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ORIGINAL PAPER

Environmental distribution and health impacts of As and Pb in crops and soils near Vinto smelter, Oruro, Bolivia

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Abstract The Vinto Sb–Sn smelter (Oruro, Bolivia) has been linked to arsenic and heavy metal pollution in air, soils, residual waters of the smelter, and hair and urine of workers, but crop concentrations had not been assessed previously. In this article, alfalfa, onions, and carrots, separated into roots and shoots, were analyzed for As and Pb, together with corresponding soil samples. The aim was to assess the environmental distribution and potential health impacts of these toxic elements and to compare them to levels observed at other sites around the world. As and Pb concentrations in all analyzed crop samples exceed the FAO/WHO, UK or Chilean limits by 1.5–2 orders of magnitude and As health risk indices were 286 (carrot) and 651 (onion), showing that the potential health risk due to consumption of these products is extremely high. As and Pb soil–plant transfer factors are similar to other contaminated sites around the world, but daily intake and health risk index for As are much higher in Vinto area due to very high concentrations in soils. Arsenic and lead soil and crop concentrations suggest increasing trends toward VMC. Correlations are significant for Pb in some crop fractions, but not for As, possibly due to considerable geogenic contributions to soil As in the area. In future surveys, larger numbers of soil and crop samples should be analyzed, and additional analyses should be carried out to distinguish anthropogenic and geogenic sources of As and Pb in soils and crops in the area.

Keywords Soil–plant transfer factors · Daily intake · Health risk index

Introduction

Contamination of soils, vegetation, and animals by As, Pb, and other heavy metals emitted from smelters has been reported in numerous studies since the early twentieth century (e.g. Haywood 1907; Nriagu and Pacyna 1988; Dudka and Adriano 1997). Soil As and Pb concentrations can reach several hundred or even thousand mg/kg (e.g. Carrizales et al. 2006). Concentrations in vegetation near smelters can reach tens or sometimes hundreds of mg/kg As or Pb (e.g. Chopin and Alloway 2007). While human As and Pb exposure has decreased considerably in developed countries in recent years, it remains high in many developing countries (Tong et al. 2000; ATSDR 2007a).

In December 1993, prompted by community health concerns, the Pan American Health Organization (PAHO) commissioned a study on community and occupational exposure to As, Pb, and other metals close to the smelter of the Vinto Metallurgical Company (VMC) in Oruro, Bolivia (Sussell and Singal 1995). Of 15 workers selected for exposure monitoring, 14 had hazardous exposures to As, 11 had hazardous exposures to Cd, and eight had hazardous exposures to SO_2. Nine of the 15 workers displayed high urine concentrations of As, and five of the 15 workers had high blood Pb levels. In further studies carried out in and

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around VMC, As, and Pb, contamination was detected in air (Yapari 1999), residual waters of the smelter (Fuentes 1993), and hair and urine of workers (Huanca 1997; Philco 2003).The information network ERBOL, in the bulletin of December 19, 1997, also warned about the high environmental contamination caused by the Vinto smelter. The report indicates an annual emission to the air of 160 t of arsenic and the presence of a high quantity of heavy metals, mainly lead (ERBOL 1997). Moreover, VMC emits 239 kg of SO_2 per ton of concentrate produced (Yapari 1999), even though the Bolivian Environment Law No. 1333, issued in 1992, only permits 42 kg of SO_2 per ton for Sn smelters. These emissions are aggravated due to the fact that thermal inversion (the formation of an immobile layer of cold air close to the ground that inhibits contaminant dispersion) occurs frequently in Oruro. The analyses of toxic elements in soil samples in the city of Oruro show that 92.3 % of the analyzed samples exceed the permissible limits for lead (Mendizábal 2001).

The Vinto smelter originally started operation in 1970, it was privatized in 1999, and re-nationalized in 2007, without significant upgrades of the smelting process. In recent years, it produced an average of about 10,000 t tin concentrates per year. An additional, modern Sn smelter is currently being built at Vinto, planned to increase smelting capacity by 38,000 t Sn concentrates and to produce about 18,000 t tin metal per year.

Arsenic is a micronutrient required in trace quantities by plants, animals, and possibly humans (Uthus 2003). However, at higher levels, this element produces cancer and may cause death (ATSDR 2007a; WHO 2001). Lead is highly toxic, affecting the nervous system, kidneys, and reproductive system (ATSDR 2007b), and it can be accumulated in organisms as it does not have a defined biological function. The most important sources of human exhibition to arsenic and a major pathway for lead are food and water (WHO 2001; ATSDR 2007a, b).

Plants can hyperaccumulate metal ions that are toxic to other organisms (Baker and Brooks 1989, and references therein). Complex interactions of transport and chelating activities control the rates of metal uptake and storage (Clemens et al. 2002). This mechanism can be used to remediate metal-contaminated soils (e.g. Salt et al. 1998), but it may also transfer contaminants into the food chain, particularly if crops for human consumption or animal feed are grown on contaminated soils. The degree of contaminant uptake from the soil to the plant can be expressed through the transfer factor which relates the contaminant concentration in the crop to that in the host soil (e.g. Cui et al. 2004).

The before-mentioned studies indicated the possible contamination of agricultural products in the vicinity of the VMC smelter, but contaminant levels in crops had not been determined previously. In the present investigation, the Pb and As levels in soils and in the roots and shoots of onion (*Allium cepa* L.), carrot (*Daucus carota* subsp. *sativus*), and alfalfa (*Medicago sativa* L.) are analyzed at different distances from the smelter. The objectives are to study the contaminant distribution in soils and crops with respect to distance from VMC and within the crops, to assess the potential health risk for consumers of these products, and to compare the observed contamination levels with other studies worldwide.

Materials and methods

Site and field sampling

The VMC smelter is located on the eastern border of Oruro city and the Poopó lake (Fig. 1). The climate is semi-arid with an annual average temperature between 8 and 10 °C and average precipitations of >400 mm/year (UNEP 1996). Geomorphologically, the area belongs to the western flank of the Eastern Cordillera (EC) of the Andes, made-up of intensely deformed, lower Paleozoic, marine clastic sedimentary rocks, overlain locally by folded continental Cretaceous and early Tertiary sedimentary rocks, undeformed unconsolidated late Tertiary continental sediments, and late Oligocene to Pliocene volcanic rocks (Cunningham et al. 1991). The sampled agricultural fields are located on Quaternary deposits of glacial, fluvial, eolic, and lacustrine origin. The EC hosts most of the mineral resources of the Oruro Department, including the Bolivian tin belt, the gold-antimony belts, and the lead–zinc belt (Ahlfeld 1967). This wealth of mineral resources causes elevated geochemical background values for heavy metals and metalloids in soils of the Oruro area and the altiplano (Tapia et al. 2012).

