

Arsenic and Mercury in the Soils of an Industrial City in the Donets Basin, Ukraine

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Soil and house dust collected in and around Hg mines and a processing facility in Horlivka, a mid-sized city in the Donets Basin of southeastern Ukraine, have elevated As and Hg levels. Surface soils collected at a former Hg-processing facility had up to 1300 mg kg⁻¹ As and 8800 mg kg⁻¹ Hg; 1M HCl extractions showed 74–93% of the total As, and 1–13% of the total Hg to be solubilized, suggesting differential environmental mobility between these elements. In general, lower extractability of As and Hg was seen in soil samples up to 12 km from the Hg-processing facility, and the extractable (1M HCl, synthetic precipitation, deionized water) fractions of As are greater than those for Hg, indicating that Hg is present in a more resistant form than As. The means (standard deviation) of total As and Hg in grab samples collected from playgrounds and public spaces within 12 km of the industrial facility were 64 (±38) mg kg⁻¹ As and 12 (±9.4) mg kg⁻¹ Hg; all concentrations are elevated compared to regional soils. The mean concentrations of As and Hg in dust from homes in Horlivka were 5–15 times higher

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than dust from homes in a control city. Estimates of possible exposure to As and Hg through inadvertent soil ingestion are provided.

Keywords Arsenic, mercury, soil, house dust, Ukraine, extractable fraction, trace elements

Introduction

The influence of environmental factors on human health in urban areas has been a concern for decades. Of particular concern are cities located near industrial facilities where large populations could be exposed to potentially toxic substances. During mining and extractive processing of metal-rich ores, trace elements can enter the local environment in a number of ways, including gaseous and particulate emissions from point sources and the resultant wet or dry deposition, and as wind-blown dust or run-off from tailings piles.

In the Donets Basin of eastern Ukraine, more than 1200 mine-waste heaps (primarily from coal mining; many at risk for self-ignition) have accumulated over more than 200 years of mining (Panov et al., 1999). Ore processing and the use of metal-enriched coal in coal-fired electric generation and home heating has led to widespread contamination of the environment (Panov et al., 1999; Kolker et al., 2009). Of the 26 elements considered to be pollutants in the Donets Basin, arsenic (As) and mercury (Hg) are of primary concern; most of the As-polluted soils in this region are near burning-coal waste heaps (Panov et al., 1999). For more than 50 years, the largest Hg production facility of the former Soviet Union operated in Horlivka (*Gorlovka*, Russian spelling) a city of approximately 300,000 residents in the Donets Basin (48.3° N, 38.0° E). During this period, about 30,000 metric tons of Hg were produced from ore extracted from the adjacent Mykytivka (*Nikitovka*) mines. The Hg ore was processed in furnaces that were fueled by metal-enriched coal; the fraction of Hg recovered from this process was about 85%, resulting in substantial pollution of the environment (Rubinstein and Barsky, 2002). Byproduct coals from these mines have elevated concentrations of As (5–10 times) and Hg (75–150 times) compared to the averages for U.S. coal (Kolker et al., 2009). Numerous tailing piles are located throughout the city in close proximity to homes and apartment complexes, and are a continuing source of contamination via wind-blown dust. Commercial extraction of Hg ended in 1995, but a part of the Hg-processing facility has been used since 2000 for Hg recycling from batteries and fluorescent-light tubes.

The As and Hg content of the present-day, local surficial soil layer is a composite derived from the weathering of the natural parent material and that coming from anthropogenic atmospheric deposition, both wet and dry. Chronic (long-term) exposure to As is causally associated with increased risks of cancer in the skin, lungs, bladder, and kidney, as well as skin changes such as hyperkeratosis and pigmentation changes (IPCS, 2001). Chronic exposure to Hg is associated with damage to the central nervous systems and kidneys (ATSDR, 2006) and has been linked to diseases of the thyroid gland, and immune and reproductive systems (Holmes et al., 2009). In the industrial areas within the Donets Basin, including the city of Horlivka, the rates of circulatory, digestive, and oncologic diseases are 1.5 to 2 times greater than in non-polluted areas (Panov et al., 1999). Soils (and house dust) near mining and processing activities are often contaminated with mixtures of metals that can adversely affect human health because the combined toxicity could be more serious than the individual toxicities alone (Calderón et al., 2003).

Elements sequestered in the soil represent a reservoir of potential contamination to humans through several pathways, including leaching to the water table, increasing the

metal content of food crops, and through inadvertent ingestion of soils and dust. Children are most at risk for exposure to soil contaminants via this pathway because of their normal hand-to-mouth behavior, and because of the child's smaller body mass (Ljung et al., 2006). Soil can be brought into homes by track-in or by fugitive dust emissions through open windows and doors. Because humans spend the majority of their time indoors, the analysis of house dust provides a measure of indoor contamination for use in human exposure assessment. Carpets can hold large amounts of dust and soil, and the U.S. Environmental Protection Agency (USEPA) has recognized that carpets are both a source and a sink for pollutants in the home (USEPA, 1995).

In the present study, the objective was to delineate the distribution of Hg and the co-contaminant As in the surface soil near the former Hg-processing facility and in the residential areas in Horlivka. Additional objectives were to assess the potential environmental mobility of these elements in the soil and to estimate the role of inadvertent ingestion as a possible route of environmental exposure of As and Hg. A portion of the study was conducted during a two-week field visit in September 2005, when soil samples were collected in conjunction with a biomarker study of occupational Hg exposure among the workers at the former Hg-processing facility, now used to recycle Hg from batteries and fluorescent light-tubes. During this study, our group was permitted to sample house dust from the homes of five of the participants. In our companion study, Gibb et al. (2008) found that workers with direct occupational exposure to Hg had blood and urine levels that have been reported in other studies to be associated with sub-clinical effects. Workers without direct exposure (office and cafeteria staff) had lower blood and urine Hg levels than those directly exposed, but still exceeding those for residents of Horlivka not working at the facility. As detailed in a follow-up study comparing residents of Horlivka and a control municipality without past mercury production, Gibb et al. (2011) found that Hg concentrations in surface soil and house dust were good predictors of blood and urinary mercury.

Material and Methods

Sample Collection

A total of 69 soil samples were collected, including: (1) samples within the former Hg-processing facility; (2) samples collected at regular intervals along two transects; and (3) samples collected from residential areas at various distances from the Hg facility. Three samples of surface (0–2 cm) soils were collected from within the former Hg-processing facility (Figure 1) on the site currently used for Hg recycling. The samples were collected (1) near a fluorescent light tube crushing station; (2) a sorting yard across the road from the operating Hg-roasting furnace; and (3) immediately adjacent to the operating Hg-roasting furnace. These three soil samples were collected at a shallow sampling depth to specifically target the dust-like material with which the workers at the Hg-recycling facility would be in direct daily contact.

A total of 54 bulk surface soils (0–10 cm) were collected in Horlivka along two 1–2 km transects adjacent to areas of past mining and/or processing at intervals of 10–100 meters (Figure 1). Transect samples were collected in a manner consistent with a long-term geochemical mapping study of the Donets basin, Ukraine (Panov et al., 1999). Transect-1 (T1) extends outward from the Hg-processing facility in separate west- and northeast-trending segments. Transect-2 (T2) includes west- and east-trending segments at opposite (north and south) sides of abandoned mine workings.

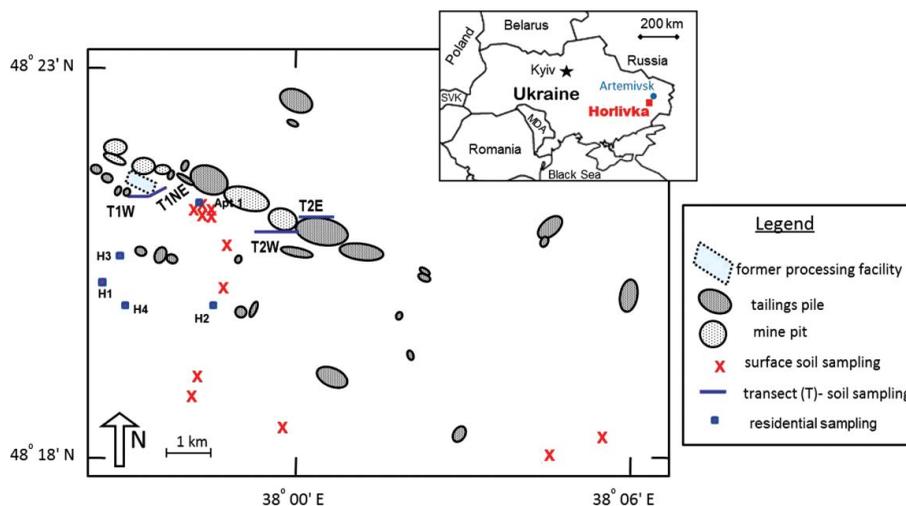


Figure 1. Generalized map of Horlivka, Ukraine, showing the locations of the former Hg-processing facility and locations of environmental samples (surface soil, transect, and residential) that were collected to evaluate the sources of As and Hg. Small map shows the location of the study site, Horlivka, and the control city, Artemivsk, with relationship to the capital city, Kyiv (Color figure available online).

