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ENVIRONMENTAL INFLUENCES OF MERCURY ORE PROCESSING

CASE STUDIES SELECTED AT SLOVENIAN, MEXICAN, HUNGARIAN GROUP MEETING IN IDRIJA IN JULY 2012

Geological Survey of Slovenia & Idrija Mercury Mine, Ltd. - in liquidation

Environmental influences of mercury ore processing - Case studies selected at Slovenian, Mexican, Hungarian group meeting in Idrija in July 2012

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Front cover photograph: Close-up of a mercury ore roasting vessel fragment filled with elementary mercury from an ancient ore processing site in the surroundings of Idrija (bottom) (Photo and image editing: Tamara Teršič & Zoran Gričar) and photograph of a painting by Janko Trošt: Cooking charcoal in Idrija's forests (top) (Courtesy of Photo Library of the Idrija Municipal Museum).
Back cover photograph: Calcite vein with cinnabar mineralization in abandonet Podljubelj mine (Photo: Mateja Gosar).

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Ljubljana, 2012

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Foreword by the director of Geological Survey of Slovenia

It is my greatest pleasure to see the results of a joint International Workshop of Mexican, Hungarian and Slovenian researchers titled *Significance of historical small scale ore processing for mercury dispersion at Idrija area*, organised in summer 2012 by the Idrija mercury Mine, Ltd. – in liquidation and the Geological Survey of Slovenia being published in a book. This is clearly a sign of the importance of the topic and of the interesting content of papers that were presented at the Workshop.

Idrija and its mercury mine have a unique status in Slovenian geology and even wider in natural sciences. The discovery of mercury in Idrija at the end of the 15th Century has since then shaped the development of this beautiful valley and has recently culminated with inclusion of Idrija Mercury Mine on the UNESCO's World Heritage List. In late 16th Century when mining activities began to advance, the economical importance of mercury paved the way for medieval and latter industrial progress, research in geology, mining, mineralogy, and even botanics. The uniqueness of the mineralisation along the Idrija fault enabled many prominent Slovenian and foreign geologists to perform their studies, develop their theses and confirm or reject them. But along with mercury exploration came also pollution of the environment that affected also local population and wildlife. As a consequence of environmental awareness that began 30 to 40 years ago another branch of research developed – environmental geochemistry. Researchers in the field of geochemistry have fully taken the advantage of Idrija's past activities and invisibly transformed the area into the natural laboratory to study long-term impacts of mercury on the environment.

Nowadays, every new piece of information we have about Idrija's environment (or similarly exposed areas elsewhere), the processes within it and especially about the interactions of mercury with the living and non-living environment will help us better understand the impacts of this mining legacy through space and time on the society, humans and animals. I am positive that contemporary research activities in mercury related areas are substantially contributing to the development of these regions by helping towards a cleaner and healthier environment and should be regarded as an opportunity to foster the scientific development and should hence be fully exploited.

Although common problems are present in the areas of past (and present) mercury exploitation around the globe, differences between these areas and their peculiarities also exist. That is why the experience, research results and knowledge sharing between experts tackling the challenges of mercury's impact on the environment are so important. These were the main drivers of the joint Workshop of Hungarian, Mexican and Slovenian researchers and the papers published in this book are a solid proof that the abovementioned goals were achieved.

As knowledge transfer is also one of the major priorities of the IGCP, the joint programme between IUGS and UNESCO, it is almost a logical consequence that the two organisations are patrons of this publication.

In the name of the publisher, the Geological Survey of Slovenia, I wish to thank all the contributors, patrons and editors for enabling this book to be brought in front of you, dear reader. May you have an interesting reading!

Assist. Prof. Marko Komac, Ph.D.Geol.

Foreword by the director of Idrija Mercury Mine

The Idrija Mine, as the second largest mercury mine in the world, operated continuously for more than 500 years. Over many centuries of digging, miners completely changed this once wild and inaccessible basin and left behind them, alongside a technical heritage that was entered in UNESCO's World Heritage List in 2012, also a degraded and polluted environment. When reflecting on the greatness of this technical heritage, we tend to forget much too easily that generations of Idrija miners and their families lived and worked in impossible living and working conditions, and that the environment from Idrija to the Gulf of Trieste has been polluted with mercury.

As many as 107,692 tons of mercury were extracted in the entire period of the mine's operation, which accounts for 13% of the world's total production of this metal so far. During its processing, however, more than 37 tons of mercury was »lost« or disappeared into all components of the environment. The greatest losses occurred in primitive methods of burning in piles and later in clay retorts. Owing to the massive amounts of wood used in this method of burning, the forest in the vicinity of Idrija was soon cleared. Because there were no suitable supply routes for transporting wood, relatively small quantities of rich ore were carried to suitable locations in the surroundings of Idrija. These old burning sites additionally polluted the environment outside the impacted area of the mine.

Environmental pollution with mercury is not only the consequence of long-lasting mining activities in this basin. Even if the legendary »tubmaker« had not discovered mercury in the far-off year of 1492, increased concentrations of this metal would still have been found today in the Idrijca and Soča rivers and in the Gulf of Trieste. This is because primary outcrops of rocks mineralised with mercury can still be found in the surroundings of Idrija.

The inhabitants of Idrija and the entire impacted area of the Mine once lived and continue to live with increased concentrations of this toxic metal in the environment. Even the oldest researchers were aware of the negative impact of mercury on the environment and human health. Through various technical measures they constantly attempted to reduce this negative impact that, to an extreme extent, decisively influenced the working capacity and life expectancy of miners. Precisely because of the need to study the impacts of mercury, a great deal of knowledge and awareness about its impacts on the health of humans and animals, and possible measures for mitigating such impacts, have accumulated. In our opinion, in the same way as the technical heritage of mercury is universal and the property of all mankind, so is the knowledge and awareness of its harmful effects. By organising workshops of this kind and through our further cooperation in joint research, we would like to pass our knowledge on to others who are facing similar problems and are interested in such issues.

Marko Cigale, M.Sc.Geol.

MONITORING AND ASSESSMENT OF MERCURY POLLUTION IN THE IDRIJA MINING AREA

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The Idrija ore deposit is the second largest ore deposit in the world in terms of mercury concentration, being second only to Almadén in Spain. But the Idrija ore deposit is not only a 'giant' among mercury deposits; it has gained international repute and professional significance primarily because of the conditions in which it was formed, its exceptionally rich and unusual ores, geochemical and mineralogical compositions, and the extraordinary transformations into its extremely complex present-day state. The Idrija ore deposit lies directly below the town of Idrija and extends in the direction NW-SE. It is approximately 1500 m long, 400-600 m wide and 450 m deep. 158 ore bodies were found, of which 141 contain cinnabar (14 ore bodies with mostly syngenetic mineralisation and 127 with epigenetic mineralisation). Native mercury is predominant in the remaining 17 ore bodies (Mlakar & Drovenik, 1971).

Closing-down of the Idrija Mine

In 1989 the Slovenian National Assembly passed a decision on the gradual shutdown of the Idrija mine. In respect to the fact that, in the span of 500 years of mining, the town of Idrija was established and expanded partially above very mine, it has been necessary to carry out the closing of the mine in such a manner that the town will not be endangered by the expected deformations on the surface (Likar et al., 2006). Mining of mercury ore directly under the town of Idrija had a significant impact on the surface above the mine (Bajželj et al., 2007). Under the mine shutdown project adopted in 1996, the mine's closure was foreseen by the end of 2006. However, all shutdown works in the pit had been completed by 2009 and the restoration of surface facilities above the mine was completed in 2011.

On the basis of the legislative provisions for shutdown of mercury mine, the final rehabilitation and elimination of the consequences of mining, a mining project “Monitoring of the Affected Area of the Idrija Mercury Mine after the Completion of Shutdown Works” was prepared in 2006. The implemented monitoring programme of the narrower and broader region after the mine closure comprises of visual monitoring to observe the sinking and sliding of ground above the mine, geodetic, geo-mechanical, monitoring of the ground water and environmental monitoring, which comprises of monitoring of concentrations of mercury in soil, water, air and vegetation, and the effect of the mercury pollution to humans (Dizdarevič et al., 2006; Dizdarevič et al., 2011).

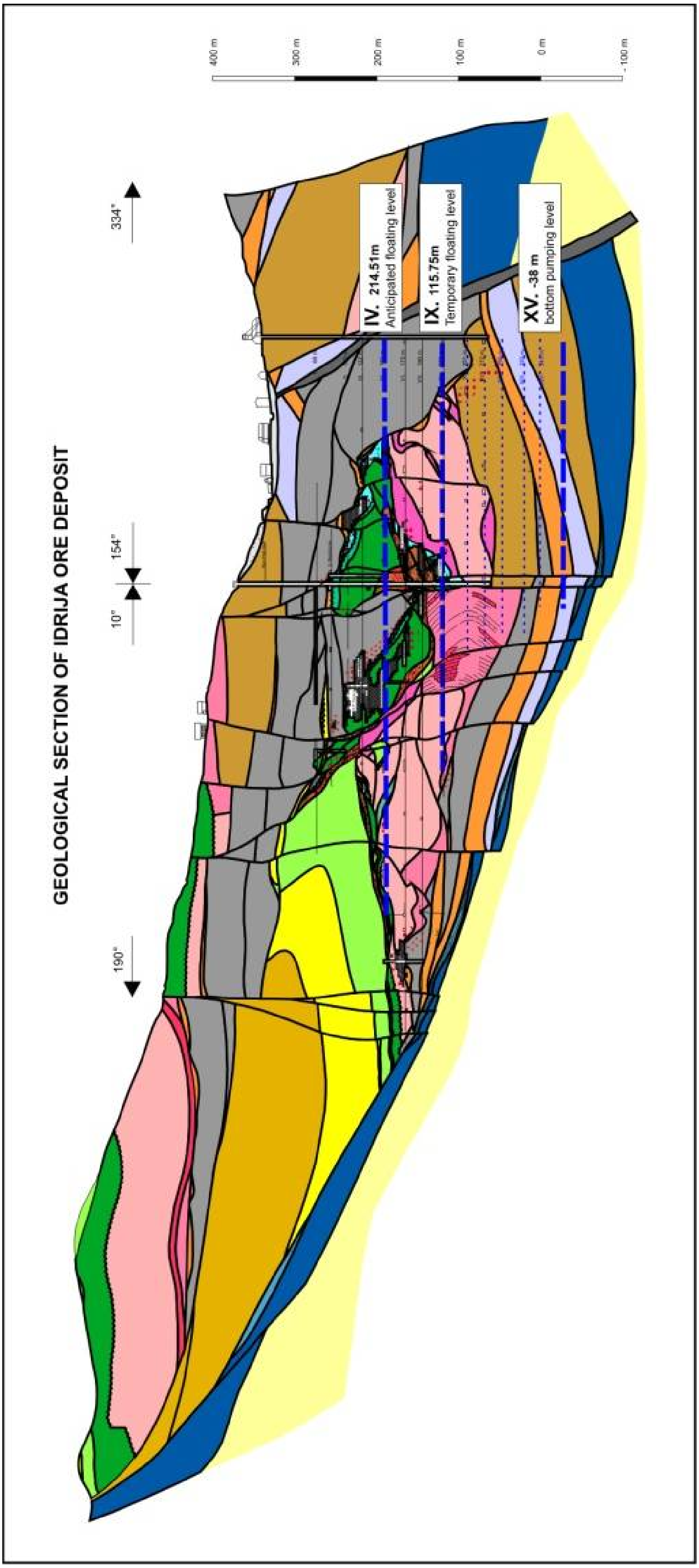

Figure 1: Geological cross section of Idrija ore deposit

Mercury pollution in Idrija Area

In the 500-year history of the mine (1490 – 1995), over 12 million tons of ore were excavated and a total of 153.309 tons of commercial mercury was extracted, which represents over 13% of the entire world production to date (Mlakar & Drovenik, 1971; Mlakar, 1974; Cigale, 1997; Kavčič, 2008). Over this period approximately 38.000 tons of mercury were lost to the environment, mostly in the form of mercury vapour, deposited as smelting residues into the river Idrijca and its banks, or used as construction material (Dizdarevič et al., 2009). Anthropogenic releases from the ore smelter significantly increased the exposure of the inhabitants to mercury, especially in the 70's when Hg production reached its final peak, when first systematic measurements of mercury in the environmental compartments in Idrija region were introduced.

Figure 2: During high waters, the Idrijca River carried away the burnt ore deposited on its banks (Idrija Mercury Mine Archive, 1970)

Since 1995, when smelting plant finally stopped with its operation, Hg concentrations in the air have been much lower (Kotnik et al., 2005; Kocman et al., 2011). But today, tailings and contaminated soils in the Idrija region are eroded and serve as a continuous source of Hg pollution, ultimately of the Gulf of Trieste (Kotnik et al., 2006). This is confirmed by the fact that even after more than 15 years after the cessation of mercury production, the Hg concentrations in river sediments and water show no trend toward the expected decrease in the Gulf of Trieste (Biester et al., 2000; Gosar & Šajn, 2001; Horvat et al., 2002; Kotnik et al., 2006; Gosar, 2008; Kocman & Horvat, 2009; Gosar & Žibret, 2011). The results of the last research works (Kocman, 2008) reveal that the quantity of Hg stored in the catchments, soils and sediments of the Idrija River significantly exceeds the annual quantity of Hg leaving the catchment, i.e. 890 kg/y (Kocman & Horvat, 2011).

As expected, the natural outcrops of mercury and past atmospheric deposition of mercury still burden the soil and consequently the vegetation in this region and mercury levels in soil do not seem to decrease with time (Gnamuš, 2002; Gosar, 2008; Miklavčič et al., 2012).

At the current level of exposure to Hg in the town of Idrija, no directly perceivable toxic effects are expected. Nutritional habits of inhabitants have changed in the past decades. The latest study on mercury exposure revealed that pregnant woman and children living in the area of the former mercury mine are not under any significantly elevated risk of mercury exposure (Kobal et al., 2004, 2007).

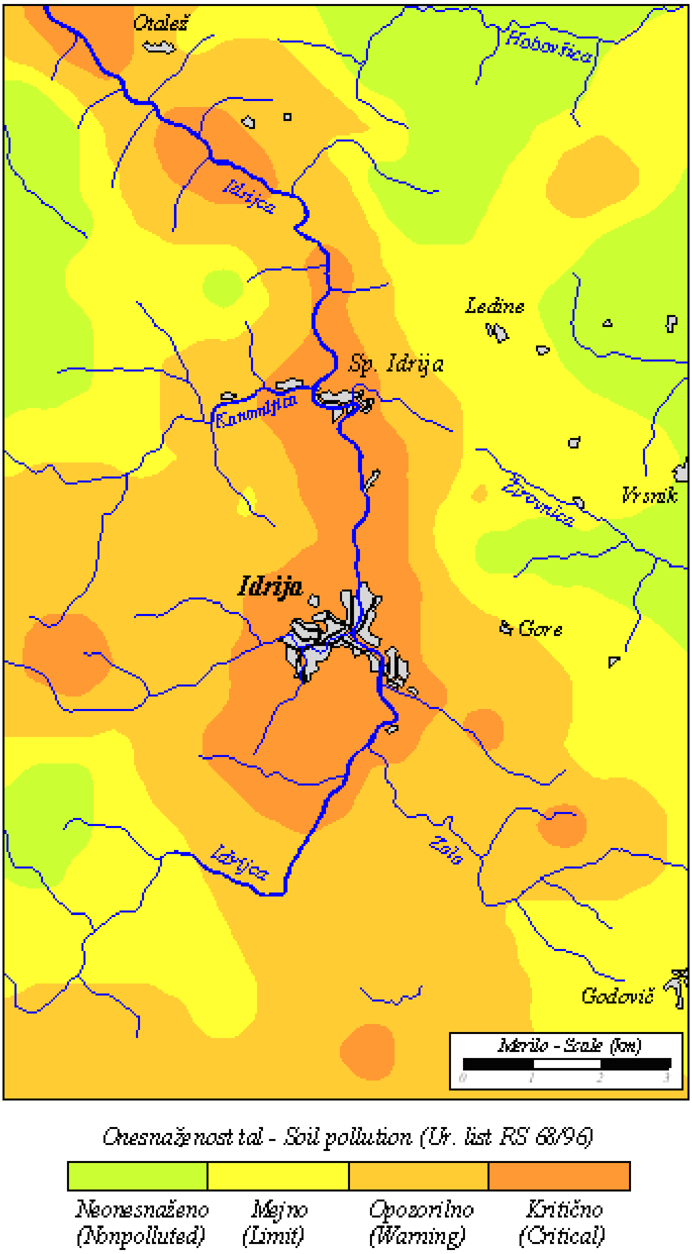

Figure 3: T-Hg distribution in soil in wider Idrija area (after Šajn & Gosar, 2004; data also in Gosar et al., 2006)

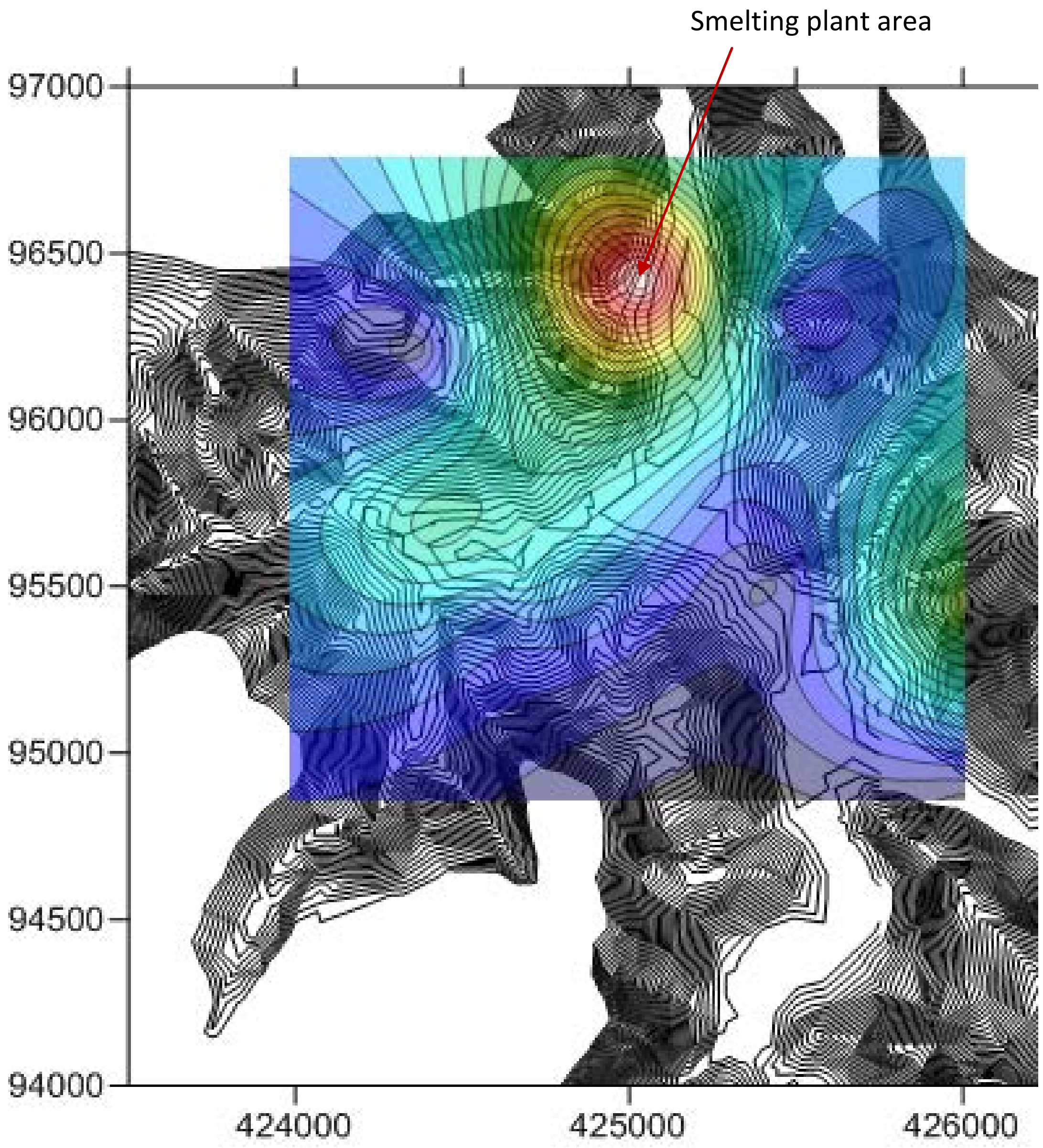

Figure 4: T-Hg distribution in soil in nearer Idrija area in 2012

Conclusion

The results of environmental studies have served as a basis in preparing low term rehabilitation measures for reducing the effects of mining activities accumulated in the past. Although in the past decade there have been several attempts at modelling mercury transport and transformations in the wider Idrija region, it will be necessary to develop an integrated model system that will provide us with a better understanding of the numerous segments of mercury circulation in the polluted area (entire catchment area and inshore sea waters). The model and results will be combined into a tool designed to provide support in decisionmaking, and thus help us to implement the EU Directive on Mercury and the EU Framework Water Directive. A new approach is the integration of environmental sciences with a socio-economic approach (Horvat et al., 2003; Žagar et al., 2006). Also the primary strategic goal of the Municipal Environmental Protection Program (February 2009) is the setup of an effective environmental management system (ISO 14001), reduction of environmental pollution, regulation of public utility infrastructure, waste management, sustainable use of energy, protection of natural resources and biotic diversity, as well as raising environmental awareness and informing citizens.

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Factors that influenced mercury dissemination in the Idrija environment

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Mining and processing of mercury ore in one of the largest natural mercury deposits in the world - the Idrija mercury mine - left behind serious pollution problems in different environmental compartments. There were many different mechanisms of mercury dispersion in Idrija and its surroundings through history.

Before mining activities in Idrija had started, were mercury levels in the environment of Idrija hightened as a consequence of natural, geogenic conditions. The outcrop is very small. Natural migration of mercury into the wider surroundings of the deposit is limited owing to impermeable Carboniferous clastites and tectonic zones filled with clay (Čar, 1998).

The production of mercury in Idrija started in 1492 and was soon moved to the neighbouring forests. Because enormous quantities of timber were required by the mining works, forests in the nearby surroundings of Idrija soon disappeared. Consequently, the miners had to transport relatively small quantities of rich ore to various places in the surroundings of Idrija that were suitable for ore roasting. This way, mercury was brought far into the Idrija surrounding areas and later misled ore prospectors who accidentally found traces of mercury in creeks. Until recently, most interpretations of the investigations resulted from the belief that the town of Idrija with the mine, the smelter and waste material dumps, were the only source of pollution. The detailed study on different ways of ore roasting techniques in the first 150 years of mercury production (Čar & Terpin, 2005), revealed numerous localities of historical ore roasting sites in the woods around Idrija; large quantities of broken pottery can be found in soils and sediments at these sites (Figure 1). Up to now 21 localities of ancient roasting sites were established on the neighbouring hills and in more distant localities; taking into account their extent and numerousness they represent a constant source of mercury emissions (Čar & Terpin, 2005; Gosar & Čar, 2006; Teršič & Gosar, 2009; Teršič, 2010, 2011; Teršič et al., 2011a; Teršič et al., 2011b). Up to the middle of the 17th century, ore was roasted on the neighbouring hills and in more distant localities. It should be stressed that the ignition of ore at that time resulted in considerable losses (Gosar & Čar, 2006; Teršič, 2010; Teršič & Gosar, 2009; Teršič et al., 2011a; Teršič et al., 2011b).