According to CORDEOR data (Corporation of Development of Oruro, pers. comm.), in the Cercado province where VMC is located, 7,000 l of milk is produced daily, and the region is one of the main sources of agricultural produce for the city of Oruro (30 % of the total consumption).

The sampling of soils and agricultural products was designed following the recommendations of LaGrega et al. (2010); according to the stack height of 80 m at VMC, the maximum deposition distance of the smelter is estimated to be 5 km. We extended this distance by factor 2.5 in order to study the spatial contaminant distribution (Fig. 1). The soil samples (arable layer, upper 30 cm) and agricultural products were taken by random selection (chessboard method, 5 samples per field), in order to obtain a higher homogeneity (LaGrega et al. 2010). The crops were excavated with the surrounding soil in order to facilitate the

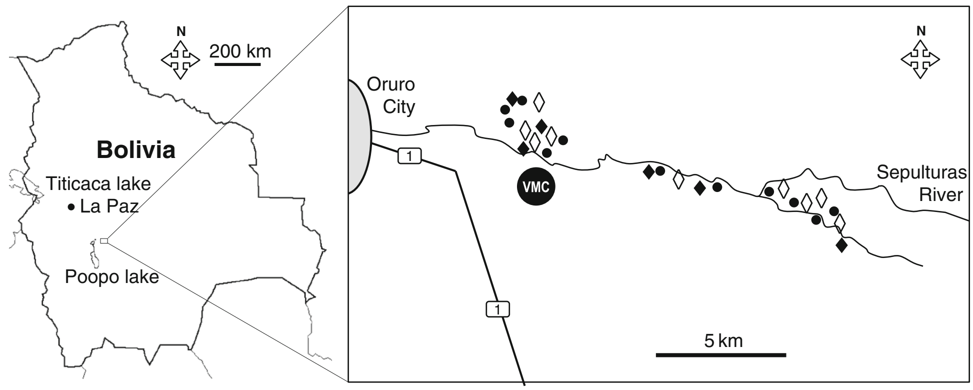

Fig. 1 Study area (*left*), and location (*right*) of the sampling points in relation to the Vinto Metallurgical Complex (VMC). *Solid rhombi* show the sampling areas with alfalfa, *solid circles* show the areas with carrots, and *open rhombi* show the areas with onion

total extraction without damage and were separated into root and shoot fractions. In the case of alfalfa, the root, which may grow several meters deep, was cut at about 50 cm depth. The samples were cleaned with a plastic brush to remove soil and surface contamination and stored in sealable polythene bags.

Laboratory analyses

Gravimetric water content of the soil samples was determined by mass difference after drying at ambient temperature during 4 weeks. All soil samples were sieved through a 2-mm sieve. Soil pH was determined in an aqueous filtrated extract (soil:water 1:2 v/v slurry) using an Eutech pH 11 meter calibrated with pH 4, 7, and 10 buffer solutions, and conductivity was measured in the same extract using an Eutech Cond 6+meter.

For the agricultural products, each sample was washed with deionized water and then dried shortly on tissue paper to determine fresh weight. To determine dry weight and gravimetric water content of the crops, each sample was weighed, cut, frozen to −80 °C, freeze-dried, and weighed again.

All analyses were carried out in the Hydrochemistry Laboratory of Instituto de Investigaciones Químicas at Universidad Mayor de San Andrés de La Paz. In order to determine the total concentration of lead and arsenic in soil and agricultural products, the samples were acid-digested in a microwave oven (Sah and Miller 1992) using HNO_3 (70 % w/w) and H_2O_2 (30 %). All digested samples were first analyzed by flame atomic absorption spectroscopy (FAAS). Those samples whose values were below the detection limit of FAAS (150 ppm for arsenic and 15 ppm for lead) were reanalyzed by AAS with graphite furnace (AASGF) for lead (0.06 ppb detection limit) and AAS with hydrate generator (AASHG) for arsenic (0.03 ppb detection limit) according to Meyer and Keliher (1992) and Tracy and Moeller (1990), respectively. Correlation coefficients obtained during calibration of the different methods ranged from 0.989 to 1.000, and deviations from the concentrations of certified reference samples (NIST 1640A) were <10 %. Concentrations in soils are reported on dry weight basis, and concentrations in crops on fresh weight basis.

Water content of soils and crops, and soil pH and electrical conductivity were determined in the all the samples taken, but due to budget limitations, it was not possible to analyze As and Pb in all the samples. In total, 42 crop samples and 13 soil samples were analyzed.

Data analysis

Basic statistics and correlations

Mean values, standard deviations, and linear (Pearson's) and nonparametric (Spearman's) correlations of the measured parameters with distance from VMC smelter were calculated using the software IBM SPSS Statistics 20. Cases were excluded pairwise, and statistical significance of the correlations was determined two-tailed. The significance of differences between mean values of different subgroups was determined by Student's *t* test.

Comparison of crop As and Pb concentrations with maximum permissible values

Regarding crop Pb, the FAO and WHO have established maximum levels in different products. For bulb, root, and tuber vegetables (i.e. onion and carrot), the maximum level is 0.1 mg/kg fresh wt. For leafy vegetables, the limit is 0.3 mg/kg fresh wt., which was applied to alfalfa in this study.

FAO and WHO have not established maximum levels of As in food, due to the large toxicity variations between the different inorganic and organic As species (Codex Alimentarius Commission 2010). However, other countries have established legal limits for the maximum content of As, for example, the UK Arsenic in Food Regulations

(1959/831) have set a general limit of not more than 1 ppm (1 mg/kg fresh wt.) of total arsenic in food, and the Chilean Food Sanitary Regulation (Decree 977) prescribes a maximum of 0.5 mg/kg fresh wt.

