

Assessment of potential health risk for inhabitants living near a former lead smelter. Part 1: metal concentrations in soils, agricultural crops, and homegrown vegetables

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Abstract Soil contamination by metals engenders important environmental and health problems in northern France where a smelter (Metaleurop Nord) was in activity for more than a century. This study aims to look at the long-term effects of the smelter after its closedown by combining data on the degree of soil contamination and the quality of the crops grown (agricultural crops and homegrown vegetables) in these soils for a better

assessment of the local population's exposure to Cd, Pb, and Zn. Seven years after the Metaleurop Nord close-down, (1) the agricultural and urban topsoils were strongly contaminated by Cd, Pb, and Zn; (2) the kitchen garden topsoils were even more polluted than the agricultural soils, with great variability in metal concentrations within the gardens studied; (3) a high proportion of the agricultural crops for foodstuffs did not conform with the European legislation; (4) for feedstuffs, most samples did not exceed the Cd and Pb legislation limits, indicating that feedstuffs may be an opportunity for most agricultural produce; and (5) a high proportion of the vegetables produced in the kitchen gardens did not conform with the European foodstuff legislation. The high contamination level of the soils studied continues to be a risk for the environment and the population's health. A further investigation (part 2) assesses the associated potential health risk for local inhabitants through consumption of homegrown vegetables and ingestion of soil particles by estimating the site-specific human health assessment criteria for Cd and Pb.

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Introduction

Mining and smelting activities are the main sources of metals in the environment, which can result in

considerable soil contamination. The accumulation of metals in soils can have adverse effects on environmental health, crop growth, and food quality and is of great concern because of the potential health risk to the local inhabitants if directly ingested or transferred through food (Alam et al. 2003; Bermudez et al. 2011; Finster et al. 2004; Hough et al. 2004; Wang et al. 2005). The consumption of crops produced in contaminated soils, as well as ingestion or inhalation of contaminated soil particles, are the main pathways of human exposure to metals. Cultivation of crops on contaminated soils can potentially lead to the accumulation of metals in the edible plant parts with detrimental effects on soil ecosystems resulting in a risk to human and animal health (Cui et al. 2004; Hough et al. 2004; McBride 2007; Moolenaar and Lexmond 1999; Nabulo et al. 2010; Wang et al. 2005). Cd exposure may pose adverse health effects, including kidney dysfunction, and skeletal disorders, and may also affect bones and result in fractures (Jarup 2003). Long-term exposure to Pb may cause neurological disorders such as memory deterioration, prolonged reaction times, and reduced cognitive ability (Jarup 2003; Oliver 1997). Although Zn is an essential element, its excessive concentration in food plants is of great concern because of its toxicity to humans (Kabata-Pendias and Mukherjee 2007).

Soil quality is a major concern in the North of France, especially in the former mining areas, due to the past industrial context and the strong demographic pressure. For more than a century up to 2003, Metaleurop Nord, the main European lead smelter situated in Noyelles-Godault, generated significant quantities of dust (Frangi and Richard 1997; Godin et al. 1985; Sterckeman et al. 2000, 2002). The emissions generated by this smelter have led to substantial contamination of the surrounding soils. The pollutants were mainly Cd, Pb, and Zn but also to a lesser degree As, Hg, Sb, and In (Sterckeman et al. 2000, 2002). The epidemiological studies carried out during the industrial activity showed that 10–15 % of children (2–4 years old) living near the smelter had blood Pb levels higher than $100 \mu\text{g Pb L}^{-1}$ (elevated blood Pb level defined by the Centers for Disease Control and Prevention). This reached 30 % in the town situated close to the smelter and under the prevailing winds (Leroyer et al. 2000; 2001).

In 1999, a General Interest Project (GIP) was set up following a request from the authorities based on the

Pb and Cd concentrations in topsoils: the first zone with soil concentrations over $1,000 \text{ mg of Pb kg}^{-1}$ and $20 \text{ mg of Cd kg}^{-1}$ of soil and the second zone within the range of $500\text{--}1,000 \text{ mg of Pb kg}^{-1}$ of soil. Soils with a concentration below $500 \text{ mg of Pb kg}^{-1}$ were not included in the GIP. For any land use, the GIP defined very strict recommendations on how to manage the contaminated land. The GIP planned to exclude the most heavily contaminated fields ($>500 \text{ mg of Pb kg}^{-1}$ of soil) from agricultural production and to stabilize the soil by herbaceous and planted tree coverage. As for homegrown vegetables, however, no ban has been imposed on their production and consumption.

Economic problems closed Metaleurop Nord in 2003, leaving behind a large area of spoiled agricultural and urban soils but also a serious socioeconomic crisis. Since the closedown and the industrial site renovation, dust emissions have entirely ceased. However, the environmental and health problems induced by high contamination of the area remained worrisome, especially the urban soils, which exceeded metal concentrations of agricultural soils located in a similar environmental context (Douay et al. 2008a; Sterckeman et al. 2002). This is explained by gardeners who add various contaminated materials to their garden soils (smelter slag, water collected from dusty roofs, etc.). Various studies have shown that vegetables grown in kitchen gardens close to Metaleurop Nord, both before and just after closing, frequently exceeded the European legislation limits for Cd and Pb concentrations (Douay et al. 2008b, c; Pruvot et al. 2006).

In 2010, the authorities decided to conduct a new study in order to verify the relevance of the measures defined within the GIP. The topsoils, agricultural crops, and homegrown vegetables were sampled in a large area around the former smelter. This work aims to look at the long-term effects of the Metaleurop Nord closedown by combining data on the degree of soil contamination and the quality of the crops grown in these soils for a better assessment of the population's exposure to metals. The present study focuses on the quality of soils and was conducted on both agricultural and urban lands as follows: (1) evaluation of the degree of soil contamination by Cd, Pb, and Zn in agricultural fields and kitchen gardens and (2) determination of the metal concentrations of agricultural crops and vegetables. In addition, the crops' metal concentrations were examined with regard to the European legislation maximum levels for foodstuffs and feedstuffs. Part 2 of this study, which will

appear in a separate publication (Pelfrène et al. 2012), will be devoted to assessing the potential health risk associated with local inhabitants through consumption of homegrown vegetables and ingestion of soil particles by estimating site-specific Cd and Pb criteria for human health assessment.

Materials and methods

Sampling sites

Ninety-one sampling sites were selected in the vicinity of the former Metaleurop Nord smelter (50°25'41.08" N and 3°00'53.08" E), including 57 agricultural fields (named AF-1 to AF-57) and 34 kitchen gardens (named KG-1 to KG-34), in order to consider various environmental contexts (Fig. 1). These sites extended over the zone that was highly affected in the past by smelter dust emissions (approximately 30 km²). The distance of the sampling sites varied from 0.7 to 3.3 km from the former large smokestack (main dust emissions) of the smelter. Soils around the former Metaleurop Nord smelter originate from loessic materials and occasionally have developed from alluvial deposits (Sterckeman et al. 2000, 2006). The surface layers of the soils studied showed mainly a loamy texture that was sometimes carbonated and where the clay and more particularly the sand contents vary considerably (Sterckeman et al. 2000).

