Impact of Dust Filter Installation in Ironworks and Construction on Brownfield Area on the Toxic Metal Concentration in Street and House Dust (Celje, Slovenia)

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Abstract This article presents the impact of the ecological investment in ironworks (dust filter installation) and construction works at a highly contaminated brownfield site on the chemical composition of household dust (HD) and street sediment (SS) in Celje, Slovenia. The evaluation is based on two sampling campaigns: the first was undertaken 1 month before the ecological investment became operational and the second 3 years later. The results show that dust filter installations reduced the content of Co, Cr, Fe, Mn, Mo, W and Zn on average by 58% in HD and by 51% in SS. No reduction was observed at sampling points in the upwind direction from the ironworks. By contrast, the impact of the construction works on the highly contaminated brownfield site was detected by a significant increase (on average by 37%) of elements connected to the brownfield contamination in SS. Such increase was not detected in HD.

Keywords House dust · Street sediment · Toxic metals · Industrial dust filters · Ironworks · Celje

INTRODUCTION

The World Steel Association (2010) reports that world production of steel in the year 2008 was approximately 1.4×10^9 ton, 71% of it in countries with questionable environmental standards or with insufficient environmental monitoring. The World Bank Group (2007) reports that production of 1 ton of steel can generate as much as 4 kg of particulate matter. Thus, steel production in developing and third-world countries has a huge potential for polluting the atmosphere and surrounding terrestrial environments with dust containing toxic metals.

Knowledge about the chemical composition of dust, especially in urban areas, is important because this is a material to which we are exposed daily. The main exposure pathways are lungs (inhalation) and stomach (ingestion). These can be very important pathways for toxic metals in the body. Rasmussen et al. (2001) showed that ingestion of house dust (HD) is the main Pb exposure pathway (69%) for small children in contaminated areas. This is because of the very small nature of the particles, which means that a high proportion of toxic metals in the HD is bioavailable (Cu, Pb, Zn between 80 and 100%; Mn and Ni between 60 and 80%) (Turner and Simmonds 2006). This is why contaminated HD can present a health risk, especially for children, and its study might be a key to evaluating the exposure of people to toxic metals in contaminated areas.

As demonstrated by many authors, past environmental burdens, heavy industry, metallurgy, steel production and other factors can significantly increase toxic metals concentrations in HD and street sediment (SS) when sufficient pollution prevention measures are not undertaken. However, this study goes in the opposite direction. Can ecological investment in dust filters (dust filter producer: Intensiv-Filter group, Germany) in ironworks in a previously heavily contaminated area (Celje, Slovenia) decrease the content of toxic metals in HD and SS? The main reasons for doing such a study in this area are that “baseline” data from past studies of the same materials (Žibret and Rokavec 2010) are available and Štore ironworks are the only ironworks in the wider Celje area, and consequently, the only important source of “ironworking” elements in the atmosphere. The expected result is that, as a consequence of the ecological investment, there is the decrease of concentrations of metals connected with the past dust emissions from Štore ironworks (Co, Cr, Fe, Mn, Mo, W and Zn) in the SS and HD. To the author’s knowledge, this is the first study that presents and compares

the data at the time of daily atmospheric dust emissions from ironworks, which were visible from several km away, and the data from the same locations 3 years after the dust filters became fully operational.

In the meantime, improperly planned construction works without proper means of preventing dispersion of toxic metals began on the highly contaminated brownfield site, where concentrations of toxic metals exceed action values several hundred times. These construction works produce material's dispersion into the nearby environment (dusting in dry weather conditions and mud dispersion due to traffic from the construction site). Increased concentrations of elements connected to brownfield contamination are expected in SS and HD, because of dusting and mud dispersion from the heavy machinery.

Therefore, the results of this study represent a sound scientific background for environmental decision makers considering investment in clean technologies or planning the use of contaminated areas. There is additional reference for environmental scientists studying HD and SS contamination and assessing different influences on HD and SS composition.

Celje Area

Celje is a small town in central Slovenia with less than 50 000 inhabitants. Characteristic of the area is large-scale contamination of soil due to the historical 100-year Zn smelting tradition between 1870 and 1970. The most problematic elements are Zn (max. 8600 mg kg⁻¹), Cd (max. 59 mg kg⁻¹) and Pb (max. 1500 mg kg⁻¹). The main causes of the contamination are 11 pyrometallurgical furnaces which dispersed toxic metals up to 20 km away (Žibret and Šajn 2008). In the last 40 years, the factory switched to other products, and today its main product is TiO₂ pigment. The only detectable emissions in HD and SS from this factory are emissions of Ti and Nb (Šajn 2005; Žibret 2002; Žibret and Rokavec 2010).