Soil–plant transfer factor and transportation index

Soil–plant transfer factors TF were calculated as (e.g. Cui et al. 2004):

$$TF = \frac{c_{\text{crop fw}}}{c_{\text{soil dw}}}$$

where $c_{\text{crop fw}}$ is concentration in crop (mg/kg fresh weight) and $c_{\text{soil dw}}$ is concentration in soil (mg/kg dry weight).

The transportation index (TI) describes the ability of the plant to translocate the pollutant from roots to shoots (Ghosh and Singh 2005):

$$TI = \frac{c_{\text{shoot fw}}}{c_{\text{root fw}}} \times 100$$

Estimation of health risks

The health risk associated with the consumption of the analyzed crops by humans or animals was assessed by calculating the daily intake of metals and metalloids, the estimated daily exposure, and the health risk index (HRI). The daily intake DI of contaminants was estimated as:

$$DI = c_{\text{crop fw}} m_{\text{d}}$$

where m_{d} is the daily crop consumption.

The estimated daily exposure EDE was calculated as:

$$EDE = \frac{DI}{\text{Body mass}}$$

For onion and carrot for human consumption, we assumed an intake m_{d} of 345 g per day for an adult of 60 kg body mass. As alfalfa is used for animal feeding and not for humans, we assumed a consumption m_{d} of 10 kg per day for a cow of 500 kg body mass.

For As, the Integrated Risk Information System (IRIS) of the US EPA (http://www.epa.gov/iris/subst/0278.htm, *last accessed 13/03/2013)* has set a reference oral dose (RfDo) of 0.0003 mg As per kg body weight per day as the safe level of oral intake for a life-long exposure. Therefore, we calculated the HRI for As exposure as:

$$HRI = \frac{EDE}{RfDo}$$

If the risk index is equal or greater than one, there is a potential health risk due to arsenic intake from food.

For Pb, the US EPA has not set an RfDo, because some negative health effects, “particularly changes in the levels of certain blood enzymes and in aspects of children’s neurobehavioral development, may occur at blood lead levels so low as to be essentially without a threshold.” (http://www.epa.gov/iris/subst/0277.htm, *last accessed 13/03/2013*). Accordingly, we did not calculate a risk index for Pb, because any exposure to lead can have potential negative health effects.

Literature review

We reviewed publications on As and Pb concentrations in plants and soils contaminated by smelters, mines, and other sources to compare the observed levels and transfer factors with our findings, and to assess the severity of the contamination near VMC. We also calculated DI, EDE, and HRI for these studies. Where plant concentrations were reported on dry weight basis, they were converted to fresh weight basis assuming a water content of 90 %.

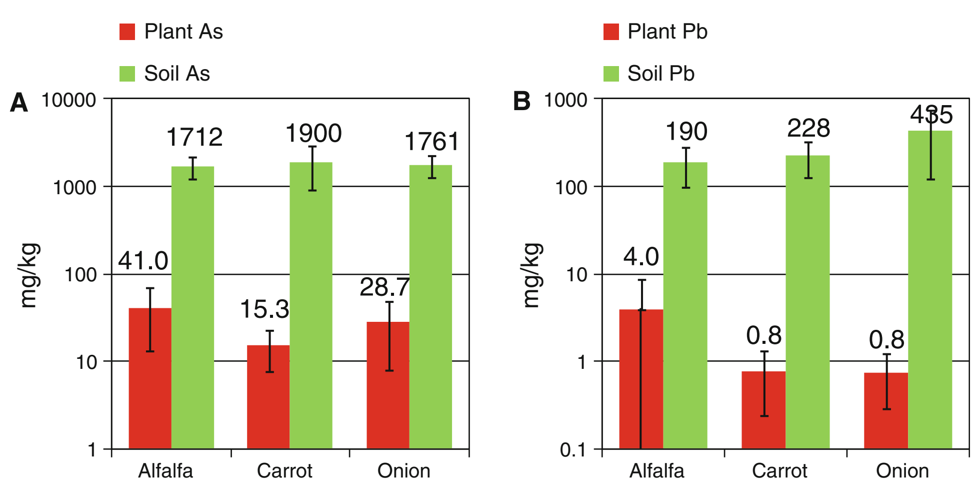

Fig. 2 Mean concentrations of As (*left*) and Pb (*right*) in all samples of each crop and in the soil samples underneath, with standard deviations

Table 1 Comparison with As data from other studies

Location	Sampling site description	Crop	Crop conc [mg/kg fw]	Soil conc [mg/kg dw]	TF (–)	DI [mg/d]	EDE [mg/(kg·d)]	HRI (–)	Source
Southern Ontario, Canada	Near two Pb-smelters	Vegetation (unwashed foliage)	**0.49**[a]	**71**	0.0069	0.169	0.0028	9.4	Temple et al. (1977)
	Near other urban and industrial sources	Vegetation (unwashed foliage)	**0.09**[a]	**13**	0.0064	0.029	0.0005	1.6	
Germany, growth experiments on soil and soil–slag mixtures	Control soil	Carrots	**0.011**[a]	**17**	0.0006	0.004	0.0001	0.2	Bunzl et al. (2001)
	Red slag-soil mixture 1:1	Carrots	**0.12**[a]	**115**	0.0010	0.041	0.0007	2.3	
	Black slag-soil mixture 1:1	Carrots	**0.036**[a]	**420**	0.0001	0.012	0.0002	0.7	
Samta village, south-west Bangladesh		Vegetables	0.22[b]	**13**	0.0166	**0.028**	0.0005	1.6	Alam et al. (2003) (crop data), Islam et al. (2000) (soil data)
Hunan province, south China	Fields affected by Chenzhou lead/zinc mine spill	Vegetables, village 1	**0.53**[a]	**459**	0.0012	0.183	0.0030	10.2	Liu et al. (2005)
		Vegetables, village 2	**4.1**[a]	**709**	0.0058	1.42	0.0236	78.6	
		Vegetables, village 3	**0.13**[a]	**192**	0.0007	0.045	0.0007	2.5	
Zlatna, western Romania	Near a Cu smelter	Spring onions from vegetable plots	**0.13**	**66**	0.0020	0.045	0.0007	2.5	Pope et al. (2005)
North Carolina, USA	Soil contaminated by lead arsenate pesticide	Carrot roots	**<1.5**[a]	**178**	<0.0084	0.518	0.0086	28.8	Pendergrass and Butcher (2006)
Eastern South Korea	Near ceased Songcheon Ag-Au mine	Green onion leaves	**4.7**	**175**	0.027	1.62	0.0270	90.1	Lim et al. (2008)
		Green onion root	**33**	**175**	0.19	11.39	0.1898	632.5	
Gyöngyösoroszi village, Northeast Hungary	Near a ceased Pb–Zn mine	Leafy vegetables	**0.17 (0.005–0.49)**[a]	**109 (31–184)**	**0.0022 (0.006–0.052)**	0.060	0.0010	3.3	Sipter et al. (2009)
Huelva province, southwest Spain	Tharsis mine and smelter	Plantago coronopus	**0.6**[a]	**37**	0.0162	0.207	0.0035	11.5	Chopin and Alloway (2007)
	Rio Tinto mine and smelter	Plantago coronopus	**2.0**[a]	**94**	0.0213	0.690	0.0115	38.3	
	Near Huelva Cu smelter	Plantago coronopus	**0.7**[a]	**14**	0.0500	0.242	0.0040	13.4	
Huelva province, southwest Spain	Rio Tinto mining region	Natural vegetation	**0.6**[a,c]	**869**	0.0007	0.206	0.0034	11.4	de la Fuente et al. (2010)
Soils from Florida	Greenhouse study on soils with arsenical pesticide	Rice (*oryza sativa* L.), whole plant	**10.7 (1.8–24.3)**[a]	**675**	0.0158	3.678	0.0613	10.7	Quazi et al. (2011)