Twelve grab samples of surface soil (0–2 cm) were collected exclusively in residential areas and focused on playground areas and public spaces within 12 km of the facility (Figure 1). These samples were collected to specifically target the surficial “dust-like,” fine-grained, unconsolidated material from areas stripped bare of vegetation by heavy foot traffic; pebbles or other debris were avoided. Particular attention was paid to areas under playground equipment where children would come in direct contact with the soil. The samples were collected by scooping the loose soil from grass-free areas with pre-cleaned plastic hand trowels into plastic zip-top bags; where available, multiple grabs were collected within the same playground. Approximately 50–75 g of sample were collected for each location.

Five participants of the Gibb et al. (2008; 2011) biomarker study in Horlivka and four in the control city, Artemivsk (*Artemovsk*) (48.59° N, 38.08° E), allowed access to their homes for the collection of house dust. Artemivsk, about 30 km to the north, is demographically similar to Horlivka, but lacks geologic Hg enrichment and does not have the Hg-production history of Horlivka. One home in Horlivka is an apartment, the others in Horlivka and all in Artemivsk are individual structures. House dust was collected from carpets using protocols similar to those for lead analysis in dust (USEPA, 1995), with the exception that larger areas of carpet were vacuumed to collect more sample for analysis and to produce a more representative sample. Carpet dust was collected on a dust-sampling sock using a trace-evidence vacuum cleaner (3M Co., St. Paul, MN). The dust-sampling sock (X-cell 100, Midwest Filtration, Cincinnati, OH) retained particles with a mean pore size of approximately 7 μm or greater. Dust samples were passed through a 500- μm stainless-steel sieve to remove large particles (e.g., fluff and fibers) but retain enough material for an accurate analysis.

Sample Analysis

All soil samples were subject to a total digestion and analysis of As, Hg, aluminum (Al), calcium (Ca), iron (Fe), sulfur (S), and silicon (Si) at the U.S. Geological Survey (USGS)

Energy Resources Program laboratories in Denver, Colorado. Samples were wet-ashed with a combination of acids, including hydrofluoric, nitric, and hydrochloric; sub-samples for As analysis were analyzed using a Perkin-Elmer ELAN 6100 inductively coupled plasma-mass spectrometer (ICP-MS) and sub-samples for Hg were assayed using Milestone DMA-80 Hg analyzer. The determination of loss on ignition (LOI) at 525°C was also performed on an aliquot of sample at the same laboratory; LOI is a measurement of moisture and organic carbon (OC) in the sample (Dean, 1974).

Soil samples were also evaluated for extractable As and Hg at the USGS laboratory in Reston, VA, using operator-defined selective extractions. All chemicals used for the selective extractions were analytical grade purity; ultra-pure (18 MΩ resistance) deionized water (DI) was used. Sampling and laboratory plasticware was cleaned by a three-day soak in a solution of 4M HNO₃ followed by thorough rinsing with DI.

All soil samples were leached with 1M HCl using a 1:20 solid:solution ratio, with end-over-end rotation on a mechanical shaker for four hours at 20°C followed by filtration (0.45 μm). Soils from the Hg facility and from residential areas were also evaluated by extraction using the synthetic precipitation leaching procedure (SPLP) (method 1312; USEPA, 1994). In this method, the soils were extracted with a solution of 60% H₂SO₄:40% HNO₃, at pH 5.0, with a 1:20 solid:solution ratio with end-over-end rotation on a mechanical shaker for 18 hours at 20°C and filtered (0.45 μm). The water soluble fraction (method 38 414-S4; DIN, 1984) was also determined on a sub-set of soil samples having high total- and HCl-extractable As and Hg concentrations (the three surface soils from the Hg-processing facility, nine soils from T1, and two soils from T2). In this procedure, the samples were extracted with deionized water at a 1:10 ratio with end-over-end rotation for 24 hours and filtered (0.45 μm). Filtered solutions from all extractions were preserved to 2% HNO₃ with distilled acid.

House dust samples were wet-ashed using a total digestion of sub-boiling concentrated HNO₃ and H₂O₂, with a 1:10 solid:solution ratio, at the USGS laboratory in Reston, VA. The samples were brought to volume with DI water such that the final concentration of HNO₃ in the matrix was approximately 5%.

Arsenic was analyzed using a Perkin-Elmer ELAN 6000 ICP-MS calibrated with five matrix-matched standards. Internal standards (Ge and Tb) were used to correct for instrument drift and several aqueous reference solutions within the range of the sample concentrations were included for quality assurance. Mercury was determined by cold vapor-atomic absorption spectroscopy (CV-AAS) using a Mercury Instruments Lab Analyzer 254. The instrument was calibrated with a blank and seven standards; an aqueous reference solution was diluted in the sample matrix to prepare three separate solutions of varying concentrations within the expected concentration range of the samples. This reference solution was analyzed to verify the standard curve and again after every 20 samples to check for instrument drift. Precision was evaluated by extracting and analyzing 20% of the samples in triplicate; the percent relative standard deviation did not vary more than 5% for any sample. Descriptive statistics (mean, standard deviation, median) were calculated by Microsoft Excel 2000.

National Institute of Standards and Technology (NIST) SRM 2710 and 2711 (Montana soils with highly and moderately elevated trace-element concentrations) were used to evaluate the accuracy and precision of the total digestion of the house dust procedure and the precision of the soil extractions with 1M HCl and SPLP. For each procedure, aliquots of 2710 and 2711 having the same soil:solution ratio as the samples were processed along with the sample unknowns. Although the NIST certified values of the SRM are for a total analysis, the results of the SRM extractions are listed in Table 1 to illustrate the range of concentrations expected from each type of analysis. Recoveries are calculated relative to

Table 1

Reported total concentrations of two NIST standard reference soils (2710 and 2711) compared to the results (mean \pm standard deviation) of three types of sample analysis in this study. Recovery is calculated relative to the total element concentration. n = number of replicate analyses, SPLP = synthetic acid rain extraction, n.d. = not determined.

	n	Measured concentration mg kg ⁻¹	NIST certified concentration mg kg ⁻¹	Analytical recovery %
NIST 2710				
Total As	4	573 (56)	626 (38)	92
1 M HCl As	8	499 (10.9)		80
SPLP As		n.d.		n.d.
Total Hg	3	31.5 (0.12)	32.6 (1.8)	97
1 M HCl Hg	8	4.14 (0.26)		13
SPLP Hg		n.d.		n.d.
NIST 2711				
Total As		n.d.	105 (8)	n.d.
1 M HCl As	7	63.1 (1.46)		60
SPLP As	4	8.8 (0.36)		8.4
Total Hg	2	6.20	6.25 (0.19)	99
1 M HCl Hg	7	0.54 (0.05)		8.6
SPLP Hg	3	0.012 (0.0021)		0.34

the NIST-certified total concentration; recoveries of 100% are not expected for the 1 M HCl and SPLP because of the nature of the weak acid (sometimes called partial) extraction. All concentrations are reported in mass units based upon air-dry weight.

