	203.2
Pb	159	34	8714	215	33	6182
Pr	7.4	2.5	14.1	2.6	0.0	6.6
Rb	145	59	271	99	44	376
Sb	2.1	0.2	28.6	1.5	0.3	56.7
Sc	6.6	2.6	10.3	3.1	1.0	7.6
Sm	5.3	2.2	9.0	2.4	0.8	4.7
Sn	3.4	0.4	19.3	2.3	0.6	22.1
Sr	199	129	1610	922	332	1684
Tb	0.68	0.22	1.81	0.28	0.04	0.68
Th	17.6	5.6	31.0	4.8	0.9	16.8
Tl	0.82	0.38	7.39	0.70	0.15	4.59
U	4.70	2.26	11.06	1.83	0.53	5.48
V	66.87	17.50	122.17	23.44	8.53	54.70
W	1.37	0.29	4.90	0.73	0.14	2.80
Y	17.8	7.1	28.2	6.9	1.5	18.3
Yb	2.34	0.95	3.59	0.93	0.27	2.29
Zn	137	44	1637	471	132	1652
Zr	74.7	7.7	227.0	7.8	1.1	51.7

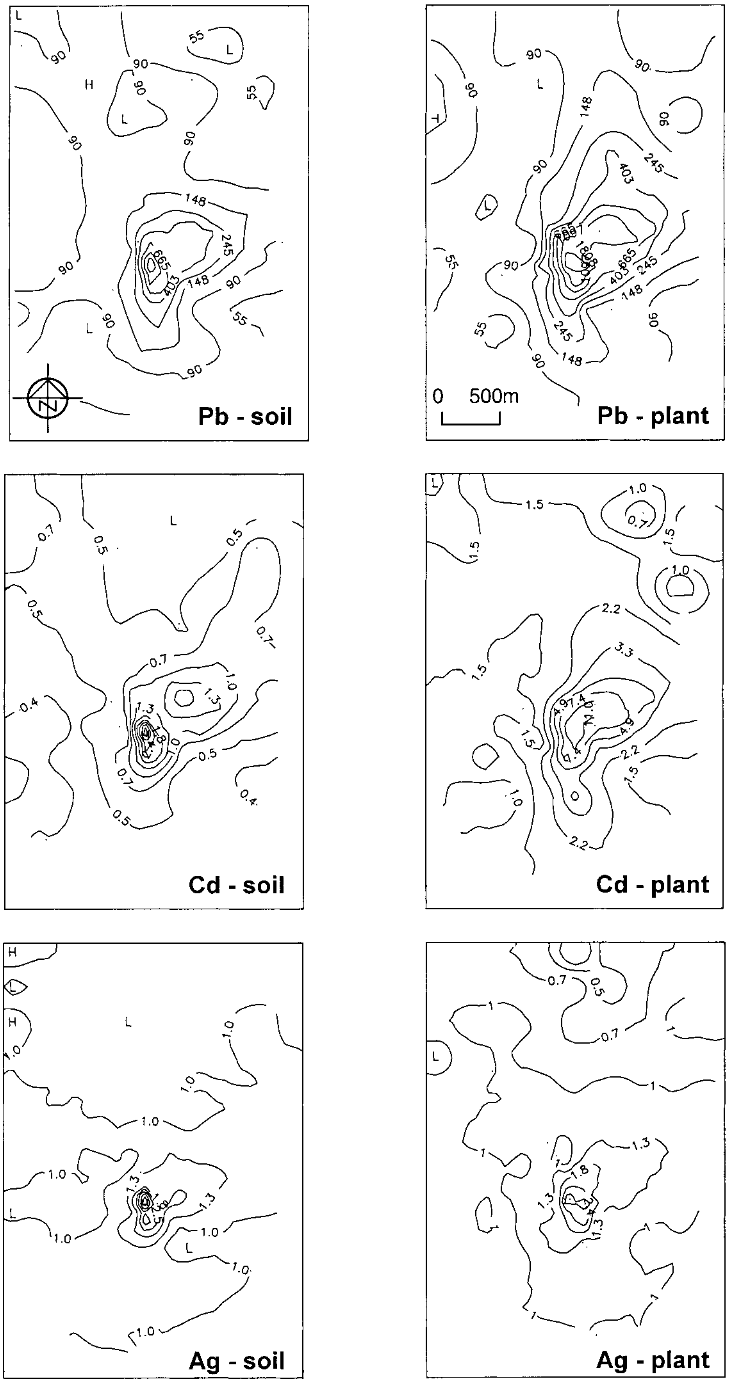

Figure 4. Contour maps of Pb, Cd and Ag in surface soils and ashed unwashed plants (*Sida rhombifolia*, Malvaceae). Contour levels expressed as mg kg^{-1}. L and H, lower and higher concentrations than those observed in contour maps.