Table 1 continued

Location	Sampling site description	Crop	Crop conc [mg/kg fw]	Soil conc [mg/kg dw]	TF (–)	DI [mg/d]	EDE [mg/(kg·d)]	HRI (–)	Source
Bestari Jaya, Malaysia	Former tin mining district	Natural vegetation, roots	**56.9** (28.9–79.2)[a,d]	**2,478** (2,232–2,878)	0.0229	19.6	0.3269	93.4	Ashraf et al. (2011)
		Natural vegetation, shoots	**13.9** (1.3–31.3)[a,d]	**2,478** (2,232–2,878)	0.0056	4.79	0.0798	22.8	
Arithmetic mean			**6.22**	**445.6**	**0.019**	**2.14**	**0.04**	**60.0**	
Min			0.005	13.0	0.0001	0.004	0.00006	0.21	
Max			56.9	2478.4	0.19	19.62	0.33	632.5	

Crop concentration (fresh weight basis), soil concentration (dry weight basis), soil–plant transfer factors (TF), daily intake (DI), estimated daily exposure (EDE), and health risk index (HRI). DI, EDE, and HRI are calculated supposing a daily consumption of 345 g by a human of 60 kg body weight. Bold values were published in the source, and other values have been calculated from published data

n. r. not reported

[a] Crop concentration published on dry weight basis was converted to fresh weight assuming a mean water content of 90 %

[b] Calculated from DI based on daily ingestion of 130 g/habitant given in the publication

[c] Arithmetic mean of 97 plant species

[d] Arithmetic mean of 7 terrestrial plant species

Results and discussion

Mean As and Pb concentrations in crops and soils

In Fig. 2, the mean concentrations in all samples of each crop and in the corresponding soil samples are given. Overall, As concentrations are an order of magnitude higher than Pb concentrations, both in crops and in soils.

Arsenic concentrations are highest in alfalfa, intermediate in onion, and lowest in carrot (Fig. 2a). The As crop values (global mean of all analyzed crop samples: 25.6 mg/kg, range 6.2–110 mg/kg) exceed Chilean and UK regulations by 1–2 orders of magnitude. These concentrations are higher than most values found in other publications reviewed in this study (Table 1). The highest crop Pb values are also found in alfalfa, while concentrations are similar in carrot and onion (Fig. 2b). Pb crop concentrations (global mean 1.45 mg/kg, range 0.11–12.8 mg/kg) exceed FAO and WHO limits by a factor of 8 for onion and carrot, and 13 for alfalfa. These values are in the range of crop Pb concentrations observed at other contaminated sites around the world (Table 2).

Soil As values ranged from 825 to 3,390 mg/km dry wt. (global mean: 1,755 mg/kg). These concentrations are much higher than those observed at all but one of the sites from the literature review (Table 1), indicating that As contamination in the studied area is very severe. Soil Pb concentrations ranged from 118 to 656 mg/km dry wt. (global mean 245 mg/kg). These values are in the low to medium range of concentrations observed at other sites (Table 2). The differences between the means of soil As or Pb under the three different crops (Fig. 2a, b) are not statistically significant even at the 0.05 level (Student's *t* test), indicating that the crop type has no influence on soil concentrations.

Soil pH, conductivity, and As and Pb concentrations according to distance from VMC smelter

Soil pH was near-neutral to slightly alkaline in all samples (Table 3; Fig. 3a); it did not show a statistically significant correlation with distance to the Vinto metallurgical complex. Soil electrical conductivities were highly variable (0.04–1.05 mS/cm; Fig. 3a; Table 3) and did not correlate either with distance to VMC. As and Pb soil concentrations show no clear trends when plotted against soil pH or electrical conductivity (not shown). For both As and Pb soil concentrations, linear least squares regression shows increasing trends with vicinity to VMC (Fig. 3b), but correlations are not statistically significant (Table 3)

The very high soil As concentrations suggest that As content is not only caused by atmospheric deposition. Supposing that As emissions have been constant at