Results and Discussion

Total As and Hg in the Soil

Soils developed on parent material in this region of geologic enrichment, particularly of As and Hg (Kolker et al., 2009), can be expected to show elevated concentrations of these elements. Anthropogenic sources contribute additional loadings. These sources include: (1) locally and regionally derived wet and dry atmospheric deposition from coal combustion (Kizilshtein and Kholodkov, 1999); and (2) aerial deposition and wash-off from mining and processing activities, including reworking from various tailings piles throughout the city (Panov et al., 1999). Under oxidizing conditions such as those encountered in the aerobic soils sampled in Horlivka for this study, Hg²⁺, the mercuric cation, and AsO₄³⁻, the arsenate anion, are the likely forms of mercury and arsenic in the soil (Schuster, 1991; Matschullat, 2000). Binding of these forms to charged sites on clay minerals, Fe and Mn-hydroxides, and soil organic matter will occur. Cinnabar (HgS) is abundant in the mined rock (Kolker et al., 2009) and thus an expected mineral in the soil. The chemistry of As and Hg in oxidized soils is complex and the mobility of either would depend upon numerous soil characteristics, including specific ion concentration, bonding partners, pH, associated ions, organic matter, and minerals. Our objectives in this study were to observe specific

behaviors of these elements when subject to synthesized environmental conditions rather than to define specific geochemical processes.

Table 2 lists the concentrations of the total As and Hg from the soils at the processing facility. The mean total concentrations and the large standard deviations of As ($623 \pm 590 \text{ mg kg}^{-1}$) and Hg ($4290 \pm 3900 \text{ mg kg}^{-1}$) in the three surface soils collected within the boundaries of the Hg-processing facility illustrate the level of localized contamination as well as the associated site heterogeneity. The soil sample that was collected immediately adjacent to an operating furnace used to recover Hg from recycled waste materials contained the highest concentrations of As and Hg (1310 mg kg^{-1} and 8800 mg kg^{-1} , respectively). As a comparison, surface soils collected in a historic Hg-mining area in NW Slovenia (Teršič et al., 2009) ranged from 8.0 to 49 mg kg^{-1} for As, and 0.35 to 244 mg kg^{-1} for Hg. A sample collected near a former Hg-ore roasting furnace in that study contained 719 mg kg^{-1} of Hg (Teršič et al., 2009). However, the median and maximum Hg concentrations in soil collected at a historic Hg-ore roasting site near Idrija, Slovenia (370 and $19,900 \text{ mg kg}^{-1}$, respectively; Teršič et al., 2011), are comparable to the Hg concentration in the soil next to the Hg-furnace at the processing site in Horlivka.

The sample T1W1 (Table 3a), taken just outside of the boundary of the Hg-processing facility, had an exceptionally high concentration of total Hg ($28,000 \text{ mg kg}^{-1}$) and the second highest total As concentration (760 mg kg^{-1}) of the transect soils. The Hg concentration was more than 100 times that of the next highest concentration of Hg in the transect soil (10 m away), and three times that of the surface soil collected inside of the Hg-processing facility. This site was suspected to have been contaminated by elemental Hg, as drops of liquid Hg were visible in a breached conduit just a few meters away. This sample (T1W1) is excluded in the summary of the Hg data discussed here, although it reinforces our finding that very high levels of As accompany Hg contamination at this site.

The concentrations of both As and Hg in the soils collected along transect T1 (centered on the Hg-processing facility) were highest in samples within 100 m of the facility (Table 3a). The range of total concentrations in T1 was from 38 to 830 mg kg^{-1} for As, and from 2.7 to 250 mg kg^{-1} for Hg. The range of concentrations from T2 (Table 3b), which is bisected by a former Hg mine and tailings piles, was from 41 to 290 mg kg^{-1} for As, and from 1.7 to 44 mg kg^{-1} for Hg. There is a general trend of decreasing soil concentrations with increasing distance from the Hg-processing facility, but the concentrations of As and Hg show a large spatial inhomogeneity. It is evident that even though the Hg-processing facility is a major point-source, it is not the only source of contamination, as the Hg mine workings and tailings piles are extensive and there are coal waste piles located throughout the city.

A comparable site to Horlivka is documented around the Muzhievo metal deposits in the Transcarpathian region, Ukraine, where the local soils have been contaminated by a suite of toxic elements (including As and Hg) from waste material used in local construction, and by effluents from the mining/processing site (Shumlyanskyy et al., 2005). The range of As concentrations in the Muzhievo soils (12.0 to 120.0 mg kg^{-1}) is similar to the range of As concentrations in the Horlivka transect soils; but even the lowest Hg concentrations in the Horlivka soils exceed the range of Hg in the Muzhievo soils (0.034 to 1.522 mg kg^{-1}) (Shumlyanskyy et al., 2005). In Lousal, Portugal, soils in contaminated areas near a former pyrite mine contain As concentrations (597 to 6377 mg kg^{-1}) that exceed those found in the Horlivka soils (Ferreira et al., 2005). The Hg concentrations at this site in Portugal (1 to 130 mg kg^{-1} ; Ferreira et al., 2005) are comparable to Hg concentrations in the soils collected in the transects and the residential areas in Horlivka, but are still an order of magnitude lower than the Hg concentrations in the soil collected within the Hg-processing facility.

Table 2

Total As, Hg, Al, Ca, Fe, S and Si, 1 M HCl-extractable and synthetic precipitation (SPLP) extractable As and Hg concentrations, and loss on ignition (LOI) percentage for three surface soils collected from the Hg-processing facility. Locations: (1) near fluorescent light tube crushing station (48° 21' 32.5" N, 37° 57' 2.8" E); (2) sorting yard across the road from Hg-furnace; (3) adjacent to currently operating Hg-furnace (B and C 48° 21' 30.6" N, 37° 57' 11.9"E).

Site	As total mg kg ⁻¹	As HCl mg kg ⁻¹	As SPLP mg kg ⁻¹	As water mg kg ⁻¹	Hg total mg kg ⁻¹	Hg HCl mg kg ⁻¹	Hg SPLP mg kg ⁻¹	Hg water mg kg ⁻¹	LOI %	Al total %	Ca total %	Fe total %	S total %	Si total %
1	310	240	1.2	0.57	1900	14	0.27	0.2	4.2	2.0	1.6	5.6	0.24	33
2	250	230	1.2	1.7	2100	19	0.03	1.3	3.9	1.7	0.91	6.6	0.19	33
3	1300	1200	2.9	7.9	8800	1200	18	16	11	1.9	1.4	37	1.2	12

Table 3a

Total As, Hg, Al, Ca, Fe, S and Si, 1 M HCl-extractable and water extractable As and Hg concentrations, and loss on ignition (LOI) percentage for surface (0–10 cm) soils collected in transect-1 from the west through the former Hg-processing facility to the northeast. The distance listed is measured from the Hg-processing facility. Only samples having $>6 \text{ mg kg}^{-1}$ of HCl-extractable As and at least 5 mg kg^{-1} of HCl-extractable Hg were chosen for analysis by water extraction (n.d. indicates not determined). Transect T-1W $48^{\circ} 21' 27'' \text{ N}$; $37^{\circ} 57' 5'' \text{ E}$ to $48^{\circ} 21' 25'' \text{ N}$ $37^{\circ} 56' 41'' \text{ E}$, transect T-1NE $48^{\circ} 21' 27'' \text{ N}$; $37^{\circ} 57' 5'' \text{ E}$ and ends 500 meters to the NE (latitude and longitude are unavailable).