The sampled agricultural sites were selected based on knowledge on the expected spread of Pb and Cd contamination of this area and on agricultural land management (Sterckeman et al. 2000, 2002). The studied crops included wheat (grain and straw; *Triticum aestivum* L.), barley (grain and straw; *Hordeum vulgare* L.), maize (grain and forage; *Zea mays* L.), horse bean (*Vicia faba* L.), potato (*Solanum tuberosum* L.), and sugar beet (*Beta vulgaris* L.). At each sampling site, paired soil (0–25 cm deep) and plant samples were collected. Twelve random soil samples on each plot were taken and bulked together as one composite sample ($n=57$).

For the kitchen gardens, few data are available on management practices. In the studied area, aerial photos identified approximately 310 kitchen gardens adjoining houses. These gardens were selected based on their location, exposure, and the gardener's willingness to participate in the study. A total of 45 gardeners participated in our door-to-door survey and

different approaches were undertaken: (1) a questionnaire was administered in the studied area in April–May 2010 to determine gardeners' practices; (2) at least one soil profile (up to 120 cm) was carried out with a hand auger for each garden to determine heterogeneity, complexity, presence, and relative importance of anthropogenic material, etc.; (3) the average contamination level of the topsoil (0–25 cm deep) was assessed with one composite sample comprising at least 20 subsamples for each garden. A total of 34 completed questionnaires were usable. The data recorded included the garden's characteristics (age, surface area, gardening practices, etc.), the vegetables grown, the age and gender of the gardener, and the number of family members in the household. From the questionnaire, the main vegetables produced and selected for study were radish (*Raphanus sativus* L.), lettuce (*Lactuca sativa* L.), French bean (*Phaseolus vulgaris* L.), carrot (*Daucus carota* L.), leek (*Allium porrum* L.), tomato (*Solanum lycopersicum* L.), and potato (*S. tuberosum* L.). The gardeners received the same vegetable cultivars (seeds and seedlings) in order to reduce variability in metal accumulation within species and grew all the vegetables themselves. We sampled the vegetables at their consumption stages, taking care to obtain a representative sample (of the vegetable) and sufficient dried matter for the analyses. At each sampling plot, paired soil (0–25 cm deep) and vegetable samples were collected. From three to seven random soil samples on each plot were taken and bulked together as one composite sample. Because of gardening crop failures, certain vegetables were missing in some kitchen gardens. So a total of 207 samples of vegetables and corresponding soil samples were collected from the kitchen gardens and packed into polyethylene bags.

Because urban soils such as kitchen garden soils can be highly disturbed by human activities, at least one soil profile was carried out for each garden studied to describe and characterize them. The kitchen gardens (1–150 years old) were situated in a highly urbanized area, adjoining houses. In most cases, the garden soils were developed on composite materials and showed signs of disturbance as deep as 60 cm, with the presence of coarse elements, slags, fragments of brick, coal ashes, and various other materials. From the questionnaire, most gardeners (>70 %) affirmed that large amounts of chemical fertilizers and/or herbicides were applied to their gardens over a long period.

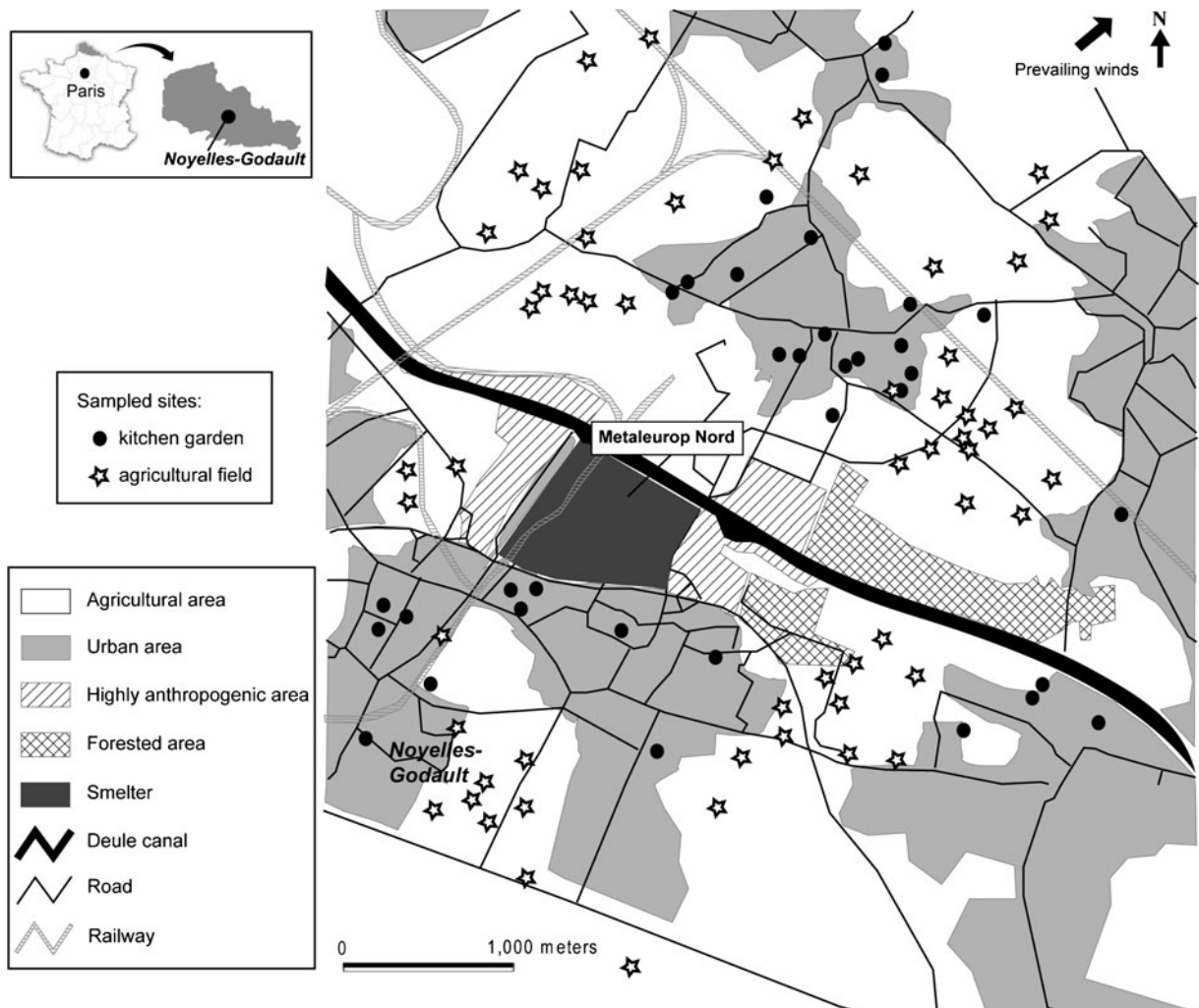


Fig. 1 Location of the sampled sites in northern France

Moreover, in past times, most gardeners added exogenous materials to the soil to improve its permeability and facilitate cropping practices.