Table 2 Comparison with Pb data from other studies

Location	Sampling site description	Crop	Crop conc (mg/kg fw)	Soil conc (mg/kg dw)	TF (–)	DI (mg/d)	EDE [mg/(kg·d)]	Source
Southern Ontario, Canada	Near two Pb-smelters	Vegetation (unwashed foliage)	**16.65**[a]	**3,199**	0.0052	5.744	0.0957	Temple et al. (1977)
	Near other urban and industrial sources	Vegetation (unwashed foliage)	**7.83**[a]	**717**	0.0109	2.703	0.0450	
Three industrial/smelter sites in Sweden	Contaminated garden soils	Carrot	**0.025**	**47**	0.0005	0.009	0.0001	Jorhem et al. (2000)
Germany, growth experiments on soil and soil–slag mixtures	Control soil	Carrots	**0.027**[a]	**20**	0.0014	0.009	0.0002	Bunzl et al. (2001)
	Red slag-soil mixture 1:1	Carrots	**0.91**[a]	**800**	0.0011	0.314	0.0052	
	Black slag–soil mixture 1:1	Carrots	**0.41**[a]	**2,740**	0.0001	0.141	0.0024	
Samta village, south-west Bangladesh		Vegetables	0.57[b]	**28**	0.0205	**0.075**	0.0012	Alam et al. (2003) (crop data), Islam et al. (2000) (soil data)
Hunan province, south China	Fields affected by Chenzhou lead/zinc mine spill	Vegetables, village 1	**1.77**[a]	**305**	0.0058	0.611	0.0102	Liu et al. (2005)
		Vegetables, village 2	**5.9**[a]	**1,088**	0.0054	2.036	0.0339	
		Vegetables, village 3	**0.39**[a]	**321**	0.0012	0.135	0.0022	
Zlatna, western Romania	Near a Cu smelter	Spring onions from vegetable plots	**0.55**	**1,772**	0.0003	0.190	0.0032	Pope et al. (2005)
North Carolina, USA	Soil contaminated by lead arsenate pesticide	Carrot roots	**2.0**[a]	**585**	0.0034	0.690	0.0115	Pendergrass and Butcher (2006)
Huelva province, southwest Spain	Tharsis mine and smelter	*Plantago coronopus*	**4.5**	**85**	0.0529	1.553	0.0259	Chopin and Alloway (2007)
	Rio Tinto mine + smelter	*Plantago coronopus*	**6.1**	**172**	0.0355	2.105	0.0351	
	Near Huelva Cu smelter	*Plantago coronopus*	**5.5**	**45**	0.1222	1.898	0.0316	
Eastern South Korea	Near ceased Songcheon Ag–Au mine	Green onion leaves	**0.8**	**95**	0.008	0.276	0.0046	Lim et al. (2008)
		Green onion root	**3.8**	**95**	0.04	1.311	0.0219	
Gyöngyösoroszi village, Northeast Hungary	Near a ceased Pb–Zn mine	Leafy vegetables	1.14	**953 (21–2,825)**	**0.0012 (0.006–0.017)**	0.395	0.0066	Sipter et al. (2009)
Huelva province, southwest Spain	Rio Tinto mining region	Natural vegetation	**0.5**[a,c]	**1,094**	0.0005	0.187	0.0031	de la Fuente et al. (2010)
Nord province, northern France	Near a Zn–Pb smelter in Mortagne du Nord	Carrot	**0.09**	**456**	0.0002	0.031	0.0005	Douay et al. (2007)
Hubei province, central China	Near Daye smelter in Huangshi	Leafy vegetables *(Brassica chinensis* L.)	**3.28**[d]	**400**	0.0082	1.132	0.0189	Yan et al. (2007)
Guangdong province, south China	Villages near Dabaoshan mine	Carrot, village 1	**0.09**	**130**	0.0007	0.031	0.0005	Zhuang et al. (2009)
		Carrot, village 2	**0.18**	**151**	0.0012	0.062	0.0010	
		Leafy vegetables average	n. r.	n. r.	**0.007–0.016**			
		Root vegetables average	n. r.	n. r.	**0.002–0.009**			

Table 2 continued

Location	Sampling site description	Crop	Crop conc (mg/kg fw)	Soil conc (mg/kg dw)	TF (–)	DI (mg/d)	EDE [mg/(kg·d)]	Source
Guangdong province, south China	Near an e-waste processing site	Carrot	**0.48**	68.6	**0.007**	0.166	0.0028	Luo et al. (2011)
Liaoning province, east China	Near Huludao Zinc plant	Edible vegetable parts average	**1.6**	**319.6**	0.005	0.552	0.0092	Zheng et al.(2007)
		Carrot leaf	**5.5**[a]	14.7	**0.375**	1.898	0.0316	
		Carrot root	**0.5**[a]	15.6	**0.032**	0.173	0.0029	
Five abandoned Cu mine spoil sites in China	Wugongli, Anhui Province	Wild plants, average	**3.76**[a]	**1,680**	0.0022	1.297	0.0216	Xiao et al. (2008)
	Tongguanshan, Anhui Province	Wild plants, average	**2.4**[a]	**860**	0.0028	0.828	0.0138	
	Fenghuangshan, Anhui Province	Wild plants, average	**1.32**[a]	**164**	0.0080	0.455	0.0076	
	Tongshan, Jiangsu Province	Wild plants, average	**1.91**[a]	**694**	0.0028	0.659	0.0110	
	Xiaojiancu, Zhejiang Province	Wild plants, average	**1.94**[a]	**797**	0.0024	0.669	0.0112	
El-Sadat city, Eqypt	Wastewater pond in an industrial zone	*Typha domingensis* - root in winter	**1.5**[a]	**59.1**	0.0252	0.514	0.0086	Hegazy et al. (2011)
		Typha domingensis - root in summer	**2.0**[a]	**59.1**	0.0338	0.690	0.0115	
		Typha domingensis - shoot in winter	**0.66**[a]	**59.1**	0.0112	0.229	0.0038	
		Typha domingensis - shoot in summer	**0.90**[a]	**59.1**	0.0153	0.312	0.0052	
Bestari Jaya, Malaysia	Former in mining district	Natural vegetation, roots	**43.5**[a,d] **(11.5–68.9)**	**2362.0 (100–3,589)**	0.0184	15.02	0.2503	Ashraf et al. (2011)
		Natural vegetation, shoots	**13.1**[a,d] **(2.5–27.8)**	**2,362.0 (100–3,589)**	0.0055	4.509	0.0751	
Kampala, Uganda	Wetlands in Lake Victoria basin	*Cyperus papyrus* leaf	**0.31**[a]	**30.4**	0.0103	0.108	0.0018	Nabulo et al. (2008)
		Cyperus papyrus stem	**0.88**[a]	**30.4**	0.0288	0.302	0.0050	
		Cyperus papyrus root	**1.11**[a]	**30.4**	0.0366	0.384	0.0064	
		Colocassia esculenta leaf	**0.6**[a]	**98.2**	0.0061	0.207	0.0035	
		Colocassia esculenta tuber	**0.2**[a]	**98.2**	0.0020	0.069	0.0012	
		Curcubita maxima (pumpkin) leaf	**1.3**[a]	**98.2**	0.0128	0.434	0.0072	
Sakaraya, Turkey	Plants grown on sewage sludge in pots	*Brassica juncea* root	**2.18**[a]	**34.0**	0.064	0.751	0.0125	Dede et al. (2012)
		Brassica juncea shoot	**0.34**[a]	**34.0**	0.010	0.117	0.0020	