Distance meters	As total mg kg^{-1}	As HCl ex mg kg^{-1}	As water ex mg kg^{-1}	Hg total mg kg^{-1}	Hg HCl ex mg kg^{-1}	Hg water ex mg kg^{-1}	LOI %	Al total %	Ca total %	Fe total %	S total %	Si total %
W14	46	6.1	n.d.	31	6.4	n.d.	14	4.9	0.17	2.4	0.028	35.8
W13	400	110	0.06	63	14	0.07	11	7.8	0.97	3.7	0.074	34.0
W12	300	76	n.d.	53	12	n.d.	13	5.0	0.57	2.9	0.099	37.8
W11	200	50	0.01	44	7.6	0.01	10	3.9	0.08	2.3	0.042	38.9
W10	100	89	0.05	230	22	0.02	11	7.1	0.99	3.7	0.093	34.1
W9	90	55	13	97	8.2	n.d.	9.0	10	1.7	5.6	0.030	29.3
W8	80	100	n.d.	88	2.3	n.d.	10	10	1.6	4.8	0.069	29.3
W7	70	38	n.d.	25	4.8	n.d.	11	9.0	1.7	4.7	0.050	31.0
W6	60	100	0.17	110	12	0.02	8.8	8.0	0.80	4.6	0.077	32.6
W5	50	100	0.04	49	4.7	0.07	9.4	7.9	0.58	5.6	0.096	31.5
W4	40	260	0.46	55	6.6	0.13	7.0	7.5	0.55	5.5	0.070	31.7
W3	30	210	0.12	50	6.6	0.07	7.7	8.4	0.51	7.2	0.072	29.8
W2	20	190	0.16	250	110	0.03	19	7.5	0.52	5.4	0.041	32.4
W1	20	760	1.4	28000	770	5.6	31	9.0	0.92	4.9	0.10	30.5
Transect -1 centered on Hg-processing facility												
NE1	10	110	n.d.	13	0.51	n.d.	8.4	5.7	0.27	2.8	0.055	37.2
NE2	20	130	n.d.	24	1.2	n.d.	7.9	6.8	1.8	3.7	0.049	33.9
NE3	30	85	n.d.	10	0.46	n.d.	9.7	9.0	1.0	5.6	0.040	31.5
NE4	40	75	n.d.	47	0.35	n.d.	7.6	7.2	4.4	4.1	0.17	30.5
NE5	50	170	n.d.	22	0.05	n.d.	7.2	8.1	0.87	6.1	0.78	30.7
NE6	60	830	n.d.	22	0.53	n.d.	2.6	6.1	1.2	7.8	0.56	29.9
NE7	70	490	n.d.	33	0.32	n.d.	3.7	4.7	4.2	16	1.2	21.4
NE8	80	130	n.d.	21	0.03	n.d.	6.4	2.8	6.7	20	1.3	19.0
NE9	90	58	n.d.	69	0.14	n.d.	5.8	4.0	5.2	15	2.3	20.4
NE10	100	51	n.d.	68	0.73	n.d.	7.8	11	0.99	6.4	1.1	27.4
NE11	200	320	n.d.	9.8	1.4	n.d.	6.3	5.0	2.4	13	0.91	24.2
NE12	300	44	n.d.	2.7	1.1	n.d.	7.4	8.2	2.3	5.1	0.033	30.9
NE13	400	53	n.d.	6.7	0.02	n.d.	12	8.2	1.7	4.4	0.16	31.6
NE14	500	86	n.d.	3.3	0.40	n.d.	9.7	10	0.99	4.5	0.14	30.3

Table 3b

Total As, Hg, Al, Ca, Fe, S and Si, 1 M HCl-extractable and water extractable As and Hg concentrations, and loss on ignition (LOI) percentage for surface (0–10 cm) soils collected in transect-2 from the west to east beginning on opposite sides of a mine workings. The distance listed is measured from the Hg-processing facility. Only samples having >6 mg kg⁻¹ of HCl-extractable As and at least 5 mg kg⁻¹ of HCl-extractable Hg were chosen for analysis by water extraction (n.d. indicates not analyzed). Transect T-2W 48° 50' 54" N; 37° 59' 34" E to 48° 20' 59" N 37° 59' 6" E, transect T-2E 48° 21' 6" N; 37° 59' 50" E to 48° 20' 58" N; 38° 0' 24" E.

Distance meters	As total mg kg ⁻¹	As HCl ex mg kg ⁻¹	As water ex mg kg ⁻¹	Hg total mg kg ⁻¹	Hg HCl ex mg kg ⁻¹	Hg water ex mg kg ⁻¹	LOI %	Al total %	Ca total %	Fe total %	S total %	Si total %
W10	290	110	n.d.	14	0.017	n.d.	16	8.9	0.11	5.62	0.10	32.6
W9	61	7.5	n.d.	5.2	0.28	n.d.	10	8.2	1.08	5.11	0.36	31.5
W8	170	56	n.d.	24	0.18	n.d.	7.8	5.0	0.556	3.42	0.27	36.1
W7	45	1.0	n.d.	1.7	0.46	n.d.	6.6	9.0	0.243	5.44	0.33	31.5
W6	85	21	n.d.	4.1	0.005	n.d.	29	8.0	0.459	5.54	0.49	31.0
W5	180	17	n.d.	1.8	0.21	n.d.	29	2.9	1.64	1.69	0.11	34.5
W4	59	12	n.d.	6.9	0.006	n.d.	39	10	0.073	6.04	0.18	31.6
W3	59	16	n.d.	2.8	0.002	n.d.	15	7.2	4.59	4.55	0.029	30.0
W2	69	19	n.d.	2.8	0.005	n.d.	36	5.1	1.94	4.83	0.078	30.9
W1	220	38	n.d.	13	0.069	n.d.	36	6.5	1.05	6.23	0.51	31.6
Transect-2 centered on a mine workings												
E1	140	28	n.d.	32	1.3	n.d.	5.7	5.3	1.0	3.37	0.15	35.3
E2	41	7.4	n.d.	6.4	1.2	n.d.	8.7	7.6	0.90	4.75	0.090	32.9
E3	110	3.8	n.d.	9.8	0.66	n.d.	12	7.8	0.78	5.56	0.14	33.1
E4	190	49	n.d.	44	0.040	n.d.	6.8	8.5	0.42	5.43	0.10	32.0
E5	140	19	n.d.	12	0.019	n.d.	12	8.0	0.32	6.45	0.057	33.5
E6	120	8.6	n.d.	6.5	0.34	n.d.	19	6.6	0.28	4.5	0.06	35.0
E7	210	44	n.d.	24	0.049	n.d.	5.1	6.1	0.28	3.64	0.05	36.5
E8	160	34	n.d.	20	0.028	n.d.	11	5.6	1.3	9.81	0.95	28.7
E9	99	7.4	n.d.	38	5.4	n.d.	10	8.1	1.0	5.12	0.28	30.6
E10	240	75	n.d.	24	0.073	n.d.	6.4	7.4	3.7	5.18	0.02	29.4
E11	200	51	n.d.	5.7	3.1	n.d.	12	7.2	1.4	4.11	0.039	32.3
E12	180	53	n.d.	21	2.3	n.d.	17	7.9	2.5	4.51	0.037	30.2
E13	190	52	n.d.	22	3.7	n.d.	13	8.8	1.6	4.94	0.049	31.2
E14	120	24	0.03	24	6.0	0.061	9.4	8.4	0.57	5.45	0.046	31.1
E15	230	56	0.08	29	5.3	0.84	12	8.6	0.92	6.16	0.094	30.6
E16	160	48	n.d.	14	2.4	n.d.	8.5	8.3	0.96	5.03	0.058	31.6

Table 4 shows the range of the total concentrations of As and Hg in the soil samples that focus exclusively on the urban residential areas. The mean total As and Hg concentrations in the soils were $64 (\pm 38) \text{ mg kg}^{-1}$ and $12 (\pm 9) \text{ mg kg}^{-1}$, respectively, and range from 20 to 150 mg kg^{-1} for As, and from 3.7 to 29 mg kg^{-1} for Hg. These concentrations are an order of magnitude higher than the median As and Hg concentrations in playground soils in urban Uppsala, Sweden; 3.22 and 0.52 mg kg^{-1} , respectively (Ljung et al., 2006). Horlivka soils are also elevated compared to the mean (maximum) concentrations of As and Hg in high-density residential areas in Berlin, Germany, of 4.9 (42.3) and $0.48 (3.5) \text{ mg kg}^{-1}$, respectively (Birke and Rauch, 2000), and an industrial city Avilés, Spain, of 20.9 (117) and $0.57 (2.41) \text{ mg kg}^{-1}$, respectively (Balyuk et al., 2008). When compared to soils from a highly polluted environment such as Idrija, Slovenia, a city with a history of 500 years of Hg mining and processing (Gosar et al., 2006), the urban soils collected in Horlivka have similar median (maximum) concentrations for As [$64(150) \text{ mg kg}^{-1}$ for Horlivka vs. $19 (57) \text{ mg kg}^{-1}$ for Idrija (collected 0–10 cm depth; Gosar and Šajin, 2005)]. In contrast, Hg concentrations in the soil (0–15 cm) at Idrija are noticeably higher than at Horlivka [$12(29)$ for Horlivka vs. $47 (973) \text{ Hg mg kg}^{-1}$ for Idrija (Gosar et al., 2006)].

