Heavy Metal Contamination of the Mining and Smelting District in Mitrovica, Kosovo

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Abstract

Mitrovica had the largest metallurgic and mining complex (Trepca) in Europe which commenced activities in 1993 with the extraction of lead, cadmium and zinc. Many industrial plants existed in the complex such as lead smelter, fertilizer production plant, refinery, battery factory, zinc electrolysis facility and a sulfuric acid plant. The significant amount of heavy metal pollutants were released to the surrounding area including populated residential areas and therefore associated with human health risk. The minority communities in three refugee camps in Mitrovica, Kosovo have been significantly exposed to environmental lead originated from large-scale mining and smelting industries since 1999. Even the smelter was closed down in 2000 by United Nations but the impacts of the abandoned mining dumps, tailing dams are still left behind. The initial risk assessment by WHO in 2004 indicated children's blood lead levels in these communities are dangerously high. Soil contamination due to historical and ongoing pollution from these complexes is also considered as a key source of exposure. A systematic investigation for the soil contamination by lead and other heavy metals was performed in year 2006. Most soil samples contain significantly high lead amount exceeding the US Environmental Protection Agency standard of 400 mg kg-1. The highest amount of lead, 151,000 mg kg-1 with the average of 134,000 mg kg-1 was found in the sample close to the former smelter. Soil lead existed as relatively high amount of bioavailability fraction which may be confirmed with the recent study that no lead bearing phases could be observed directly by XRD. The resemble trend of lead isotope ratios (206Pb/207Pb) in tailings (1.175+0.003), soils from former smelter (1.175+0.014) and from the relocated area (1.173+0.011) revealed that tailings may be one source of lead. However, sustainable monitoring of environmental condition and continuous risk assessment are required to prevent lead and other heavy metal exposure in this area.

Keywords: heavy metal, mining, smelting, Mitrovica, Kosovo

1. Introduction

Lead is one of the best known toxic heavy metals, and has become a general environmental contaminant. Lead in the environment has multiple sources (e.g. petrol, industrial process, paint, solder in canned foods, water pipes) and reaches people via a numbers of pathways such as air, household dust, street dirt, soil, water food. While Pb concentration measurements may provide useful information about potential enrichment of this element, the source of Pb will be ambiguous. Lead isotopes have thus been introduced as "fingerprints" of environmental pollution. Each source of lead can have distinct or sometimes overlapping isotopic ratio ranges. Lead is present in the environment as four main isotopes include 208 Pb (52%), 206Pb (24%), 207Pb (23%) and 204Pb (1%) (Komarek et al., 2008). The first three are radiogenic isotopes and are produced by the radioactive decay of 232Th, 235U and 238U respectively (204Pb is non-radiogenic). Lead isotope analysis are widely used to study environmental pollution as the Pb isotope composition does not change during industrial and environmental processes, but always reflects the sources origin (Cicchella et al., 2008).

WHO and Centers for Disease Control and Preventions recognize 10 microgram per deciliter as the safety threshold for the concentration of lead in human blood. Lead exposure can cause many adverse health effects. Severe lead poisoning, at levels exceeding 70 µg/dl of blood can lead to encephalopathy and death. Other health effects associated with less severe exposures include hypertension, anemia, and impaired nerve conduction (National Research Council, 1993). Young children under age of six are especially vulnerable to lead's harmful health effects because their brains and central nervous system are still being formed (ENHIS, 2007).

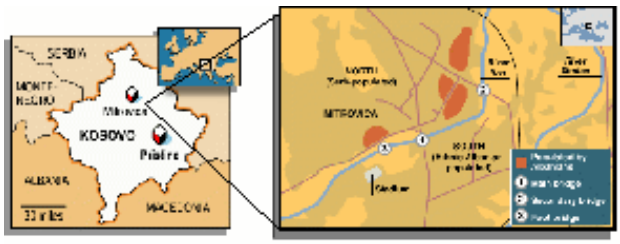

Figure 1. Map of Mitrovica.

Mitrovica is a city and municipality in northern Kosovo (Figure 1). It has population about 110,000 which 70% are Albanian and 30% are Serbian. Since the religion conflict in 1999, Mitrovica has been divided physically by the Ibar River. Northern part is occupied Serbian who are Christian Orthodox. The southern part is occupied by Albanian who is Muslim (Figure 2). Mitrovica is a very important district as it had the largest metallurgic and mining complex in Europe named "Trepca". Mining was operated since 1939 with the extraction of lead, cadmium and zinc. Recently, there are three camps of the Roma, Ashkali and Egyptian (RAE) internally displaced persons (IDP) and some other camps in northern Mitrovica are located near to the mine waste tailing dams which are polluted with lead and heavy metals. According to the concern on environmental contamination and its health risk, the complexes were shut down in July 2000 by UN. However, lead and other heavy metals such as cadmium, nickel, arsenic and zinc from the abandoned waste tailing dams and contaminated soil from mining and smelting activities continuously influence the environment and cause health effects to the people in this area (WHO, ECEH, 2005).