In the vicinity of the city centre and next to the locations of the old smelting furnaces, a large brownfield area has been established. Remains of the bricks, demolition waste, tar, pyrometallurgical waste and other debris have been placed here. Its thickness varies between 0.5 and 5 m. Concentrations of metals are very heterogeneous and can reach extreme values (Voglar and Leštan 2010). The most problematic elements are Cd (max. 344 mg kg⁻¹), Pb (max. 5.9%), Zn (max. 11%), Cu (max. 1%) and As (max. 528 mg kg⁻¹). Other elements, not all measured in the aforementioned study, can also have significantly high values (Romih et al. 2010), such as Fe, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb and Zn. In the last year, this extremely contaminated area has been the site of construction works, where roads and other infrastructure are being built for a

planned commercial and residential zone, according to the municipality decree from 2005 (OG 2005). Dispersion of toxic elements is due to dust emissions in the dry periods and soil and dirt dispersion by traffic from the brownfield area in wet periods.

Another important pollution factor affecting this area is the ironworks, which has a more than 150-year tradition in the Štore area. According to past studies and the visible dust plumes, this factory has been emitting metals into the atmosphere and has produced an anomaly of increased concentrations of Cr, Mn, Fe, Co and Ni (Šajn 2005; Žibret 2008; Žibret and Šajn 2010) in soil and attic dust. In the summer of 2005, emissions of the aforementioned metals and Mo were detected in HD and SS (Žibret and Rokavec 2010). The most important fact for the current study was that in the autumn of 2005, the Štore ironworks undertook an ecological investment. Dust filters became fully operational, and no red dust emissions are visible any more.

MATERIALS AND METHODS

Sampling Procedure

Two sampling campaigns were undertaken. The first one was in September 2005 (data from Žibret and Rokavec 2010), just before dust filters became operational and before any construction activities started at the brownfield site. The second was undertaken in September 2008 at the same locations, 3 years after the dust filters became fully operational and approximately 1 year after construction works began at the brownfield site. Similar atmospheric conditions (no precipitation or strong winds in the previous 7 days) existed during both sampling campaigns.

Seven sampling points were chosen (Fig. 1). These sampling locations are Bukovžlak (BUK), Štore (STO), ironworks gate (IW) and unpolluted Nova Cerkev reference point (NC). Sampling locations Delavska street (DEL), Teharska street (TEH) and Lava area (LAV) are placed in the town of Celje. At each sampling point, samples of top soil (only in the 2005 campaign), HD and SS were taken. Topsoil was sampled in the following way. In order to minimise the influence of unwanted factors, a composite sample was taken. It was composed of at least 15 subsamples of A horizon (2–10 cm) of autogenic soil from an area of 50 × 50 m, each weighing approximately 200 g. Anthropogenic soils were not sampled. The composite sample was then mixed in situ, roots and grass were removed, and 1 kg was taken (the rest was discarded).

Samples of the SS were taken along the road or street sections from an area of 100 × 100 m at 15 microlocations. Special attention was given to the selection of subsample microlocations so that no soil or plant remains were

Fig. 1 Position of the sampling points, main pollution factors and dominant wind direction (GovRS 2009). HD house dust, SS street sediment, BUK Bukovžlak sampling point, STO Štore sampling point,

LAV Lava sampling point, DEL Delavska street sampling point, TEH Teharska street sampling point, NC Nova Cerkev sampling point, IW ironworks sampling point

visible on the road. Before sampling, sand and other coarse-grained materials were removed with a soft plastic brush. Fine-grained material was then collected with a hard plastic brush and stored in a plastic bag. Approximately 0.5 kg of street sediment was taken at each sampling point. Sampling was conducted after at least 1 week of dry weather conditions during both sampling campaigns.