Mineralized rock dumps and especially smelting residues that still contain rather high amounts of mercury are also sources of mercury. Since 1652, when the first smelter in Idrija was built, the mercury rich side products of smelting have been deposited along the river. The main reason for complex spatial distribution of roasting tailings in Idrija and its surroundings are changes in roasting technology over the centuries, continuously growing quantities of processed ore accompanied by decreasing mercury content and various methods of further treatment of ore residues. From the environmental protection point of view, depositories of poor quality ore and remains from roasting, which contain large quantities of mercury, are equally important (Biester et al., 1999).

In time, less and less mercury rich ore was excavated. In order to maintain mercury production on the same level larger and larger quantities of ore had to be excavated and larger roasting facilities were needed. In 1867, a modern roasting plant was built on the right bank of the Idrijca River. New dumps of roasted ore occurred also on the right banks of the Idrijca River. Through atmospheric emissions of the new big roasting plant chimney, mercury was brought far into the Idrija surrounding areas. Roasting process produced gaseous and particulate matter emissions, which were the major cause of creating huge geochemical halo around the Idrija mercury mine (Gosar & Šajn, 2001; Gosar et al., 2006). The research of mercury speciation and total mercury contents in soil and attic dust in 160 km^2 big area confirmed the impact of air emissions on the wider area around Idrija. Furthermore the spatial mercury distribution in the attic dust showed that the influence of atmospheric emissions caused by the Idrija roasting plant resulted in impacts on environment on a regional scale (Gosar et al., 2006). The portions of non-cinnabar compounds increase with distance from the mercury source in both sampling media. Non-cinnabar fractions were found to be enriched in distant areas where fine grained material was deposited. Hg gasses and dust particles (including small paticles of cinnabar) have spread far into the Idrija environs. Mercury is therefore present in soils and attic dust far from Idrija at localities far from the outcrops of ore-rich rocks (Gosar et al., 2006).

Figure 1: Closer look at roasting vessels fragment; cinnabar coatings are visible

From 1868 to 1977 most roasting remains were dumped directly into the Idrijca River, which carried the material to the Soča River and Adriatic Sea. For this reason, the river sediments have high mercury contents (Gosar et al., 1998; Biester et al., 2000; Gosar, 2003; Gosar, 2004; Gosar, 2008; Žibret & Gosar, 2006; Gosar & Žibret, 2011). During high waters, mercury rich material was deposited on the floodplains in the lower part of the Idrijca and

Soča River valleys. These sediments represent a large accumulation of mercury enriched sediments.

Sketch diagram presenting mechanisms of mercury dispersion in the Idrija area through history, which created geochemical mercury halo in Idrija area is presented in Figure 3.

Figure 2: Dry stream bed below Pšenk roasting site with roasting vessels fragments

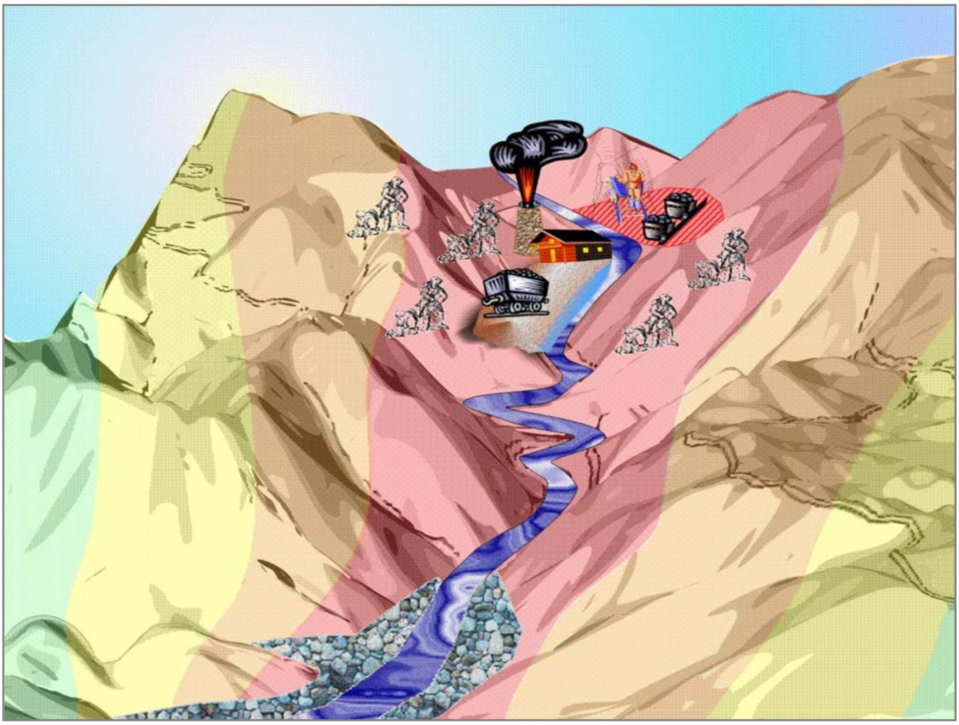

Figure 3: Sketch diagram presenting mechanisms that create geochemical Hg halo at Idrija area

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Influences of ancient ore processing sites in surroundings of Idrija on the mercury dispersion in soil

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In the initial period of mining activities in the Idrija basin (the 16th and the first half of the 17th centuries), mercury ore processing was performed at various small-scale sites in the woods surrounding Idrija, by roasting ore in earthen vessels. The recovery rate of this method was very low; about half of mercury was lost, causing soil contamination and considerable amounts of waste material that could potentially leach Hg into the surrounding environment. The determined mercury contents in soils at old roasting sites are very high, and they surpass all up to now described localities at Idrija and in its surroundings. It was estimated that there are about 40 tons of mercury still present at ancient roasting sites (Gosar & Čar, 2006).

Localities Pšenk and Frbejžene trate were studied in detail. They are two out of 21 localities of ancient roasting sites established on the hills surrounding Idrija (Čar & Terpin, 2005; Gosar & Čar, 2006). We started detailed investigations on mercury contents in soils at these 2 historical roasting site locations (Figure 1) (Gosar & Čar, 2006; Teršič & Gosar, 2009; Teršič et al., 2008; Teršič, 2010, 2011; Teršič et al., 2011a, 2011b). The purpose of the research was to find out the extension of mercury pollution at old roasting sites and their significance for mercury dispersion locally and also in the wider Idrija area, to determine the contents and vertical distribution of mercury in soils and sediments and to establish the changes in mercury speciation with depth in the soil profile. As several anomalies were discovered during geochemical soil survey (Gosar et al., 2006) where increased mercury contents could not be the consequence of main Hg sources such as atmospheric emissions, mineralized rock dumps and roasting residues or their use in construction, we wanted to find out if old roasting sites could be the reason for these anomalies.

At Pšenk site, detailed soil sampling was performed on 210 x 180 m large area to establish the extension of mercury pollution and to investigate mercury transformations and transport characteristics through the 400 year-long period. The organic matter-rich surface soil layer (SOM) and soil samples were collected from 73 sampling points. 3 soil profiles were sampled to determine vertical distribution of Hg in soil (Teršič, 2010; Teršič et al., 2011a) (Figure 2). The main mercury phases were determined by the mercury-thermo-desorption technique. The determined Hg contents in soil samples of the investigated area vary from 5.5 to almost 9,000 mg/kg with the median of 200 mg/kg. In SOM Hg contents are ranging from 1.4 to 4.200 mg/kg with the median of 20 mg/kg (Teršič, 2010; Teršič & Gosar, 2009; Teršič et al. 2011a). Extremely high Hg contents were found in investigated soil profiles where it riches 37,020 mg/kg. In general Hg concentrations in all three studied profiles show a gradual decrease with depth (Figure 3).

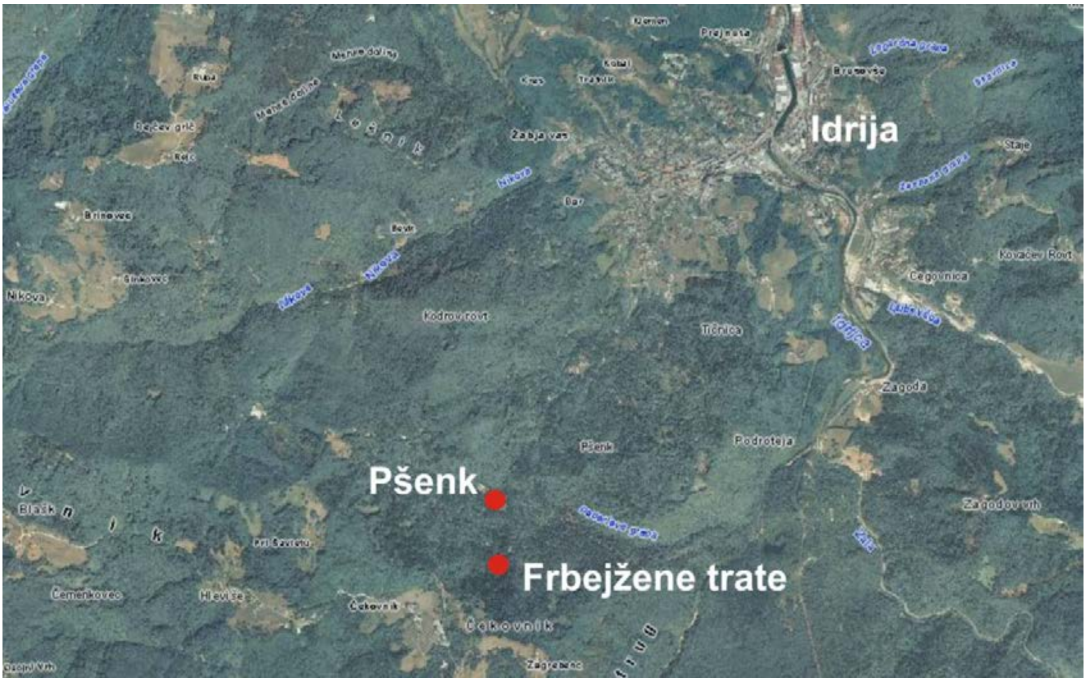

Figure 1: Localities of old roasting sites Pšenk and Frbejžene trate in Idrija area

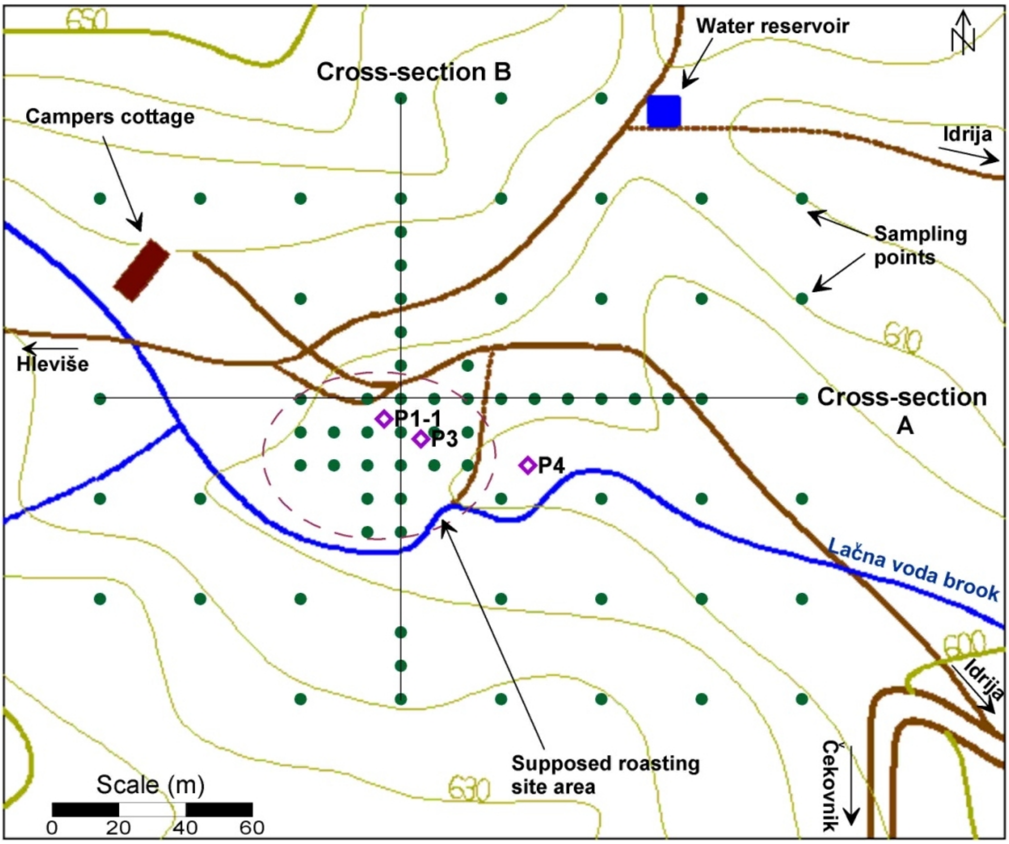

Figure 2: Roasting site Pšenk with soil (green dots) and soil profiles (P1-1, P3 and P4) sampling locations and indicated cross-sections A (E–W direction) and B (N–S direction) (after Teršič, 2010)

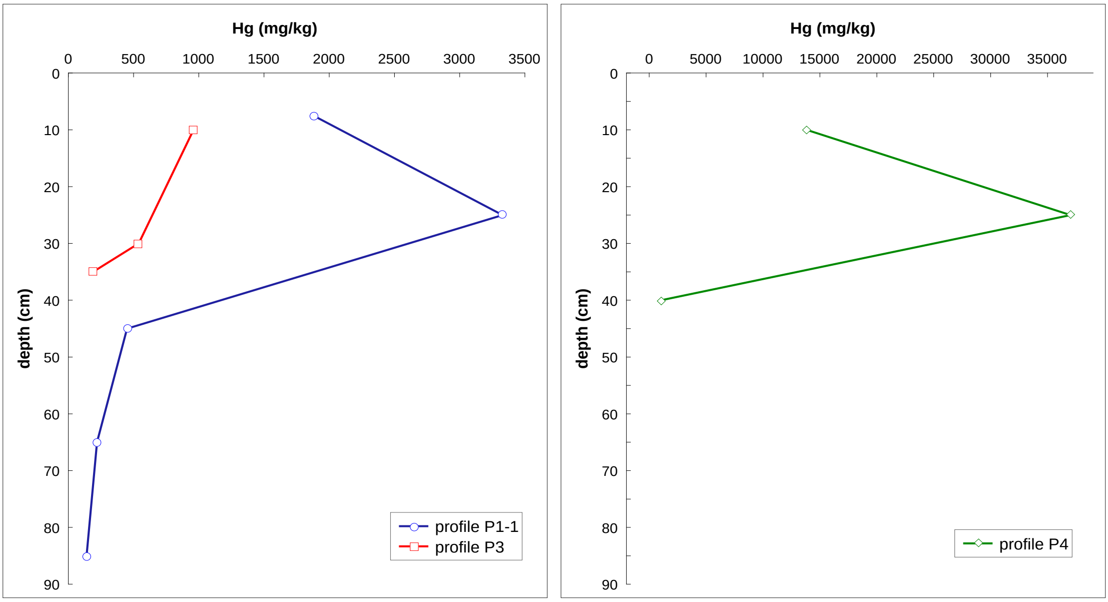

Figure 3: Vertical distribution of mercury contents in soil profiles (after Teršič, 2010)

Determination of Hg phases by solid-phase-Hg-thermo-desorption is based on the specific thermal desorption or decomposition of Hg compounds from solids at different temperatures, and the continuous determination of released volatile Hg°. Mercury thermo-desorption curves were determined by means of using an in-house apparatus, consisting of a furnace and a Hg detection unit. The samples show double peak curves with one maximum between 200°C and 250°C and a second one between 250°C and 350°C. The first peak indicates non-cinnabar compounds. Compared to the standard Hg compounds curves it is most reasonable that this peak represents Hg bound or sorbed to the matrix components. The distribution of mercury species in soil and SOM show almost equal distribution of cinnabar and non-cinnabar Hg compounds in investigated samples (Teršič et al., 2011a).

At Frbejžene trate site soil sampling was performed at the area of the former roasting site. The organic matter-rich surface soil layer (SOM) and underlying mineral soil were sampled at 63 sampling locations (Teršič et al., 2011b) (Figure 4). The results indicate extremely high mercury concentrations with a maximum of 37,000 mg/kg in SOM and 19,900 mg/kg in mineral soil. The established Hg median in soil was 370 mg/kg and in SOM 96.3 mg/kg. Spatial distributions of mercury in SOM and soil showed very high mercury contents in the central area and decreased rapidly with distance.

The results of Hg thermo-desorption measurements indicated that significant portion (35–40 %) of Hg in the investigated soil and SOM samples was comprised of non-cinnabar compounds, which are potentially bioavailable (Teršič et al., 2011b). The distribution of Hg phases does not vary to a large extent throughout the investigated areas and no significant changes in the portion of both fractions could be observed. In Figures 5 and 6 the distributions of mercury phases in SOM and soil (5–20 cm) samples of cross-section C from the western to the eastern part of the investigated area are presented.

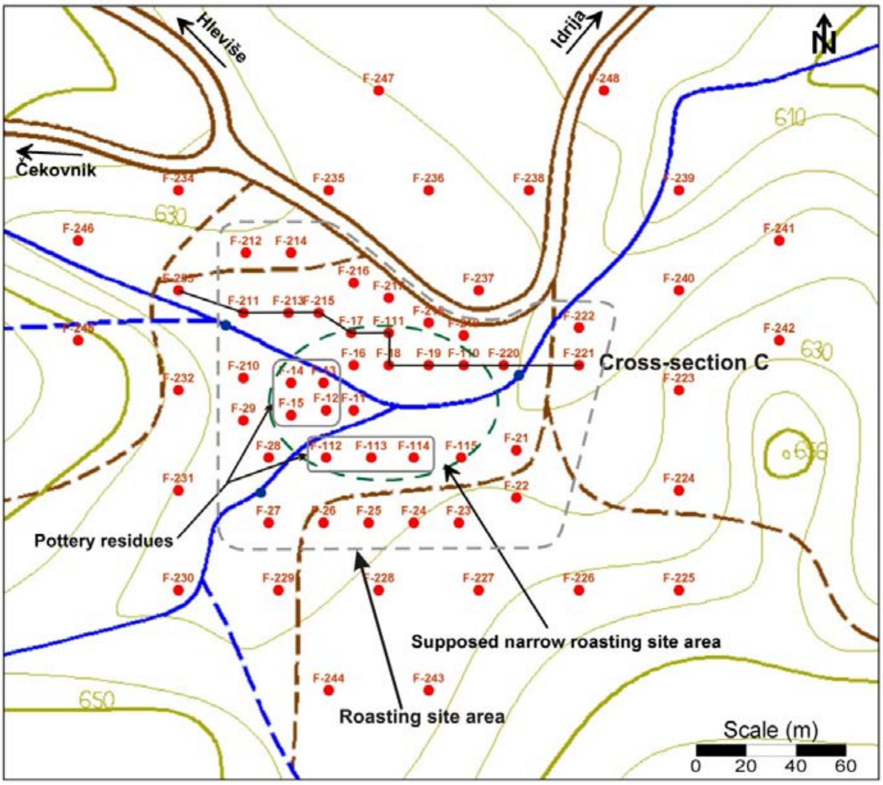

Figure 4: Investigated roasting site Frbejžene trate with sampling locations (red dots) and indicated cross-section C (modified after Teršič et al., 2011b; Teršič, 2010)

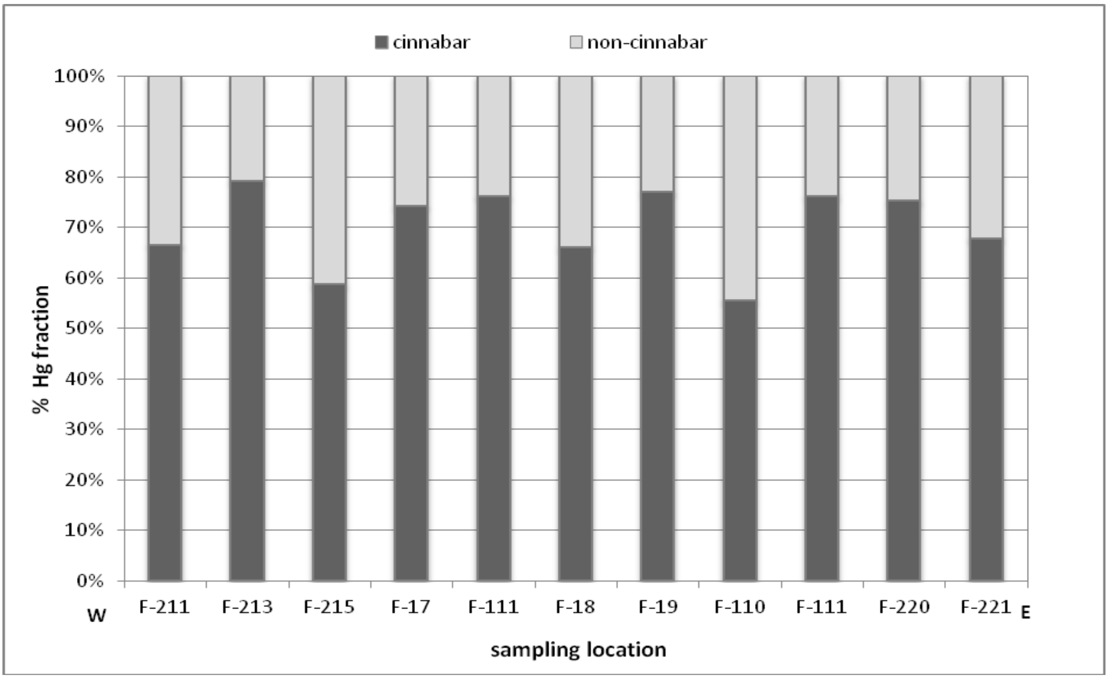

Figure 5: Distribution of mercury phases in SOM samples from cross-section C at Frbejžene trate (after Teršič, 2010)

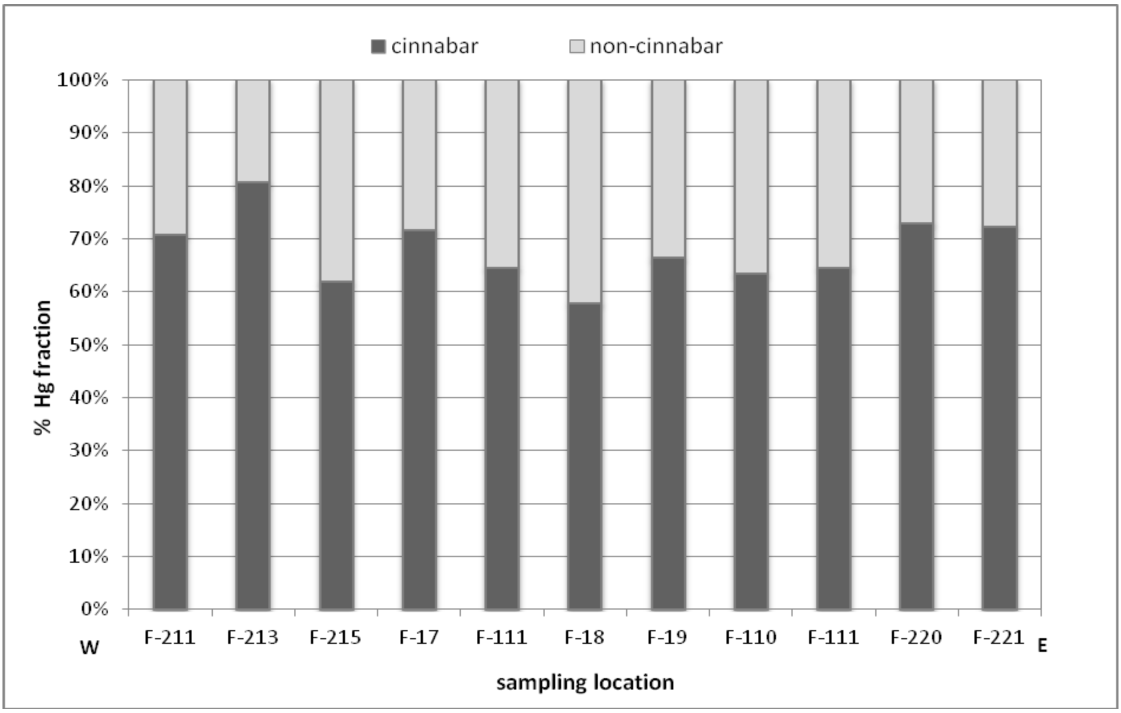

Figure 6: Distribution of mercury phases in soil (5–20 cm) samples from cross-section C at Frbejžene trate (after Teršič, 2010)

Detailed geochemical surveys carried out at these two sites proved that the unique way of historical ore processing in the surroundings of Idrija resulted in extremely polluted sites which influence today's extension and spatial distribution of mercury in the Idrija area. Several Hg anomalies in sediments which were discovered in upper Idrijca River Valley (Gosar, 2008; Gosar & Žibret, 2011) and in the soils on the hills around Idrija (Gosar & Šajn, 2001; Gosar et al., 2006), where increased mercury contents could not be the consequence of main anthropogenic Hg sources, are now interpreted as a consequence of ancient ore roasting sites impacts.