Other Elements in the Soil

Tables 2, 3a, 3b, and 4 list the results of the analysis for major elements including OC (measured as LOI). The major elements in the soil samples, with one exception (site 3 at the Hg-processing facility), have very similar characteristics. The mean (and standard deviation) of the Si, Fe, and Al concentrations in the transect soils are 31% (3.8), 5.7% (3.3), and 7.3% (1.9), respectively, compared to 31% (2.0), 3.6% (1.2), and 4.8% (1.7) in the residential soils. In general, the three major element oxides (SiO_2 , Fe_2O_3 , and Al_2O_3) account for approximately 70 to 80% of the mass of the soil composition. The sulfur concentration ranges from 0.02 to 2.3% and the carbon concentration ranges from 2.6 to 39% for the soils.

No correlations exist here with Fe, Al, S, or OC and As, or Hg, which suggests anthropogenic sources in addition to geologic processes alone. Deposition from the stack emissions of the Hg-processing furnace will reflect the differing volatility of Hg and As from the source materials; for example, Liu et al. (2006) have shown greater volatile loss of Hg as compared to As during coal gasification. At Horlivka, with its multiple sources of contaminants (tailings piles, Hg furnace, etc.), simple patterns of differential behavior are unlikely to be discerned in surrounding soil samples.

HCl-extractable As and Hg in the Soil

The 1 M HCl extraction was used in this study to evaluate the relative mobility and availability of As and Hg. This procedure has been used for As and other trace elements in sediments to identify the phase that includes iron and manganese oxyhydroxides, carbonates, and hydrous aluminosilicates (Huerta-Diaz and Morse, 1990). Dmytriw et al. (1995) used 1 M HCl to extract Hg associated with reactive iron and manganese phases of sediments, and Kot and Matyushkina (2002) reported that this would remove the weakly bound non-organic fraction. Saulnier and Gagnon (2006) suggested that the 1 M HCl extraction would solubilize the bioavailable fraction of trace elements, including As and Hg in sediments. The concentrations in the 1 M HCl extractions of the three surface-soil samples collected at the Hg-facility ranged from 235 to 1190 mg kg^{-1} for As, and 14.1 to

Table 4

Total As, Hg, Al, Ca, Fe, S and Si, 1 M HCl-extractable and synthetic precipitation (SPLP) extractable As and Hg concentrations, and loss on ignition (LOI) percentage for surface (0–2 cm) soils collected as random grabs from playgrounds and public spaces in Horlivka, Ukraine. The distance listed is measured from the Hg-processing facility.

Latitude N	Longitude E	Distance km	As total mg kg ⁻¹	As HCl mg kg ⁻¹	As SPLP mg kg ⁻¹	Hg total mg kg ⁻¹	Hg HCl mg kg ⁻¹	Hg SPLP mg kg ⁻¹	LOI %	Al total %	Ca total %	Fe total %	S total %	Si total %
48° 21' 13"	37° 58' 12"	1.4	150	42	1.8	29	0.023	0.012	8.6	4.0	2.1	2.9	0.14	32
48° 21' 10"	37° 58' 19"	1.6	110	25	1.5	31	0.011	0.003	9.7	3.9	1.4	2.8	0.13	32
48° 21' 8"	37° 58' 17"	1.6	32	10	0.45	7.8	0.021	0.004	4.7	2.0	0.52	1.5	0.054	34
48° 21' 7"	37° 58' 18"	1.6	36	8.5	0.43	6.1	0.010	0.004	7.0	2.4	1.2	1.7	0.056	34
48° 21' 6"	37° 58' 15"	1.6	53	9.7	0.16	18	0.13	0.001	8.3	4.5	2.4	4.6	0.059	31
48° 20' 49"	37° 58' 46"	2.4	65	19	0.59	5.5	<0.001	<0.001	13	8.2	1.5	4.3	0.36	28
48° 20' 21"	37° 58' 32"	2.7	71	18	0.71	7.4	0.008	0.001	13	4.5	3.1	3.5	0.30	31
48° 19' 8"	37° 58' 14"	4.5	36	9.0	0.06	4.4	0.018	0.010	4.6	4.9	4.1	3.1	0.14	32
48° 19' 00"	37° 57' 57"	4.6	20	1.7	0.04	6.1	0.31	0.002	8.0	5.3	0.79	4.4	0.040	32
48° 18' 26"	37° 59' 38"	6.4	44	9.7	0.23	3.7	0.066	0.005	14	6.3	1.3	4.5	0.12	30
48° 17' 58"	38° 04' 31"	11.0	49	14	0.97	14	0.024	0.006	20	6.1	3.8	5.5	0.45	28
48° 18' 22"	38° 05' 33"	11.9	110	33	0.33	13	0.011	0.004	11	5.2	4.2	4.1	0.76	29

1150 mg kg⁻¹ for Hg; these concentrations are 74–93% of the total As, and 1–13% of the total Hg (Table 2). Although the concentrations of total Hg are much higher than total As in soil samples from the Hg-processing facility, for the HCl-extractable fractions As is greater than Hg, indicating that the majority of the Hg is present in more resistant, and potentially less bioavailable forms than the As. Previous studies from our group (Landa, 1978a) have shown elemental mercury vapor, likely the major vapor phase here, to be labile (~60% average removal) from soils via 1 M HCl extraction. Hg²⁺ ions introduced to the soil by dry or wet deposition of particulates and subsequently retained by cation exchange sites are also likely mobilized by such an extraction. Hg in unprocessed ore and in the most Hg-enriched coal occurs as HgS (Kolker et al., 2009). The solubility of HgS in 1 M HCl is minimal (Mikac et al., 2002). The observed low solubility of Hg in the samples shown in Table 2 is consistent with the occurrence of Hg as HgS. Methylation of mercury is unlikely under the oxidizing conditions present in these soils. The mercury deposited in the soil as Hg²⁺ is subject to subsequent volatilization as Hg⁰ (Landa, 1978b); likewise, sorbed Hg⁰ can be oxidized to Hg²⁺ by microbial action or abiotic processes (Fang, 1981). Mercury emission will generally increase with soil temperature (Landa, 1978b; Rinklebe et al., 2010). Hence the mercury inventory in the soil is a dynamic quantity, at this site and at other sites where similar anthropogenic inputs of mercury occur.

Of the organomercury compounds, methylmercury is the most stable and is the primary concern regarding bioexposure (Holmes et al., 2009). Methylmercury production is a biologically mediated process, predominantly associated with sulfate-reducing bacteria (Compeau and Bartha, 1987). During site reconnaissance, several areas where conditions that might favor the production of methylmercury were identified and sampled. Sediment analysis from the edges of tailings/catchment ponds in the vicinity of the Mykytivka mines showed that the proportion of total Hg occurring as methyl Hg was very small, ranging from 0.04 to 0.28% for four samples (Kolker, unpublished data, 2005; Kolker, 2007). These results indicate that Hg exposure to the population from the edge of the tailings pond sediment was primarily as inorganic Hg, although there may have been some higher concentrations of methyl Hg in the deepest areas of the ponds.

In general, the samples collected along the transect in or near the Hg-processing facility or the mine workings had the highest HCl-extractable fractions of As and Hg. For As, the range of concentrations (excluding T1W1) mobilized by the 1 M HCl extraction from T1 (Table 3a) were from 2.5 to 381 mg kg⁻¹, with a mean concentration of 54 (±85) mg kg⁻¹. For Hg, the range extracted was from 0.02 to 140 mg kg⁻¹, with a mean concentration of 8.5 (±22) mg kg⁻¹. For T2 (Table 3b), these extractable concentrations ranged from 1.0 to 110 mg kg⁻¹ for As, with a mean concentration 33 (±26) mg kg⁻¹, and from <0.01 to 6 mg kg⁻¹ for Hg, with a mean concentration of 1.3 (±1.9) mg kg⁻¹. These soils are highly variable; the range of extraction efficiencies was 2–87% for As, and 0.2–55% for Hg. There is no correlation between the HCl-extractable As versus HCl-extractable Hg concentrations from the transect soil.

For the 12 residential soils, between 9 and 33% of the total As concentrations (Table 4) were extracted in 1 M HCl, compared to less than 2% of the total Hg. The pH of the 1 M HCl solution is approximately 0.1; after extraction of the alkaline soils, the pH was still strongly acidic (<0.5). The mean HCl-extractable concentration in the residential areas was 17 (±12) mg kg⁻¹ As and 0.057 (±0.090) mg kg⁻¹ Hg. Not only are the total concentrations lower in the residential areas as compared to the soils in the transects that are closer to industrial workings, but the As and Hg concentrations are less extractable and presumably less bioavailable.