The HD sample was approximated with at least three full vacuum cleaner bags from houses next to the places where the soil and SS samples were taken. Special attention was given to sampling only vacuum cleaner bags which were used exclusively for vacuuming the interior of apartments or houses inhabited by non-smokers. Vacuum cleaner bags used for cleaning cars, garages or workshops, or for cleaning possible renovation debris were not sampled. Conversation with the owners assured the correct sampling procedure. Although the number of the sampling points was relatively small (6), sampling took a lot of time and effort to ensure maximum quality of the results.

Sample Preparation and Chemical Analysis

Pre-analytical sample preparation consisted of drying at 303 K until constant weight. Possible soil and SS aggregations were gently crushed in the ceramic mortar. Skeletal

particles (stones) were not crushed and were discarded. Soil and SS were then sieved and 5 g of the material (<0.125 mm) was analysed. HD was prepared differently. The material inside the vacuum cleaner bag was rubbed through a 1-mm sieve to extract dust and dirt. Fibres (hair, textiles, etc.) were discarded. The further procedure consisted of removing as many fibres as possible. This was done by sieving through a 0.5-mm sieve and then through a 0.125-mm sieve. Sieving was done manually with several hand strokes. With this procedure, it was possible to extract only the fine-grained atmospheric deposit and to discard the majority of the fibres, skin particles and other unwanted material. Longer machine sieving was not applied because fibrous particles fall through the sieve using such a procedure.

Chemical analysis was done in the ACME analytical laboratories in Vancouver, using aqua regia digestion and inductively coupled plasma mass spectrometry. Precision was controlled with four duplicates, and the accuracy with five analyses of two standard materials. Precision parameter, relative percent difference (RPD), was calculated according to the following equation: $RPD = \frac{100}{4} \sum_{i=1}^4 \frac{2|A_i - B_i|}{A_i + B_i}$, where A is first analytical measurement and B is second analytical measurement. Accuracy parameter, percent recovery (%R), was calculated

using following equation: $\%R = \frac{100}{5} \sum_{i=1}^5 \left(\frac{C_i - C_{true}}{C_{true}} + 1 \right)$, where C is measured concentration and C_{true} is standard concentration. In cases where concentrations were below the detection limit, they were assumed to be 50% of the detection limit. In cases where double analysis was made for the purpose of the precision tests, the average value of both analyses was used for further data processing.

Data Processing

As a quantitative measure of the difference in concentration between both sampling periods, concentrations were compared by calculating percent difference value (DIF) with the following equation:

$$DIF = \frac{100 * (C_{2008} - C_{2005})}{C_{2005}}$$

where C_{2008} and C_{2005} represent the concentration of the element in the year 2008 and 2005 respectively.

Further data processing measures aimed toward removing the possible influence of the previously contaminated soil on the composition of the HD and SS, and to separate temporal variations, not produced by the ecological investment in the ironworks or construction activities at the brownfield site (the former two are regarded as “signal”), such as the influence of the coal power plant 25 km NW of Celje, population, traffic, regional influences (Sahara and volcanic dust, pollen, etc.), regarded as “noise”. Enrichment factors (EF) were used for this purpose.

According to the analysis of the mineral fraction in house (office) dust (Molhave et al. 2000), the dominant minerals of natural origin are silicates (apatite, biotite, feldspar, hornblende, quartz, etc.) and other minerals (sea salt, limonite, haematite, etc.). Si should normally be used as a reference element for this case, but because samples were digested in aqua regia, which fails to fully dissolve silicates, Al was used as a reference element instead. Taking into account that Celje is not an extensive farming area (Al can be found in fertilisers), substituting Al with Si as a reference element is not likely to yield biased results. EF has been calculated by the following equation:

$$EF = \frac{C_{dust}/C_{Al,dust}}{C_{soil}/C_{Al,soil}}$$

where C_{dust} and C_{soil} represent the concentration of the element in dust (SS or HD) or soil, $C_{Al,dust}$ and $C_{Al,soil}$ represent the concentration of the aluminium in HD or SS and soil. The differences between EF in the year 2005 and 2008 were evaluated by enrichment factor difference parameter (EFDIF), calculated by the analogy with the DIF of concentrations.

To distinguish between noise and signal, upper and lower limit values were set. For this purpose, EFDIF values for naturally distributed elements (La, Mg, Sc, U and V; Šajn 2005; Žibret 2002; Žibret and Rokavec 2010) were calculated. The second lowest and the second highest obtained values were used as noise threshold limits. This procedure was carried out for HD and SS separately. EFDIF values for other elements (decrease/increase), which fell outside the noise interval, were regarded as a signal. Finally, the detected signals were then plotted on the map for a visual estimation of the temporal and spatial differences and to test the working hypotheses.