The purpose of this study is to examine the current level of heavy metal pollution and lead isotope composition in environmental samples from relocating and surrounding area of lead smelting in Mitrovica, Kosovo. The result will be the key data for the following lead risk assessment study for the minority community in Mitrovica, Kosovo and to further trace the source of lead by comparison of stable lead isotope ratios in blood with those in environmental samples.

2. Methods

Soil samples were collected from seven sites included former smelter (FS), minority community (Osterode, OS and Cesmin Lug, CL), relocation area (Roma Mahala, RM), public residence area (PH), agricultural land (AL) near to the relocation area and suspected hot spot (2KP). Tailings samples were also taken from the mining dumps (MS). Soil and tailing samples were taken from the upper 5 cm of the soil profile. Then they were air-dried in the laboratory to constant weigh, sieved through a 2 mm sieve and homogenized. A mass of 0.4 g of the sample will be extracted in 4 ml of aqua regia (1 ml HNO_3 + 3 ml HCl) solution. Total Pb concentrations will be determined by Flame Atomic Absorption Spectrophotometer, Perkin Elmer 5100 PC.

Lead isotopes were analyzed in GIST by an Aligent 7500 series Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Calibration against the Pb isotope standard reference material NIST 981 was performed in order to correct mass bias. Stock solutions were prepared by digesting a portion of the Pb metal in 3M HNO3. The following lead isotopes include ^{204}Pb, ^{206}Pb, ^{207}Pb and 208Pb were measured. Subsequently, only ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios will be discussed as they show the most significant differences between contaminated and natural background materials and are mostly interpreted in environmental studies (Monna et al., 1998). The measurement of Pb isotopes (^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios) by ICP-MS proved to be a powerful tool for tracing the pollution in soil heavily polluted by metallurgy (Ettler et al., 2004).

In this study, X-ray diffraction analysis was performed to determine the dominant mineralogy. The samples were analyzed on the XRD using a scan region from 3 to 70° 2Ø in 0.03° steps using count times of 1 s. The XRD unit is a Rigaku DXR-3000 powder diffracto-meter that uses a 40 kV, 30mA Cu anode for X-ray production.

3. Results and Discussion

The XRD results (Figure 2) showed that bulk mineralogy of tailings (MS) was dominated by quartz (SiO2) and gypsum ($CaSO_4.2H_2O$) with minor amount of jarosite ($KFe_3(SO_4)2(OH)_6$), muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), albite ($NaAlSi_3O_8$) and calcite ($CaCO_3$). Soil samples were also identified the predominant minerals present as quartz, albite, and muscovite. No lead-bearing phases were detected in most samples except former smelter site (FS) which thenardite ($NaSO_4$) and galena (PbS) were remarkably found on the diffraction peak. Thenardite, jarosite and gypsum are the common form occurred during oxidation of sulfide mineral (Alpers et al., 1994). Gypsum is an ordinary phase in oxidized zone of sulfide-rich mine tailings or coal wastes (Alpers et al., 1994). The presence of jarosite indicates acidic conditions (pH<3) (Dutrizac et al., 2000). Galena (PbS) could reflect the large amount of Pb remaining in the form of unsmelted primary minerals and or the Pb in silicate glasses in the slag (Li and Thorton, 2001). It is

noticeable that despite the relatively high contents of lead in many samples, no metal bearing phases could be observed directly by XRD. A previous study about Kosovo soil by Ko et al., (2008, personal communication) found relatively high exchangeable lead concentrations with averaged of 24.97% and it clearly illustrates that Pb in soil is potentially soluble and bioavailable.