Acid Precipitation— and Water Soluble— As and Hg in the Soil

The SPLP uses a dilute solution of H_2SO_4 and HNO_3 (at pH 5.0) to determine the potential for groundwater impact from contaminated soils when subjected to acid precipitation. This method has been used to evaluate the relative mobility of As and Hg, as well as other trace elements, in contaminated sediments and soils (Adams et al., 2007; Jang et al., 2010). The SPLP was performed on the three soils from the Hg facility (Table 3a and 3b) and the 12 soils from the residential areas (Table 4). The pH of the soils in deionized water (1:10) ranged from 7.8 to 9.4. Because of the alkaline nature and strong buffering capacity of the soils, the pH of the SPLP solution after the 18 hours of soil extraction was between 7.2 and 8.6. The concentrations of As and Hg in the SPLP leachate in the soils from the facility ranged from 1.2 to 2.9 mg kg^{-1} for As and from 0.03 to 18 mg kg^{-1} for Hg; this is 0.2% to 0.5% of the total As, and 0.002% to 0.8% of the total Hg in these samples. The range of As concentrations leached from the residential soils with the SPLP varied from less than 0.05 to 1.8 mg kg^{-1} ; this procedure extracted less than 3% of the total As, and less than 0.2% of the total Hg.

The samples selected for the water extraction were only those with the highest total and extractable As and Hg concentrations. The water-soluble fraction of the soils from the Hg facility (Table 2) ranged from 0.57 to 7.9 mg kg^{-1} As and from 0.2 to 16 mg kg^{-1} Hg; this represented 0.2 to 0.7% of the total As and 0.01 to 0.2% of the total Hg. It is an interesting note that in sample 3—collected adjacent to a currently operating Hg furnace—the water soluble fractions of both As and Hg are higher than the very dilute acid leachate SPLP fraction. The range of concentrations of As and Hg in the water leachate samples from T1 and T2 was 0.01 to 1.4 mg kg^{-1} As (0.6% or less of the total As), and 0.01 to 5.6 mg kg^{-1} Hg (0.01 to 3% of the total Hg). This is similar to the range of water-soluble fraction of As (0.82–1.7%) and Hg (0.06–0.16%) fraction to that reported for industrially impacted soil reported from Estarreja, Portugal (Rodrigues et al., 2010), and to the range of water soluble As (0.02–0.5%) in soil from the La Parrilla mine, Spain (Anawar et al., 2006). Even though the water-soluble Hg fraction of sample 1W from T1 was only 0.02% of the total, the concentration of Hg is 5.6 mg kg^{-1} , which is more than double the Ukraine soil MAC of 2.1 mg kg^{-1} Hg (SRIOSCP, 1994; Shumlyansky et al., 2005).

Total As and Hg in the Carpet Dust

The median and maximum concentrations of As (5.1 and 12.9 mg kg^{-1}) and Hg (1.2 and 21.5 mg kg^{-1}) in Horlivka carpet dust were higher than carpet dust collected in the control city of Artemivsk (1.1 and 1.3 mg kg^{-1} As and 0.7 and 0.9 mg kg^{-1} Hg). However, they are not elevated compared to concentrations in home dust reported in the literature. For example, in Ottawa, Canada, a city without a major sector of heavy industries, median and maximum concentrations in house dust for As (4.1 and 79.5 mg kg^{-1} , respectively) and Hg (1.61 and 37.1 mg kg^{-1} , respectively) were reported by Rasmussen et al. (2001). In Idrija, Slovenia, near one of the largest Hg deposits in the world (Gosar et al., 2006), average and maximum concentrations for home attic dust [9 and 141 mg kg^{-1} for As (Gosar and Šajn, 2005) and 129 and 1055 mg kg^{-1} for Hg (Gosar et al., 2006)] are a point of comparison for house dust from a highly contaminated area.

The carpet dust in Apt 1 (Figure 2), within 1 km of the Hg facility and 500 m of a large tailings pile, had $12 \pm 2.6 \text{ mg kg}^{-1}$ As and $21.5 \pm 1.4 \text{ mg kg}^{-1}$ Hg. Dust in this home, closest to the Hg facility, had concentrations of Hg nearing the USEPA human-health soil screening levels (SSL) of 23 mg kg^{-1} (USEPA, 2011). Here the carpet dust had a higher

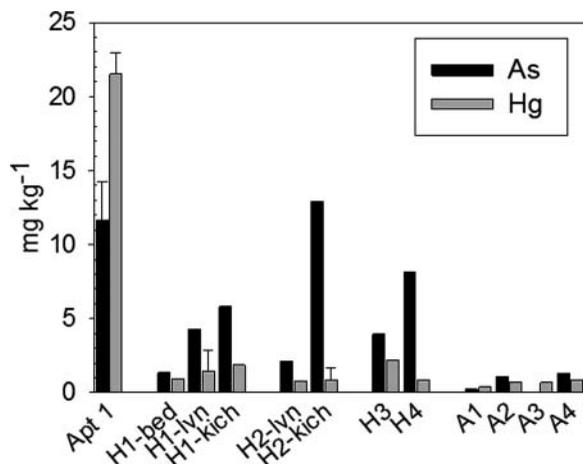


Figure 2. Concentrations of As and Hg in vacuumed carpet dust from homes in Horlivka (H) compared to homes in the control city Artemivsk (A). b: bedroom; l: living room; k: kitchen.

concentration of Hg than As, which differs from dust collected in the other homes (H1–H4 in Figure 2). In these other homes, approximately 1 to 3 km away from the Hg facility, the range of concentrations was from 1.3 to 12.9 mg kg⁻¹ for As and from 0.8 to 2.2 mg kg⁻¹ for Hg. Two of the homes (H1 and H2) were sampled in more than one room. In each of these homes, samples from the kitchen contained the highest concentrations of As and Hg. The range of concentrations in carpet dust in the homes in the control city of Artemivsk was from 0.2 to 1.3 mg kg⁻¹ of As and from 0.4 to 0.9 mg kg⁻¹ of Hg. In a companion study, Gibb et al. (2011) reported a significant correlation between the concentration of Hg in home vacuum dust and the urinary Hg of the resident.

Soil Regulatory Guidelines

Ukraine does not have soil regulatory guidelines specific to industrial soils, but soil screening values for potentially unacceptable human-health risk in the European Union (EU) nations for industrial soils range from 50 to 500 mg kg⁻¹ for As, and 5 to 480 mg kg⁻¹ for Hg (Table 4.8 in Carlon, 2007). Note that the As and Hg concentrations in the 1 M HCl-extractable fraction of sample 1 (Table 2) exceed the highest EU industrial soil screening value (500 mg kg⁻¹ for As, 480 mg kg⁻¹ for Hg) based on health risk (Carlon, 2007).

In Ukraine, national standards exist for maximum allowable concentrations (MAC) of As and Hg in soils, and reflect national environmental targets (Palekhov et al., 2008). In environmental assessments done in Ukraine, total soil concentrations are typically normalized to these MAC values of 2.0 mg kg⁻¹ for As and 2.1 mg kg⁻¹ for Hg (SRIOSCP, 1994; Shumlyansky et al., 2005). The nations of the EU have soil screening values that are based on potentially unacceptable health risk for residential soils; these range from 10 to 300 mg kg⁻¹ for As, and 1 to 56 mg kg⁻¹ for Hg (Table 4.6 in Carlon, 2007).

Potential Exposure from Ingestion

One of the potential exposure pathways to As and Hg is through inadvertent ingestion of these soils. Indoor exposure to heavy metals has been well documented, especially for

small children (Landrigan and Baker, 1981; Lanphear et al., 1998). Based upon a range of studies, 100 mg d⁻¹ is a mean estimate for inadvertent soil ingestion for a child (Table 5–21 in USEPA, 2006). Using this daily rate and the mean total concentration of the soils from the residential area, we calculated possible total amounts of metal ingested for As of 6.4 μg d⁻¹ and for Hg of 1.2 μg d⁻¹. This amount would be equivalent to as much as one-third of the estimated daily intake of total As (between 20 and 300 μg day⁻¹; WHO, 2001) and Hg (4.3 μg d⁻¹; Holmes et al., 2009) from food and beverages. As a comparison, the calculated inadvertent soil ingestion for As and Hg from a comprehensive study of playgrounds in Uppsala, Sweden, was 0.54 and 0.065 μg day⁻¹, respectively (extrapolated from Table 4 in Ljung et al., 2006). These calculated ingestion rates are only what a child might inadvertently take into his/her mouth, and are not meant to imply that these concentrations would be absorbed into the body.