Table 2 continued

Location	Sampling site description	Crop	Crop conc (mg/kg fw)	Soil conc (mg/kg dw)	TF (–)	DI (mg/d)	EDE [mg/(kg·d)]	Source
Arithmetic mean			**3.28**	**550.6**	**0.023**	**1.13**	**0.019**	
min			0.03	14.7	0.0001	0.009	0.0001	
Max			43.5	3,199.0	0.38	15.2	0.25	

Crop concentration (fresh weight basis), soil concentration (dry weight basis), soil–plant transfer factors (TF), daily intake (DI), and estimated daily exposure (EDE). Bold values were published in the source, and other values have been calculated from published data

n. r. not reported

[a] Crop concentration published on dry weight basis was converted to fresh weight assuming a mean water content of 90 %

[b] Calculated from DI based on daily ingestion of 130 g/habitant given in the publication

[c] Arithmetic mean of 97 plant species

[d] Arithmetic mean of 7 terrestrial plant species

160 t/year during the 42 years of operation of VMC, and that deposition is uniform in a radius of 5 km (affected area 78.5 km^2 or 7 854 ha), the annual As deposition would have been 20.4 kg/ha As. Assuming that this mass is distributed by tillage in the upper 30 cm of soil (equivalent to about 4,000 t/ha of dry soil), the annual increase in soil As would be 5.1 mg/kg year (dry weight), or a total increase in 204 mg/kg since the start of operation of Vinto, eight times less than the mean observed As concentration. This calculation suggests that the high observed soil As concentrations are mostly due to the high geogenic background values found in the region (Tapia et al. 2012), which may blur trends with respect to distance from VMC.

Tapia et al. (2012) also investigated As and Pb in soils with respect to distance to Vinto smelter. For As, they did not find a significant trend toward Vinto smelter, consistent with our findings here. For Pb, however, they observed a significant correlation with distance to VMC, with decreasing Pb concentrations up to a distance of about 60 km from the smelter.

Reuer et al. (2012) and Reif et al. (1989) investigated contamination by Pb, As, and other heavy metals near the smelter of La Oroya, Junin department, Peru and found that soil metal levels dropped exponentially or linearly with distances up to 56 km from the smelter. De Gregori et al. (2000) investigated heavy metal levels in agricultural soils impacted and non-impacted by mining activities in Chile. Near Las Ventanas smelter, they found Cu and As levels decreasing with distances of up to 26 km. Near Chagres smelter, however, Cu and As concentrations were high, but not clearly correlated with distance. In this valley, smelter slag had been used for road construction, which may have artificially increased soil metal concentrations at larger distances.

Probably, in our study, the correlation for Pb is not significant due to the low number of analyzed soil samples, and due to the presence of one very high Pb value at 5 km distance, which may be due to another unidentified Pb source. Regarding As, probably geogenic As concentrations (for example from arsenopyrite, e.g., Ramos et al. Ramos Ramos et al. 2012) are so high in the studied area that they partly cover the influence of VMC.

In future studies, a larger number of soil samples should be analyzed, the range of distances from the smelter should be extended, and mineralogical analyses or sequential extractions should be carried out to determine the nature and origin of the As and Pb compounds in the soils.

As and Pb concentrations in shoot and root fractions

In onion (Table 3), mean concentrations in the roots (bulb) are higher than in the shoots for both As (transportation index $TI_{As} = 41.7$ %) and Pb ($TI_{Pb} = 56.0$ %), indicating that onion transports only about half of the absorbed

Table 3 Statistics of As and Pb concentrations in soils (dry weight basis), crops and crop fractions (fresh weight basis), and soil pH and electrical conductivity

	Soil pH (−)	Soil el. cond. (mS/cm)	Crop As (mg/kg fw)								Crop Pb (mg/kg fw)							
			Soil As (mg/kg dw)	All crop samples	Alfalfa shoots	Alfalfa roots	Onion shoots	Onion roots	Carrot shoots	Carrot roots	Soil Pb (mg/kg dw)	All crop samples	Alfalfa shoots	Alfalfa roots	Onion shoots	Onion roots	Carrot shoots	Carrot roots
Mean	7.76	0.33	1,755.2	25.6	39.2	55.7	14.2	34.0	16.2	14.9	245.1	1.45	2.87	12.77	0.48	0.85	1.44	0.51
Std. Deviation	0.47	0.24	664.0	20.5	29.0	n.d.	5.9	21.8	5.3	8.5	151.3	2.48	3.46	n.d.	0.25	0.50	0.34	0.32
Minimum	6.33	0.04	824.7	6.2	20.8	55.7	9.8	8.2	10.3	6.2	117.8	0.11	0.39	12.77	0.21	0.11	1.06	0.18
Maximum	8.24	1.05	3,389.7	109.7	109.7	55.7	22.9	80.2	23.2	37.7	655.9	12.77	11.07	12.77	0.71	1.71	1.83	1.12
No. of samples	37	37	13	42	8	1	4	11	5	13	13	42	8	1	4	11	5	13
Pearson's correlation coefficient with distance from VMC	0.098	0.173	−0.386	−0.296	−0.452	n.d.	−0.529	−0.492	−0.046	−0.547	−0.243	−0.301	−0.553	n.d.	−0.956*	−.0724*	−0.422	−0.580*
Significance (two-tailed)	0.565	0.306	0.192	0.057	0.261	n.d.	0.471	0.124	0.942	0.053	0.423	0.053	0.155	n.d.	0.044	0.012	0.479	0.038
Spearman's correlation coefficient with distance from VMC	0.268	0.172	−0.242	−0.271	−0.618	n.d.	−0.738	−0.300	−0.053	−0.486	−0.330	−0.463**	−0.618	n.d.	−0.949	−0.764**	−0.527	−.0752**
Significance (two-tailed)	0.109	0.308	0.426	0.082	0.102	n.d.	0.262	0.370	0.933	0.092	0.271	0.002	0.102	n.d.	0.051	0.006	0.361	0.003