Total content of lead in soil and tailings ranged from 480 to 125094 mg kg-1 (Table 1). The highest concentration was found in the sample taken from the former smelter which lead in soil was more than 300 times of the US EPA standard of 400 mg kg-1 for lead in bare soil for children. The lead isotopic ratios measured in all the soil and tailings samples are shown in Table 1. . Based on the 206Pb/207Pb ratios the soil and tailings analyzed in this study have distinct ratios. The minority community, Cesmin Lug (CL), posses the least isotope ratios range from 1.154 to 1.163 (average: 1.159+0.005) whereas the other, Osterode (OS) and Roma Mahala (RM) have much higher 206Pb/207Pb ratios ranging from 1.158 to 1.175 (average: 1.169+0.009) and 1.163 to 1.184 (average: 1.173+0.011). The soil samples from hot spot (2KP) have slightly higher 206Pb/207Pb ratios than any of the samples in this study. Lead isotope of mine tailings (MS) (1.175+0.003), soil samples from former smelter (FS) (1.175+0.014) and Roma Mahala (RM) (1.173+0.011) are identical. This is reasonable to assume that lead from tailing dams may be one important source. Dust particles from the tailing dams may also be a primary source of lead which was dispersed to the vicinity area. As the smelter was shut down, the abandoned mine waste may still be the primary source in Mitrovica area. The resemble trend of lead isotopes were also found in Osterode (OS) samples (1.169+0.009) and agricultural area (AL) samples (1.166+0.010) which can imply the contamination from the equivalent source of lead.

Contamination of lead in soil can cause the health effects to human beings. In Mitrovica, lead poisoning of children in the north Mitrovica region of Kosovo is considered as one of the most serious children' s environmental health crisis in the contemporary Europe (WHO ECEH, 2005). Currently, identification of second source of lead, other than tailing dams is difficult because there is not enough information. According to a report of WHO (WHO ECEH, 2005), secondary smelting activities in this area and IDP camps are suspected to be an important source of lead. Home smelting lead batteries is a potential source of lead as it is an important source of income for many RAE families.

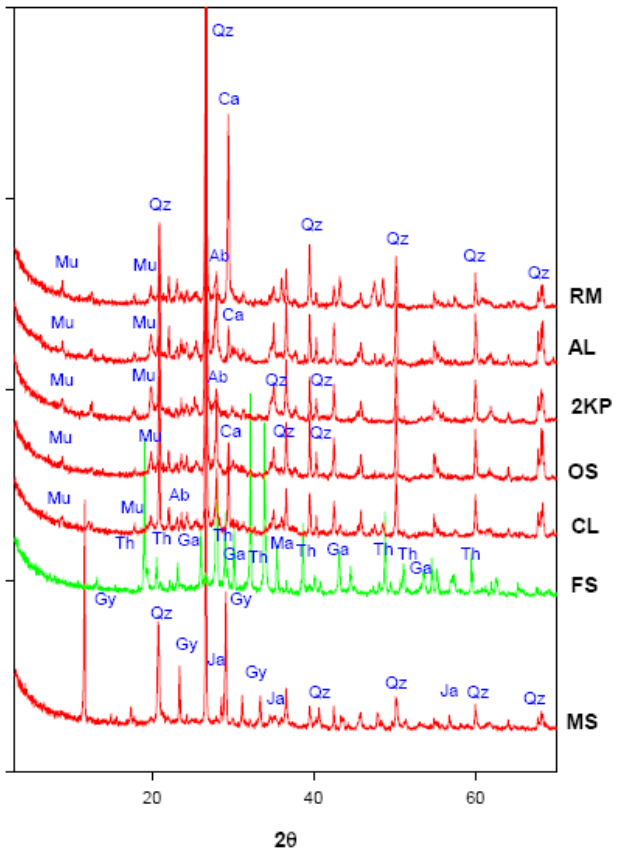

Figure 2. XRD pattern of tailings and soil samples. Ab; albite, Ca; calcite, Gy; gypsum, Ja; jarosite, Mu; muscovite, Ga; galena; and Th; Thenardite.

Table 1. Lead concentrations and its isotope ratios of the tailings and soil samples from Mitrovica, Kosovo

	Pb content mg kg-1	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
MS-1	1780	1.175 ± 0.003	2.098 ± 0.005
MS-2	21100	1.172 ± 0.002	2.076 ± 0.003
MS-3	480	1.172 ± 0.023	2.111 ± 0.010
FS	125094	1.175 ± 0.014	2.122 ± 0.021
OS	8920	1.169 ± 0.009	2.101 ± 0.023
CL	9390	1.159 ± 0.005	2.096 ± 0.009
2KP	4460	1.193 ± 0.003	2.070 ± 0.056
RM	570	1.173 ± 0.011	2.127 ± 0.018
AL	840	1.166 ± 0.011	2.118 ± 0.003