Because the 1 M HCl extraction is less aggressive than the total extraction, using the results of this experiment would be a more conservative estimate of the bioaccessibility of inadvertent soil ingestion for As and Hg. Thus, using the mean and maximum concentrations of these extractions from the residential soils (primarily collected from playgrounds), we can make a general estimate of acid-extractable intakes of 1.7 and 3.3 μg d⁻¹As. The lower HCl-extractable fractions for Hg in these residential soils results in estimates of the mean and maximum ingestion rates of 0.06 and 0.3 μg d⁻¹. This is, of course, a much smaller fraction of the total daily estimated intake of these elements from food and beverages noted earlier considering total concentrations.

Using the mean and maximum concentration of As in residential vacuum dust in Horlivka and a child's daily soil ingestion rate of 100 mg, we estimated mean and maximum ingestion rates for As of 0.63 and 1.2 μg d⁻¹, respectively. These estimates are comparable to calculated mean and maximum ingestion rates for As (0.47 and 1.3 μg d⁻¹, respectively) that are based on elements in house dust predominantly from industrial (contaminated) sites described in a literature review by Oomen et al. (2008). The maximum inadvertent ingestion from residential dust exposure would represent 6% or less of the estimated daily intake of total arsenic from food and beverages (between 20 and 300 μg day⁻¹; WHO, 2001).

The same calculations for the mean and maximum ingestion rates of Hg for the Horlivka homes resulted in ingestion rates of 0.38 and 2.2 μg d⁻¹, respectively. These are an order of magnitude higher than the calculated rates by Oomen et al. (2008) of 0.012 and 0.25 μg d⁻¹, and at the maximum rate, nearly half of the estimated average daily intake of inorganic mercury from food and drinking water sources of 4.3 μg d⁻¹ (Holmes et al. 2009).

Conclusions

In this pilot-scale case study, we have described the total concentrations of As and Hg in soil and home dust in Horlivka, Ukraine, an area of natural and anthropogenic enrichment of these elements but one that has not been well documented in English language literature. Because loosely bound elements are more bioavailable, a total element analysis alone was not sufficient to estimate environmental mobility or potential human risk; our environmental assessment also included a series of weak acid extractions. Our data for each type of element speciation (total, weak acid extractable, SPLP, water extractable in soil and in home dust) has been put into context by comparison to other similar published studies in Europe; for example, Portugal (Ferreira et al., 2005; Rodrigues et al., 2010), Spain (Anawar et al., 2006; Balyuk et al., 2008), and Slovenia (Gosar et al., 2006; Gosar and Šajn, 2005; Teršič et al., 2009).

We have also compared the results of the soil and home dust to soil quality guidelines and have attempted to model oral bioaccessibility. Most significantly, Hg concentrations in soil and home dust from this study have been shown to be good predictors of blood and urinary Hg (Gibb et al., 2011). Concentrations of extractable As and Hg that exceed recommended total soil concentrations for industrial soils indicate that the soil may represent a potential source exposure to workers at the Hg facility. Estimates of possible exposure to As and Hg through inadvertent ingestion of soil or house dust by children in Horlivka are within an estimated range of daily dietary intake. Leaching studies suggest that As in the soils is more labile in dilute acids and potentially more biologically available than Hg. For this reason, future studies in this region should consider evaluating both As and Hg concentrations in biological tissues. Even though the risk of acute exposure to As and Hg for the general population of Horlivka may not be significant, the long-term chronic exposure to low levels of these elements, individually or in combination, may have health consequences. However, a more thorough and detailed study of this city would be needed to accurately gauge the full human-health impact.

Acknowledgments

This research was supported, in part, by U.S. Civilian Research and Development Foundation Cooperative Grant UKG1-2633. We would like to thank Michael Doughten (USGS) for his analytical assistance, and Suzette Morman and Mark Engle (both from the USGS) for their review of the manuscript.

References

- Adams, C., Witt, E. C., Wang, J., Shaver, D. K., Summers, D., Filali-Meknassi, Y., Shi, H., Luna, R., Anderson, N. 2007. Chemical quality of depositional sediments and associated soils in New Orleans and the Louisiana Peninsula following Hurricane Katrina. *Environ. Sci. Technol.* **41**, 3437–3443.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2006. *TOX FAQs Chemical Agency Briefing Sheets. Mercury*. Available at <http://www.atsdr.cdc.gov/MMG/MMG.asp?id=106&tid=24#bookmark02>. Accessed May 22, 2011.
- Anawar, H. M., Garcia-Sanchez, A., Murciego, A., and Buyolo, T. 2006. Exposure and bioavailability of arsenic in contaminated soils from the La Parrilla mine, Spain. *Environ. Geol.* **50**, 170–179.
- Balyuk, S. A., Miroshnichenko, N. N., and Fateev, A. I. 2008. Concepts of ecological rating of permissible anthropogenic impact on the soil cover in Ukraine. *Eurasian Soil Sci.* **41**, 1327–1334.
- Birke, M., and Rauch, U. 2000. Urban geochemistry: Investigation in the Berlin metropolitan area. *Environ. Geochem. Health* **22**, 233–248.
- Cachada, A., Rodrigues, S. M., Mieiro, C., Ferreira da Silva, E., Pereira E., Duarte, A. C. 2009. Controlling factors and environmental implications of mercury contamination in urban and agricultural soils under a long-term influence of a chlor-alkali plant in the North-West Portugal. *Environ. Geol.* **57**, 91–98.
- Calderón, J., Ortiz-Pérez, D., Yáñez, L., and Díaz-Barriga, F. 2003. Human exposure to metals: Pathways of exposure, biomarkers of effect, and host factors. *Ecotoxicol. Environ. Saf.* **56**, 93–103.
- Carlson, C. (Ed.): 2007. *Derivation Methods of Soil Screening Values in Europe: A Review and Evaluation of National Procedures towards Harmonization*, European Commission, Joint Research Centre, Ispra, EUR 22805-EN.