Acknowledgments

The presented study was funded by the Slovenian Research Agency (ARRS) in the frame of the research programme Groundwater and Geochemistry (P1-0020) and the research project Environmental geochemistry of metal contaminated sites (J1-2065) which are performed by the Geological Survey of Slovenia. The authors would like to thank to prof. dr. Harald Biester from Technical University Braunschweig who enabled and co-operated in this geochemical study.

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Elemental contents in earthworm casts at mercury contaminated site

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Earthworms ingest both mineral and organic fragments in soil and, through comminution and mixing during digestion process, the soil material is subjected to a biochemical and physical modification. Earthworms are important for bioturbation, whereby they bring up minerals and soil materials from A and B horizon and are depositing them on the soil surface as casts. Earthworm cast consists of mixed inorganic and organic materials from the soils that are voided after passing through the earthworm intestine. Earthworm casts (Figure 1) offer micro-environmental conditions very different from those occurring in the surrounding soil, resulting from both food selection and digestion process (Kizilkaya, 2004). Total cast production is an indicator of burrowing and soil turnover, because 99.9% of ingested material is egested as casts.

Figure 1: Earthworm cast in researched locality

Applicability of earthworm casts as a sampling media for determining soil contamination was carried out at the ancient Hg ore roasting site Pšenk in the surroundings of Idrija, which is highly contaminated with Hg (Teršič, 2010; Teršič & Gosar, 2009; Teršič et al., 2011). Little information is published on the comparison between elemental contents in earthworm casts and soil and on possibility to use casts as a sampling medium for determining soil contamination. The objectives of our research which was recently published (Teršič & Gosar, 2012), were to compare the Hg and other element contents in earthworm casts to the values in SOM (soil organic matter) and soil (0–15 cm) and to determine whether or not earthworm casts could be applied as sampling material for estimating the dispersion and distribution of contaminant in soil.

32 earthworm cast samples were collected in the research grid 30 x 30 (on approximately 150×150 m large area) in order to compare the Hg and 36 other element contents and spatial distributions in earthworm casts to the values and distributions in SOM and soil (0–15 cm) determined in previous investigation.

Extremely elevated Hg concentrations were determined in earthworm casts from the studied area ranging from 5.4 to 4,330 mg/kg with the median of 31 mg/kg (Table 1) (Teršič & Gosar, 2012). The Hg values in casts are somewhat lower than in soil (6.3–8600 mg/kg) and slightly higher compared to SOM (1.5–4200 mg/kg). Spatial distribution of Hg in earthworm casts show the highest concentrations in the central part of investigated area, similar to the distribution in soil. Hg contents rapidly decrease from the centre towards the margins of the studied area, where they reach values of less than 50 mg/kg. At investigated area earthworm casts proved to be a convenient sampling media for determining Hg contamination in soil (Teršič & Gosar, 2012).

Beside extremely elevated Hg contents, also high contents of As were determined in casts from investigated roasting site, reaching as much as 65 mg/kg (median 26 mg/kg). Additionally Ca (0.61–6.3 %, with the median of 1.8 %), Cd (0.20–1.2 mg/kg with the median of 0.7 mg/kg), Mo (0.80–83 mg/kg with the median of 6.5 mg/kg), Pb (26–91 mg/kg with the median of 47 mg/kg) and U (0.60–12 mg/kg with the median of 1.9 mg/kg) contents are elevated (Table 1). All of these elements except Ca express elevated concentrations also in soil and SOM samples from investigated roasting site (Table 1).

Till now we did not find an explanation for elevated concentrations of As, Cd, Mo and Pb. Idrija ore deposit is classified as a monometal deposit; mercury is the only metal found in the Idrija ore deposit in economically important quantities, while other elements appear only in traces or insignificant quantities (Mlakar & Drovenik, 1971). Therefore high contents of above mentioned elements in studied soils are probably not the consequence of historical ore roasting, with the exception of uranium, whose increased concentrations might be the result of roasting extremely rich cinnabar ore from Skonca beds, which contain on average up to 7 times the average quantity of radioactive elements such as uranium, radium, thorium and potassium, and also radon as a consequence of radioactive decay (Mlakar & Drovenik, 1971).

The determined elemental contents in analyzed cast samples were compared to elemental contents in SOM and soil (0–15 cm) determined in previous investigation of environmental impact of historical ore roasting at Pšenk area (Teršič et al., 2011). The elemental median values for casts are mostly in between SOM and soil median values, indicating that the material from casts is to a certain part a mixture of soil and SOM material (Teršič & Gosar, 2012). During sampling and field observations of the casts we observed differences in colour from light to dark brown which indicates colour of different soil layers.

Table 1: Basic statistics of element contents in earthworm casts at Pšenk roasting site (data after Teršič & Gosar, 2012)

element	N	Mean	Median	Minimum	Maximum	Std.Dev.
Mo(mg/kg)	33		6.50	0.80	82.60	22.21
Cu(mg/kg)	32	14.39	14.95	5.50	24.10	3.92
Pb(mg/kg)	33	48.03	47.40	26.00	91.40	13.37
Zn(mg/kg)	33	73.47	76.00	44.00	93.00	14.46
Ni(mg/kg)	33	13.46	13.70	5.80	24.50	5.22
Co(mg/kg)	33	5.24	5.00	2.30	10.60	2.15
Mn(mg/kg)	33	691.36	611.00	408.00	1615.00	237.52
Fe(%)	33	1.28	1.32	0.66	2.07	0.36
As(mg/kg)	33	27.69	25.70	6.10	65.00	15.53
U(mg/kg)	33	2.45	1.90	0.60	12.40	2.46
Au (mg/g)	23	3.15	1.90	0.50	8.90	2.42
Th(mg/kg)	33	2.16	2.10	1.00	3.20	0.61
Sr(mg/kg)	33	19.14	18.00	9.00	27.50	5.18
Cd(mg/kg)	33	0.67	0.70	0.20	1.20	0.24
Sb(mg/kg)	33	1.43	1.30	0.60	3.00	0.57
Bi(mg/kg)	33	0.55	0.40	0.20	5.60	0.92
V(mg/kg)	33	35.65	34.00	13.00	85.00	14.85
Ca (%)	33	2.35	1.81	0.61	6.33	1.62
P (%)	33	0.05	0.05	0.02	0.07	0.01
La(mg/kg)	33	13.42	14.00	4.00	22.00	4.32
Cr(mg/kg)	32	11.69	12.00	2.00	22.00	5.89
Mg (%)	33	1.13	0.80	0.21	3.26	0.90
Ba(mg/kg)	33	42.33	41.00	20.00	62.00	9.58
Al (%)	33	1.03	1.04	0.53	1.72	0.26
K (%)	33	0.14	0.13	0.08	0.28	0.05
W(mg/kg)	30	0.21	0.20	0.10	0.90	0.14
Hg(mg/kg)	**33**	**279.58**	**31.46**	**5.35**	**4330.00**	**778.65**
Sc(mg/kg)	33	1.38	1.50	0.10	2.50	0.58
Tl(mg/kg)	33	0.56	0.50	0.20	3.20	0.50
S (%)	33	0.11	0.11	0.07	0.21	0.03
Ga(mg/kg)	32	3.06	3.00	2.00	5.00	0.92
Se(mg/kg)	29	2.81	1.10	0.60	25.70	4.88

Positive correlations between casts and SOM were found for U (0.61), Hg (0.59), Ni (0.53), Cr (0.51), Mo (0.51), As (0.50), Sb (0.50), V (0.43) and Sr (0.38). Between casts and soil positive correlations were calculated for Hg (0.87), U (0.83), Cr (0.72), Ni (0.71), Mo (0.67), Sc (0.56), Sb (0.55), As (0.47), Ga (0.48), Co (0.44), Fe (0.38), and V (0.37). Correlation coefficients for positive correlations between elemental contents in casts and SOM and between casts and soil are compared in Figure 2. The highest correlations have Hg, U, Cr, Ni and Mo. Elemental contents in casts are mostly better correlated to contents in soil compared to SOM. However, for As, Sr and V correlation between casts and SOM is better compared to correlation between cast and soil (Figure 2).

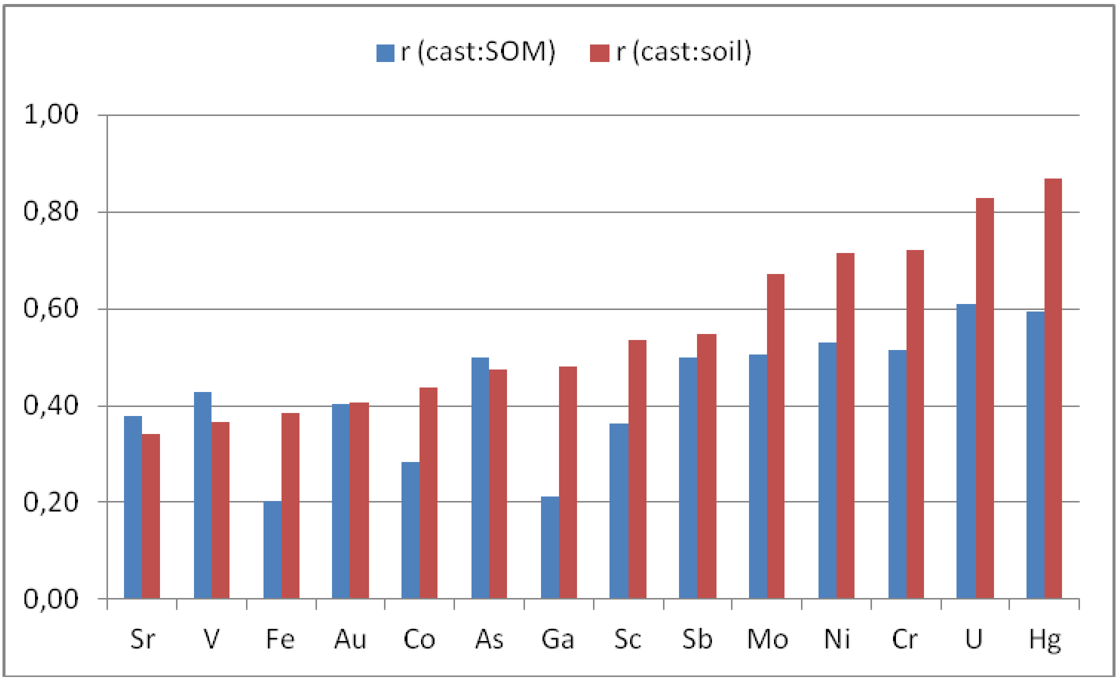

Figure 2: Comparison of significant correlation coefficients between elemental contents in earthworm cast and SOM (blue columns) and earthworm casts and soil (red columns)

At the investigated roasting site Pšenk Hg contents and distribution in casts are comparable to those in the soil. Therefore, earthworm casts can be an appropriate sampling media for determining soil contamination at this particular area.

Acknowledgments

The presented study was funded by the Slovenian Research Agency (ARRS) in the frame of the research programme Groundwater and Geochemistry (P1-0020) and the research project Environmental geochemistry of metal contaminated sites (J1-2065) which are performed by the Geological Survey of Slovenia.

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Mercury in river sediments and boreholes through the Idrijca River alluvial sediments

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Hg contamination of the Idrijca River overbank sediments because of mining and the historical dumping of ore roasting residues and mining waste into the river channel and its erosion downstream was studied. The chemical composition of the alluvial sediment profiles at two locations along the Idrijca River and recent river sediment in Idrijca and Soča has been assessed (Gosar, 2004; Gosar, 2008). Stream sediments were monitored at the 20 locations along the Idrijca and Soča rivers every 5 years since 1991. It was found out that there was no decrease in the mercury concentration in the stream sediments during the last two decades and that overbank sediments are (according to analyses at two locations along the Idrijca River) strongly enriched with mercury (Gosar, 2008). Alluvial sediments were taken between 1996 and 2008. In total, 9 localities were inspected, 20 boreholes were made with total of 33 meters and 266 samples were taken. Inspected and sampled locations are presented on Figure 1 and Table 1 (data after Gosar & Žibret, 2011).

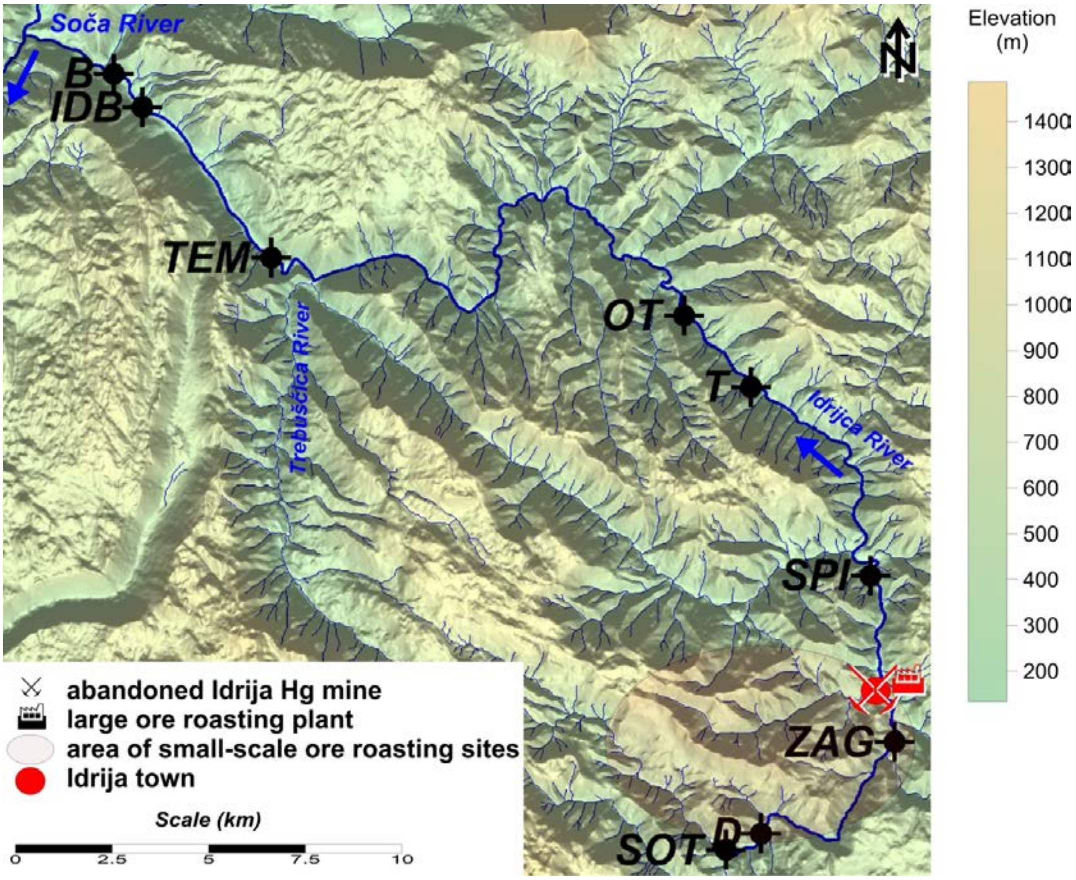

Figure 1: Locations of localities where borehole sampling have been performed between the years 1996 and 2008 (slightly modified after Gosar & Žibret, 2011)

Table 1: Basic information about sampling locations: DIST – distance from Idrija; BOR – number of boreholes on each location; DEP – total depth of boreholes; NUM – total number of samples, taken on each location; GU – sampled geomorphological units (flood – flood plain, 1st – 1st terrace; 2nd – 2nd terrace) (data after Gosar & Žibret, 2011)

Code	DIST	BOR	DEP	NUM	GU
	km		cm		
SOT-IB	-9.1	1	30	3	flood
D	-7.7	1	30	3	flood
ZAG	-2.3	1	200	20	flood
SPI-1	2.9	2	240	12	flood, 1st
T-1	10.6	2	200	10	flood, 1st
Ot-1	13.2	2	460	23	flood
TEM-1	31.1	3	278	49	flood, 1st, 2nd
IDB-1	36.1	5	704	88	flood (3x), 1st (2x)
B-1	37.8	3	1160	58	flood (2x), 1st

Calculation presented in paper by Žibret and Gosar (2006) show that more than 2000 tons of Hg has accumulated in the alluvial sediments in the narrow valley of the Idrijca River downstream of Idrija. The geomorphological property of the sampling location is highly related with its Hg content (Figure 2). Floodplains (overbanks) were found to be the most contaminated geomorphological units, with concentration dropping rapidly on the first terrace and more rapidly on the second one. Hg concentrations on the floodplains drop exponentially with the distance from the source of the pollution (Gosar & Žibret, 2011; Figure 3).

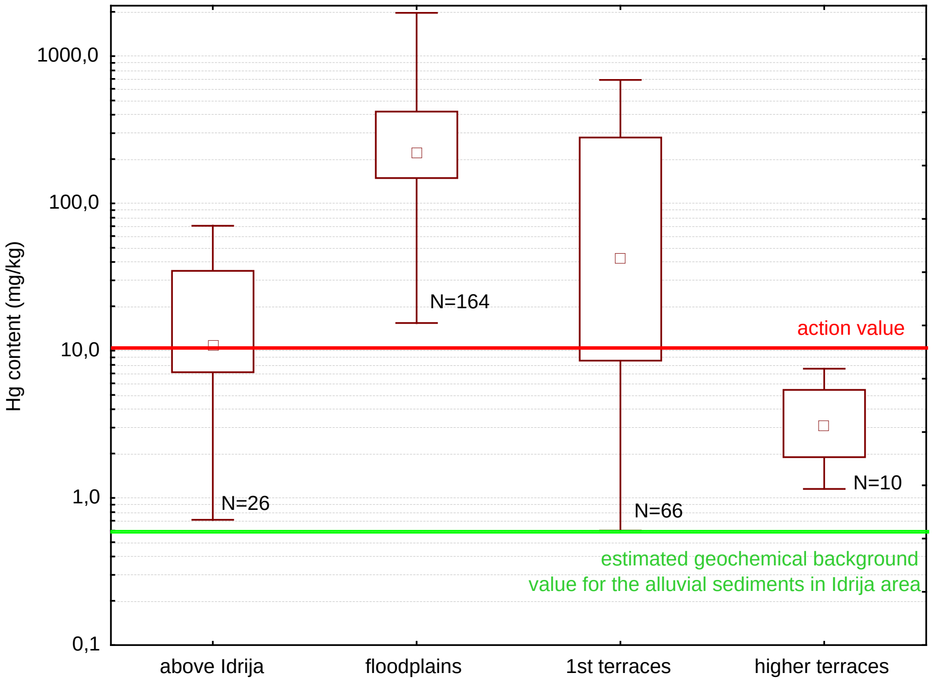

Figure 2: Influence of the geomorphological unit to the distribution of the Hg content in boreholes, located on the each of the geomorphological unit and with the indicated action value, according to the legislation, and estimated geochemical background value for Idrija area. N – number of samples

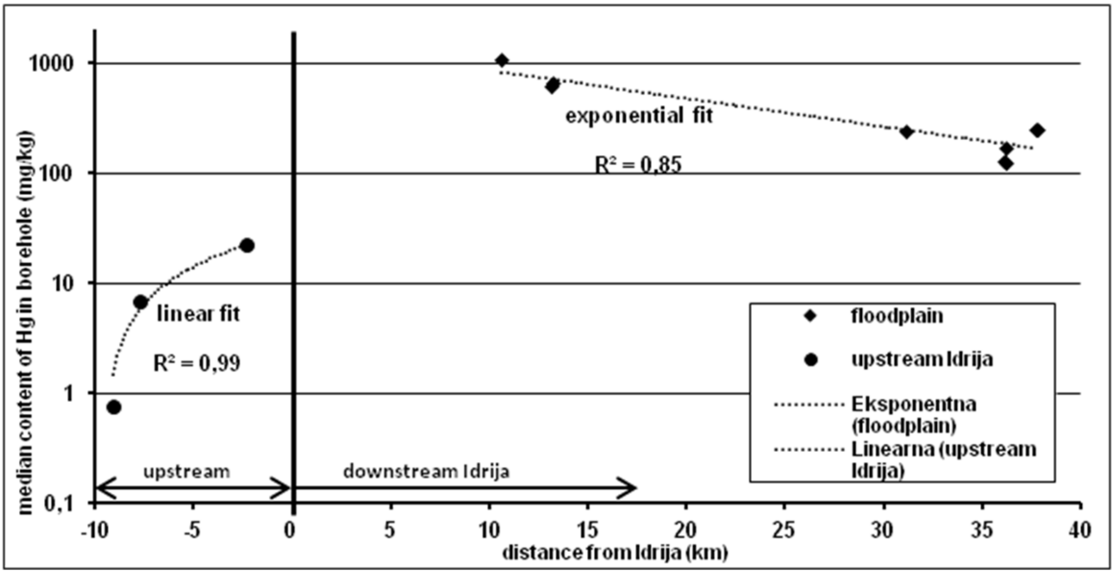

Figure 3: Median values of Hg content in floodplain boreholes and influences of the small ore roasting sites (upstream Idrija) and dumping of ore residues in the Idrijca River (downstream Idrija) to the Hg content

Results for alluvial sediments from the area upstream the Idrija showed that not only mine and ore roasting plant increased Hg levels in alluvial deposits but also contaminated sites upstream Idrija contribute to Hg contamination (Gosar & Žibret, 2011). Three floodplain profiles were sampled in the upper Idrijca Valley. Even though they were sampled upstream from the main contamination sources, the Hg values in two profiles exceeded the expected background values (Figure 4).