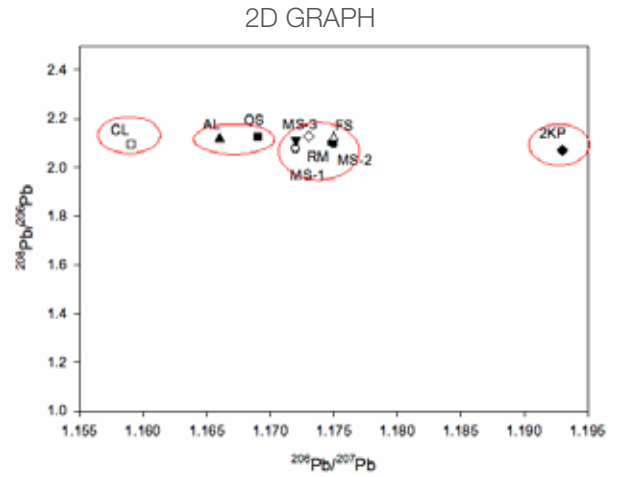

Figure 3. 206Pb/207Pb vs 208Pb/206Pb in soil and tailings from Mitrovica, Kosovo, (•) MS-1, (○) MS-2, (▼) MS-3, (Δ) FS, (■) OS, (□) CL, (♦) 2KP, (◊) RM, (△) AL.

4. Conclusions

Soil in Mitrovica contains significantly high amount of lead exceeding the acceptable level. The obtained results indicated that people in IDP camps and the relocation area, Roma Mahala, are still living in the unsafe environment even the smelter has been closed down for more than seven years. A continuous monitoring of environment and assessment of lead and heavy metals exposure should be implemented. Therefore, the future research will be focused on an update health risk assessment of lead for the minority community in Mitrovica, Kosovo. Lead concentration and isotopic ratio will be measured in environmental samples of Roma, Ashkali and Egyptian internal displaced persons (RAE IDP) camps (Osterode, Cesmin lug and Leposavic) including soil, tailings and batteries. The lead isotopes will be compared with the data of biological samples of blood lead, skeleton tissue and hair. This study will provide valuable information the properties of lead contamination in Kosovo by geochemical approaches and will be the first research which applies lead isotope analysis as a tool to identify the source of exposure in Mitrovica, Kosovo. Findings will not only add new knowledge based on the field of environmental geochemistry and lead toxicology but also benefit the exposed group and the general population in the area with the fundamental data for effective risk management and communication based on scientific evidence.

5. Acknowledgements

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References

Alpers, C., N., Blowes, D., W., Nordstrom, J., L. and Jambor, J., L., 1994. Secondary minerals and acid mine, in: Blowes, D., W., Jambor, J., L. (Eds). *The environmental geochemistry of sulfide mine-wastes, Short course handbook.* Mineralogical Association of Canada, 247-270.1.

Cicchella, D., Vivo, B.D., Lima, A., Albanese, S., McGill, R. A. R., and Parrish, R. R., 2008. Heavy metal pollution and Pd isotopes in urban soils of Napoli, Italy. *Geochemistry: Exploration, Environment, Analysis*, 8, 103-112.

Dutrizac, J., L. and Jamber, J., L., 2000. Jarosites and their application in hydrometallurgy, in: Alpers, C., N., Jamber, J., L. and Nordstrom (Eds). Sulphate minerals-crystallography, geochemistry and environmental significance. *Rev.Mineral.Geochem*, 40, 405-452.2.

Ettler, V., Mihaljevi, M., and Komárek, M., 2004. ICP-MS measurements of lead isotopic ratios in soils heavily contaminated by lead smelting: tracing the sources of pollution. *Anal Bioanal Chem*, 378, 311-317.

Jambor, J. L., 2000. Mineralogy of sulfide-rich tailings and their oxidation products, in: Blowes, D., W., Jambor, J., L. (Eds). *The environmental geochemistry of sulfide mine-wastes, Short course handbook*. Mineralogical Association of Canada, 59-102..

Komarek, M., Ettler, V., Chrastny, V., and Mihaljevic, M., 2008. Lead isotopes in environmental sciences: A review. *Environment International*, 34, 562-577.

Li, X. and Thornton, I., 2001. Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities. *Applied Geochemistry*, 16, 1693-1706.

Monna, F., Loizeau, J., L., Thomas, B., A., Guéguen, C., and Favarger, P.Y., 1998. Pb and Sr isotope measurements by inductively coupled plasma–mass spectrometer: efficient time management for precision improvement. *Spectrochimica Acta Part B: Atomic Spectroscopy* 5, 1317-1333.

National Research Council., 1993. Measuring lead exposure in infants, children and other sensitive populations. Washington DC: National Academic Press.

European Environment and Health Information System (ENHIS), World Health Organization (WHO). Blood lead levels in children. Fact sheet no. 4.5 May 2007 Code RPG4 Chem_Ex1

WHO ECEH, Bonn office., 2005. Mission report: Lead (Pb) crisis in the United Nation administered province of Kosovo.