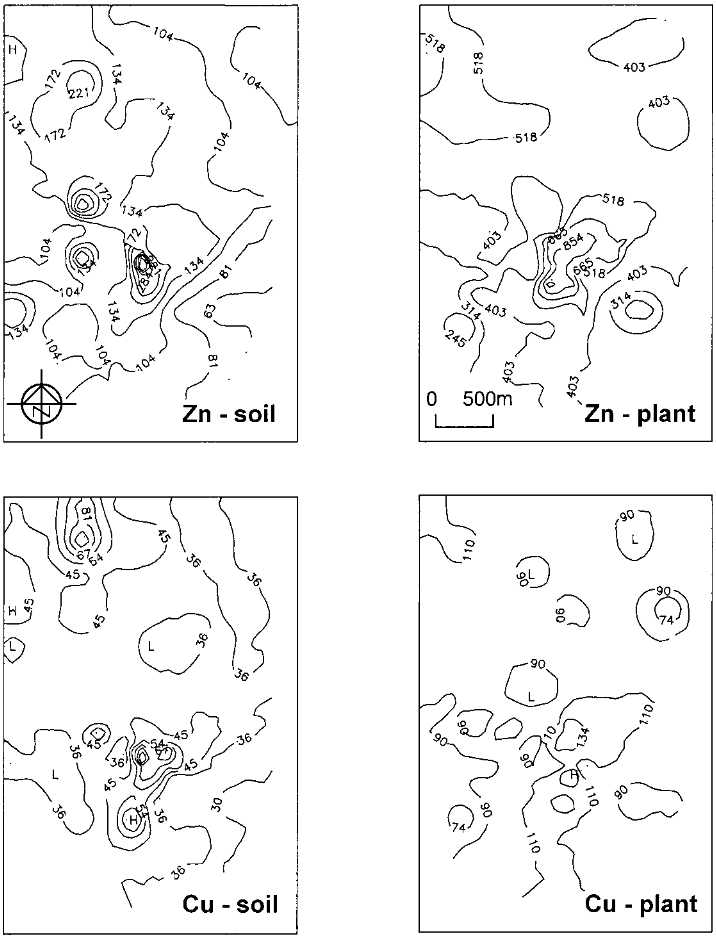

Figure 5. Contour map of Zn and Cu in surface soils and ashed unwashed plants (*Sida rhombifolia*, Malvaceae). Contour levels expressed as mg kg^{-1}. L and H, lower and higher concentrations than those observed in contour maps.

The comparison of soil and plant patterns allows for the inference of some general trends on their environmental behaviour, especially when the soil features are considered. The soil pH was neutral to alkaline and the mineralogy consisted of quartz, feldspars, calcite, illite and kaolinite. The Pb, Cd and Ag soil patterns might reflect element low mobility and their persistence in the surface soil. Despite the low bioavailability of Pb, Cd and Ag in neutral to alkaline soils (Kabata-Pendias and Pendias, 1989; McBride, 1994), the plant patterns demonstrate the pollutant distributions. The general trends shown by the Ag halos are consistent with those observed for Pb and Cd, and their worse definition could be possibly attributed to lower contents in the pollutant emissions.

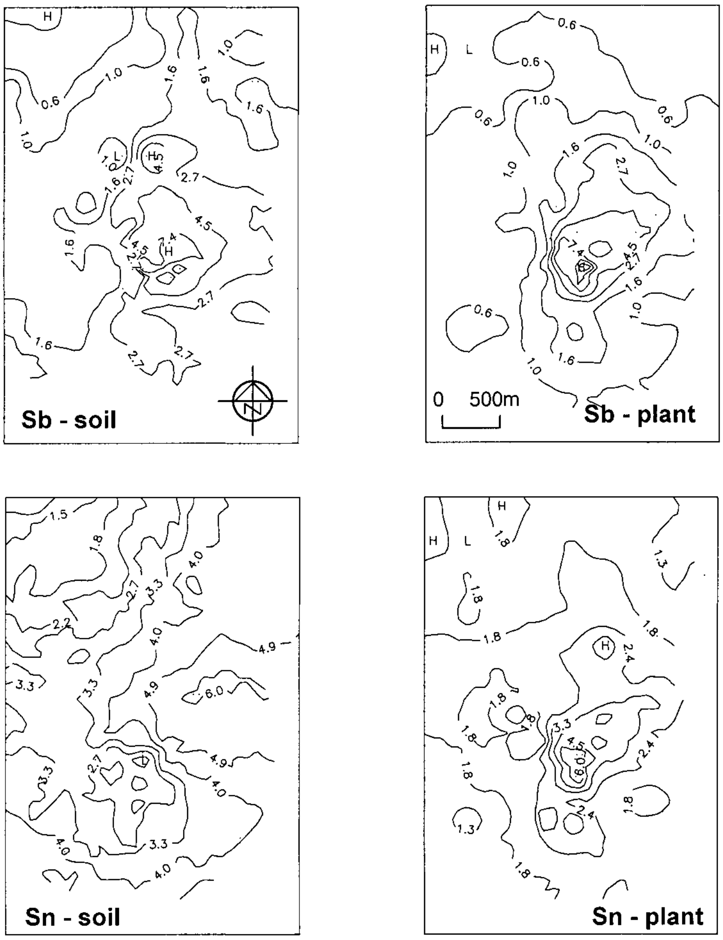

Figure 6. Contour map of Sb and Sn in surface soils and ashed unwashed plants (*Sida rhombifolia*, Malvaceae). Contour levels expressed as mg kg^{-1}. L and H, lower and higher concentrations than those observed in contour maps.