Sample preparation and analysis

The soil samples, collected in agricultural fields and kitchen gardens, were prepared according to the NF ISO 11464 standard. Samples were oven-dried at 40 °C and crushed to pass through a 2-mm stainless steel sieve. For each soil sample, a representative subsample was obtained with an automatic sieve using an ultracentrifugal mill less than 250 μm (Retsch type ZM 200, Germany) for total dissolution analysis. Calcination at 450 °C and a mixture of hydrofluoric and

perchloric acids, as described by the NF X 31–147 standard, were used for total dissolution of Cd, Pb, and Zn.

Parts of the plant not for consumption or those that were damaged were removed. Similar to agricultural and food-industry practices, the grain (wheat, barley, maize, and horse bean), straw (wheat and barley), and foraged maize were not washed. The sugar beets were meticulously brushed under a trickle of tap water. The other vegetable samples were prepared as a careful consumer would prepare them to eat, with the elimination of the inedible parts and meticulous cleaning in three successive washings of tap water. All precautions were taken to avoid possible

contamination. All samples were then cut into small pieces to obtain a representative sample, packed in a polypropylene sachet, kept cool, and transmitted as soon as possible to the laboratory where there were freeze-dried. They were crushed with a cutting mill in tungsten carbide with a 0.5-mm grid. A representative part was then digested with concentrated nitric acid and hydrogen peroxide using a closed microwave.

The concentrations of metals in soils and vegetables were quantified by the INRA Soil Analysis Laboratory (Arras, France) accredited by COFRAC according to the ISO 17025 standard. The Zn and high concentrations of Cd and Pb were measured by inductively coupled plasma atomic emission spectrometry (ICPOES, Vista Pro, Varian, France). The low concentrations of Cd and Pb were determined by inductively coupled plasma mass spectrometry (ICPMS, Série X2, Thermo, France).

Data analysis

Soil metal concentrations were expressed in milligrams per kilogram of dry weight and were compared with regional references (Sterckeman et al. 2002; Douay et al. 2009).

Crop metal concentrations expressed in milligrams per kilogram of dry weight were used to study the crop/soil behavior, i.e., to calculate the transfer factor (TF) defined as the ratio of metal concentration in the plant to the total metal concentration in soil (Cui et al. 2004; Kachenko and Singh 2006). The ones expressed in milligrams per kilogram of fresh weight were used to evaluate the inhabitants' exposure and were compared with the legislation limits (European Directive of 19 December 2006 for human consumption and French Decree of 12 January 2001 for animal consumption). These legislative limits define the maximum permissible concentrations in foods for human and animal consumption (European Commission 2006). These limit values were expressed on a 15 % humidity basis for foodstuffs and a humidity content of 12 % was considered for feedstuffs.

The data were statistically analyzed using XLSTAT 2011.3.01 (Addinsoft). The measures were expressed in terms of medians and/or means with standard deviations.

Results and discussion

Metal concentrations in agricultural and kitchen garden soils

Table 1 presents the total metal concentrations of the organo-mineral horizon in the agricultural and kitchen garden soils studied. In agricultural topsoils, the results showed a wide range of concentrations, which varied for Cd from 2.3 to 15.4 mg kg⁻¹, for Pb from 108 to 828 mg kg⁻¹, and for Zn from 193 to 1,052 mg kg⁻¹. The kitchen garden topsoils were more polluted than the agricultural soils and metal concentrations varied for Cd from 2.8 to 21.1 mg kg⁻¹, for Pb from 190 to 1,425 mg kg⁻¹, and for Zn from 199 to 2,429 mg kg⁻¹. This was explained by the soil uses, the past or present anthropogenic activities (removal and deposition of various contaminated materials, gardening practices, atmospheric fallout linked to circulating traffic, urban heating, and industrial activities), the corrosion of building materials, etc. The metal concentrations in soils were compared with the regional agricultural values; not enough data were available for the contamination degree of the regional urban soils. The comparison confirmed their high level of contamination. For the agricultural soils, the mean Cd, Pb, and Zn concentrations were 13-, 9-, and 6-fold, respectively, greater than the regional agricultural values. This difference was also considerable for the kitchen garden soils. Thus, the mean Cd, Pb, and Zn concentrations in kitchen garden soils were 21-, 16-, and 11-fold, respectively, more contaminated than regional soils. The degree of contamination appeared to be related to the use of the studied soils.

With the kitchen gardens, two types of soil sampling were carried out per garden: (1) one composite soil sample to provide an estimate of average soil concentration (Tables 1 and 2) and (2) several composite soil samples collected in each homegrown vegetable sample to determine the ranges of metal levels in each kitchen garden (Table 2). The metal concentrations among the 34 kitchen gardens varied greatly, independently of the smelter's distance. For example, the concentrations of Cd, Pb, and Zn in KG-15 soil averaged 3.0, 180, and 214 mg kg⁻¹, respectively, while those in KG-13 soil averaged 13.4, 1,669, and 2,679 mg kg⁻¹, respectively (or 4, 9, and 12 times as much, respectively). The particularly high spatial variability in concentrations observed between the 34

Table 1 Median, mean, and standard deviation (SD) values for total Cd, Pb, and Zn concentrations in the topsoils studied and in regional agricultural topsoils

	Contaminated area						Regional values		
	Agricultural fields ($n=57$)			Kitchen gardens ($n=34$)			Agricultural fields ^a ($n=232$)		
	Median	Mean	SD	Median	Mean	SD	Median	Mean	SD
Cd	4.9	5.2	2.0	7.4	8.3	4.2	0.4	0.4	0.2
Pb	254	277	110	464	526	317	29	32	17
Zn	364	377	133	621	749	461	67	68	25

Results are expressed in milligrams per kilogram of dry weight

^aFrom Sterckeman et al. (2002)

kitchen gardens can be explained by the anthropogenic soil modifications resulting from residential activities, confirming the absence of a nonlinear relationship between metal concentrations and the distance to the smelter (as reported by Douay et al. 2008a, b). Variations of metal concentrations within each garden were represented by the 3- to 7-fold range and relative standard deviation (RSD) (Table 2). Concentrations of Cd, Pb, and Zn showed relatively low variability with RSD less than 10 % within 15, 18, and 16 kitchen gardens, respectively. However, many soils (19, 16, and 18 kitchen gardens for Cd, Pb, and Zn, respectively) displayed large variations of metal concentrations (RSD>10%). For example, KG-16 showed variations for Cd from 5.3 to 8.6 mg kg⁻¹ with a RSD of 23.1 %; KG-18 provided evidence of variations for Pb from 387 to 1,484 mg kg⁻¹ with a RSD of 60.2 %; and KG-13 showed variations for Zn from 1,864 to 3,591 mg kg⁻¹ with a RSD of 26.1 %. The high RSD recorded in these kitchen gardens was consistent with soils having undergone considerable disturbance. This specific enrichment is often combined with a high heterogeneity and variability of the physicochemical parameters of soils. This can be caused by different reasons like the input of contaminated materials, especially slag resulting from the combustion of coal and used to improve soil drainage, the various industrial activities, the utilization of pesticides, the watering of vegetables with rainwater collected on dusty roofs, but also by the dust emission due to motor vehicle traffic (Finster et al. 2004). Few studies have examined the spatial variability of metal concentrations within residential soils and showed that greater numbers of samples may be required due to

disturbances of soil and contaminant concentrations resulting from residential activities (Arrouays et al. 1996; Machemer and Hosick 2004). For each garden, the comparison of average soil metal concentrations (obtained from one composite soil sample taking into account the entire garden) with the range of values (obtained from several composite soil samples collected at each vegetable sampling) often provided evidence of high spatial variability in surface soil metal contamination. As reported by Arrouays et al. (1996), this spatial variability is too great to determine a mean value with a high level of confidence and could have important implications for assessment of local inhabitants' exposure to these metals.