Particularly interesting is the profile ZAG, where maximum Hg contents has been found out at the depth of 160 cm. When taking into account all possible sources of Hg in the environment, special focus should be placed on small scale ore processing sites in the surrounding hills of Idrija, which were active in the 16th and 17th century. These localities are highly contaminated because former roasting processes led to considerable losses of Hg (Hg spills, contaminated pottery, ore losses at the transport, etc). Despite these hot spots are spatially limited, the increased Hg content in two alluvial sediment profiles can be attributed to the Hg wash out from aforementioned sites. Maximum Hg content at the depth between 140 – 200 cm at the ZAG profile can be attributed to the period of the peak Hg roasting in the Idrija surroundings in the 16th and 17th century. Recent Idrijca River sediments upstream of Idrija are mercury contents between 2-10 mg/kg which is much more than expected background values, and can be attributed to the continuous wash out of the material from several historical ore roasting sites (Figure 5).

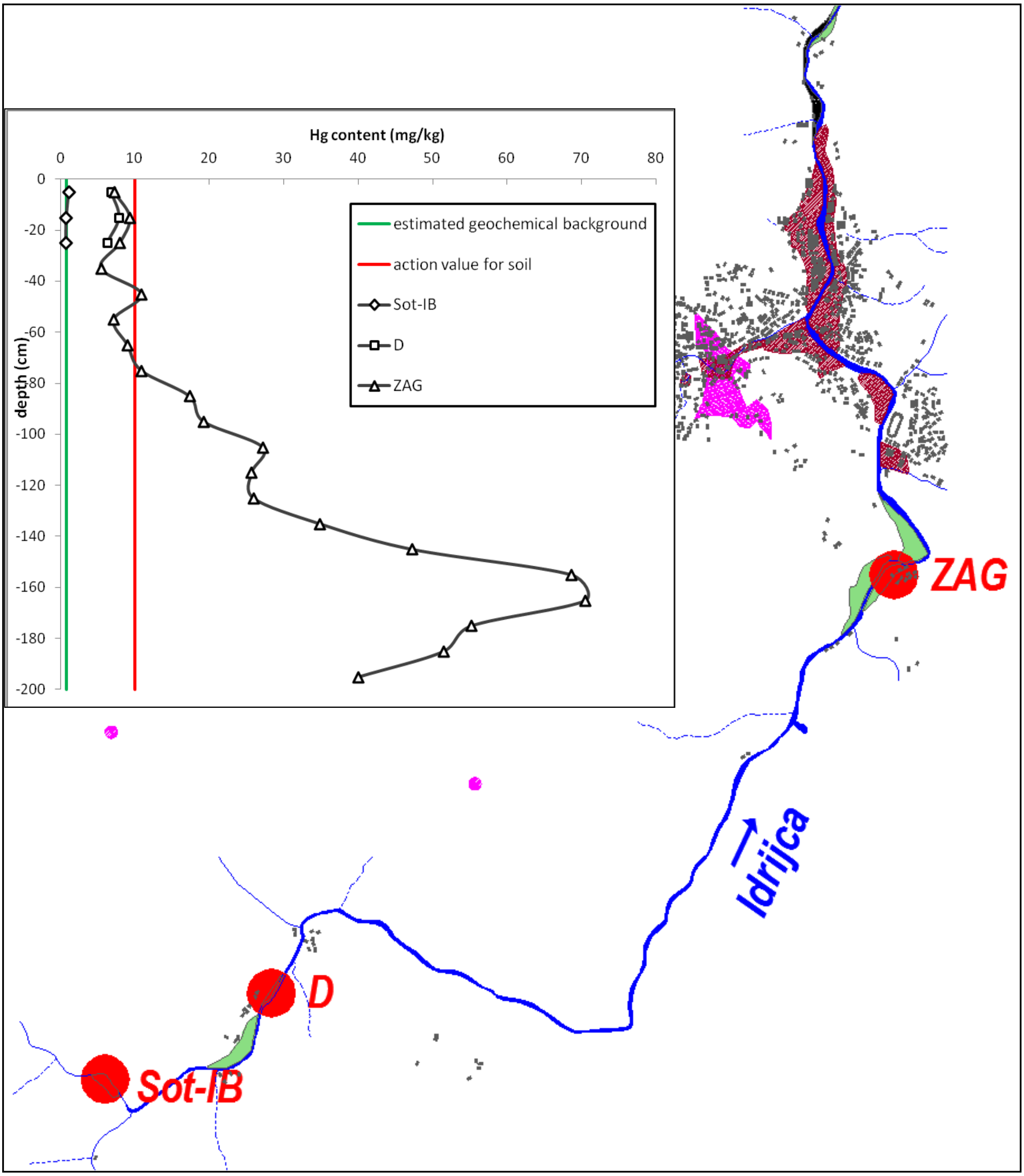

Figure 4: Hg content in the alluvial sediment profiles upstream Idrija

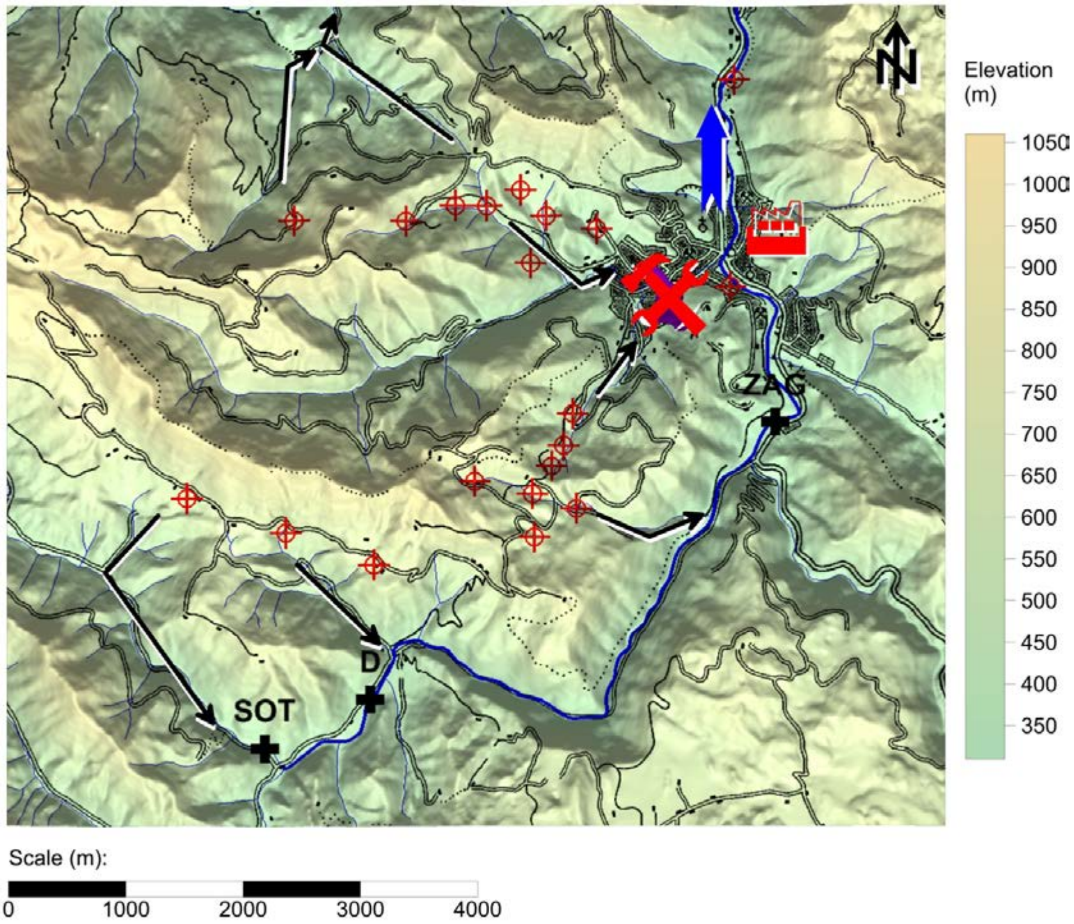

Figure 5: Possible pathways of Hg from the historical ore roasting sites to the sampled profiles (modified after Gosar & Žibret, 2011)

Acknowledgments

The presented study was funded by the Slovenian Research Agency (ARRS) in the frame of the research programme Groundwater and Geochemistry (P1-0020) and the research project Environmental geochemistry of metal contaminated sites (J1-2065) which are performed by the Geological Survey of Slovenia.

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Introduction to geochemical studies in the Idrija urban environment

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The environmental chemistry of potentially harmful elements (PHEs) is an important and growing field of research in applied geochemistry. Sources, transport, and fate of trace and toxic elements in urban environments are examined. Of particular importance is understanding the processes that affect the release, transport and uptake of these elements in urban environment.

The city is a heterogeneous complex structure that has been developed by humans as a necessity for protection, collaboration, trade, etc., which is constantly growing and changing over centuries. Today the quality of the urban environment is of concern to public health authorities following serious environmental degradation arising from the release of many toxic elements and compounds by industrial processes. Many health-related problems are linked to the state of the urban environment.

Contents of many potentially harmful elements (PHEs) are enhanced in the urban environment as a result of atmospheric and terrestrial contamination and the nature of urban ground, which is often disturbed and in-filled and frequently bears little relation to the natural soil, bedrock and superficial cover of the surrounding rural hinterland. Even in completely undisturbed urban areas, such as parks, many PHE signatures are elevated in comparison to the rural natural geochemical baseline concentrations, due to atmospheric contamination, littering, urban surface run-off and other factors. It is necessary to establish the overall urban geochemical signature, so that areas of concern within a city or town can be highlighted, and detailed site investigation and contamination studies can be assessed in terms of the urban geochemical profile in addition to the rural baseline chemical element variation.

Idrija is the oldest Slovenian mining town. Mining in this area started already at the end of the 15th century. The market town obtained municipal rights at the end of the 17th century. The most favourable economic conjuncture was attained around 1790, when the entire mine company employed 1350 workers and produced from 600 to 700 tons of mercury per year. Idrija nowadays numbers about 6000 inhabitants, and the municipal centre unites competent administrative, educational, and cultural functions.

Legacy of 500 years of mercury mining and ore processing is extremely important. Idrija and its environs has been a subject to extensive, versatile and thorough investigations of geogenic and anthropogenic pollution and new findings always raise new scientific questions. Previous research studies have shown that Idrija is burdened with geogenic, but even more by anthropogenic mercury pollution. Besides soil pollution by atmospherically derived mercury (Hg^0), considerable amounts of mercury-bearing ore residues were spilled into the environment. Mining activities (Figure 1, 2), such as mercury ore exploitation and processing, were not just the most significant in terms of pollution, but simultaneously also presented the main reason for the development of the town.

Figure 1: View on ore processing facilities with neighbouring urbanized area

Figure 2: The chimney from the roasting plant was situated up the hill, high above the valley, causing that majority of atmospheric mercury was blown away from the populated area by winds

Thus the town Idrija is nowadays amongst higher urbanized areas in Slovenia, with important electro-metal processing industry, which developed after the mine was closed towards the end of the last millennium due to lack of profitability. New industry activities represent another possible sources of metals along with other anthropogenic activities, such as traffic, small and illegal dumps, etc.

The urban area of Idrija is studied on the basis of systematic sampling of different urban materials (soil, sediment and household dust) and will further direct investigations into the research of spatial distribution of mercury and other metals along with establishing the water-soluble and bio-available portions of mercury in selected materials.

Since the investigation of soils is also included in the project URGE (Urban Geochemistry), lead by Prof. Dr. Rolf Tore Ottesen from Norwegian Geological Survey (NGU), soil samples were collected following a protocol, which was prepared as a part of the mentioned international project. A sampling model grid defined according to Gauss Krueger coordinate system was developed for collection of 9 samples per km^2. Due to higher population density, the density of samples was increased in the town centre. The working team included three people. One member was responsible for the physical work (excavation), second member for the storage of the sample and third member to determine the coordinates, taking pictures and the description of the site location and soil properties to a pre-prepared worksheet. At the end of fieldwork, 45 locations (Figure 3) were determined with 6 duplicates (for performance of within site variability). On each location the urban soil was sampled at two depths; 0-10 cm and 10-20 cm in order to see if there are any differences in soil profile.

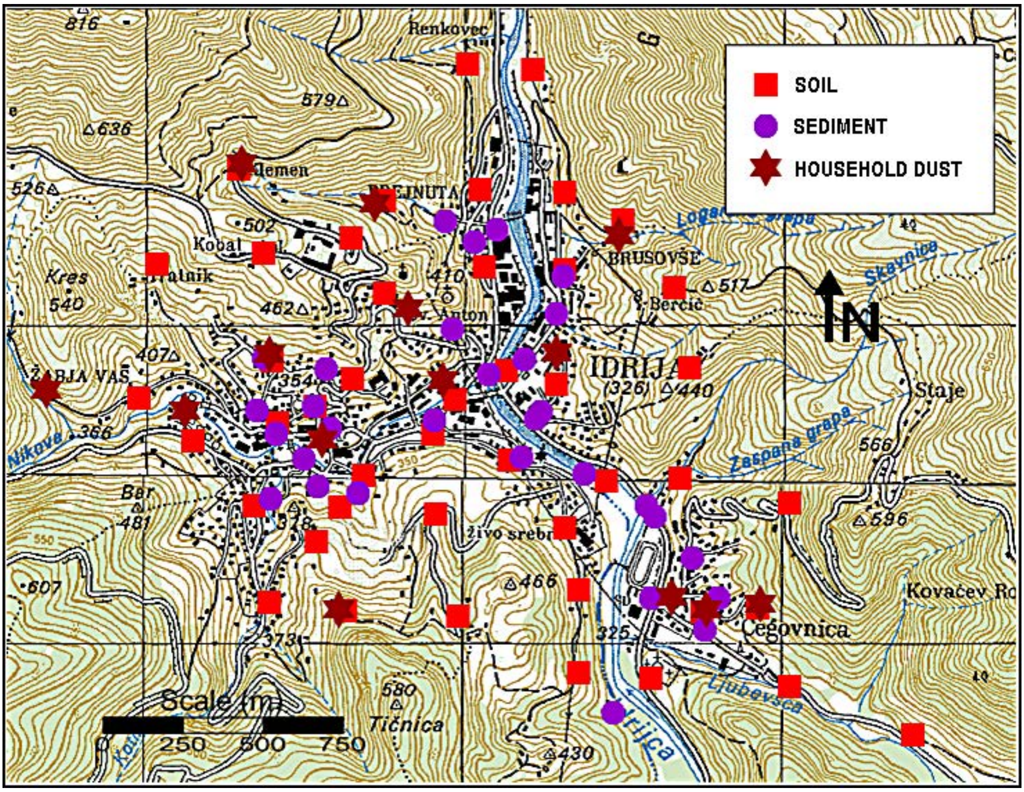

Figure 3: A presentation of sampling locations of three different collected urban materials on a map of the urban area of Idrija: urban soil samples- red squares, urban sediment samples – purple circles, household dust – brown stars

Figure 4: An example of a sampling site: road shaft from urban drainage system

Figure 5: An example of a sampling site: natural stream flowing through the urban area of Idrija

Sediments from urban area were collected from two different location types; road shafts of the urban drainage system (Figure 4) and natural streams flowing through urban area (Figure 5). In order to collect the samples from the road shafts, we had to collaborate with the officials of city utilities, since they are responsible for the management of the urban drainage system and are also well acquainted with the drainage of the natural streams flowing through the studied urban area. One of the employees joined the two members of our research group, so the collection of sediments from road shaft was even possible. Approximately 1 kg of urban sediment was collected with a scoop and stored in polyethylene bags. Sampling locations (Figure 3) were spatially defined according to Gauss Krueger system by GPS device and selected in such manner, that all the local streams flowing through the selected urban area were covered. Altogether 30 samples of urban sediment were collected.

16 samples of household dust, which is represented by dust accumulated in household vacuum cleaner, were contributed by the inhabitants of Idrija. They provided us vacuum cleaner dust bags labelled with their home address. Later on, each home address was transformed into Gauss Krueger coordinates by using GIS, so the precise locations of collected samples could be defined on the map (Figure 3).

The sampled materials were prepared in different ways for the following chemical analysis:

- Element contents in all collected samples, its randomly selected duplicates and standard materials will be analysed by inductively coupled plasma mass spectrometry (ICP-MS) after aqua regia digestion.
- For identification of water-soluble mercury fraction, leaching tests will be performed to determine the solubility of mercury in soils.
- For determination of Hg species in solid materials, thermo-desorption analysis, also called pyrolysis (Figure 6), will be performed. The method allows the separation of total mercury contents into a cinnabar and non cinnabar fraction. The latter indicates the amount of potentially bioavailable mercury.
- For determination of Hg bioaccessible fraction (mercury that is ready for absorption in a human stomach and potentially threatens human health), a standardized protocol will be performed (EN71-3).
- Determination of metal bearing mineral phases will be performed by SEM/EDS (Figure 7). The combination of scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) is used for non-destructive morphological, qualitative and semi-quantitative elemental analysis of individual particles on the micron level, and thus serves as a complementary method of conventional mineralogical and geochemical methods.

The foreseen analyses are currently in procedure. In continuation of the project we intend to analyse the gathered data with various statistical methods and produce geochemical maps to present the spatial distribution of potentially toxic elements separately for each environmental medium. In addition, water-soluble and bio-accessible portions of mercury in soil will be established in order to determine what amounts of Hg contents are actually mobile and bio-accessible in the urban area of Idrija. It is also expected that the foreseen analyses of mercury species will help to explain the origin of mercury.

Figure 6: An apparatus for determination of different Hg- species, also called pyrolysis

Figure 7: Scanning electron microscope (SEM) with energy dispersive spectrometer (EDS)

Acknowledgments

The presented study was funded by the Slovenian Research Agency (ARRS) in the frame of the research programme Groundwater and Geochemistry (P1-0020) and the research project Environmental geochemistry of metal contaminated sites (J1-2065) which are performed by the Geological Survey of Slovenia. The authors would like to thank prof. dr. Harald Biester from Technical University Braunschweig, who is cooperating in this geochemical study. We would also like to thank mag. Vesna Miklavčič and Mr. Martin Kržišnik from Komunala Idrija, d.o.o. for good cooperation during urban sediment sampling.

Applicability of SEM/EDS in environmental geochemistry – Examples from Mežica and Idrija mining areas

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Combination of scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) is used for non-destructive qualitative and quantitative elemental analysis of individual particles at micron level as well as for analysis of their morphology. Thus it serves as one of complementary methods to classical mineralogical and geochemical methods used in studies of environmental media. Conventional chemical analyses give limited information on mineralogy, morphology and composition of individual solid particles and metal-bearing phases and their stability in the environment. SEM/EDS, however, enables determination of chemical, mineralogical and morphological characteristics of particles, which are a basis for differentiation between natural and anthropogenic sources and assessment of processes responsible for their formation.

The use of SEM/EDS as a supplementary method for characterisation of micron-sized metal-bearing particles, originating from natural and anthropogenic sources, in various environmental media was already introduced to environmental studies world-wide. Hochella and co-authors (2005) observed heavy metal-mineral associations in stream and floodplain sediment samples and established, using SEM/EDS, that the source of floodplain material are mine tailings and smelter wastes. Bernaus and co-authors (2005) used the combination of SEM/EDS in order to evaluate the elemental background of ore, slag and soil samples from Almaden mercury mining area. SEM/EDS analyses of mercury and arsenic contaminated soils, calcines and tailings derived from Sb-Hg mineral deposit of the Valle del Azogue mine, confirmed that cinnabar, found in contaminated samples, is a secondary phase, precipitated after dissolution of Hg-rich pyrite (Navarro et al., 2006). Kemppainen and co-authors (2003) studied the distribution of airborne particles in the surroundings of an iron and steel factory in southern Finland and identified different particle types using SEM/EDS.

SEM/EDS has been successfully introduced to environmental studies at Geological Survey of Slovenia (Miler & Gosar, 2009, 2010, 2012; Gosar & Miler, 2009, 2011; Teršič, 2011; Miler, 2012). SEM/EDS was used for characterization of metal-bearing phases in metal-polluted environmental media (stream sediments and mine waste deposit material) from the Meža River Valley, NNE Slovenia (Miler & Gosar, 2010; Gosar & Miler, 2009, 2011; Miler, 2012). The analysis of the Meža River sediments showed that the highest contents of Pb, Zn, Mo and V in the upper Meža River Valley mostly occur in Pb-Zn ore minerals (cerussite (Figure 1a), sphalerite (Figure 1b), smithsonite, descloizite (Figure 1c) and wulfenite (Figure 1d)) of geogenic-technogenic origin, resulting from washing out of mine waste material in the Mežica mining district. In stream sediments from the lower Meža River Valley, Fe-alloys (Figure 2a), Fe-oxides and spherical metal-oxides (Figure 2b) with Cr, Ni, W, Mo and V were recognized, most probably originating from technogenic processes in steel industry in Ravne. Ce, Y and La occur in the form of geogenic accessory minerals (monazite and xenotime) originating from weathering of metamorphic bedrock in the Meža River catchment area.