RESULTS AND DISCUSSION

Data from laboratory analysis and results of analytical quality control are shown in Table 1. Precision and accuracy were found to be satisfactory. A relative percentage difference larger than 10% was found for Ba, Cd, Mo and Sb. A recovery rate of less than 90% was found for Pb, Sb and W. Other elements had a recovery rate between 90 and 110%. Table 2 presents the DIF for the raw dataset and Fig. 2 summarises the basic statistical parameters for the sampling points and the elements, influenced by the two factors of interest.

The data from past studies show that, until 2005, the ironworks were emitting dust containing Cr, Mn, Fe, Co, Ni and Mo. Taking into account the shape of the anomaly in attic dust (Šajn 2005; Žibret 2002), Zn is also very probably included in these emissions. The influence of the ironworks was assessed by only one sampling point (STO) for HD, and two points for SS (STO, IW). All the points are located in the vicinity of the ironworks, in the dominant wind direction. Points that are considered not to be influenced by the ironworks are DEL, TEH, LAV and NC. The observed elements for the calculation of the statistics are Co, Cr, Fe, Mn, Mo, W and Zn. Regarding the brownfield site in Celje, past data (Romih et al. 2010; Voglar and Leštan 2010) show that this is very heterogeneous material and the concentrations of toxic metals vary drastically. The material in the brownfield is contaminated with As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb and Zn. The influence of the construction works on this brownfield site is assessed according to the concentration change for aforementioned elements on the sampling points DEL and TEH, which are placed on the transportation routes of heavy machinery, going in and out of the brownfield.

DIF for the concentrations (Table 2) on two sampling points influenced by ironworks (IW and STO) show a significant decrease (median values are −58% for HD and −51% for SS) in the content of “ironworks elements” and relatively small standard deviation (21% for HD and 17%

Table 1 Analytical results, precision, accuracy, detection limits and basic statistical parameters