Mean, standard deviation, minimum, maximum, number of samples, and linear (Pearson's), and nonparametric (Spearman's) correlations with distance from VMC smelter

n.d. not determined

Significant two-tailed correlations are marked with ** ($p < 0.01$) or * ($p < 0.05$)

** Correlation is significant at the 0.01 level (two-tailed)

* Correlation is significant at the 0.05 level (two-tailed)

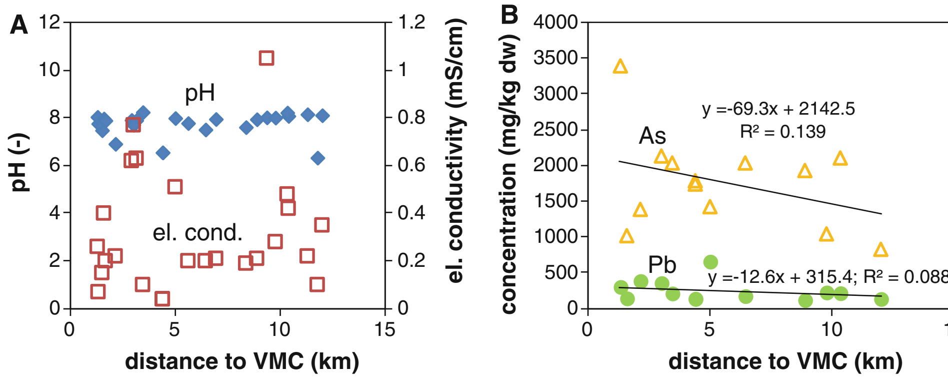

Fig. 3 **a** soil pH (*filled rhombi*) and electrical conductivity (*open squares*), **b** soil As (*open triangles*) and Pb (*filled circles*) in mg/kg dry weight

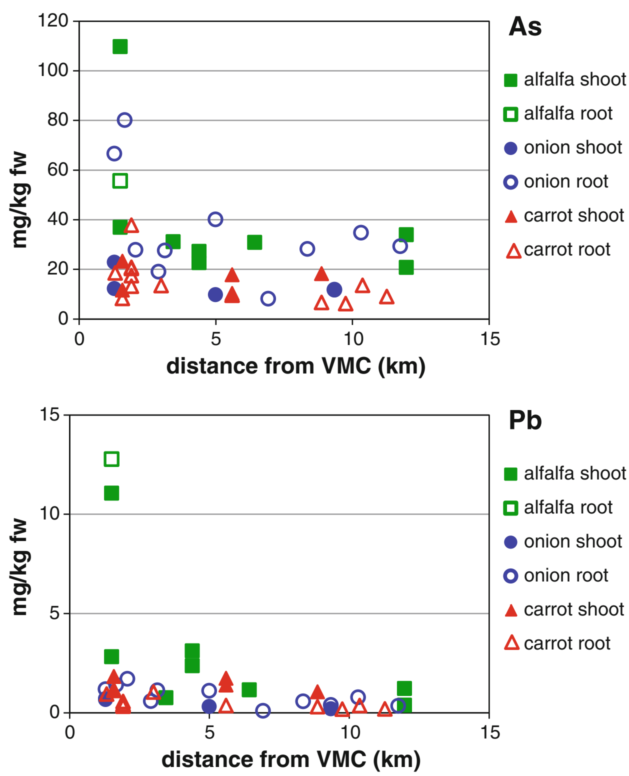

Fig. 4 Concentrations of As (*above*) and Pb (*below*) in all analyzed crop samples, separated into shoot (*open symbols*) and root (*filled symbols*) fraction, and according to distance from VMC smelter

contaminants to the aerial parts of the plant. The same is observed for alfalfa ($TI_{As} = 70.3$ %, $TI_{Pb} = 22.4$ %), but as only one root sample was analyzed, no robust conclusions can be drawn in this case. In carrot, the mean As and Pb concentrations in the root are lower than in the shoots ($TI_{As} = 108.6$ %, $TI_{Pb} = 281.4$ %), indicating that carrot tends to accumulate contaminants, particularly Pb, in the non-edible parts.

As and Pb crop concentrations show no clear trends when plotted against soil pH or electrical conductivity (not shown).

Regarding spatial correlations, the concentrations of As and Pb in the shoot and root fractions of the crops appear to increase toward VMC (Fig. 4). However, statistical analysis (Pearson's and Spearman's correlation coefficients) shows that for As concentrations, these trends are not statistically significant, neither separated by crop fractions nor considering all crop As values together (Table 3). Actually, most samples along the entire range of distances show a similar spread of As concentrations between 6 and 40 mg/kg fw, while the only samples with As >50 mg/kg fw are observed at less than 1.7 km distance from VMC. This suggests that VMC may have an impact on crop As very close to the smelter, while most crop As in the area may be from geogenic origin as hypothesized above.

It could be argued that predominant wind directions could influence the deposition pattern of contaminants around VMC. We have analyzed data from Oruro airport meteorological station (SYNOP data obtained from http://www.mundomanz.com, accessed on 13/03/2013), and the dataset for 2011–2012 (2 years) shows that during 49 % of the time, there is no wind, and wind blows during 16 % of time from the North, 13 % from the East, 12 % from the South, and 10 % from the West. So, during half of the time, deposition of emissions is expected to occur rather evenly around VMC, and in windy periods, even though there is a slight predominance of Northern winds, the fields sampled to the North and East of VMC potentially receive almost equal shares of the emissions from VMC.

For Pb, the picture is different, and Pearson's linear correlation coefficients are significant at the 0.05 level for onion shoots, onion root, and carrot root with respect to distance from VMC (Table 3); taking all crop samples together the significance is only slightly off the 0.05 limit ($p = 0.053$). Spearman's rank correlation coefficient with vicinity to VMC is highly significant (0.01 level) for Pb in all crop samples, in onion root, and carrot root. In onion shoots, the significance is slightly off the 0.05 limit ($p = 0.051$). These trends indicate that VMC contributes a significant portion of crop Pb concentrations in the area.