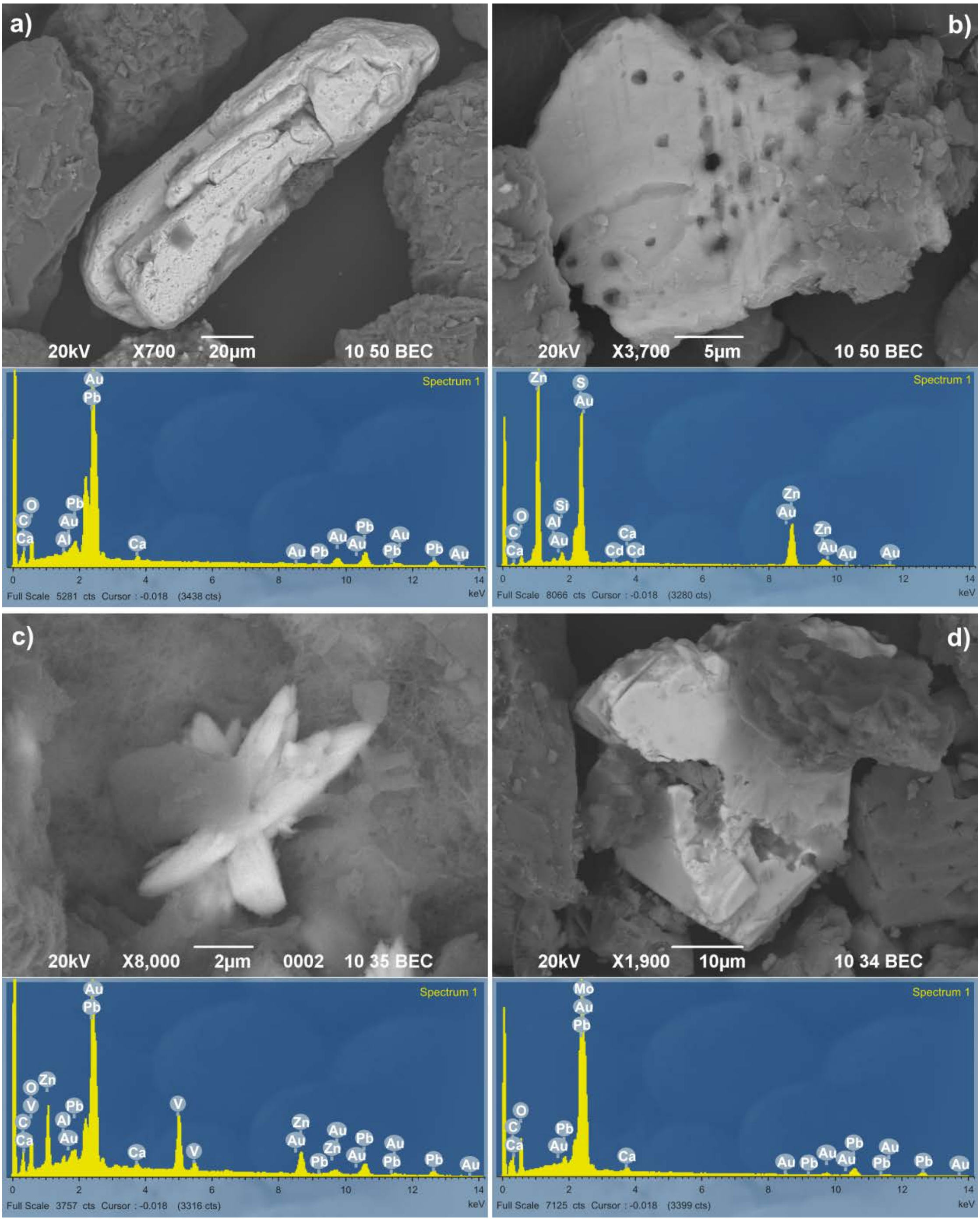

Figure 1: SEM (BSE) images and EDS spectra of geogenic-technogenic metal-bearing phases from the upper Meža River Valley: (a) porous grain of cerussite; (b) grain of sphalerite with minor contents of Cd showing corrosion pitting on its surface; (c) enantiomorphic crystal of descloizite and (d) fragment of wulfenite crystal with inclusions of carbonate. Si, Al and Ca peaks in spectra originate from clay minerals and carbonate inclusions (dark gray patches on the surfaces of grains). The sample is coated with gold

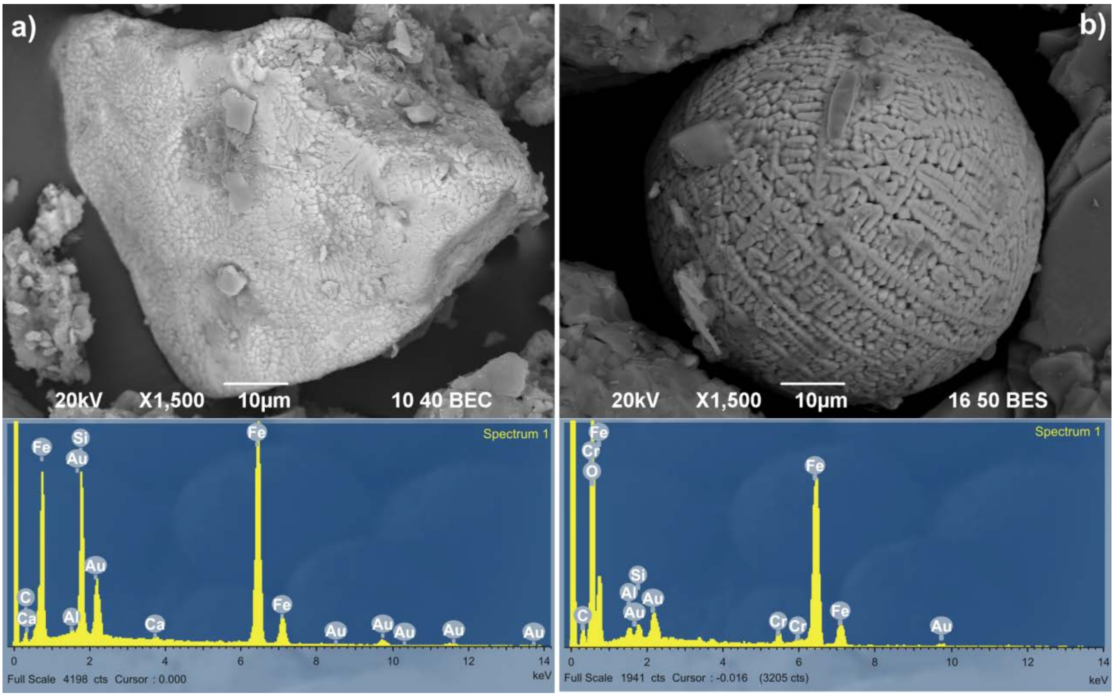

Figure 2: SEM (BSE) images and EDS spectra of technogenic metal-bearing phases from the lower Meža River Valley: (a) grain of Fe-Si alloy (gupeiite), composed of Fe-Si dendrites; (b) skeletal-dendritic sphere of Fe-oxide with minor contents of Cr. The sample is coated with gold

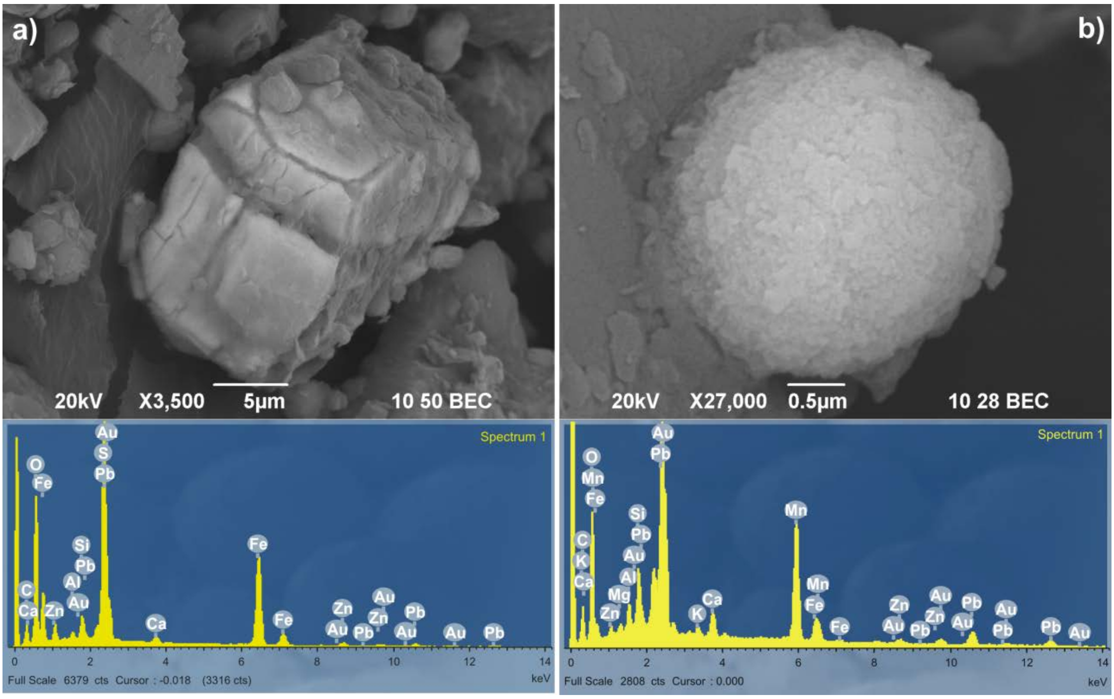

Figure 3: SEM (BSE) images and EDS spectra of secondary weathering products in mine waste deposits from the upper Meža River Valley: (a) pseudomorph of Fe-oxy-hydroxy sulfate after pyrite hexahedron. Peaks of co-precipitated or sorbed Pb and Zn can be seen in the spectrum; (b) spherical grain of Mn-oxide with minor contents of co-precipitated Pb and Zn. Samples are coated with gold

Detailed chemical and SEM/EDS analyses of three mine and ore-processing waste deposits in the Meža River Valley were carried out with the purpose of determining the influence of mine waste deposits on high contents of metals in environmental media, determining modes of occurrence of metals in waste deposit material, and assessing the stability and mobility of metals in metal-bearing phases (Miler & Gosar, 2012; Miler, 2012). SEM/EDS analysis revealed that Pb, Zn, V, and Mo in the waste deposit material occur mostly as primary ore minerals (cerussite, sphalerite, smithsonite, descloizite, and wulfenite). A considerable amount of Pb and Zn was also found bound to secondary weathering products, such as Fe-oxy-hydroxides, Fe-oxy-hydroxy sulfates (Figure 3a), Mn-oxides (Figure 3b), and Al-silicates, which act as sustainable trapping media for Pb and Zn in the investigated mine waste deposits.

SEM/EDS proved as the only suitable method for analysis of solid airborne particles in snow deposits from the Ljubljana urban area (Miler & Gosar, 2009). Using SEM/EDS, solid airborne particles were identified and classified according to their morphology and chemical composition into geogenic (quartz fragments, zircon and clay minerals) and technogenic particles (spherical carbonaceous (Figure 4a) and metal-bearing particles from high-temperature industrial combustion and steel-melting processes (Figure 4b)).

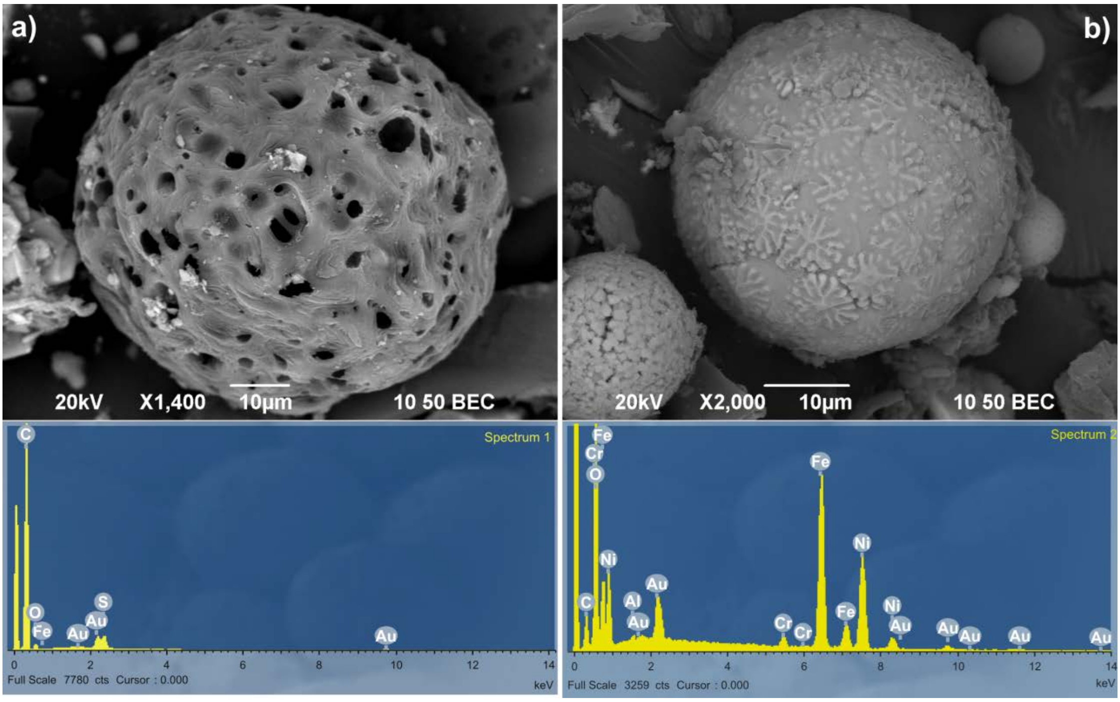

Figure 4: SEM (BSE) images and EDS spectra of technogenic solid airborne particles in snow deposits from the Ljubljana urban area: (a) porous spherical carbonaceous particle with spongy interior that formed during high-temperature combustion of coal or liquid fuel; (b) spherical (Fe,Ni)-oxide with minor contents of Cr from high-temperature steel-melting processes. Samples are coated with gold

SEM/EDS was also applied to the study of roasting vessel fragments and soil samples from ancient roasting sites in the surroundings of Idrija in order to characterize solid forms of Hg (Teršič, 2011). The analyses of vessel fragments showed HgS coatings on the surface of ceramics, forming either crusts or isolated grains (Figure 5a). In soil HgS was present as small scattered particles (Figure 5b), as coatings on quartz and clay minerals and as complex particles containing Hg, S, Si, Al, Fe and Mg, interpreted as soil aggregates impregnated with liquid mercury or vapours of mercury and sulphur.

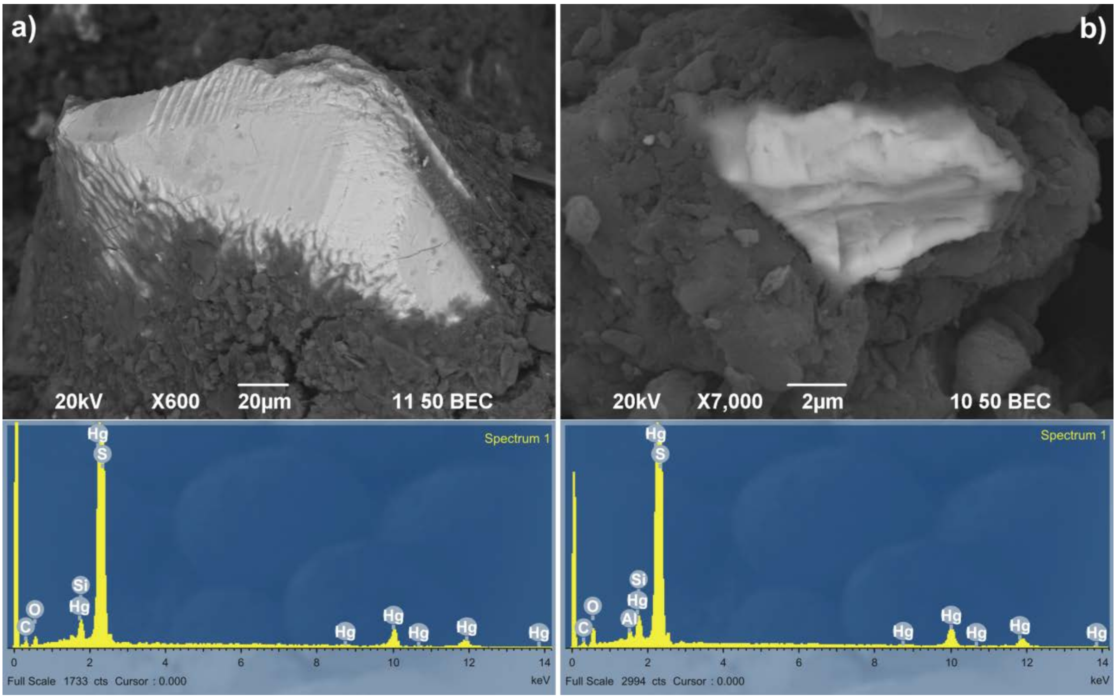

Figure 5: SEM (BSE) images and EDS spectra of Hg-bearing grains in roasting vessel fragments and soils from ancient roasting sites in the surroundings of Idrija: (a) isolated HgS crystal on the surface of ceramics; (b) HgS fragment in soil aggregate (Teršič, 2011)

Acknowledgments

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Mercury in soil and sediments as a consequence of environmental influences of abandoned Podljubelj mercury mine, NW Slovenia

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In 2004/2005 Geological survey of Slovenia conducted a research project concerning the abandoned mine and ore roasting facilities in Podljubelj. The aim of the project was to establish the contents and spatial distribution of mercury in the environment. Outcomes of the research project were published in monograph (Teršič et al., 2006) and in some papers (Teršič et al., 2005; Teršič et al., 2009). Here we merge some of the most important results of the study.

Figure 1: Calcite vein with cinnabar mineralization in abandoned Podljubelj mine

The Podljubelj mercury mine is situated in the NW part of Slovenia. The ore deposit is located between 700 and 800 m above sea level in a narrow valley. The ore deposit is of hydrothermal vein type, developed as a consequence of Ladinian (T_2^2) volcanism (Drovenik et al., 1980). The calcite vein with cinnabar is presented in Figure 1. The mine was first exploited as early as in 1557, closed in some periods and finally abandoned in 1902. The entire operating period yielded about 110,000 tons of ore, from which 360 tons of Hg was produced. A roasting facility located close to the mine had been in operation since 1855. The remainings of the roasting pottery and the roasting facilities are still present in the area (Figure 2). Before this roasting facility was built the ore was transported to Idrija for gaining out the mercury. The waste material from the mine and the roasting facility was dumped in close vicinity of the mine. Total quantity of the waste has been estimated to 170.000 tons (Mohorič, 1957). Most of the material was used for the construction of the Ljubljana–Celovec road which runs through the valley.

Figure 2: The pottery remains of the former roasting

The soil and sediment sampling was conducted in the years 2004 and 2004. There were 26 topsoil samples (0–5 cm) and 23 subsoil samples (20–30 cm) collected within a research grid of 100 x 100 m in the narrow area of the mine and smelter (Figure 3) (Teršič et al, 2006; Teršič et al., 2009). Four additional soil samples were taken in the area of abandoned ore roasting and waste material dump.(Figure 4) The fraction smaller than 0.063 mm was analyzed. Stream sediments were sampled in a wider area of the mine. Seven samples were taken from the Mošenik creek which runs through the valley, and additional 4 samples from Mošenik's tributaries (Figure 5). Each sample consisted of 5 sub-samples. Different fractions were separated by dry sieving. The fraction smaller than 0.125 mm was analyzed.

The samples were analyzed in the ACME laboratories in Vancouver, Canada. Analysis for 41 chemical elements was performed by inductively coupled plasma mass spectrometry (ICP-MS) after the (total) four-acid digestion. Hg was determined by cold vapor atomic absorption spectrometry (CV-AAS) after aqua regia digestion.

The determined Hg in soil is ranging between 0.17 and 719 mg/kg. In topsoil Hg concentrations vary from minimum 0.35 to maximum 244 mg/kg with the median of 3.67 mg/kg. The subsoil median is 1.39 mg/kg and individual values between 0.17 and 71.7 mg/kg (Table 1). In topsoil the critical Hg value for soil (10 mg/kg) is exceeded at ten sites, and in subsoil at four sites. The highest determined value, 719 mg/kg Hg, was found at the area of former roasting facilities (Table 1). Also in samples from the waste material dump the Hg concentrations are elevated. The highest Hg content in soil from the dump (108 mg/kg) is almost 7-times lower than the soil content at the roasting area. In other samples the contents are considerably lower. Soils on waste dump are poorly developed and they contain very low organic matter. In places they are overgrown by scarce tufts of grass, and in places barren, without vegetation. The skeleton consists of fragments of roasted and low-grade unroasted ore. Differences of Hg contents on dump evidently depend upon the type of material sampled (barren rocks, low-grade ore, roasted ore). Low grade unroasted ore and barren rocks most probably contain very low mercury, mostly in the form of cinnabar. Large parts of material on the dump are remains of roasted ore. As the recovery of roasting was low, the roasted ore remains still contain appreciable mercury (Teršič et al, 2006; Teršič et al., 2009).

Table 1: Medians and ranges of mercury (in mg/kg) in soils and sediments in the Podljubelj study area (data after Teršič et al, 2006)

	SOIL (all samples)	Top soil	Lower soil	Stream sediment
N	53	26	23	11
Min	0.174	0.35	0.17	0.065
Max	718.5	244.1	71.7	1.36
Me	3.041	3.67	1.39	0.64

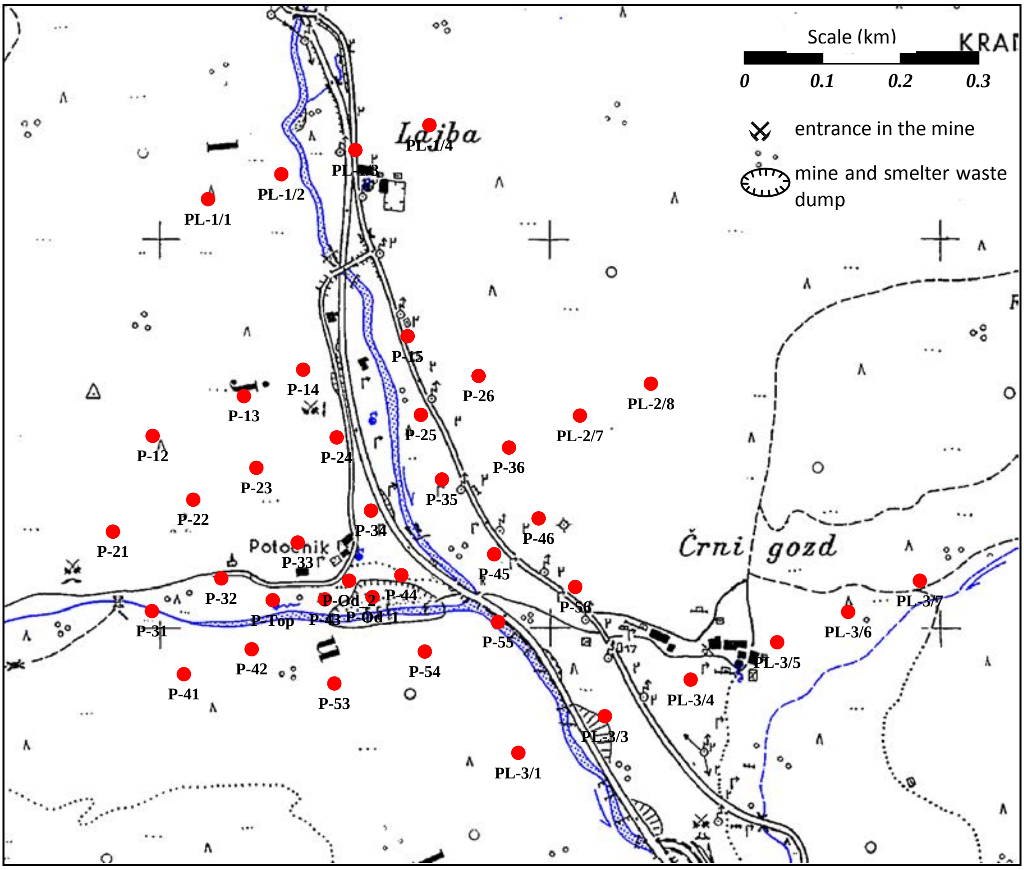

Figure 3: Sampling locations of soil (modified after Teršič et al., 2006)

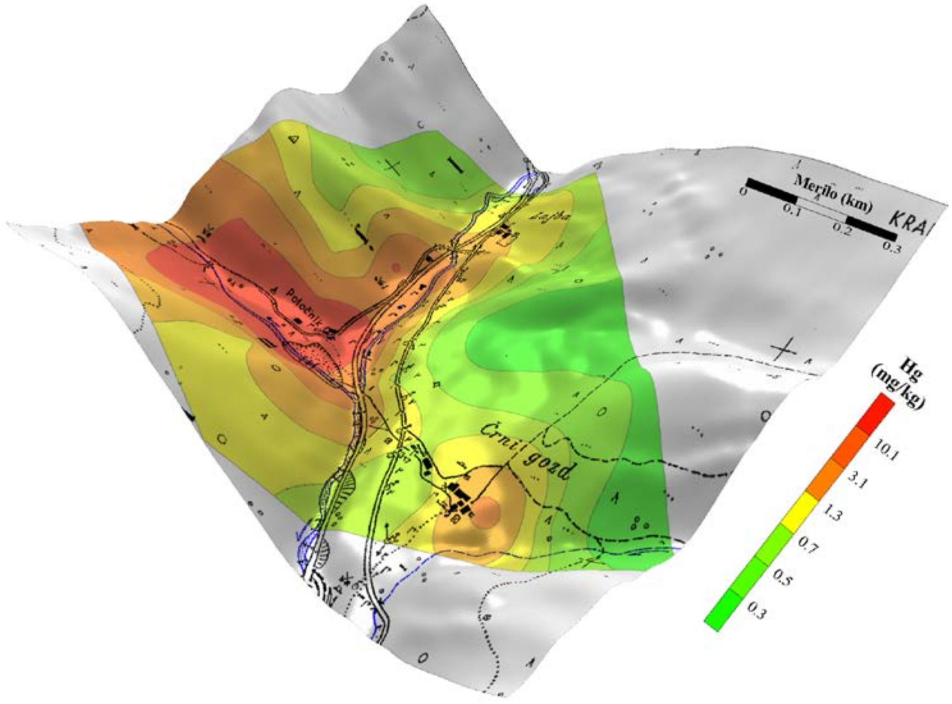

Figure 4: Spatial distribution of mercury in topsoil (0–5 cm) (after Teršič et al., 2005; Teršič et al., 2009)

The impact of Hg ore mining and processing on the environment is spatially limited to the immediate surroundings of the roasting area. On an area of about 9 hectars the Hg contents in soil exceed the Slovenian critical value for soil (10 mg/kg). The anomaly of critical values is of small extent (Figure 4) (Teršič et al, 2006; Teršič et al., 2009).