Sampling point	Material	Sampling date	Expected influential factor	Al (%)	Fe (%)	As (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Co (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Mn (mg kg ⁻¹)	Mo (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Sb (mg kg ⁻¹)	W (mg kg ⁻¹)	Zn (mg kg ⁻¹)
Detection limit				0.01	0.01	0.5	0.1	0.1	1.00	0.1	1	0.1	0.1	0.1	0.1	0.10	1
Precision	RPD		4 duplicates	4	5	4	11	3	6	4	4	12	8	5	16	3	1
Accuracy	%R		5 standards	101	98	102	103	98	103	102	98	92	98	88	75	70	92
BUK	HD	SEP 2005		0.66	1.60	16.1	9.7	10.7	157	175	352	3.6	40.0	388	4.2	0.5	3250
BUK	HD	SEP 2008		1.20	0.79	3.8	12.6	8.0	80	164	1210	3.6	22.2	126	2.3	0.6	2480
STO	HD	SEP 2005	Ironworks	0.64	4.91	8.4	3.8	19.1	724	210	1330	36.9	316	153	5.0	15.3	1830
STO	HD	SEP 2008		0.85	2.85	7.4	4.4	8.0	140	258	636	13.0	99.8	199	8.6	2.1	1360
LAV	HD	SEP 2005		0.54	1.31	6.5	2.5	7.3	114	195	393	3.4	50.5	119	4.3	1.0	1090
LAV	HD	SEP 2008		0.61	0.94	3.9	1.9	8.6	128	184	222	4.0	46.5	192	4.2	2.3	853
DEL	HD	SEP 2005		0.49	1.04	11.3	6.8	7.8	149	184	252	4.0	50.3	777	7.6	1.6	1950
DEL	HD	SEP 2008	Brownfield construction	0.50	1.21	6.4	3.0	8.7	77	125	262	4.1	46.6	119	4.8	1.5	919
TEH	HD	SEP 2005		0.53	1.35	5.5	3.7	7.5	166	222	431	6.0	103	97	7.2	2.6	1160
TEH	HD	SEP 2008	Brownfield construction	0.67	1.23	4.2	1.6	8.5	162	197	355	6.7	44.7	61	5.3	4.5	736
NC	HD	SEP 2005	Unpolluted	0.60	0.98	4.1	1.5	5.2	204	265	238	3.6	73.5	94	5.4	2.1	904
NC	HD	SEP 2008	Unpolluted	0.82	0.89	2.8	1.8	5.5	50	107	232	3.1	31.0	66	2.1	2.6	1490
BUK	SS	SEP 2005		0.31	1.29	16.4	2.2	4.3	26	74	338	2.1	21.2	121	2.6	0.1	798
BUK	SS	SEP 2008		0.23	1.01	7.9	1.4	3.1	23	50	244	2.0	12.2	60	1.7	0.1	283
STO	SS	SEP 2005	Ironworks	0.32	12.7	10.1	2.1	15.3	740	295	2970	43.3	173	179	6.2	5.2	1690
STO	SS	SEP 2008		0.30	7.35	7.8	1.6	8.7	385	164	1310	24.1	111	144	3.6	2.4	635
LAV	SS	SEP 2005		0.39	1.37	9.1	1.3	5.2	49	106	377	6.3	28.1	115	6.8	0.6	530
LAV	SS	SEP 2008		0.35	1.07	5.5	0.8	3.8	22	57	298	2.5	14.8	58	2.6	0.2	301
DEL	SS	SEP 2005		0.30	2.03	22.8	5.6	7.7	151	166	370	12.5	83.7	348	7.3	1.1	1730
DEL	SS	SEP 2008	Brownfield construction	0.36	3.19	21.1	7.2	9.6	226	263	431	15.2	124	352	7.2	2.2	2220
TEH	SS	SEP 2005		0.29	1.02	5.8	1.0	4.0	36	37	279	2.3	16.1	52	1.3	0.2	258
TEH	SS	SEP 2008	Brownfield construction	0.39	1.88	6.4	1.0	6.1	59	127	469	6.1	32.2	76	4.1	0.6	294
NC	SS	SEP 2005	Unpolluted	0.35	1.14	3.9	1.1	3.9	58	153	246	5.4	28.7	59	7.1	0.8	463
NC	SS	SEP 2008	Unpolluted	0.33	0.79	3.6	0.4	3.0	15	29	197	1.2	10.4	15	1.2	0.1	88
IW	SS	SEP 2005	Ironworks	0.25	3.33	6.2	1.4	6.1	236	211	1220	16.3	54.4	149	6.2	3.4	1260
IW	SS	SEP 2008		0.48	2.34	8.0	1.3	5.4	90	114	691	7.7	54.8	142	2.6	0.8	372
BUK	SL	SEP 2005	Previously polluted	1.45	2.05	18.7	15.8	7.7	30	49	454	0.9	23.8	255	1.3	0.1	1880
STO	SL	SEP 2005	Previously polluted	1.90	2.42	9.1	2.4	8.0	40	22	368	1.4	21.6	61	0.7	0.1	323

Table 1 continued

Sampling point	Material	Sampling date	Expected influential factor	Al (%)	Fe (%)	As (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Co (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Mn (mg kg ⁻¹)	Mo (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Sb (mg kg ⁻¹)	W (mg kg ⁻¹)	Zn (mg kg ⁻¹)
LAV	SL	SEP 2005	Previously polluted	1.66	2.28	10.8	2.3	9.3	25	26	882	0.7	23.9	64	0.6	0.1	264
DEL	SL	SEP 2005	Previously polluted	1.46	3.04	35.9	24.0	13.0	53	114	657	2.1	39.3	665	3.9	0.3	4300
TEH	SL	SEP 2005	Previously polluted	1.05	2.42	14.9	9.7	11.1	29	37	730	0.9	32.6	139	0.9	0.1	1090
NC	SL	SEP 2005	Unpolluted	1.79	2.33	6.8	0.3	8.7	34	18	530	0.8	23.5	24	0.3	0.1	76
MIN	HD			0.49	0.79	2.80	1.50	5.20	50	107	222	3.1	22	61	2.1	0.5	736
MD	HD			0.63	1.22	5.95	3.35	7.98	144	190	354	4.0	48	123	4.9	2.1	1260
MAX	HD			1.20	4.91	16.1	12.6	19.1	724	265	1330	36.9	316	777	8.6	15.3	3250
MIN	SS			0.23	0.79	3.55	0.35	3.00	15	29	197	1.2	10	15	1.2	0.1	88
MD	SS			0.32	1.63	7.85	1.35	5.30	58	120	374	6.2	30	118	3.85	0.7	497
MAX	SS			0.48	12.7	22.8	7.20	15.3	740	295	2970	43.3	173	352	7.3	5.2	2220