Table 4 Transfer factors to the edible fraction (TF), daily intake (DI), and estimated daily exposure (EDE) for As and Pb in the three studied crops

Parameter	Unit	Onion root	Carrot root	Alfalfa shoots
As TF	(–)	0.022 ± 0.008	0.0059 ± 0.0017	0.021 ± 0.011
Pb TF	(–)	0.0027 ± 0.0014	0.0035 ± 0.0027	0.010 ± 0.008
As DI (human)	(mg/day)	11.72 ± 7.51	5.15 ± 2.93	
Pb DI (human)	(mg/day)	0.29 ± 0.17	0.18 ± 0.11	
As EDE (human)	(mg/kg·day)	0.20 ± 0.13	0.086 ± 0.049	
Pb EDE (human)	(mg/kg·day)	0.0049 ± 0.0029	0.0029 ± 0.0018	
As HRI (human)	(–)	651.3 ± 417.5	286.4 ± 162.8	
As DI (cow)	(mg/day)			391.6 ± 290.1
Pb DI (cow)	(mg/day)			28.7 ± 34.6
As EDE (cow)	(mg/kg·day)			0.78 ± 0.58
Pb EDE (cow)	(mg/kg·day)			0.057 ± 0.069

For onion and carrot, a human consumption of 345 g crop per 65 kg body mass was assumed; for alfalfa, we supposed an uptake of 10 kg per day for a cow of 500 kg body mass. Mean values ± standard deviation are given

Soil–plant transfer factors, daily intake, estimated daily exposure, and health risks in edible crop fractions

In onion, the mean arsenic transfer factor to the edible fraction (root) is 0.022 (Table 4), similar to the mean observed at other sites (Table 1). The lead transfer factor to onion root is 0.003, an order of magnitude lower than the mean from our review (Table 2), but still well within the range observed at other sites (0.0001–0.38). In carrot root, the As transfer factor is considerably lower than in onion, while the Pb transfer factors are quite similar in both crops.

The average human daily intake from onion root is 11.7 mg/day As and 0.3 mg/kg Pb; the estimated daily exposure (EDE) is 0.20 mg As and 0.005 mg Pb per kg body weight per day. The resulting As HRI is 651, indicating a very high potential risk, higher than at any of the reviewed sites (Table 1). The daily intake from carrot root is 5.2 mg/day As and 0.2 mg/day Pb; the EDE is 0.09 mg As/(kg·day) and 0.003 mg Pb/(kg·day). The As HRI from carrot is lower than from onion, but still severely high (286).

The average human daily As intake from onion or carrot roots near VMC is near or above the maximum quantities found at the other reviewed contaminated sites. The mean daily human Pb intake is below the average from the review, but still Pb levels in all analyzed crops were above WHO/FAO limits. As Pb accumulates in the body, any intake of lead is considered detrimental to human health, and the consumption of contaminated vegetables from Vinto should be avoided.

In alfalfa, given that it is used for cattle feeding, we calculated the daily As and Pb intake for a cow of 500 kg body mass assuming a consumption of 10 kg/day. Accordingly, the daily intake from alfalfa shoots is 392 mg/day As and 29 mg/day Pb, the EDE is 0.78 mg/(kg·day) for As and 0.057 mg/(kg·day) for Pb. The EDE for As and Pb from alfalfa shoots is about four to twenty times higher than from onion or carrot root, because concentrations in alfalfa are higher, and the daily crop consumption relative to body weight in humans is 0.6 %, while in cows, it is assumed 2 %.

Implications of the findings

Due to the extreme As values and elevated Pb levels, none of the investigated agricultural products should be used for either human or animal consumption. An information and education campaign should be carried out within the contaminated areas and where the contaminated products are consumed, in order to increase consciousness in the population on the effects of arsenic and heavy metals in the human organism. It should be recommended to only consume products from uncontaminated areas. Detailed soil sampling campaigns should be carried out in the region in order to determine whether all fields in the region are contaminated or whether some are suitable for crop farming.

Regarding the farmers working in the contaminated areas, it would be advisable to switch production to species that are not used for food or forage, for example, flowers and ornamental plants, energy crops, fiber plants, aromatic plants for essential oil production or perhaps trees for construction wood (Puschenreiter et al. 2005, and references therein). However, such a fundamental change is not easily implemented.

Regarding the VMC smelter, appropriate steps should be taken by the authorities and the company to reduce the toxic emissions from the complex as soon as possible. Despite high geogenic metal/loid background values in soils in the area, any additional emissions are harmful to the population and the environment. Currently, a new smelter with state-of-the-art technology is being built in Vinto. If the production capacity is moved toward the new smelter, contaminant emissions may be reduced, but if the new facilities only increase production and the old smelters continue to operate at current capacity, contamination will not decrease.

Conclusion

The present study is the first investigation on As and Pb concentrations in crops in Vinto area. It shows that agricultural products (alfalfa, onions, and carrots) are severely contaminated by As and Pb in the studied region up to a distance of 12 km from the smelter "Vinto Metallurgical Complex" (Bolivia). Not a single crop sample, even in the long distance, was below the FAO/WHO, UK, or Chilean reference concentrations for As or Pb. For arsenic, the HRI of onion is 651 and that of carrot is 286. These figures show that the potential health risk due to consumption of these products is extremely high and that none of the studies crops should be consumed.

Arsenic and lead soil and crop concentrations showed increasing trends toward VMC. Pb concentrations displayed significant Pearson's and Spearman's correlations with distance to VMC for onion root and carrot root, and significant Spearman's correlations for all crop Pb concentrations together, suggesting that VMC has a significant impact on crop Pb levels close to the smelter. However, correlations for As were not statistically significant in soils or crops, possibly due to considerable geogenic contributions to soil As in the area.

In future surveys, larger numbers of soil and crop samples should be analyzed to study the spatial contaminant distributions in more detail, and additional analyses (e.g. more elements, As speciation, mineralogy, soil organic matter, isotopes, or sequential extractions) should be carried out to elucidate the anthropogenic and geogenic contributions to the very high observed As and Pb levels in soils and crops in the area.

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