In most of collected samples the Hg content is higher in topsoil than in subsoil. This proves that the increased Hg contents in soils are caused by anthropogenic impacts. The average enrichment factor in topsoil with respect to subsoil is the highest for Hg (3.3 mg/kg), followed by Cd (3.2), Pb (2.7), Ca (2.4) and P (1.9). The average enrichment factor in studied soils with regard to the established Slovenian soil averages is the highest for Hg, amounting to 19 for topsoil and 13 for subsoil (Teršič et al., 2006; Teršič et al., 2009).

The analysed Hg contents in sediments vary from 0.065 mg/kg to the maximum of 1.36 mg/kg (Table 1, Figure 5) (Teršič et al, 2006; Teršič et al., 2009). The highest Hg value was determined in the Potočnikov graben, where the material from the dump of roasted ore remains is washed to the creek. During operation of the mine a part of the dumped material was discharged most probably directly into the creek. The highest determined Hg value from the Mošenik creek was in the sample collected just downstream of the confluence of Potočnikov graben. The Hg contents then consistently decrease downstream. The average Hg content of the analyzed samples (0.64 mg/kg) is 7 times higher than the estimated Slovenian average for stream sediment, 0.09 mg/kg (Sotlar, 1995). The enhanced Hg concentrations in stream sediments of the studied area are most probably the consequence of a higher natural background as well as of the anthropogenic influence. Pollution owing to mining is best expressed in the Potočnik graben and below the confluence of Potočnik graben into the Mošenik creek, but farther downstream it rapidly dies off.

The impact of mining and processing of Hg on the environment in the area of Podljubelj is spatially limited. The Hg contents are very high in the close vicinity of the mine and decrease with depth in soil profile and with the distance from the source of pollution. High contents of Hg in soil around the abandoned roasting facilities are a consequence of former atmospheric emissions and technological losses.

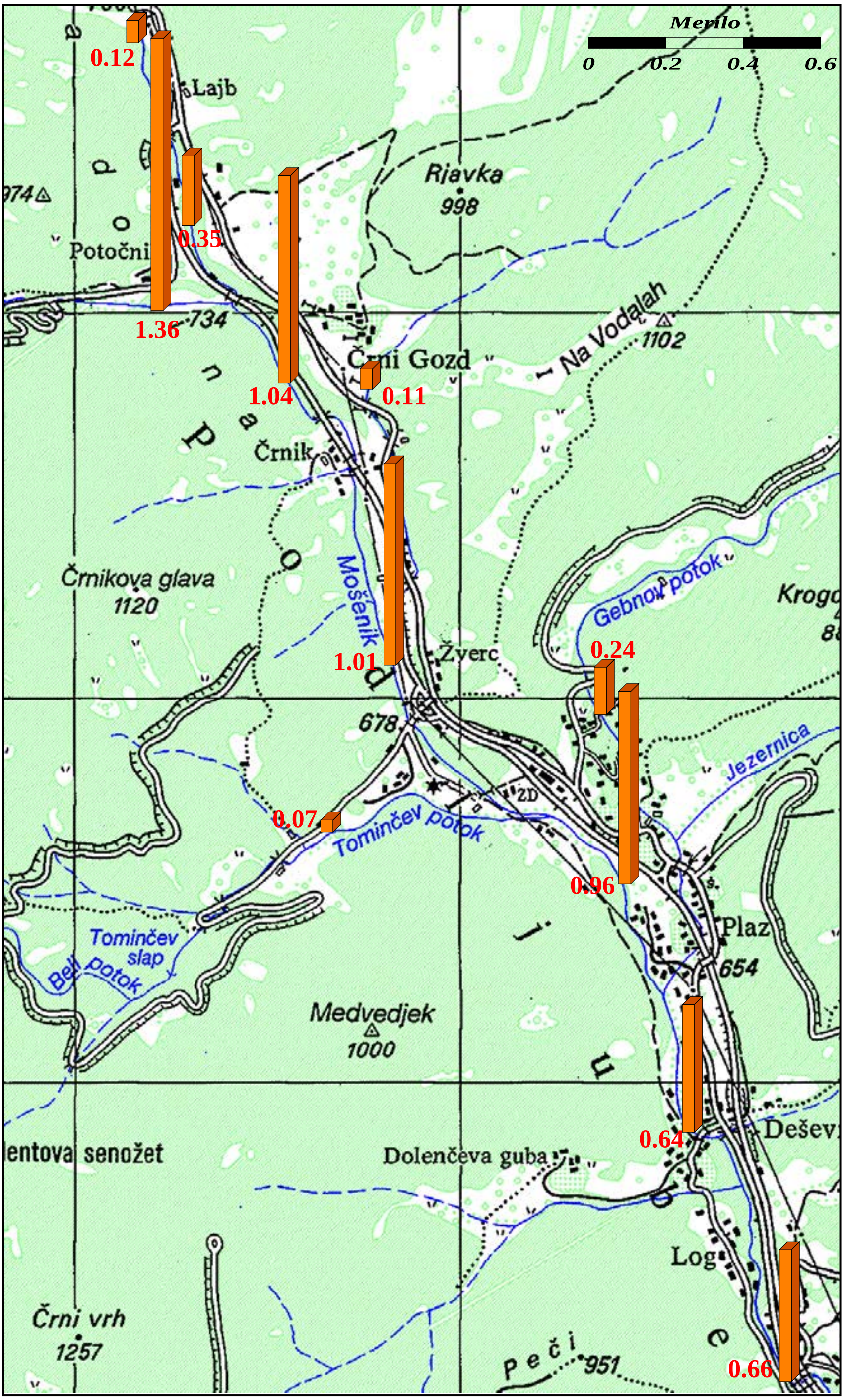

Figure 5: Stream sediment sampling locations with mercury contents (in mg/kg) (modified after Teršič et al., 2006)

Acknowledgments

The presented study was funded by the Slovenian Research Agency (ARRS) in the frame of the research programme Groundwater and Geochemistry (P1-0020) which is performed by the Geological Survey of Slovenia.

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Interdisciplinary Approach on Mercury, Arsenic and Radon Gas Study in the Southern of Sierra Gorda of Querétaro, México

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Some Considerations about the Project

We want to face the cinnabar mining activities and the impact in Man and Nature in the southern part of the Sierra Gorda in Querétaro, México by grouping and linking several disciplines. One of the main bases of this project is to invite and to join disciplines and institutions that can be interested in these kinds of topics. It is not so frequent to involve disciplines that are apparently far away from one another. This region offers the opportunity to study it from several points of view, which could be undertaken only by joined efforts, association of infrastructure and the combining of experiences and qualified academic personnel of different disciplines and proceeding from the natural sciences, social sciences and public health. In the project scheme, all the disciplines have the same importance and level. The path traveled upon thus far and the link between the connected topics and others, apparently not so connected, permits us to think of the appearance of hybrid subjects. At all times, Man and Nature have existed close together. Why then should we not face and link them in the same way as the social and natural sciences should?

Interdisciplinary Paradigm

The word Nature paradigm is strongly influenced by the Earth Sciences concept. The planet at the present time is still changing. Nature itself provides essential trail in deal with how the Earth has arrived at its present physical, chemical and biological state and leads to an understanding of the large-scale processes which bring about changes in our planet. The word Man is considered in this approach in the most extensive term; it involves as an individual itself but as a connected individual into the society. Therefore the linkages and interactions that take place between Earth (Nature) and Man (Sociology and Public Health) along the different groups of disciplines will be explored.

This approach is an integrated paradigm that provides a complete view (that it is possible in our circumstances) of Man and Nature interactions with an open mind. It attempts to encompass several parts of the Man-Nature relationship, offering a new level of integration, from deep Earth (gravity, magnetism), superficial processes (air, biota, soil, water) until the impact of mining activity into the society, economy and public health in the South of Sierra Gorda. In addition, this presentation has implications, which reach far beyond the way in which we do science, extending the realms of environmental management and policy. We need to explore the Man and Nature concepts and integrate them as a whole, rather than simply as a series of separate entities. This approach paradigm incites to the interdisciplinary topics to an exploration of the processes, which link the different disciplines, in order to describe them and then to quantify the exchanges that take place. First of all, it is necessary to define some proceedings as chemical processes, cycles, translocations, residence times, fluxes, transport mechanisms, bioaccumulation, etc., and later on, to determine what is happening between the sensitive boundaries of the traditional disciplines.

There is a recognition that natural systems are open to and interact with other systems outside of themselves and through this interaction they acquire new properties and evolve over the time. The Earth System Sciences examine the Earth itself as a synergistic physical, chemical and biological system, governed by complex processes including its terrestrial crust, land surface, atmosphere, hydrosphere and biosphere.

However, it is necessary to add to the Nature, the Man's Environment, provided that any society lives over a region with determined physical (Nature) characteristics; therefore, a society (Man) receives directly the consequences of living there; it's so simple. Like the processes of the living world, some processes of the nonliving world are in a delicate balance, and some are remarkably resilient. An ideal situation is to try to know how the total system works and to determine their connections.

Earth Science Systems places a strong emphasis on quantifying processes as a prelude to mathematical modeling. In the project structure, models for Earth's modern climate system are becoming increasingly mathematically sophisticated with the intention of producing comprehensible climate models. Similarly, a major goal of modern geochemistry is to quantify elemental fluxes into and out of major Earth reservoirs. This type of approach is possible for processes which we can quantify now. It is clear that there is a trade off between the timescale of the model and its mathematical complexity.

The Structure Scheme

The simplest way to represent the project meaning can be seen in Figure 1; Hg, As and radon gas establish the central axis of the work, which considers the impact that it has imposed and imposes over Human and Nature in southern region of Sierra Gorda. Figure shows the organization scheme with the integration of different disciplines. It exhibits a clear structure and sequential linkage of diverse disciplines. In this presentation Nature and Man are considered as a whole system, which is composed of several subsystems or sub disciplines. The information, material interchanges and energies coming from other disciplines or groups of disciplines which enter within one another. These movements are in several directions and the diverse figures of these structures are interpreted in the simplest pattern. The first column is related to different groups of disciplines and the conformed diverse topics. The scheme interpretation starts from the bottom with the geophysics (gravity and magnetism) and geological (stratigraphy) background of the Sierra Gorda in order to have an idea of the type of materials that could be in the Earth's depth. Ore deposits are the sources of Hg pollution and radon gas emanations from rocks, soils and water of unknown reach in the region and its impact in human health. The Earth's "stratigraphy" helps us to understand how both Hg vapor and Rn gas emerge to the Earth surface. The cinnabar mining activity through many centuries has affected Terrestrial Systems (air, biota, soil and water). Each compartment of the Terrestrial System plays an important role because of their physical and chemical transformations and the material transported between the compartments. Ecology is a complex matter and in its extensive concept treats the relations among all organisms (life forms) and their inorganic surroundings; on this discipline we introduce sub disciplines as Land changes (Land cover changes), Landscape ecological analysis (Fragmentation and Soil erosion), Carbon & Hg sequestration and Ecosystems and fluxes of energy. Biogeochemistry allows us to determine the Hg cycles in the different compartments of the terrestrial systems, the different chemical forms of Hg in each step of the cycle, mass balance, transference and toxicity levels that affect man and the environment. The studies on Remediation through Bioremediation, Phytoremediation, Electroremediation and Environmental Engineering propose mechanisms of rehabilitation of polluted sites. The knowledge of its social impact establishes the contemporary economic relevancy of the Hg mining activity; some social effects in the population are determined by Hg and As pollution. The cultural, political and economical frames identify the power structure that connects with economical activities related to Hg. Archaeology and Anthropology point out that the cinnabar mining activity in the Pre-Hispanic age could have seriously affected the health of cinnabar workers. At the present moment, Toxicology establishes the effects on the health of the workers who are still alive.

PROJECT FRAMEWORK

Hg, As Hg, As & Rn	HUMANS	HEALTH SCIENCE	Present Toxicity
			Pre-Hispyanic Bioaccumulation
		SOCIAL SCIENCE	Political-Cultural Framework
			Social & Economic impact
			Archeology & Anthropology
	NATURE	REMEDIATION	Environmental Engineering
			Electroremediation
			Phytoremediation
			Bioremediation
		BIOGEOCHEMISTRY	Biogeochemical Cycle
			Speciation
			Analytical Chemistry
		ECOLOGY	Ecosystems & Fluxes
			Landscape Ecology
			Nature
			Land Use Change
			Carbon Sequestration
		TERRESTRIAL SYSTEMS	Biotas
			Oil
			Air
			Water
		EARTH SCIENCES	Environmental Geology
			Geohydrology
			Radon Gas
			Radioactivity
			Ore Deposits
			Geological Framework

Figure 1: The simplest way to represent the project meaning

Some considerations

The extensive mercury exploitation during almost two thousand years has resulted in a widespread contamination that impacted both Man and Nature in the Southern Sierra Gorda. Both arsenic and radon gas dispersion in the area, are only in the early part of the research, although the present results are concerned. This paradigm serves as the first approach to try to understand their connections and the fluxes between the different disciplines and their beginnings. Probably combining several different approaches may determine more accurately how the fluxes of interchange work. This presentation encourages interdisciplinary thinking and an exploration of the processes, which link the diverse topics in order to describe first and then, to quantify the exchanges that take place and seek for new frontiers in different disciplines.

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Soil organic matter role in Hg stability in an ancient mining site

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Introduction

Organic matter (OM) is fundamental for buffering soil functions offered into terrestrial systems. According to the humic substances (HS) quality and complexity, it could regulate their capacity for binding potentially toxic elements such as mercury (Hg). Mercury dynamics in soils is conditioned by biological processes, as well as by their physical and chemical soil properties; in fact, many studies show that OM is the most important soil component controlling Hg^{2+} absorption and desorption processes, affecting its retention and release in environment (Zhang et al., 2009). Colloidal character of HS, allows their interaction with diverse cations, favoring or restricting their mobilization through soils. In such a way, HS form stable compounds with Hg, and reduce its mobility and availability for other systems. Because of the complexity of this issue, few studies have examined the OM role in the retention and/or emission of mercury into the atmosphere.

In the study area, Mesozoic sedimentary rocks were shaped during Jurassic and Cretaceous periods. There are also formations of continental origin from the Paleogene and Neogene. Anticlinal and synclinal ripples are common. Also faults and fractures form veins rich in mercury that were mineralized along with hydrothermal and skarn deposits (Martínez et al., 2010). Climate varies from temperate semiarid shifting to sub-humid, temperate to sub-humid subtropical in a transect from south to north within the study area. Mean annual precipitation varies from 400 to 1500 mm. Soil groups are Leptosols, Regosols and Luvisols. The vegetation is constituted by forest communities of coniferous and coniferous- deciduous, also cloud forest, xerophytic scrubs, sub-montane scrubs and desert scrubs in close relation with the landscapes (INEGI, 1992).

The aim of this study was to determine mercury content in soils from two different land usages and the proportion of Hg binding to soil organic matter fractions.

Material and methods

The study area is located in the southern part of the Sierra Gorda, in the mining region of San Joaquín, Querétaro State, México, within Gatos hydrological basin that covers 172 km^2, between 99°40´ and 99°30 N; 21°10´ and 20°50´ W.

Soil samples were obtained from depth of 20 cm at sites close to cinnabar mines in a forest stand (*Quercus* sp., *Cupressus lusitanicus* sp., *Juniperus depeana* sp. and *J. flaccida)* and from an agricultural site. Both soils were air-dried and then sieved through a 2 mm sieve for measurements of pH, texture and extraction of humic substances. An aliquot was ground to pass through a 0.125 mm sieve for determination of total organic carbon, cation exchange capacity and Hg in soil. Physical and chemical soil properties were measured according to ISRIC (2002). Total soil organic carbon (TOC) was measured according to Walkley & Black.

Total mercury (THg) content in soils and in each humic fraction was determined using a Perkin Elmer hydride generation MHS-15, in an atomic absorption spectrometer Perkin Elmer AAnalyst 100, after HNO_3 (1 mL sample + 5 mL HNO_3 INSTRA) digestion in a microwave MarsExpress unit. Standards of suitable mercury concentration (5 μg/kg – 50 μg/kg) were employed for determination of the mercury concentration in each sample solution by triplicate.

Organic matter fractions were extracted and purified according to Dabin (1971) and the International Humic Substances Society method (Swift, 1996); obtaining light organic matter (LOM), fulvic acid (FA_{H3PO4}), fulvic and humic acid extracted with alkaline reagents (FA and HA) and humin (HU) fractions. Total mercury (THg) content was determined for each HS's fraction by microwave digestion, as already described for soil. The results were analyzed by statistical treatments mainly non-linear and factorial discriminant analysis (Statistica ver 8.2).

Results and Discussion

Soils show a slightly acidic to neutral reaction (Table 1), with silty clay texture, and high to medium CEC, diminishing strongly in the cropping site that is subjected to annual maize cultivation, as well as organic matter that is related to the CEC decrease.

Table 1: Physical and chemical characteristics of the studied soils

Soil	**pH 1:2.5 H_2O**	**Sand**	**Silt**	**Clay**	**CEC**	**COT**
		$g \cdot kg^{-1}$			**$cmol \cdot kg^{-1}$**	**$g \cdot kg^{-1}$**
C3 forest	**6.50**	**290**	**350**	**350**	**46.06**	**26.6**
C4 agricultural	**6.88**	**270**	**400**	**330**	**13.97**	**11.6**

Humic substances in forest soil retained 53.78 % of total mercury, whereas the crop soil retained 60.27 %. The higher C content in the LOM could be a result of the residual organic debris after fallow (C4) in relation with the forest soil (C3) (Table 2, Figure 1); as well, the decline of TOC in the agricultural land use is related to the traditional maize management. During the dry season, solar radiation and heat influence aromatization processes of the humic substances, increase humic acid proportions in this site in relation with the forest soil humic acids.

Table 2: C distribution in organic matter fractions from both soils

Soil	**% C_{LOM}**	**% C_{FA}**	**% C_{HA}**	**% C_{HU}**	**HA:FA**
C3	**19.8**	**16.1**	**40.4**	**23.7**	**2.5**
C4	**47.6**	**12.9**	**36.3**	**3.1**	**2.8**

LOM=light organic matter, FA=fulvic acids, HA=humic acids, HU=humins

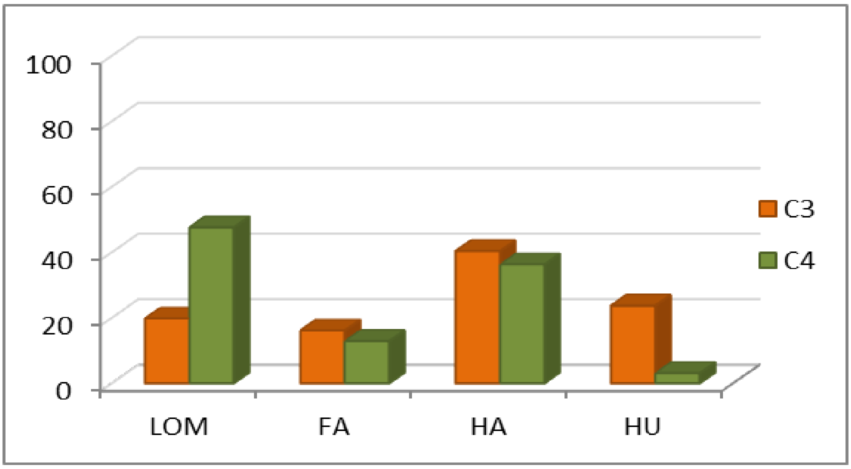

Figure 1: Comparison of the distribution of soil organic matter between the studied sites

	Organic carbon distribution in humic substances				
	LOM	HA	FA	HU	Soil
C3	0.2908 ± 0.9940	0.5927 ± 0.0410	0.2356 ± 0.0515	0.3473 ± 0.0471	2.6033 ± 0.0551
C4	0.5092 ± 0.0096	0.3890 ± 0.0726	0.1390 ± 0.0840	0.0331 ± 0.0045	1.1567 ± 0.0586

Higher mercury concentrations were obtained in the LOM, following the next sequence, in relation to the other fractions: LOM > HU > HA > FA. Hence, we suggest that Hg redeposition on the surficial layer could be part of the dynamics in both sites, and that the main reason of its decline is that Hg is released by reduction from Hg^{2+} to Hg^0 by biotic and/or abiotic processes as has been documented by several authors (Wang et al., 2003).

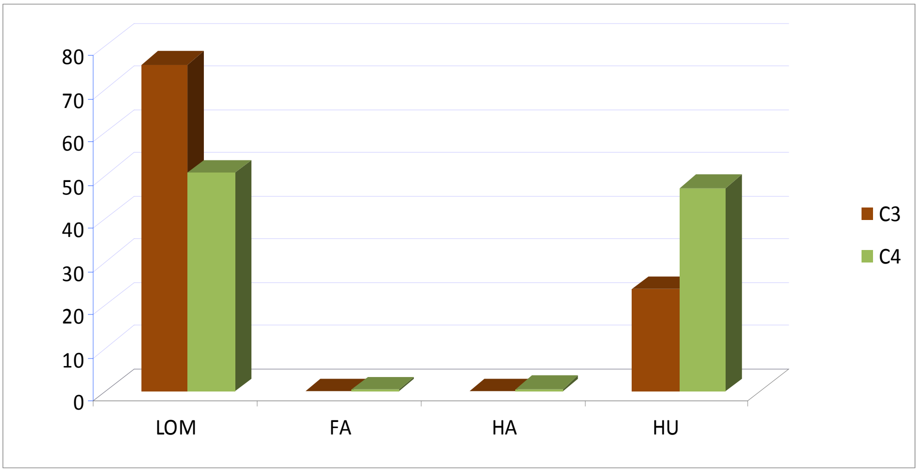

Figure 2: Proportion of mercury binding to organic matter fractions

	Mercury content ($mg.kg^{-1}$) in humic substances					
	LOM	HA	$FA\_H_3PO_4$	FA	HU	Soil
C3	18.295 ± 6.300	0.040 ± 0.004	0.0047 ± 0.000	0.039 ± .004	5.734 ± 1.158	10.83 ± 0.0915
C4	14.358 ± 0.085	0.214 ± 0.025	0.005 ± 0.001	0.172 ± 0.001	13.463 ± 6.521	12.083 ± 0.849

During LOM mineralization, mercury emission occurs, and its concentration diminishes drastically in HA and FA. Instead, part of the mercury concentrates in the HU fraction. In fact, the total net increasing content of Hg and the transforming rate of organic-bound Hg has been documented as a common process for maintaining Hg forms in humus, in this case, it could be the reason for its content in the HU. We suggest than this fraction can play a more important role in pollution control of Hg^{2+} in environment as has been studied also by Zhang et al. (2009).