Agricultural crops and homegrown vegetables

Metal concentrations in agricultural crops and homegrown vegetables

Tables 3 and 4 present the mean values and the standard deviations of Cd, Pb, and Zn concentrations measured in agricultural crops and homegrown vegetables (in fresh weight). For the agricultural crops, the results showed that: (1) the highest concentrations of Cd were measured in wheat straw and foraged maize, and, to a lesser extent, in wheat grain, horse bean, barley straw, and sugar beet, while the lowest concentrations were recorded in barley and maize grains as well as potato; (2) the Pb concentrations were under the detection limit in most cases, except in wheat and barley straw, foraged maize and sugar beet; and (3) the highest concentrations of Zn were found in horse bean and foraged maize, while the lowest concentrations

Table 2 Total Cd, Pb, and Zn concentrations (minimum, maximum, mean, standard deviation (SD) and relative standard deviation values) in the topsoils of the 34 kitchen gardens (KG)

		Range of metal concentrations at each vegetable														
		Cd			Pb			Zn								
		Min (mg kg ⁻¹)	Max (mg kg ⁻¹)	Mean (mg kg ⁻¹)	SD (mg kg ⁻¹)	%	Min (mg kg ⁻¹)	Max (mg kg ⁻¹)	Mean (mg kg ⁻¹)	SD (mg kg ⁻¹)	%	Min (mg kg ⁻¹)	Max (mg kg ⁻¹)	Mean (mg kg ⁻¹)	SD (mg kg ⁻¹)	%
KG-1	7.1	6.4	7.3	6.8	0.3	4.9	4.10	5.39	4.71	3.8	8.2	5.34	7.82	6.48	7.8	12.0
KG-2	8.9	8.2	9.0	8.5	0.3	3.0	5.52	6.24	5.85	2.5	4.3	6.86	9.80	8.63	9.5	11.0
KG-3	6.3	5.8	7.2	6.6	0.5	7.1	3.61	4.26	3.87	2.3	6.0	5.38	6.25	5.93	2.8	4.7
KG-4	5.1	3.8	5.8	5.0	0.7	13.9	2.91	4.18	3.53	4.6	13.0	3.89	5.41	4.72	5.9	12.4
KG-5	6.1	3.63	7.5	6.2	0.8	13.7	3.43	4.32	3.81	3.3	8.7	4.12	5.07	4.50	3.6	8.0
KG-6	3.8	3.6	4.0	3.8	0.2	4.2	2.17	2.36	2.25	7	3.3	3.51	3.92	3.78	1.4	3.7
KG-7	12.6	11.2	14.3	12.5	1.3	10.4	8.15	9.42	8.81	5.5	6.2	9.28	1.103	1.036	8.2	7.9
KG-8	7.7	5.8	7.9	7.3	0.8	10.8	3.74	6.62	4.66	10.5	22.4	4.70	7.68	6.60	12.3	18.6
KG-9	7.7	6.4	7.2	6.8	0.3	4.6	3.84	5.49	4.24	6.3	14.9	5.39	6.43	5.82	3.9	6.7
KG-10	7.7	7.3	8.6	8.0	0.4	5.1	4.56	5.11	4.80	2.0	4.2	5.30	6.19	5.66	3.0	5.2
KG-11	14.7	14.1	16.1	15.0	0.8	5.6	9.77	1.145	1.064	6.9	6.5	1.270	1.442	1.347	6.9	5.1
KG-12	10.3	5.98	11.7	10.7	1.7	15.7	4.91	7.25	6.75	8.2	12.2	7.33	1.160	8.51	1.50	17.6
KG-13	12.6	12.0	14.4	13.4	0.9	7.0	1.314	2.040	1.669	3.02	18.1	1.834	3.591	2.679	6.98	26.1
KG-14	4.3	3.6	4.7	4.1	0.5	12.0	2.71	3.36	3.00	2.7	9.1	4.07	6.06	4.79	7.7	16.2
KG-15	2.8	2.8	3.3	3.0	0.2	6.8	1.74	1.93	1.80	7	4.0	1.97	2.33	2.14	1.4	6.7
KG-16	7.3	5.3	8.6	6.8	1.6	23.1	3.88	5.30	4.53	6.7	14.8	6.86	8.61	7.79	9.2	11.8
KG-17	12.7	10.5	16.9	14.0	2.3	16.4	7.61	1.048	8.67	1.19	13.8	7.76	1.183	9.86	1.46	14.8
KG-18	10.5	5.33	10.8	9.0	1.3	14.2	3.87	1.484	6.34	3.81	60.2	4.94	7.82	6.31	1.16	18.5
KG-19	21.1	15.7	23.1	19.7	2.9	14.8	1.109	2.145	1.458	3.57	24.5	1.602	2.584	2.009	3.12	15.5
KG-20	19.3	18.5	20.6	19.1	0.8	4.1	1.092	1.238	1.174	5.2	4.4	1.473	1.784	1.614	1.15	7.1
KG-21	10.6	11.3	15.0	13.3	1.6	12.1	6.36	9.24	7.87	1.16	14.8	8.83	1.179	1.041	1.34	12.9
KG-22	3.9	3.5	4.4	3.9	0.4	9.5	1.61	2.12	1.93	2.0	10.3	3.03	3.94	3.53	3.3	9.4
KG-23	7.5	5.1	7.7	7.0	0.9	12.8	4.43	5.53	4.90	3.3	6.8	4.09	7.19	5.70	9.5	16.7
KG-24	4.6	4.2	5.7	4.8	0.5	10.3	2.13	2.60	2.39	1.5	6.4	3.29	3.99	3.59	2.5	7.1
KG-25	7.5	6.3	9.8	7.5	1.2	16.0	4.00	6.27	4.77	7.8	16.4	5.47	7.07	5.95	5.9	9.9
KG-26	6.5	6.7	8.1	7.2	0.8	11.4	3.98	4.65	4.23	3.6	8.6	4.61	5.12	4.78	3.0	6.2
KG-27	5.7	5.2	5.8	5.5	0.2	4.4	3.13	3.65	3.39	2.3	6.7	4.20	5.35	4.70	5.2	11.0
KG-28	4.4	2.4	4.9	3.8	1.0	26.7	1.48	2.33	1.96	4.0	20.6	1.90	3.22	2.70	6.0	22.1
KG-29	4.6	4.2	4.9	4.6	0.3	5.5	2.35	2.68	2.55	1.1	4.3	4.26	4.87	4.59	1.9	4.2
KG-30	6.8	6.7	7.9	7.3	0.4	5.9	2.75	2.94	2.85	7	2.6	5.81	6.30	6.00	1.7	2.8
KG-31	6.4	5.9	8.8	7.5	1.0	13.0	5.34	1.358	7.97	2.87	36.0	1.105	1.807	1.530	2.44	15.9
KG-32	8.4	5.07	6.86	12.7	1.6	14.7	4.98	8.50	7.07	1.43	20.2	6.94	1.165	8.43	1.90	22.5
KG-33	4.8	4.5	5.0	4.8	0.2	3.3	2.54	2.75	2.63	9	3.4	5.70	6.49	6.25	2.6	4.2
KG-34	10.8	9.4	12.8	11.1	1.4	13.0	5.61	7.96	6.95	1.20	17.2	6.72	1.077	9.08	2.04	22.5