HD house dust, SS street sediment, SL topsoil (0–5 cm), RPD relative percent difference parameter, %R percent recovery parameter, MIN minimum value, MD median value, MAX maximum value, BUK Bukovžlak sampling point, STO Store sampling point, LAV Lava sampling point, DEL Delavska street sampling point, TEH Teharska street sampling point, NC Nova Cerkev sampling point, IW ironworks sampling point

for SS) can be recognised. However, at the sampling points that were not affected by the past ironworks pollution, changes in the concentrations of these elements express a much higher standard deviation (41% for HD and 73% for SS), and the median is almost exactly zero (0% for HD and –3% for SS). DIF distribution is very well balanced (Fig. 2a), so these changes can be attributed to variations which are not caused by past ironworks pollution, but are of other origin. Results show that dust emission reduction with industrial dust filters at ironworks can have a significant positive impact (reduction of the selected toxic metals on average by 50%) to the HD and SS contamination nearby.

The influence of the construction works at the highly contaminated brownfield site on the chemical composition of HD and SS was evaluated according to the two nearest sampling points, TEH and DEL. STO, IW, LAV and NC were taken as references. As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, and Zn were used for calculating the non-parametrical statistics. It was expected that the influence of the construction works on the brownfield site would be detected in HD because of dusting, and in SS, because of mud dispersion by increased truck traffic from the site. The obtained changes in the concentrations in HD are not significant. Both populations are quite similar, with similar median and percentile distribution (Fig. 2b). However, this is not the case for SS. A significant increase in the concentrations of almost all of the “brownfield elements” was measured at both sampling points around the brownfield site. A maximum increase is observed for Cu at TEH sampling point, from 37.2 mg kg⁻¹ in the year 2005 to 127 mg kg⁻¹ in the year 2008 (DIF is 241). It can be concluded that the construction works at the brownfield site have a negative impact only on the SS (median DIF is 37%). Considering the average decrease in the concentrations in SS at reference sampling points (median DIF is –21%), construction works might increased the concentrations of “brownfield elements” in SS by almost 60%.

To exclude the possible influence of previously contaminated soil and other factors regarded as noise on the composition of SS and HD, further evaluation of the temporal differences was done by evaluating the differences in EF, using the calculated EFDIF parameter. The obtained lower limits which distinguish the signal from the noise (calculated from EFDIF values of 5 naturally distributed elements) are –60% for HD and –50% for SS, and the upper threshold limit is 10% for both media. Table 3 shows the EFDIF for the selected elements at all sampling points. It is evident that points TEH and DEL have the most values higher than the upper threshold limit, which shows the increasing trend in the concentrations of metals around the brownfield site, and STO and IW have the most values lower than the lower threshold limit, which

Table 2 Percentage difference value for the concentrations for the selected elements in house dust and street sediment between years 2005 and 2008, and corresponding median values

Sample	Influenced	Material	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sb	W	Zn
Calculated DIF of concentration																
STO	IWR	HD	32	-13	16	-58	-81	23	-42	-52	-65	-68	30	71	-86	-26
STO	IWR	SS	-6	-23	-24	-43	-48	-44	-42	-56	-44	-36	-19	-42	-54	-62
IW	IWR	SS	90	29	-11	-11	-62	-46	-30	-43	-53	1	-4	-59	-78	-71
BUK	IWR and BF	HD	82	-76	30	-25	-49	-6	-51	245	0	-45	-67	-45	20	-24
BUK	IWR and BF	SS	-26	-52	-36	-28	-13	-33	-22	-28	-5	-42	-50	-35	-50	-65
DEL	BF	HD	2	-43	-56	12	-48	-32	16	4	2	-7	-85	-37	-6	-53
DEL	BF	SS	20	-7	29	25	49	58	57	16	22	49	1	-1	100	28
TEH	BF	HD	26	-24	-57	13	-3	-11	-9	-18	12	-57	-37	-26	73	-36
TEH	BF	SS	34	10	0	53	65	241	84	68	165	100	46	215	200	14
LAV	T?	HD	13	-40	-24	18	12	-6	-28	-44	18	-8	62	-2	130	-22
LAV	T?	SS	-10	-40	-38	-27	-55	-46	-22	-21	-60	-47	-50	-62	-67	-43
NC	REF	HD	37	-32	20	6	-75	-60	-9	-3	-14	-58	-29	-61	24	65
NC	REF	SS	-7	-9	-68	-23	-75	-81	-31	-20	-78	-64	-74	-84	-88	-81