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Total mercury content in some crops, in San Joaquín, Querétaro, México

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Introduction

At the mining region of San Joaquin, Queretaro, the presence of mercury (Hg) has been sustained as a steady environment for several years, favoring Hg accumulation and the possibility of its transference to other environmental systems accessing the trophic chain; however, mercury dynamics in soils is highly complex and it is strongly controlled by physical and chemical properties of the soil (Patra et al., 2004).

Intervening processes for mercury to access vegetables are the same as those used by the nutrients. Even when crops have developed selective mechanisms for the access of nutrients, they occasionally fail and elements such as Hg are allowed to enter. The amount of metals that can be absorbed by plants depends on the ability of the element to move through the soil towards the superficial roots; transport from the rhizosphere towards the root and the translocation from the root to the stem (Patra et al., 2004; Peralta et al., 2009). Factors such as concentration and chemical speciation of mercury in soil solution, time of exposure and edaphic characteristics, influence their bioavailability and determine the conditions of toxicity for organisms (Notten et al., 2005; Patra et al., 2004; Peralta et al., 2009). Atmospheric dynamics also intervene in this process; mercury gas exchange varies significantly between plant species; for trees, the elementary mercury exchange is fast and absorption and desorption depend on environmental concentration (Staiger, 1983).

Environmental Hg can have a natural origin; nonetheless anthropogenic activities favor and increase its presence, especially those referred to mining activities. At the San Joaquin municipal entity mining activity has been vital for a long time; historic registers report mining activities dating to Pre-Hispanic times (Herrera, 2009) utilizing cinnabar for religious and social activities. By the middle of the 20th century a great demand for this metal existed and mining of mercury ore became the main economic activity for the entire region. Repercussions of such activities have been manifested by the presence of mining waste deposits highly enriched in mercury, which have remained exposed to the environment for several years, becoming punctual Hg sources. For this work, we quantified total Hg in fractioned farm activities mostly comprising corn and beans (root, stem, leaves, grains) as well as the soil for each crop, and along with the work, we sampled plants endemic for the region.

Material and method

San Joaquin mining zone is located south of Sierra Gorda, state of Querétaro (Figure 1). The extents of the study area were based on the concept of a hydrologic basin, with a surface of 172 km^2. Its furthest coordinates (vertexes) are 99°40’ and 99°30’ west and 21°10’ and 20°50’ north. The basin is naturally limited by Río Moctezuma to the southeast and its convergence with Río Extóraz to the north. The zone exhibits great differences in height, which vary from 800 to 3100 masl.

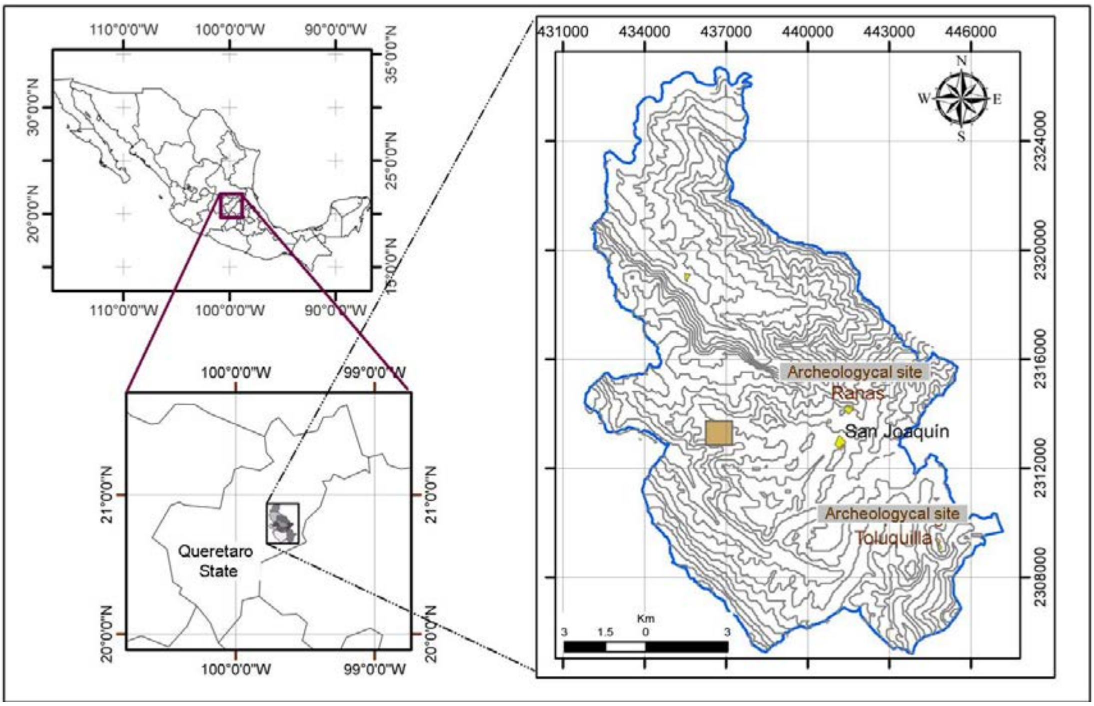

Figure 1: Study region and hydrographic micro-basin limits

In order to define the sampling sites, we located the lands with seasonal farming activities. Locations were referenced with a hand GPS and the sampling was done during harvest time in October 2006; November 2007 and November 2010. During these sampling years, even when sampling sites were the same, the lands were not always harvested. We collected complete samples (corn and beans), fractioning each sample and attending to its anatomy in root, steam, leaves and grains. Each fraction was kept in brown paper bags and sent to the laboratory. We took the necessary amount using plastic bags previously washed with a 30 % nitric acid.

Each crop fraction was washed in a 10 % nitric acid solution diluted with de-ionized water and air dried at a temperature of 22-25°C. For grinding an agate mortar and an electric mill were used; samples were sieved with a nylon mesh to obtain a particle size below 0.13 mm. For each fraction we took 0.10 g of sample, which was digested with 5 ml of concentrated (INSTRA) nitric acid in a microwave oven (Marspress). Concentrated hydrochloric acid drops were added and filled with de-ionized water (18.2 μS/cm) to 200 ml. Samples were digested and kept in cold storage until they were analyzed (not over 2 weeks). Mercury was quantified using spectrophotometry ICP-MS with a Mass Spectrometer (Thermo Electron Corp model X series II coupled with a self sampler) CETAC ASX-510 at the mass spectrometry laboratory of Centro de Geociencias.

Soil samples were air dried at room temperature and sieved with a #10 nylon mesh (2 mm). We determined texture; organic matter; pH in water and cationic exchange capacity according to ISRIC (2002) methodology. Mercury quantification was done with a spectrophotometer of atomic absorption specific to analyze mercury AMA 254. For digestion, 37 % HCl, 65 % HNO_3 and 30 % H_2O_2 of high purities were used. For reference materials Hungarian sediments MOSTAR, ISE 982 from Slovakia and WEPAL ISE were used. Analyses were conducted at the Hungarian Institute of Geology (Bartha et al., 2009). For the obtained results we used a statistical algorithm using STATISTICA 8.2 and mapped with GIS software (ArcGIS 8.1).

Results

Thirteen seasonal plots with 52 samples (Figure 2) were located. The distribution of Hg mercury of different fractions was as follows. The highest concentrations were present in roots and leaves, diminishing in stems and grains (Figure 3). The total Hg contents show a wide variation per site; we assumed that the influence of environmental differences within the basin modify the distribution and dispersion of mercury, as well as the close relation with the type of material.

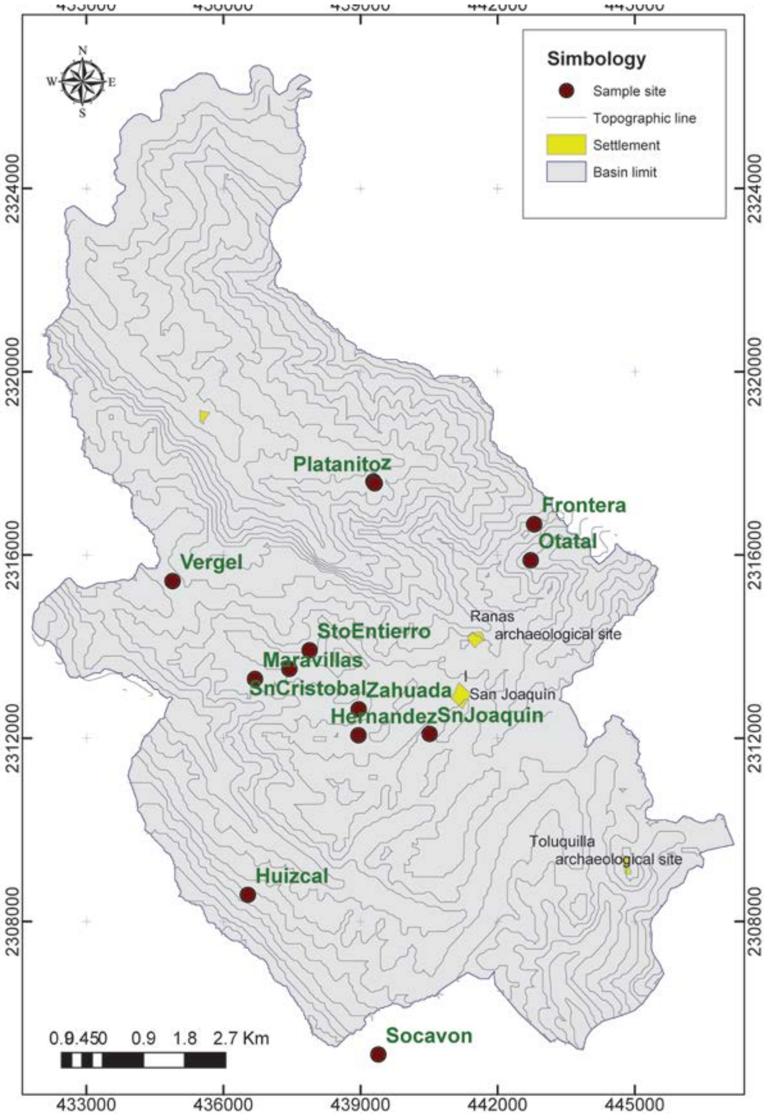

Figure 2: Sampling sites

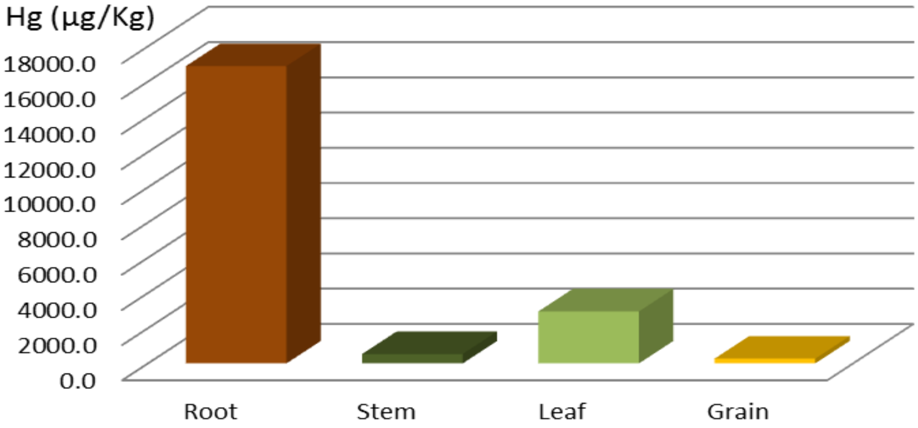

Figure 3: Distribution of total and average mercury contents (mg/kg) in analyzed corn fraction samples

Soil properties show high variations with clay contents (10-49 %); pH values with narrower margins 5.22-7.72 (slightly acidic to slightly alkaline); organic matter content from very low (0.9 %) to very high (7.8 %).

Discussion

Mercury intake to farm products represents a major factor to be incorporated to the trophic chain. Highest Hg concentration in analyzed crop structures were found in the root; followed by the stem; the leaves and finally the grain. Because the intake of Hg to corn is preferentially through the roots, their content is proportional to the surrounding concentrations. For this case of the containing material, being sediments or soils, the dynamics of mercury inside corn are unknown; however, root of the crops are expected to present a higher Hg concentration because they are in direct contact with mercury in the soils (Tammerman et al., 2009). Once mercury accesses the root, either organic or inorganic, the crop transports it to the foliage, where it might be transformed into inorganic mercury and volatilized via the stomas, as well as the process of gas exchange within the crop (Bargagli et al., 1986; Siegel & Siegel, 1983). Stem presents the lowest Hg concentration because amongst other things the function of this structure is mainly transport.

Through the leaves, Hg can enter as elementary mercury (Hg^0) all along the stem or by atmospheric deposition. Because mercury is highly volatile it can be released in the same way, through the stoma; nonetheless, Hg deposited in the leaves can be absorbed irreversibly being thus accumulated within the vegetable structure (Rea et al., 2002).

Tammerman et al. (2009) confirm that the foliage of several vegetable species exchange Hg^0 vapor rapidly and that the speed of the process depends on Hg concentration within the media. If concentration is too high, the leaves do not have the speed necessary to volatize it, and by mercury being in excess their only choice is to store it. This might be the process for the study area, suggested by the higher Hg content in the leaves and whose origin might be from atmospheric deposition.

Total Hg content found within the grains might be an alert indicator because it occupies the part consumed by humans. Total Hg contents in corn are indicators averaged, and show its ability to accumulate this element.

Mercury distribution in sampled soils is very variable ranging from 0.5 up to 4164 mg/kg; being the highest in terraces and sediments; in contrast with those locations where material is soil and show less HgT content; this agrees with the reviewed references, where total Hg within soils is rapidly transformed via volatilization to the atmosphere; the presence of micro organisms and organic matter to form chelates and other products that can trap mercury.

Conclusions

The Hg contents in these agricultural products might be indicators of the element accessing into the trophic chain and especially to human consumption representing a potential hazard to human health. These results allow us to establish precedents for starting specific studies in regard to Hg accumulation in important agricultural products such as corn and beans, illustrating bio-accumulation and therefore, toxicological impacts on the inhabitants of the region. These results show the necessity to conduct more thorough studies in this field so we can become aware of the dynamic accuracy for this element within the trophic chain and the possible hazard to the public health.

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Understanding the mercury effects on RNA in *Bacillus subtilis*

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DNA (deoxyribonucleic acid) is the genetic material in every living organism. From this molecule, **RNA** (ribonucleic acid) molecule is synthesized, this process is called transcription. The sequence of RNA is then capable of directing the process of translation where the proteins are synthesized.

RNA degradation plays an important role and is a major component of RNA metabolism in all organisms. In bacteria, there is a growing body of evidence to show that changes in RNA turnover play an essential role in stress adaptation, growth phase changes, pathogenesis and quality control (Grunberg, 1999; Anderson & Dunman, 2009). In *Escherichia coli*, and other bacteria such as *Bacillus subtilis*, it is clear that RNA degradation is a carefully controlled biochemical pathway, involving a number of different endo- and exoribonucleases (Wang & Bechhofer, 1996; Condon, 2003; Oussenko et al., 2005; Deutscher, 2006). Although some RNases display significant functional overlap, in *E. coli,* for example, cells lacking the 3'-5'-exonucleases polynucleotide phosphorylase (PNPase) in combination with RNase II or RNase R, which are also 3'-5'-exonucleases, are inviable or their growth is deficient (Grunberg, 1999; Mohanty & Kushner, 2000). These findings have shown the existence of vital functions of these RNases in RNA metabolism.

tRNAs (transfer ribonucleic acid) are adapter molecules, that play an essential role during translation and expression of genetic code. Thus, the mechanisms that generate mature tRNAs are vital in all organisms. In *Escherichia coli* as well as *Bacillus subtilis*, endo- and exoribonucleases participate in the generation of mature and functional tRNAs from primary transcripts (Grunberg, 1999; Campos et al., 2010). The degradation of defective tRNA molecules through quality control is essential in the metabolism of all cells (Deutscher, 2006; Campos et al., 2010). It has been shown in *E. coli* that polyadenylation by poly(A) polymerase and polynucleotide phosphorylase (PNPase) activity promote degradation of defective tRNA^{Trp} molecules (Li et al., 2002). Although processing by PNPase and RNase II is obstructed by stem loop structures (reviewed by Grunberg, 1999), RNase R can process through these structures (Cheng & Deutscher, 2005; Cairrao et al., 2003). Recently, the participation of RNase R in quality control of tRNA^{Cys} in *Bacillus subtilis*was has been shown (Campos et al., 2010).

In all organisms, several essential transition metals, such as copper, cobalt, iron, manganese and zinc, play important roles in the control of metabolic and signaling pathways, but a growing amount of evidence has shown the deterioration of biomolecules, such as proteins, nucleic acids, as a result of the ability of these metals, as well as metals like cadmium, chromium, vanadium, nickel and mercury, to produce reactive radicals in cells (Valko et al., 2005). Mercury is found to be among the most toxic elements to living organisms. The cycle of this element beginning as the emission from natural sources had not represented a life threat risk for thousands of years; nonetheless, during the last 150 years, the anthropogenic mercury emissions have at least doubled the natural sources in as far as the atmosphere's mercury entrance. Although the mechanisms involucrate in mercury detoxification in bacteria have been intensively analyzed, the toxicity at molecular level remains unclear. Until this moment, we have results that shown that the addition of $HgCl_2$ during bacterial exponential phase immediately reduces cell division and during this response, interestingly, we observed that the degradation or maturation of tRNA was affected. We found out that the shorter species increase up to 80 % after mercury addition when an exonuclease mutant strain is used, but this proportion changed as bacteria improved the growth, activated the ability to restore the maturation of tRNA, probably due to expression or activation of enzymes involucrate with quality control and/or quelation of mercury.

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Electroremediation of mercury polluted soil by complexing agents

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Electrochemical remediation is a promising technology in removing recalcitrant soil contaminants that uses electroosmosis, electromigration, and/or electrophoresis processes in an imposed electric field to migrate subsurface contaminants. However, several improvements, such as chemical composition, higher buffering capacity, and metal speciation are necessary to efficiently use electroremediation for heavy metal remotion. One strategy that enhances the efficiency of electroremediation is the use of complexing agents. Electroremediation of mercury polluted soil, aided by complexing agents, is an attractive treatment for mercury removal. One area which can benefit from this type of soil remediation is the mining region of the Sierra Gorda in Querétaro, Mexico. Mercury removal can hopefully improve the living conditions and general health of the population in this region. It is possible to remove up to 75 % of metal contaminants in mercury polluted soil samples by wetting them with 0.1M EDTA, placing them in an experimental cell equipped with Ti electrodes, and then applying a 5 V electric field for 6 hours. Electromigration of the coordination complexes that form between the terminal hydroxyl groups in EDTA and divalent mercury (Hg^{2+}) facilitates efficient mercury removal. Supramolecular interactions between unshared electrons at EDTA's tertiary amino nitrogen and Hg^{2+} strengthen the interaction of these complexes.

Introduction

The San Joaquin mining district of Querétaro, Mexico is located in the north of the state, at the southern tip of the Sierra Gorda, Sierra Madre Oriental mountain range. Hydrothermal processes, originating from Tertiary magmatism, have operated in the region for millions of years, creating a mineral-rich area (Martínez-Reyes et al., 2009). However, extensive use of cinnabar by pre-Hispanic and present day populations has polluted the environment of San Joaquin with high concentrations of mercury (Hernández-Silva et al., 2011). In addition, mercury-based mining was an extremely important industry until the 1970's with the mines not abandoned until the end of 1990's, causing further mercury pollution. Mercury, which bioaccumulates, can cause serious health problems when present in the environment. Since chronic mercury toxicity affects the brain and central nervous system and results in mental impairment, mercury must be removed from both soil and solid wastes (Davis et al., 1997). Accepted methods for mercury removal include thermal desorption, phytoextraction, phytovolatilization and recently, electroremediation (Mendoza et al., 2005; ArgenBio, 2003). Electroremediation has successfully removed contaminants in many soil remediation studies, having the advantage of simultaneous chemical, hydraulic and electrical gradients. Indeed, the application of either an electric field or direct current through two electrodes (anode and cathode) is required in electroremediation to efficiently remove mercury from a saturated soil. Usually, the electrodes are inserted into wells that contain a supporting electrolyte made from inert salts for improved electric field conduction (Rajeshwar et al., 1994; Huang et al., 2001; Acar & Alshawabkeh, 1993). This study focuses on implementing mercury electroremediation in the San Joaquin region. Past studies (Reddy et al., 2003a, b) have specifically used complexing agents like ethylendiaminetetraacetic acid (EDTA), KI, and NaCl under a constant potential gradient for mercury polluted soil electroremediation. Based on this precedent, electroremediation aided by extracting agents was used to remove mercury in soil samples from San Joaquin.

Methodology

By following published protocols (Reddy et al., 2003a, b), mercury was extracted from soil samples using 0.1 M solutions of several complexing agents: KI, KCl, KOH, EDTA, and CTAB. A 0.2 g soil sample was treated with 2.5 ml of each solution and then left to stand at room temperature for 72 h. To achieve soil electroremediation, a 5 g sample was mixed with 2.5 ml of extractant solution containing the complexing agent and placed in a two-electrode electrochemical cell. The two electrodes, the anode and cathode, were both titanium. Several electrolyses were carried out at potentials of 5, 10, 15, 20, 25 and 30 V for 20 min. For each variation, three 0.2 g samples were collected: near the anode, in the middle and near the cathode.

Results and Discussion

Out of all the complexing agents, EDTA (2.55 ppm) and KI (1.76 ppm) were the most efficient in mercury removal (Figure 1). EDTA extraction was approximately 57 % more effective than KI extraction at room temperature without stirring. CTAB and KCl were less effective extractants. A molecular structural analysis shows that EDTA is a good chelator for divalent cations (Hg^{2+}), likely because it has two tertiary amino groups and two carboxylic groups which promote coordination. The tertiary amino groups coordinate with metals by using non-shared electron pairs, while the terminal carboxyl groups can create coordination complexes with mercury (Sagdinc & Pir, 2009; Ghabbour & Davies, 2005). In contrast, CTAB has only one tertiary amine, several terminal methyl groups, and a bromide counterion, which prevents molecular recognition between CTAB and ionic mercury (either Hg^{+} or Hg^{2+}). Only the best extractants, EDTA and KI, were used as supporting electrolytes for new 0.1 M extractant solutions. Electric potentials of 5, 10, 15, 20, 25 and 30 V were applied for 6 hours. Afterwards, the residual concentration of the mercury extracted from the treated soil was compared as a function of the applied electric potential. EDTA had better extraction efficiency (75 %) and lower energy consumption (5 V) than KI (62 %, 15 V).