The soil and plant patterns of Zn and Cu are more irregular spatially, probably due to the relative solubility and availability of anionic hydroxy complexes of both Zn and Cu in neutral and alkaline soils (Kabata-Pendias and Pendias, 1989; McBride, 1994). Antimony and Sn patterns suggest an important mobility in soils in such way that they can be easily taken up by *S. rhombifolia*.

Stack emissions from the lead smelter are deemed to be mainly responsible for the patterns of Pb, Cd, Ag, Zn, Cu, Sb and Sn in soils and plants. The element depositions were produced from the smelter on the dominant SW–NE and N–S emitting directions (Figure 2). The larger amplitude of the northeastern plume is explained as a consequence of the wind dispersal characteristics from the SW quadrant (SMN, 1992).

As might be expected, given the chimney height, the soil and plant contamination patterns show that the most polluted zones are less than 1,000 m from the smelter. Fly ash and volatiles fell mainly in the first 400 m from the plant. The distance affected by pollution is comparable in the northeastern and in the southern zones and reflects similar wind characteristics (SMN, 1992). Furthermore, the influence of wind patterns on the plant storage area is likely to contribute to the high pollution levels observed near the smelter.

The concentrations of Pb, Cd, Ag, Zn, Cu, Sb and Sn in the polluted zones exceed the mean variations observed in uncontaminated soils and are similar to the levels found in contaminated soils associated with the metal processing industry (Table II). Some of these elements, especially Pb, reach levels thought to cause serious health and environmental problems in the residential zones located in the smelter pollutant plumes. Ingestion and inhalation of Pb enriched soil and atmospheric particulate material are common sources of excessive lead intake to man and animals. Thus, exposure to Pb and other pollutants is likely to exert potentially serious health effects, especially on children.

The metal uptake by plants in allotments could be an input to the food chain. Consequently, high Pb levels are generally reported for leafy vegetables (mainly lettuce) grown in areas surrounding non-ferrous metal smelters (Kabata-Pendias and Pendias, 1989; Kabata-Pendias, 1995). Lettuce leaves sampled 250 m SW from the plant (Table III) show that only Pb concentration reaches the values generally observed in metal industry processing soils (Kabata-Pendias and Pendias, 1989).

TABLE II

Trace elements in surface soils (mg kg^{-1}) from the study area, average contents in different sites around the world (compiled from Kabata-Pendias and Pendias, 1989), and ranges for maximum acceptable concentrations (MAC) proposed as phytotoxic in agricultural soils in different countries (after Kabata-Pendias, 1995)

	This study range	Uncontaminated soils variation of means	Metal industry processing contaminated soils range or mean	Phytotoxic MAC agricultural soils
Pb	34–8,714	10–84	72–12,123	50–1,000
Cd	0.27–30.68	0.06–1.10	0.6–160	1–5
Ag	0.54–14.92	< 1.0	n.a.	n.a.
Zn	44–1,637	17–125	155–12,400	150–600
Cu	21–242	6–80	24–3,700	50–200
Sb	0.2–28.6	0.19–1.77	up to 200	n.a.
Sn	0.4–19.3	< 11	n.a.	n.a.

n.a., not available

TABLE III

Trace element content in lettuce leaves (mg kg^{-1}) from a sample of the study area and from different sites around the world (after Kabata-Pendias and Pendias, 1989)

		This study	Lettuce grown in uncontaminated soils variation of means	Lettuces grown in metal industry processing contaminated soils range and/or mean
Pb	AW	1775	5–13	n.a.
	DW	479	0.7–3.6	45–69/596
Cd	AW	2.27	3.00	5.2–14.1/45
	DW	0.61	0.12–0.66	n.a.
Ag	AW	1.45	n.a.	n.a.
Zn	AW	400	240–520	n.a.
	DW	108	44–73	213–393/316
Cu	AW	56	42–58	n.a.
	DW	15	6–8.1	64
Sb	AW	2.34	n.a.	n.a.
Sn	AW	3.96	n.a.	n.a.

AW, ash weight basis; DW, dried weight basis; n.a., not available.

5. Conclusions

The spatial variability of trace element concentrations in surface soils and plants (*S. rhombifolia*), sampled around a lead smelter, show that both sampling media are adequate to determine the extent of the polluted area, as well as to assess the current level of pollution in the zone. The area studied is extensively contaminated with Pb, as expected as this was the main metal worked in the smelter, as well as with Cd, Ag, Zn, Cu, Sb and Sn. The contour maps of these metals show two well-defined plumes of dispersion from the factory in accordance with the prevalent wind directions. The most polluted zones are located less than 400 m from the smelter. Exposure to high contents of metals, especially Pb, such as those observed in urban zones of Lastenia could give rise to adverse health effects. Therefore, assess this and if necessary to propose measures to protect the local population and environment should be carried out.

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