DIF percent difference, IWR ironworks, BF brownfield, T? town, REF reference point, BUK Bukovžlak sampling point, STO Štore sampling point, LAV Lava sampling point, DEL Delavska street sampling point, TEH Teharska street sampling point, NC Nova Cerkev sampling point, IW ironworks sampling point

Median values of DIF's for "ironworking elements" (Co, Cr, Fe, Mn, Mo, W and Zn): HD at STO sampling points, -58; SS at STO and IW sampling points, -51; HD at DEL, TEH, LAV and NC sampling points, 0; SS at DEL, TEH, LAV and NC sampling points, -3

Median values of DIF's for "brownfield elements" (As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb and Zn): HD at DEL and TEH sampling points, -21; SS at DEL and TEH sampling points, +37; HD at STO, IW, LAV and NC sampling points, -18; SS at STO, IW, LAV and NC sampling points, -43

Fig. 2 Percentage difference between sampling periods (2005 and 2008) in the concentrations for the elements **a** connected to the past ironworks atmospheric emissions (Co, Cr, Fe, Mn, Mo, W and Zn) and **b** connected to the brownfield contamination (As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb and Zn). Data used to draw this figure were taken from Table 2. HD house dust, SS street sediment, BF two sampling

points nearby brownfield, IWR two sampling points nearby ironworks, other the other sampling points (four points in both cases). Outliers and extremes are values outside of the following interval: $[(P25 - k * (P75 - P25)), (P75 + k * (P75 - P25))]$, where $k = 1.5$ for outliers and $k = 3$ for extremes. P25 and P75 are the 25th and 75th percentile values

shows that the "ironworks signal" (operational dust filters) has been detected.

The last step is the inspection of the spatial distribution of the increase/decrease of EF in different media, which will make it possible to evaluate whether the dust filter

installation in the ironworks contributes to the decrease in the content of some metals and metalloids in the HD and SS. Furthermore, it will make it possible to evaluate also whether dust generation by traffic on and from the brownfield site conversely contribute to the increase of the

Table 3 Percentage difference value of the enrichment factors (EFDIF) between years 2005 and 2008 for the selected elements in house dust and street sediment

Sample	Influenced	Material	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sb	W	Zn
			Calculated EFDIF values													
STO	IWR	HD	0	–34	–12	–69	–85	–7	–56	–64	–73	–76	–2	30	–90	–44
STO	IWR	SS	0	–18	–19	–39	–45	–41	–38	–53	–41	–32	–14	–38	–51	–60
IW	IWR	SS	0	–32	–53	–53	–80	–72	–63	–70	–75	–47	–50	–78	–88	–85
BUK	IWR & BF	HD	0	–87	–29	–59	–72	–48	–73	90	–45	–70	–82	–70	–34	–58
BUK	IWR & BF	SS	0	–35	–14	–3	17	–10	6	–3	28	–22	–33	–12	–33	–52
DEL	BF	HD	0	–45	–57	9	–49	–34	14	2	0	–9	–85	–38	–8	–54
DEL	BF	SS	0	–23	7	4	25	32	31	–3	1	24	–16	–18	67	7
TEH	BF	HD	0	–40	–66	–10	–23	–30	–28	–35	–12	–66	–50	–42	37	–50
TEH	BF	SS	0	–18	–26	13	23	154	37	25	97	49	9	135	123	–15
LAV	T?	HD	0	–47	–33	4	–1	–17	–37	–50	4	–19	43	–14	104	–31
LAV	T?	SS	0	–33	–31	–19	–50	–40	–13	–12	–56	–41	–44	–57	–63	–37
NC	REF	HD	0	–50	–12	–23	–82	–71	–34	–29	–37	–69	–48	–72	–9	21
NC	REF	SS	0	–2	–66	–17	–73	–80	–25	–14	–76	–61	–72	–83	–87	–80

IWR ironworks, *BF* brownfield, *T?* town?, *REF* reference point, *BUK* Bukovžlak sampling point, *STO* Štore sampling point, *LAV* Lava sampling point, *DEL* Delavska street sampling point, *TEH* Teharska street sampling point, *NC* Nova Cerkev sampling point, *IW* ironworks sampling point. Elements with larger EFDIF as the upper threshold value are in bold letters and values below the lower threshold limit are italicised

amount of toxic metals in HD and SS. Figure 3 shows the spatial distribution of the detected signals. Thus, a “signal” was detected for Co, Cr, Mn, Mo, W and Zn near the ironworks in both HD and SS and for Cr, Cu, Fe, Ni and W near the brownfield site (only in SS).