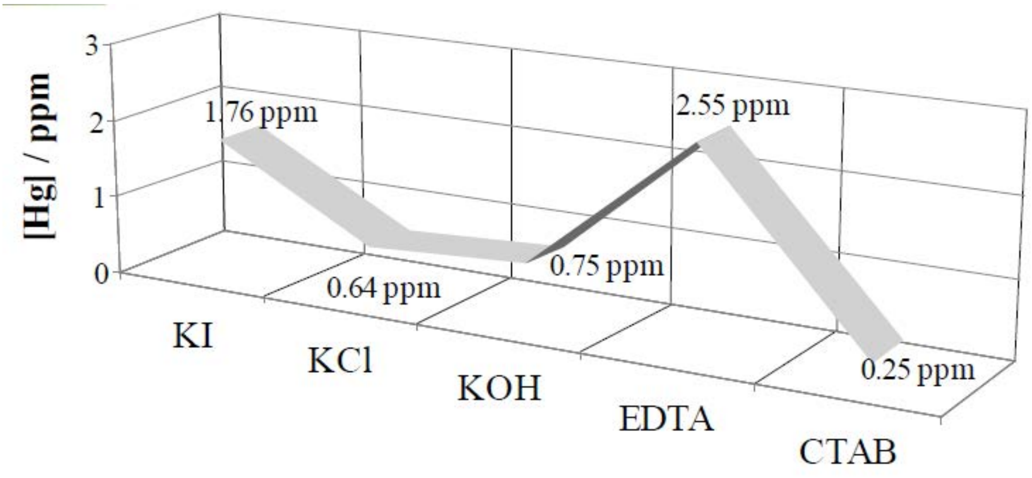

Figure 1: Hg extracted from 0.2 g of soil using 0.1 M solutions of different extractant agents for 72 h at 278 K without stirring

Conclusions

When mercury polluted soil from the San Joaquin mining zone underwent electroremediation, seventy-five percent of mercury contaminant was extracted when a 5 V electric potential was applied for 6 hours to an electrochemical cell of Ti electrodes inserted into soil wetted with 0.1 M EDTA. The high observed efficiency was facilitated by the migration of coordinated complexes by electromigration and electrophoresis in the presence of an electric charge.

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Design, construction and characterization of an electrochemical sensor of mercury in soil

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Heavy metal contamination, especially of cadmium, mercury, lead and chromium, is a serious environmental problem, since heavy metals are extremely toxic in high concentrations. Contrary to organic residuals, metals do not degrade and instead accumulate in water, soils and silt. Since heavy metals accrue easily and are highly toxic, quantitative determination is needed to measure heavy metal residual concentrations.

Current regulations state that the maximum safe concentration of mercury in potable water is around 1 ppm, which makes measuring mercury a priority because of public health reasons. Mercury can pollute drinking water and soil, so residual concentrations must be quantified to prevent possible toxic poisoning.

Analytical methods that determine mercury in water and soil include atomic absorption, ICP spectrometry and electrochemical methods (e.g. differential pulse polarography using a dropping mercury electrode).

Consequently, we have designed, constructed and characterized an electrochemical sensor that detects mercury in soil, which uses sequential injection-square wave-anodic voltammetry and anodic stripping voltammetry using mercury film and carbon electrodes under acidic conditions for chemical speciation.

Introduction

The San Joaquin mining district of Querétaro, Mexico is located in the north of the state, at the southern tip of the Sierra Gorda, Sierra Madre Oriental mountain range. Hydrothermal processes, originating from Tertiary magmatism, have operated in the region for millions of years, creating a mineral-rich area (Martínez-Reyes et al., 2009). However, extensive use of cinnabar by Pre-Hispanic and present day populations has polluted the environment of San Joaquin with high concentrations of mercury (Hernández-Silva et al., 2011).

Mercury, which bioaccumulates, can cause serious health problems when present in the environment. Since chronic mercury toxicity affects the brain and central nervous system and results in mental impairment, mercury must be removed from both soil and solid wastes (Davis et al., 1997). Accepted methods for mercury removal include thermal desorption, phytoextraction, phytovolatilization and more recently, electroremediation (Mendoza et al, 2005; ArgenBio, 2003).

Due to the toxicity of mercury, measuring mercury is a priority for health reasons, as the maximum safe concentration of mercury in potable water is around 1 ppm. Mercury can pollute drinking water and soil, so residual concentrations must be quantified to prevent possible toxic poisoning. Different analytical methods, such as atomic absorption, ICP spectrometry and electrochemical methods like differential pulse polarography using a dropping mercury electrode, can measure mercury concentration in water and soil.

Methodology

Anodic dissolution voltammetry, an electrochemical technique, was used to measure mercury concentration in soil. A three-electrode cell with a glassy carbon (GC) working electrode, a platinum counter electrode, and a reference electrode Ag/AgCl electrode was used. The supporting electrolyte was 3 M KCl. The GC electrode was polished with 1.0, 0.3 and 0.05 µm Al_2O_3 suspensions on Buehler felt pads, and rinsed with deionized water between each change in particle size. Afterwards, residual alumina was removed by a sonic cleaning of the GC for 5 min in Milli-Q water.

Results and Discussion

Anodic dissolution voltammetry was carried out in 0.1 M HCl solution with a hexadistilled mercury pre-concentrated for 3 minutes followed by a 30 s hold on the GC electrode. The mercury signal was observed at -0.250 V using a scan rate of 0.020 V s^{-1} (Figure 1) (Pineda et al., 2009).

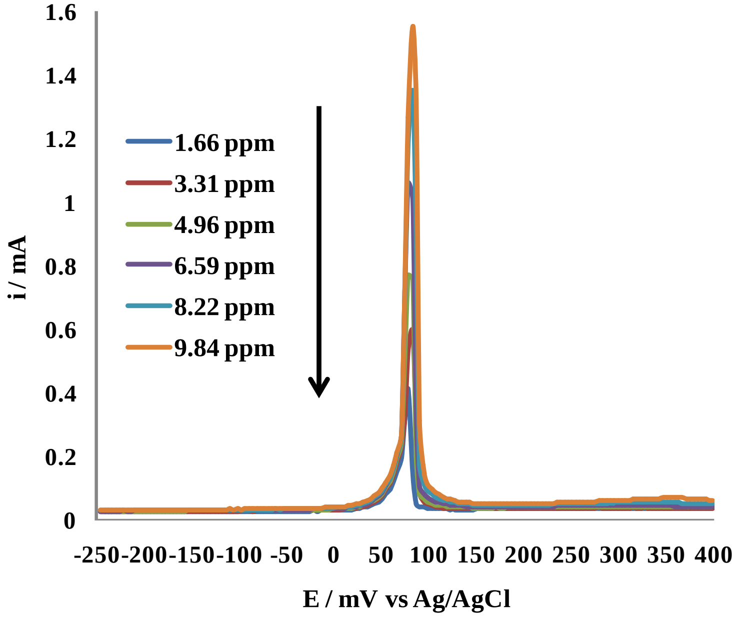

Figure 1: Voltammetries obtained to construct calibration curves without anodic dissolution

A calibration curve for mercury was made with electric current data generated from each voltammogram (Figure 2). An internal standard of 666 ppm mercury was used, anticipating a detection limit of 18.5 ppb and a quantification detection limit of 61.6 ppm.

Conclusions

Anodic dissolution voltammetry successfully quantified mercury content in soil with a detection limit of 18.5 ppb and a quantification detection limit of 61.6 ppm since mercury signals could be observed at -0.250 V using a scan rate of 0.020 V s^{-1}.

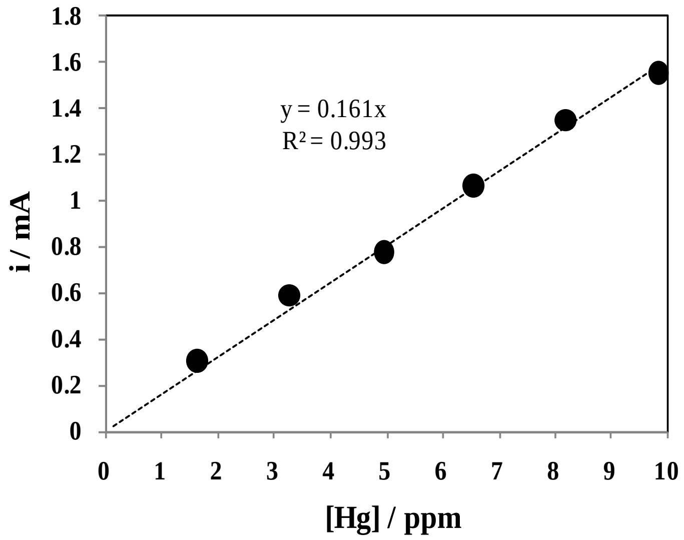

Figure 2: Calibration curves of Hg in 0.1 M HCl with pre-concentration for 3 min with a 30 s hold, Ep = -0.250 V and $\nu = 0.020\ \mathrm{V\ s^{-1}}$

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Determination of total Hg contents of soils and sediments in the Geological and Geophysical Institute of Hungary (MFGI)

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Objects

The Chemical Laboratory of MFGI (Geological and Geophysical Institute of Hungary, its former name is Geological Institute of Hungary, MÁFI) is specialized for the mercury and other heavy metal analysis for EuroGeoSurveys. It has participated in the Geochemical Baseline Mapping Program of FOREGS (Forum of European Geological Surveys) and the preparation of the Geochemical Atlas of Europe. The aim of the present work was the wide range of investigation of the Mexican samples according to our former experiences and reference samples and the geological interpretation as well.

Methodology

1. Sample preparation

1.1 Washing procedures

The hair and nail samples were washed before analysis and decomposition. Washing procedure: Double rinsing with 3:1 ratio of ethylether-acetone mixture for 20 minutes. Then drying at 85°C and rinsing with 5 % EDTA (Ethylene diamine tetra acetic acid) solution for 1 hour. Rinsing three times with deionised water and then drying at room temperature.

1.2 Sample decomposition

The Hg analyses were performed on the undecomposed washed hair and nail samples and the bone samples as well.

For other elements (As, Cd, Cr, Cu, Ni, Pb, Sb, Zn) the bone samples were decomposed by aqua regia. The decomposition procedure was as follows: 0.25 g sample was weighed into a 150 ml glass beaker and a mixture of 3.8 ml of cc. HCl and 1.2 ml of cc. HNO_3 was added to the sample. It was evaporated up to dry on a waterbath and the residue was dissolved by 5 ml of 1:1 HCl and finally filled up to 50 ml.

The hair and nail samples were decomposed by microwave decomposition unit (Milestone MLS 1200 MEGA) using a mixture of HNO_3 and H_2O_2. The decomposition procedure was as follows: 0.25 g of sample (or less if it is not enough) was weighed into the PTFE vessel of the microwave unit. A mixture of 0.25 ml of H_2O_2 (30 %) and 3ml of cc. HNO_3 was added. The vessel was tightly closed. Digestion program lasted 7 minutes at 300W. The sample solutions were then filled up to 50 ml.

2. Instrumentation

2.1 AMA 254 Advanced Mercury Analyser

The Hg content was analyzed by a direct AAS mercury analyser (AMA 254 Advanced Mercury Analyser).

The instrument operating parameters are listed below:

Arrangement:	single beam, serial arrangement of cuvettes
Light source:	low pressure mercury lamp
Wavelength:	253.65 nm
Interference filter:	254 nm, half-width 9 nm
Detector:	silicon UV diode
Detection limit:	0.01 ng Hg, in the case of 0.100g sample: 0.1 ppb
Working ranges:	automatic switching at switching point A=0.8
1st range	0.05-50 ng Hg
2nd range	50-600 ng Hg
Reproducibility:	<1.5 %
Typical analysis time:	5 minutes
Sample treatment:	programmable
Drying period:	9-999 s
Decomposition period.	1-999 s
Calibration:	solution, reference material
Number of standards:	unlimited
Sample characteristics:	solid material, solution
Dosing volume:	
External sampling, max:	500 µl, 1000 µl (sample boat number2)
Internal sampling:	depended on sampling device
Weight of sample, max.:	300 mg, 700 mg(sample boat number2)
Possibility of preconcentration:	max. 10 times
Carrier gas:	oxygen
Inlet pressure:	200-250 kPa
Flow rate:	200 ml/min

Detection limit and expected uncertainty of the mercury content in bone, hair and nail samples by solid sampling direct AAS technique using 0.1 g of sample is given in Table 1.

Table 1: Detection limit and expected uncertainty of the mercury content in bone, hair and nail samples by AAS technique

Element	**Analytical wave-length nm**	**Detection limit mg/kg**	**RSD %**		
			±20	**±5**	**±2**
			Concentration range in the proper unit (mg/kg)		
Hg	253.650	0.0001	0.0001-0.001	0.001-0.005	>0.005

2.2 JY ULTIMA 2C ICP-AES instrument

For other elements (As, Cd, Cr, Cu, Ni, Pb, Sb, Zn) the analysis of the bone samples were performed by a JY ULTIMA 2C ICP-AES instrument.

The ICP-OES instrument operating parameters are listed below:

RF power:	1000 W
Reflected power:	<10 W
Plasma gas flow rate:	12 l/min
Sheath gas flow rate	: 0.2 l/min
Nebuliser type:	cross-flow
Nebuliser flow rate:	0.4 l/min
Nebuliser pressure:	2.7 bar
Observation height:	15 mm (above load coil)
Integration time:	0.5 s (poly) to 5 s (mono)
Nitrogen generator	For purging the monochromator for the determination of the UV lines

Detection limits and expected uncertainties of trace elements by ICP-AES technique are give in Table 2.

Different concentration ranges of the samples are grouped in the three columns on the right side of the table. The RSD value valid in the proper range is indicated at the top of the three columns. If the results are in the right column of the table, the RSD value is ± 2 %. In the column to the left the RSD value is ± 5 % and the results in the first column means RSD is ± 20 %. In this last case it would be better choosing a more sensitive analytical technique.

Table 2: Detection limits and expected uncertainties of trace elements by ICP-AES

Element	**Analytical wavelength nm**	**Detection limit mg/kg**	**RSD %**		
			±20	**±5**	**±2**
			Concentration range in the proper unit (mg/kg)		
As	189.042	0.6	0.6-6	6-30	>30
Cr	205.552	0.2	0.2-2	2-10	>10
Cu	324.754	0.2	0.2-2	2-10	>10
Ni	231.604	0.4	0.4-4.0	4.0-20	>20
Pb	220.353	0.6	0.6-6	6-30	>30
Zn	213.856	0.10	010-1.0	1.0-5.0	>5.0
Cd	228.802	0.06	0.06-0.6	0.6-3.0	>3.0
Sb	206.833	0.6	0.6-6	6-30	>30

2.3 Perkin-Elmer ELAN DRC II ICP-MS instrument

For the nail and hair samples the analysis were performed for the next elements: As, Cd, Cr, Cu, Ni, Pb, Sb, Zn by a Perkin-Elmer ELAN DRC-II ICP-MS instrument.

The ICP-MS instrument operating parameters are listed below:

Generator	40.68 MHz
RF power	1200 W
Plasma gas flow rate	15 l/min
Auxiliary gas flow rate	1.20 l/min
Nebulizer gas flow rate	0.99 l/min
Nebulizer	Meinhard
Spray chamber	Cyclonic, quartz
Cones	Ni
Quadrupole operating frequency	2.5 MHz
Dwell time	50 ms
Acquisition time	60 s

Detection limits and expected uncertainties of trace elements by ICP-MS technique are given in Table 3.

Different concentration ranges of the samples are grouped in the three columns on the right side of the table. The RSD value valid in the proper range is indicated at the top of the three columns. If the results are in the right column of the table, the RSD value is ± 2 %. In the column to the left the RSD value is ± 5 % and the results in the first column means RSD is ± 20 %. In this last case it would be better choosing a more sensitive analytical technique.

Table 3: Detection limits and expected uncertainties of trace elements by ICP-MS

Element	**Detection limit mg/kg**	**RSD %**		
		±20	**±5**	**±2**
		Concentration range in the proper unit (mg/kg)		
As	0.2	0.2-2	2-10	>10
Cr	0.1	0.1-1	1-5	>5
Cu	0.2	0.2-2	2-10	>10
Ni	0.2	0.2-2	2-10	>10
Pb	0.05	0.05-0.5	0.5-2.5	>2.5
Zn	0.1	0.1-1	1-5	>5
Cd	0.02	0.02-0.2	0.2-1	>1
Sb	0.04	0.04-0.4	0.4-2	>2

Reagents, standards

37 % HCl (Scharlau, Ultrapure) and 65 % HNO_3 (Scharlau Chemie, Spain) and 30 % H_2O_2 a.r. (Reanal, Hungary) were used for the decomposition of the samples.

Stock solution of mercury was a mono-elemental solution from BDH, 'SpectrosoL' grade. Calibration standard solutions were made by stepwise dilution of this stock solution. Final acid concentration was 10 ml/l sulphuric acid. (Merck, "Suprapur"). The concentrations of calibration solutions in doses of 100 μl are as follows: 5, 10, 20, 50, 100, 200 and 500 ng/100 μl solutions.

The following stream sediment samples (SRMs) were used for checking the solution calibration of the AMA 254 mercury analyser:

MOSTAR Hungarian stream sediment standard	recommended Value: 0.2245 ppm
Slovakian reference material (ISE 982)	recommended Value: 0.020 ppm
WEPAL monitor sample: (ISE 921)	recommended Value: 1.210 ppm

For mercury analysis more than 98 % recovery was reached.

Multi-elemental standard solutions (SPEX industries, Inc. Edison, NJ, USA) were used for the calibration of the ICP-AES and ICP-MS instruments.

Over 95 % recovery was reached for the elements analyzed by the ICP-AES technique. SRMs water solutions (TMDA 51.3, SLRS-2, NIST 1640) were used for checking the calibration and the recovery.

All solutions were appropriately diluted by high purity water (glass distillation unit, made by SIMAX, former Czechoslovakia, followed by Purite HP Still Plus system, Purite Ltd., Thame, Oxfordshire, U.K.). This system produced ultrapure water with a resistivity of 18 $M\Omega cm^{-1}$.

Results

On the basis of the performed analyses the main statistical parameters of total Hg content of the samples of **soils, sediments and mining wastes** in San Joaquin region (Mexico, Querétaro State) are presented below:

Number of samples: 103

Minimum:	0.21	mg/kg
Maximum:	4164	mg/kg
Medium:	181.83	mg/kg

The Figure 1 indicates the distribution of the number of samples per domain.

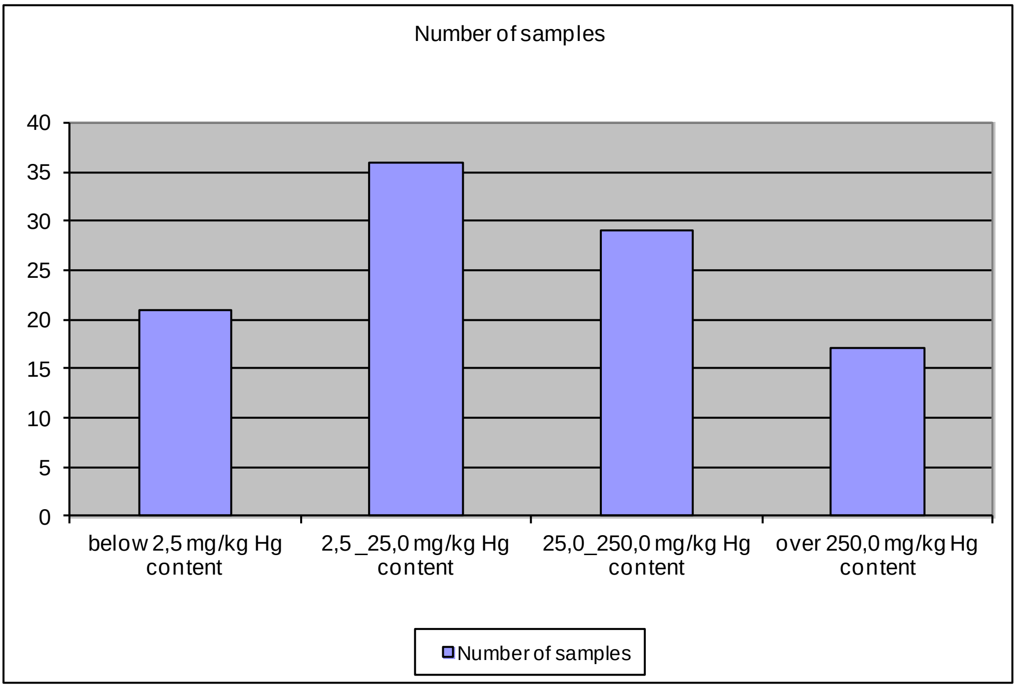

Figure 1: The distribution of the number of samples per domain

The Figure 2 shows the distribution of the total Hg content by domains on the map.

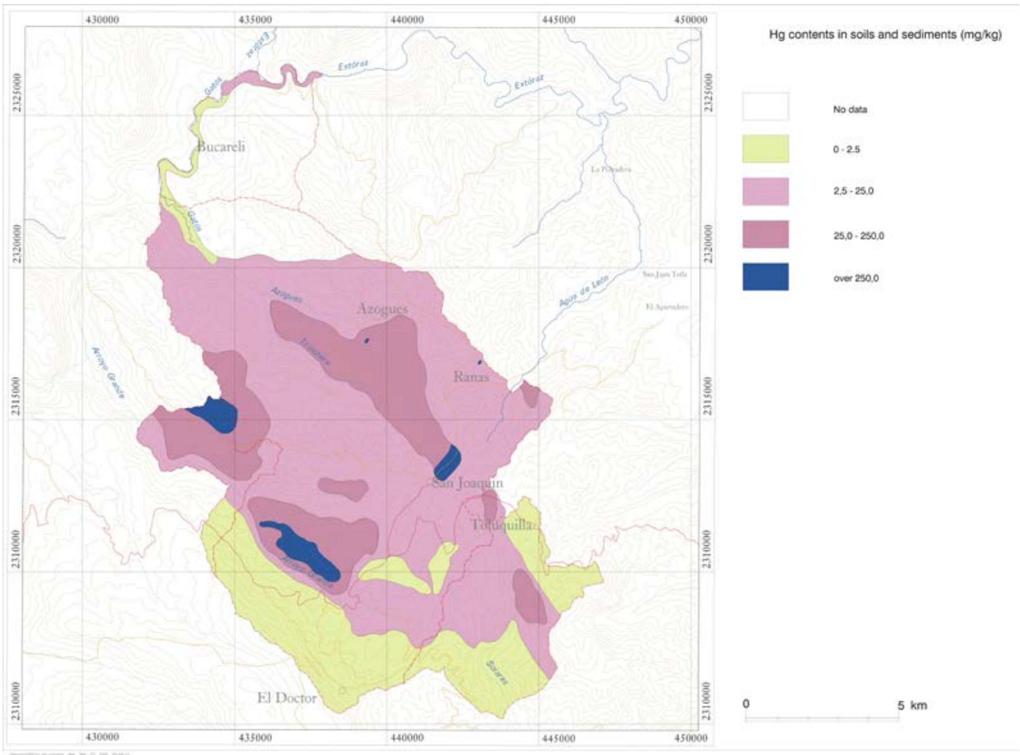

Figure 2: The distribution of the total Hg content by domains on the map

As a result of the correlation of the samples with specific geological formations it was concluded that the samples taken in the vicinity of the mines fell invariably in the highest domain, whereas the Hg-content of the sequences more distant from the mines could be assigned to the domain between 2.5 and 25.0 mg/kg showing the background value of the territory. The Hg-content of the soil samples overlying the Soyatal Formation remains commonly under 2.5 mg/kg similarly to the sediments of the river Gatos upstream of Bucareli.

The transitional domain between 25.0 and 250.0 mg/kg of Hg-content appears commonly in the sequences covering the formations Las Trancas and Tamaulipas. It occurs typically along some ridges in zones affected by hydrothermal processes.

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