Table 3 Cd, Pb, and Zn concentrations in the agricultural crops with regard to the legal values (European Directive of 19 December 2006 for human consumption and French Decree of 12

January 2001 for animal consumption) and the noncompliance ratio (the number of samples not in compliance with the legislation compared with the total sample number)

	Cd		Pb		Zn		Legislation limits		Noncompliance ratio
	Mean	SD	Mean	SD	Mean	SD	Cd	Pb	
Human consumption (mg kg ⁻¹ FW)									
Wheat grain	0.33	0.16	<0.19	–	35.0	6.8	0.2	0.2	13/18
Barley grain	0.16	0.07	<0.19	–	43.4	6.0	0.1	0.2	5/7
Maize grain	0.04	0.04	<0.19	–	20.7	2.2	0.1	0.2	1/10
Horse bean	0.35	0.13	<0.19	–	62.8	7.7	0.1	0.2	7/7
Potato	0.09	0.04	<0.19	–	16.1	2.9	0.1	0.1	2/4
Sugar beet	0.31	0.16	0.28	0.16	33.0	13.7	0.1	0.1	11/11
Animal consumption (mg kg ⁻¹ FW)									
Wheat grain	0.34	0.16	<0.19	–	36.2	7.0	1.0	10	0/18
Wheat straw	0.80	0.39	0.86	0.50	22.7	11.2	1.0	10	5/18
Barley grain	0.17	0.07	<0.19	–	44.9	6.3	1.0	10	0/7
Barley straw	0.34	0.16	0.66	0.30	40.0	14.0	1.0	10	0/7
Maize grain	0.05	0.04	<0.19	–	21.4	2.3	1.0	10	0/10
Foraged maize	0.85	0.72	0.87	0.45	62.4	25.9	1.0	10	4/10
Horse bean	0.36	0.14	<0.19	–	65.0	8.0	1.0	10	0/7
(mg kg ⁻¹ DW)									
Wheat grain	0.39	0.18	<0.22	–	41.1	7.9			
Wheat straw	0.91	0.44	0.98	0.57	25.8	12.7			
Barley grain	0.19	0.08	0.24	–	51.1	7.1			
Barley straw	0.39	0.18	0.75	0.34	45.5	15.9			
Maize grain	0.05	0.05	<0.22	–	24.3	2.6			
Foraged maize	0.97	0.82	0.99	0.52	70.9	29.4			
Horse bean	0.41	0.16	<0.22	–	73.8	9.1			
Potato	0.41	0.14	<0.22	–	19.0	3.4			
Sugar beet	1.38	0.69	1.23	0.69	38.8	16.1			

Mean and standard deviation values are given in milligrams per kilogram of fresh weight (FW) and in milligrams per kilogram of dry weight (DW)

were measured in maize grain and potato (Table 3). Moreover, the ratio between straw (or foraged) and grain concentrations (for wheat, barley, and maize) was quite high for Cd and Pb. The storage organs seemed to be less metal-accumulating than the foliar system. Weber and Hrynczuk (2000) found that Cd and Pb concentrations in wheat grains were almost ten times lower than those found in straw, thus explaining the low uptake and the low translocation of Cd and Pb in the vegetative organs because of a lack of specific carriers (ion exchangers), which may in a significant way influence the percentage of these elements' accumulation in wheat grains. The concentrations of metals

in wheat grain ranged from 0.15 to 0.66 mg kg⁻¹ dry weight (DW) for Cd, from 29.8 to 60.0 mg kg⁻¹ (DW) for Zn, were <0.22 mg kg⁻¹ (DW) for Pb, and were substantially higher or comparable than the concentrations recorded by other authors: 0.006–0.043 mg kg⁻¹ for Cd, 0.022–0.269 mg kg⁻¹ for Pb, and 7.8–56.4 mg kg⁻¹ for Zn by Bermudez et al. (2011); 0.070 mg kg⁻¹ for Cd, 0.007 mg kg⁻¹ for Pb, and 24.0 mg kg⁻¹ for Zn by Kabata-Pendias and Mukherjee (2007); and 0.05–0.48 mg kg⁻¹ for Cd by Rafiq et al. (2006). In potato, the concentrations of metals ranged from 0.26 to 0.58 mg kg⁻¹ (DW) for Cd, from 15.9 to 22.1 mg kg⁻¹ (DW) for Zn, and were <0.22 mg kg⁻¹

Table 4 Cd, Pb, and Zn concentrations in the homegrown vegetables with regard to the legal values (European Directive of 19 December 2006 for Cd and Pb and Chinese Food Hygiene Standard for Zn) and noncompliance ratio (number of samples not in compliance with the legislation compared with the total sample number)

	Cd		Pb		Zn		Legislation limits			Noncompliance ratio
	Mean	SD	Mean	SD	Mean	SD	Cd	Pb	Zn	
(mg kg⁻¹ FW)										
Radish	0.12	0.08	0.15	0.09	6.43	3.27	0.1	0.1	20	23/34
Lettuce	0.39	0.39	0.15	0.16	5.94	4.70	0.2	0.3	20	22/33
French bean	0.01	0.01	0.06	0.05	4.39	1.73	0.05	0.1	20	3/32
Carrot	0.15	0.09	0.21	0.13	4.03	1.28	0.1	0.1	20	26/28
Potato	0.17	0.07	0.07	0.02	5.60	1.38	0.1	0.1	20	27/30
Leek	0.16	0.10	0.09	0.05	5.44	3.16	0.1	0.1	20	19/26
Tomato	0.04	0.02	0.04	0.06	1.38	0.37	0.05	0.1	20	7/24
(mg kg⁻¹ DW)										
Radish	2.49	1.36	3.19	1.98	136.0	72.0				
Lettuce	6.76	5.54	2.72	3.27	107.7	77.3				
French bean	0.13	0.08	0.59	0.65	41.7	8.8				
Carrot	1.53	0.96	2.14	1.41	40.5	13.6				
Potato	0.83	0.38	0.35	0.11	27.2	7.6				
Leek	2.16	1.72	1.14	0.61	72.6	56.6				
Tomato	0.73	0.31	0.81	1.23	26.8	7.4				

Mean and standard deviation values are given in milligrams per kilogram of fresh weight (FW) and milligrams per kilogram of dry weight (DW)

(DW) for Pb. For Cd, the concentrations were slightly lower or comparable to the concentrations recorded by others authors: 0.3–1.0 mg kg⁻¹ by Dudka et al. (1995), 0.15–3.88 mg kg⁻¹ by Dudka et al. (1996), and 0.24–1.12 mg kg⁻¹ by McLaughlin et al. (1997). However, these concentrations were substantially higher than those recorded by Srek et al. (2010) (0.02–0.07 mg kg⁻¹). For Pb, the concentrations were substantially lower than those recorded by other authors: 0.49–1.37 mg kg⁻¹ by Srek et al. (2010); 0.5–4.5 mg kg⁻¹ by Dudka et al. (1995); 0.2–15.4 mg kg⁻¹ by Dudka et al. (1996); and 3.19 mg kg⁻¹ by Antonious and Snyder (2007). For Zn, the concentrations were comparable with values published by Srek et al. (2010) (13.6–24.5 mg kg⁻¹).