The research has demonstrated that dust emissions can have a significant impact on the concentrations of toxic elements in HD and SS. Installation of dust filters can decrease the concentrations of toxic metals which are contained in the emissions by up to 86% (the case for W, Table 2). This can drastically decrease the exposure of humans and especially children to anthropogenic pollutants.

On the other hand, the strong impact of the construction works at the highly contaminated brownfield site on the chemical composition of the SS was detected. As SS can be a major source of ambient dust in towns, measures to decrease the negative impact of such activities are recommended. Based on the findings of this study, an increased rate of street sweeping around construction sites on contaminated areas and along the pathways of the trucks, and prevention of the dispersion of the contaminated material (washing of tyres, for example) are also recommended.

CONCLUSION

In this research, the impact of the ecological investment in the Štore ironworks (dust filter installation) and construction works at the highly contaminated brownfield site on the composition of SS and HD was assessed. Five sampling

points and one reference point were sampled in two time periods: at the time of daily visible dust emissions from Štore Ironworks and 3 years after dust filters were fully operational and approximately 1 year after the construction works began on the highly contaminated brownfield site.

Elemental composition changes show that dust filters in ironworks (3 years of operational time) decreased the content of Co, Cr, Fe, Mn, Mo, W and Zn by around 50% in SS and HD. On the other hand, construction works at the brownfield site did not have a significant negative impact on HD composition, but this is not the case for SS, where the increase in the concentration of toxic elements was up to 240% (in the case of Cu at the TEH sampling point). The average increase is roughly 40% for the elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb and Zn. Changes in EFs show a similar pattern. A significant decrease of EFs between 2005 and 2008 was generally detected for Co, Cr, Mn, Mo, Ni, W and Zn (near the ironworks) in HD and SS. On the contrary, a significant increase in EFs in SS was detected for Cr, Cu, Fe, Ni and W, and only partially for Co, Mn, Mo and Sb in SS. This increase was not detected in HD.

Future studies in the Celje area will focus on the collection of more samples of HD and SS at more sampling points, and also on the evaluation of the bioavailability of metals using physiologically based extraction tests, especially in HD. Combined with hundreds of analyses of soil and vegetable samples in the Celje area, obtained in the last 20 years, assessment of exposure of the local population to toxic metals due to pollution caused by the area’s 100-year Zn smelting and 150-year ironworking history is now the focus of a team of experts, which was formed to prepare

Fig. 3 Spatial distribution of the significant decrease (in *green, underlined*) or significant increase (in *red, bold*) of elements in house dust and street sediment between the years 2005 and 2008. *HD* house dust, *SS* street sediment, *BUK* Bukovžlak sampling point, *STO* Štore

sampling point, *LAV* Lava sampling point, *DEL* Delavska street sampling point, *TEH* Teharska street sampling point, *NC* Nova Cerkev sampling point, *IW* ironworks sampling point

ecological restoration measures for this area. The author of this article is responsible for the preparation of measures to minimise the negative impact of contaminated dust on the population. Moreover, sampling should also be extended temporally to assess whether the obtained decreases of toxic metals are final, or if some further decrease is to be expected in future. In order to obtain data which will allow mathematical modelling of such events, similar studies in other areas should focus on a denser spatial and temporal sampling plan.

While a decreased exposure of humans to toxic metals due to ecological investment in the Štore ironworks was detected in our study, there are certainly many sites, especially in the developing countries, which are still polluting the environment in the form of dust emissions containing toxic metals (Alijagić and Šajn 2011; Dimovska et al. 2010; Stafilov et al. 2010a, b, c, just to mention some recent studies). Data from this and future studies can then be compared, which will lead to a better understanding of the

interrelations between atmospheric pollution, HD and SS contamination and human exposure to toxic metals.

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