- Compeau, G. C., and Bartha, R. 1987. Effect of salinity on mercury-methylating activity of sulfate reducing bacteria in estuarine sediments. *Appl. Environ. Microbio.* **53**, 261–265.
- Dean, W. E. 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: Comparison with other methods. *J. Sed. Pet.* **44**, 242–248.
- Deutsches Institut für Normung (DIN). 1984. *German Standard Methods of the Examination of Water, Waste Water and Sludge: Sludge and Sediments (Group S): Determination of Leachability by Water (S4)*, DIN 38414-S4 pub, Berlin, Germany.
- Dmytriw, R., Mucci, A., Lucotte, M., and Pichet, P. 1995. The partition of mercury in the solid components of dry and flooded forest soils and sediments from a hydroelectric reservoir, Quebec (Canada). *Water Air Soil Poll.* **80**, 1099–1103.
- Fang, S. C. 1981. Studies on the sorption of elemental mercury vapor by soils. *Arch. Environ. Con. Tox.* **10**, 193–201.
- Ferreira, E., Cardoso, E., Matos, J. X., Patinha, C., Reis, P., and Santos, J. M. 2005. The effect of unconfined mine tailings on the geochemistry of soils, sediments and surface waters of the Lousal area (Iberian Pyrite Belt, Southern Portugal). *Land Degrad. Dev.* **16**, 213–228.
- Gibb, H., Kozlov, K., Buckley, J., Centeno, J., Jurgenson, V., Kolker, A., Conko, K., Landa, E., Panov, B., Panov, Y., and Xu, H. 2008. Biomarkers of mercury exposure at a mercury recycling facility in Ukraine. *J. Occup. Environ. Hyg.* **5**, 483–489.
- Gibb, H., Haver, C., Kozlov, K., Centeno, J. A., Jurgenson, V., Kolker, A., Conko, K. M., Landa, E. R., and Xu, H. 2011. Biomarkers of mercury exposure in two Eastern Ukraine cities. *J. Occup. Environ. Hyg.* **8**, 187–193.
- Gosar, M., Šajn, R. 2005. Arsenic in the environment: Enrichments in the Slovenian soils. *Geologija.* **48**, 253–262.
- Gosar, M., Šajn, R., Biester, H. 2006. Binding of mercury in soils and attic dust in the Idrija mercury mine area (Slovenia). *Sci. Total Environ.* **369**, 150–162.
- Holmes, P., James, K. A.F., and Levy, L. S. 2009. Is low-level environmental mercury exposure of concern to human health? *Sci. Total Environ.* **408**, 171–182.
- Huerta-Diaz, M. A. and Morse, J. W. 1990. A quantitative method for determination of trace metal concentrations in sedimentary pyrite. *Mar. Chem.* **29**, 119–144.
- International Programme on Chemical Safety (IPCS) 2001. *Arsenic and Arsenic Compounds: Environmental Health Criteria 224*, World Health Organization, Geneva, Switzerland. Available at: http://www.who.int/ipcs/publications/ehc/ehc_224/en/index.html. Accessed May 23, 2011.
- Jang, Y., Jain, P., Tolaymat, T., Dubey, B., Singh, S., Townsend, T. 2010. Characterization of roadway stormwater system residuals for reuse and disposal options. *Sci. Total Environ.* **408**, 1878–1887.
- Kizilshstein, L. Y., Kholodkov, Y. I. 1999. Ecologically hazardous elements in coals of the Donets Basin. *Int. J. Coal Geol.* **40**, 189–197.
- Kolker, A. 2007. *Final Project Report*, U.S. Civilian Research and Development Foundation, Award UKG1-2633-GO-04, Washington, DC.
- Kolker, A., Panov, B., Landa, E., Panov, Y., Korchemagin, V., Conko, K., and Shendrik, T. 2009. Mercury and trace-element contents of Donbas coals and associated mine water in the vicinity of Donetsk, Ukraine. *Int. J. Coal Geol.* **79**, 83–91.
- Kot, F., Matyushkina, L. 2002. Distribution of mercury in chemical fractions of contaminated urban soils of Middle Amur, Russia. *J. Environ. Monit.* **4**, 803–808.
- Landa, E. R. 1978a. The retention of metallic mercury vapor by soils. *Geochim. Cosmochim. Acta* **42**, 1407–1411.
- Landa, E. R. 1978b. Soil water content and temperature as factors in the volatile loss of applied mercury (II) from soils. *Soil Sci.* **126**, 44–48.
- Landrigan, P., and Baker, E. 1981. Exposure of children to heavy metals from smelters: Epidemiology and toxic consequences. *Environ Res.* **25**, 204–24.
- Lanphear, B., Matte, T., Rogers, J., Clickner, R., Dietz, B., Bornschein, R., Succop, P., Mahaffey, K., Dixon, S., Galke, W., Rabinowitz, M., Farfel, M., Rohde, C., Schwartz, J., Ashley, P.,

- and Jacobs, D. 1998. The contribution of lead-contaminated house dust and residential soil to children's blood lead levels. *Environ Res.* **79**, 51–68.
- Liu, S., Wang, Y., Yu, L., Oakey, J. 2006. Volatilization of mercury, arsenic and selenium during underground coal gasification. *Fuel*. **85**, 1550–1558.
- Ljung, K., Selinus, O., Ottabong, E., and Berglund, M. 2006. Metal and arsenic distribution in soil particle sizes relevant to soil ingestion by children. *Appl. Geochem.* **21**, 1613–1624.
- Matschullat, J. 2000. Arsenic in the geosphere – a review. *Sci. Total Environ.* **249**, 297–312.
- Mikac, M., Foucher, D., Niessen, S., Fischer, J. C. 2002. Extractability of HgS (Cinnabar and metacinnabar) by hydrochloric acid. *Anal. Bioanal. Chem.* **374**, 1028–1033.
- Oomen, A., Janssen, P., Dusseldorp, A., and Noorlander, C. 2008. *Exposure to Chemicals via House Dust*, Report 609021064/2008, National Institute for Public Health and the Environment, Bilthoven, The Netherlands.
- Palekhov, D., Schmidt, M., and Pivnyak, G. 2008. Standards and thresholds for EA in highly polluted areas – The approach of Ukraine in standards and thresholds for impact assessment. In: *Standards and Thresholds for Impact Assessment*, pp. 33–48 (Schmidt, M., Glasson, J., Emmelin, L., and Helbron, H., Eds.), Springer-Verlag, Berlin.
- Panov, B., Dudik, A., Shevchenko, O., and Matlak, E. 1999. On pollution of the biosphere in industrial areas: The example of the Donets coal basin. *Int. J. Coal Geol.* **40**, 199–210.
- Rasmussen, P., Subramanian, K., Jessiman, B. 2001. A multi-element profile of house dust in relation to exterior dust and soils in the city of Ottawa, Canada. *Sci. Total Environ.* **267**, 125–140.
- Rinklebe, J., During, A., Overesch, M., DuLaing, G., Wennrich, R., Stärk, H.-J., and Mothes, S. 2010. Dynamics of mercury fluxes and their controlling factors in large Hg-polluted floodplain areas. *Environ. Poll.* **158**, 308–318.
- Rodrigues, S. M., Henriques, B., Coimbra, J., Ferreira da Silva, E., Pereira, M. E., and Duarte, A. C. 2010. Water-soluble fraction of mercury, arsenic and other potentially toxic elements in highly contaminated sediments and soils. *Chemosphere*, **78**, 1301–1312.
- Rubinstein, J. B., and Barsky, L. 2002. *Non-ferrous Metal Ores: Deposits, Minerals and Plants*, Taylor and Francis, New York.
- Saulnier, I., Gagnon, C. 2006. Background levels of metals in St. Lawrence River sediments: Implications for sediment quality criteria and environmental management. *Integ. Env. Assess Manag.* **2**, 126–141.
- Schuster, E. 1991. The behavior of mercury in the soil with special emphasis on complexation and adsorption processes – a review of the literature. *Water Air Soil Poll.* **56**, 667–680.
- Shumlyansky, B., Ivantyshyana, O., Makarenko, M., and Subbotin, A. 2005. Environmental pollution around the Muzhievo gold-base metal deposit, Ukraine. *Manage. Environ. Qual.* **16**, 593–604.
- State Research Institute of Occupational Safety in Chemical Production, Ukraine (SRIOSCP). 1994. *The Safety Levels of Harmful Substances in the Environment: Table 3: Maximum Allowable Concentrations of Chemicals in Soils*, SRIOSCP, Severodonetsk, Ukraine, 537–545 (in Russian).
- Teršič, T., Gosar, M., and Šajin, R. 2009. Impact of mining activities on soils and sediments at the historical mining area in Podljubelj, NW Slovenia. *J. Geochem. Explor.* **100**, 1–10.
- Teršič, T., Gosar, M., and Biester, H. 2011. Distribution and speciation of mercury in soil in the area of an ancient mercury ore roasting site, Frbežene trate (Idrija area, Slovenia). *J. Geochem. Explor.* **110**, 136–145.
- United States Environmental Protection Agency (USEPA). 1994. *Test Method for Evaluation Solid Waste, Physical/Chemical Methods (SW-846)*, EPASW-846.3.2B. Available at: <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1312.pdf>. Accessed May 23, 2011.
- United States Environmental Protection Agency (USEPA). 1995. *Sampling House Dust for Lead: Basic Concepts and Literature Review*, EPA747/R-95-007, USEPA, Washington, DC.
- United States Environmental Protection Agency (USEPA). 2006. *Child-Specific Exposure Factors Handbook (External Review Draft)*. Available at: <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=56747#Download>. Accessed May 23, 2011.

- United States Environmental Protection Agency (USEPA). 2011. *Regional Screening Level (RSL) Resident Soil Table June 2011*. Available at: http://www.epa.gov/reg3hwmd/risk/human/rbconcentration.table/Generic_Tables/index.htm. Accessed November 2009.
- World Health Organization (WHO). 2001. *Environmental Health Criteria 224: Arsenic and Arsenic Compounds*, 2nd ed., WHO, Geneva, Switzerland. Available at: <http://www.inchem.org/documents/ehc/ehc/ehc224.htm#1.4>. Accessed May 23, 2011.