For the homegrown vegetables, the results showed that: (1) the highest concentrations of Cd were obtained in lettuce, and, to a lesser extent, in leek, potato, carrot, and radish, while the lowest concentrations were measured in French bean and tomato; (2) carrot, radish and lettuce presented the highest Pb concentrations, while French bean, potato, leek and

tomato showed the lowest concentrations; and (3) the lowest concentrations of Zn were found in tomato (Table 4). The order of accumulation and the mean concentrations of metals measured in lettuce, carrot, and French bean were comparable with values published by Alexander et al. (2006). Compared with the values recorded by Voutsas et al. (1996), the concentrations of Cd, Pb, and Zn on carrot, leek, and lettuce were higher or comparable. For example, in the present study, the concentrations of metals in carrot varied from 0.45 to 3.97 mg kg⁻¹ for Cd, from 0.58 to 6.67 mg kg⁻¹ for Pb, and from 21.9 to 76.4 mg kg⁻¹ for Zn. In Voutsas et al. (1996), the values varied from 0.17 to 0.41 mg kg⁻¹ for Cd, from 0.08 to 0.71 mg kg⁻¹ for Pb, and from 11.9 to 113 mg kg⁻¹ for Zn. The results showed great variability in the concentrations depending on the species, the metal element, and the garden studied. Indeed, in the case of lettuce, tomato, and leek, the standard deviation values were very high, which was consistent with the high heterogeneity and variability of metal concentrations observed in some kitchen gardens. Moreover,

these results showed that the accumulation of metals in the plants vary according to the metal speciation, the vegetable species and the physicochemical parameters of the soils, as observed by other authors (Banat et al. 2005; Cobb et al. 2000).

Transfer of metal from soils to agricultural crops and homegrown vegetables

The TF was calculated as the ratio of the metal concentrations in the agricultural crops or homegrown vegetables (dry weight) to the metal concentrations in the topsoils (dry weight) (Fig. 2). The TF is an index that evaluates the transfer potential of a metal from soil to plant. A higher TF reflects relatively poor retention in soil or greater plant efficiency in absorbing a metal, and a low TF represents the strong sorption of a metal to the soil colloid (Alloways and Ayres 1997).

On average, the TFs of metal in agricultural crops were in the order $Zn=Cd>Pb$ and those in homegrown vegetables were in the order $Cd>Zn>Pb$. The TF order of metal in homegrown vegetables agreed with the results of previous studies (Khan et al. 2008; Liu et al. 2005; McBride 2003; Wang et al. 2006; Zhuang et

al. 2009). However, these TF orders differed somewhat depending on the plant species. The average TFs of Cd, Pb, and Zn were 0.118, 0.003, and 0.127, respectively, in agricultural crops, and 0.277, 0.003, and 0.104, respectively, in homegrown vegetables (Fig. 2). The average TF values for Cd and Zn were 39 and 42 times greater than for Pb, respectively, in agricultural crops, and 92 and 35 times greater than for Pb, respectively, in homegrown vegetables, indicating that it is much easier for Cd and Zn to transfer from soil to the edible parts of the plants. However, the very low TF values for Pb (<0.005 for agricultural crops and <0.007 for homegrown vegetables) were comparable to the values recorded by Wang et al. (2006) and show that it is much more difficult for Pb to transfer from soil to the edible parts of the plants.

The results showed that TF values for Cd and Zn for agricultural crops and homegrown vegetables varied greatly between plant species and sites (field or garden). For agricultural crops: (1) the highest TF values for Cd were obtained in sugar beet (0.298 ± 0.176), while the lowest TF values for Cd were recorded in maize grain (0.009 ± 0.009) and (2) the highest TF values for Zn were found in barley grain and straw, foraged maize, and horse bean

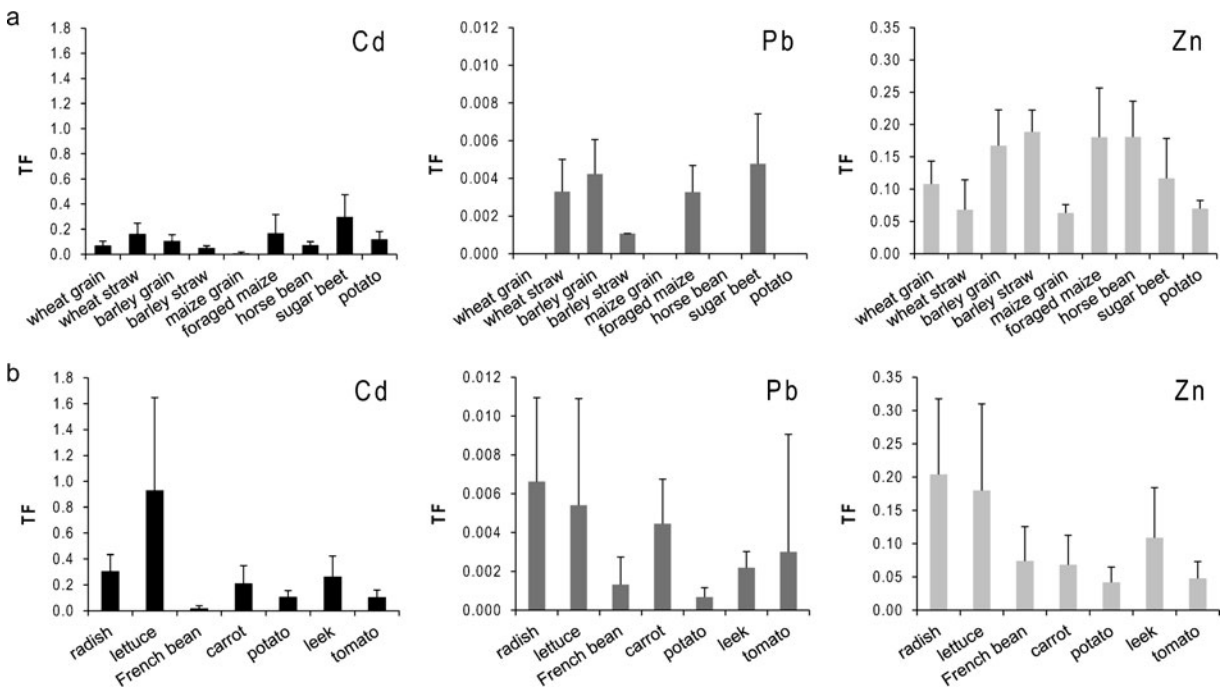


Fig. 2 Transfer factors (TF) of Cd, Pb, and Zn: **a** from agricultural soils to crops and **b** from kitchen garden soils to vegetables. The error bars indicate the standard deviation. Note that the Y scales are different

(0.167 ± 0.056 , 0.189 ± 0.034 , 0.180 ± 0.076 , and 0.181 ± 0.056 , respectively) while the lowest TF values for Zn were obtained in maize grain and potato (0.063 ± 0.013 and 0.070 ± 0.013 , respectively). For homegrown vegetables, lettuce was the vegetable that presented the highest TF values (0.929 ± 0.718) while French bean, potato, and tomato showed the lowest TF values (0.019 ± 0.021 , 0.107 ± 0.048 , and 0.105 ± 0.054 , respectively). Moreover, the highest TF values for Zn were obtained in radish and lettuce (0.204 ± 0.113 and 0.180 ± 0.130 , respectively) while potato and tomato showed the lowest TF values for Zn (0.042 ± 0.023 and 0.048 ± 0.025 , respectively). In previous studies, distinctive differences were also identified when comparing one vegetable to another, legumes (such as beans) tending to be low accumulators (Alexander et al. 2006; Flemming and Parle 1977), root vegetables (such as carrot and radish) tending to be moderate accumulators (Lehoczky et al. 1998) and leafy vegetables (such as lettuce) being high accumulators (Alexander et al. 2006; Lehoczky et al. 1998; Li et al. 2006). These results showed that the TF values differed between locations (field and garden) and plant species. The difference in TFs between fields or gardens may be related to the vegetable crop's physiological properties, soil nutrient management, and the physicochemical parameters of soils (especially pH, as reported by Golia et al. 2008). In the present study, soil pH values ranged from 7.3 to 8.3 (8.0 ± 0.3) for agricultural fields and from 6.3 to 8.3 (7.3 ± 0.3) for kitchen gardens (data not presented here). The high pH can stabilize metals in soils, resulting in decreased leaching effects of elements. Thus, the metal concentrations in the soil solution are quite low, that restrain the absorbability of the metals from the soil solution and the translocation into the crop tissues.

Metal concentrations with regard to the legal values

The concentrations of Cd and Pb obtained for agricultural crops and homegrown vegetables were compared with the legal values given in the European Directive of 8 March 2001 and the French Decree of 12 January 2001. With regard to the legislation, the crops have to contain both Cd and Pb concentration levels below the legislation limits to be considered as acceptable for human or animal consumption. However, there are no European guidelines to enforce the maximum level of Zn in crops. In China, the Chinese Food Hygiene

Standard defined a maximum permissible concentration of 20 mg of Zn per kilogram (fresh weight) for vegetables (SQMIQAC 2001). Only our homegrown vegetable Zn concentrations were compared with this limit. Tables 3 and 4 show the proportion of noncompliant samples.

A high percentage of agricultural crops for foodstuffs did not comply with the European legislation. Indeed, 72 % of the wheat grain, 100 % of the horse bean and sugar beet, 71 % of the barley grain, 50 % of the potato, and 10 % of the maize grain samples were over the foodstuff limit values (Table 3). For feedstuffs, most samples did not exceed the Cd and Pb legislation limits, and only 28 % of the wheat straw samples and 40 % of the foraged maize samples were over the feedstuff limit values (Table 3). A significant proportion of the vegetables produced in the kitchen gardens did not comply with the European foodstuff legislation (Table 4): carrot (93 %), potato (90 %), leek (73 %), radish (68 %), and lettuce (67 %). For tomato and French bean, nonconformity with the European regulations was not systematic (29 and 9 %, respectively). The highest Zn level in the vegetables studied was below the Chinese Food Hygiene Standard of 20 mg kg^{-1} of fresh weight, except for one lettuce sample (25.7 mg kg^{-1} of fresh weight). Excess Zn may be toxic to plants. However, the soil Zn threshold for producing safe vegetables is not available. Long et al. (2003) reported that leaf Zn levels in excess of 300–600 mg kg^{-1} of dry weight is considered to be toxic to plants. In the present study, the Zn concentrations in agricultural crops were less than 141 mg kg^{-1} of dry weight and those in homegrown vegetables were less than 300 mg kg^{-1} of dry weight (except for one lettuce sample with a Zn concentration of 465 mg kg^{-1}).

Most agricultural crops exceeded the legislation limits for Cd while most homegrown vegetables exceeded the limits for both Cd and Pb. Because of the high correlation between Cd and Pb concentrations in soils (Pearson coefficient, $r^2=0.969$ and 0.935 with $p<0.0001$ for agricultural and garden soils, respectively), the Cd concentration in soils was considered an indicator of pollution. Table 5 shows the proportion of plant samples for human consumption that did not respect the legal values with regard to a scale of soil Cd contamination. Four classes of soil contamination were discriminated: 2–5, 5–10, 10–15, and 15–25 mg of Cd per kg of soil. With Cd concentration in soils greater than 2 mg kg^{-1} , the agricultural crops (except

Table 5 Number of samples that were noncompliant with the European limit values for human consumption (European Directive of 19 December 2006) with regard to the total number of samples

	Cd concentrations in soils (mg kg^{-1})			
	2–5	5–10	10–15	15–25
Agricultural crops				
Wheat grain	4/7	9/11	–	–
Barley grain	5/7	–	–	–
Maize grain	0/2	1/8	–	–
Horse bean	3/3	4/4	–	–
Potato	2/4	–	–	–
Sugar beet	7/8	2/2	1/1	–
Homegrown vegetables				
Radish	2/8	12/17	6/6	3/3
Lettuce	4/8	10/17	5/5	3/3
French bean	0/8	0/15	1/5	2/4
Carrot	5/7	10/10	4/4	4/4
Potato	8/8	11/14	3/3	5/5
Leek	5/7	5/9	5/5	4/5
Tomato	1/6	1/11	3/5	2/2

This interpretation is a double analysis of both Cd and Pb concentrations in edible parts with regard to Cd soil concentration

for maize grain) were not in accordance with the regulations. Similar observations were made for radish, lettuce, carrot, potato, and leek when the soil concentration of Cd exceeded 5 mg kg^{-1} . French bean and tomato did not comply with the regulations with a concentration of Cd in soils higher than 15 and 10 mg kg^{-1} , respectively.

Long-term effects of the smelter closedown on metal concentrations in agricultural crops and homegrown vegetables

The long-term effects of the Metaleurop Nord closedown were evaluated by comparing the metal concentrations in agricultural crops and homegrown vegetables before the smelter closed down in 2003 (Douay et al. 2008b; Pruvot et al. 2006) to those obtained in the present study (i.e., 7 years after the smelter closedown).

Data from 230 agricultural crops and 79 homegrown vegetable samples, collected before 2003 (Douay et al. 2008b; Pruvot et al. 2006), were selected on soils with the same degree of Cd and Pb contamination as those selected in the present study. In 2010, a sampling campaign around the smelter was carried

out, where (1) the same cultivars were used as in 2003 for the homegrown vegetables (except for leek) and (2) for all crop samples, the same methods for sampling, sample preparation and analyses were used.

Figure 3 presents the proportion of vegetables that were noncompliant with the legislation limits (by considering Cd and Pb together) before and 7 years after the smelter closedown.

Before the smelter closedown, 89, 76, 42, and 40 % of the wheat grain, barley grain, maize grain, and potato samples, respectively, were over the European legislation limit values for foodstuffs. Seven years after the smelter closedown, 72, 71, 10, and 50 % of the samples were over the foodstuff limit values. For feedstuffs, no grain samples exceeded the legislation limits before and 7 years after the smelter closedown, except for the barley grain samples, with only 6 % over the limit values before 2003. However, for wheat and barley straw and foraged maize, 76, 56, and 79 % of the samples, respectively, were over the legislation limits before the closedown. After the smelter closedown, only 28 and 40 % of the wheat straw and foraged maize samples, respectively, were over the feedstuff limit values. Before the smelter closedown, 55, 67, 80, 47, 79, and 92 % of the radish, lettuce,

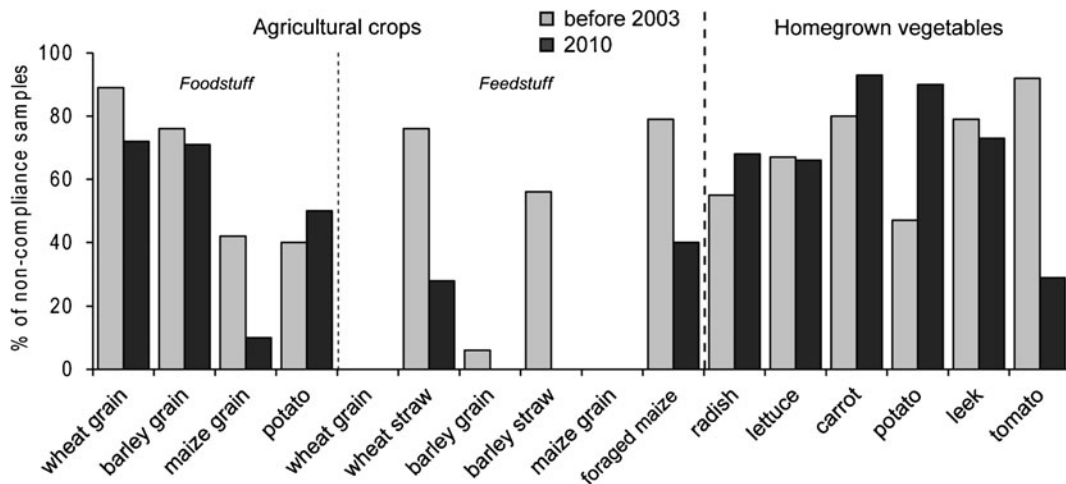


Fig. 3 Proportion of agricultural crops (foodstuffs and feedstuffs) and homegrown vegetables in compliance with the legislation limits (for both Cd and Pb) before the smelter closedown (2003; Douay et

al. 2008b; Pruvot et al. 2006) and 7 years after the smelter closedown (2010; this study)

carrot, potato, leek, and tomato samples, respectively, were over the European limit values for human consumption. Seven years after the closedown, 68, 66, 93, 90, 73, and 29 % of the samples were over the limit values.

Seven years after the smelter closedown, the results showed that (1) little change or a slight decrease in the proportion of agricultural foodstuffs were noncompliant with the legislation limits, which indicates a slight decrease in the foodstuff metal concentrations; (2) a noticeable decrease in the metal concentrations (mainly Pb concentrations) in feedstuff agricultural crops; and (3) little change or an increase in the homegrown vegetable metal concentrations.

For the agricultural crops, the decrease in plant contamination seemed to result from the decrease in dust fallout, which indicates that the smelter dust emissions played an important role in the Pb contamination of crops. Indeed, the contamination pathways for the plants resulted from root uptake but also from dust deposition on the foliar system (Douay et al. 2008b; Moolenaar and Lexmond 1999; Uzu et al. 2010). Dalenberg and Van Driel (1990) found that direct atmospheric deposition contributed considerably (up to 95 %) to Pb concentrations in wheat grain and straw. However, the decrease in Pb concentrations observed should be treated with caution because various parameters could have an influence when comparing before and 7 years after the smelter closedown. Because of crop rotations and management practices

(e.g., changing land use to increase profitability), the agricultural crop samples, collected in the present study, were not exactly the same cultivars as those collected before 2003, and many authors have shown that the accumulation of metals in plants varied not only according to the element, its speciation, the physicochemical parameters of the soils, and the vegetable species but also the type of vegetable cultivar (Banat et al. 2005; Cobb et al. 2000; Georgieva et al. 1997; Tokalioglu and Kartal 2003). These results point out (1) the importance of interrupting atmospheric fallout in the crop contamination pathways for Pb and (2) that after a period of 7 years, natural attenuation of the metal’s bioavailability alone may not be sufficient to explain the observed decrease.

For the homegrown vegetables, the smelter closedown did not result in a noticeable decrease in the (sample) metal concentrations (except for tomato), but in an increase in the radish, carrot, and potato metal concentrations. However, comparing the two sets of data was difficult because of the great variability of metal soil contamination between and within the gardens; this was even more problematic since, before 2003, only one composite soil sample was collected to provide an estimate of average soil concentration in each garden.

Seven years after the smelter closedown, agricultural crops did not meet compliance standards for Cd, while homegrown vegetables were noncompliant for both Cd and Pb, which can be explained by the

different contamination levels in urban soils and agricultural soils and the high heterogeneity and variability of the physicochemical parameters (e.g., organic matter) in urban soils (Karapanagiotis et al. 1991; Martinez and Motto 2000). Kitchen garden soils' high organic matter contents stem from gardening practices using local composts from contaminated green wastes. In spite of organic matter, which is responsible for the formation of stable complexes with Pb, the intensification of cultural practices in the kitchen gardens could lead to increasing the mobility and phytoavailability of this element. Indeed, the application of acidic fertilizers and pesticides and frequent plowing generate a more oxidizing environment, which favors Pb mobilization in soils (Spuller et al. 2007) with its release from decomposing soil organic matter (Klitzke and Lang 2009).

Conclusions

After more than a century of activity, and 7 years after the Metaleurop Nord closedown, the agricultural and urban topsoils located around the smelter were strongly contaminated by Cd, Pb, and Zn, at a level much greater than the regional values. The kitchen garden topsoils were more polluted than the agricultural soils, with a great variability of metal concentrations in soils within the gardens studied. This observed heterogeneity, at a relatively short distance from the smelter, could have important implications for assessing local inhabitants' exposure to the metals studied as well as investigations of remediation techniques.

This study showed that the Metaleurop Nord closedown had an effect on the Cd and Pb concentrations of agricultural crops. However, a large share of these crops used for foodstuffs did not comply with the European legislation. For feedstuffs, most samples (except for some wheat straw and foraged maize samples) did not exceed the Cd and Pb legislation limits, suggesting that feedstuffs may be a possible opportunity for most agricultural produce. Seven years after the smelter closedown, a considerable proportion of the vegetables produced in kitchen gardens did not comply with the European foodstuff legislation.

The consumption of kitchen garden produce might contribute to exposing the population to metals. Seven years after the smelter closedown, the high contamination level of the surrounding soils continues to

indicate a risk for the environment and the health of the local population. A further investigation (part 2; Pelfrène et al. 2012) is needed to assess the associated potential health risk to local inhabitants through consumption of homegrown vegetables and ingestion of soil particles by estimating site-specific human health assessment criteria for Cd and Pb.

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