Mercury speciation determined by thermo-desorption analysis at two sites contaminated by mining

DISSERTATION

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Statement of originality

This dissertation is the result of my original research and is presented for the degree of "Doctor of Philosophy" at the Faculty of Science, Charles University in Prague.

The dissertation contains no material previously published or written by another person except where due reference is made in the dissertation itself. It has not been submitted to any other university for any degree or other qualification.

M.Sc. Maria Hojdová

Statement of co-authors

On all co-authors behalf, I can confirm that Maria Hojdová performed the majority of the field, analytical and research work in the studies included in this dissertation. The co-authors contributed by sampling, analytical work and their critical comments helped to improve the final version of the manuscripts.

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ABSTRACT

Historic mercury mining represents an environmental threat due to high Hg concentration in waste material. Mercury ores were mined for more than 150 years at two sites in the central Czech Republic, but the extent of Hg contamination in the vicinity of former Hg mining sites has not been yet investigated. The objectives of the study were to evaluate the Hg sources in mine wastes, assess the extent of Hg contamination in historical mining area and to estimate potential mobility of Hg in the mine waste and soils. The method of thermal desorption in combination with ICP-OES (TDA-ICP-OES) has been applied to determine Hg speciation in solid samples.

Mine waste material was sampled at two mining sites, Jedová Hora and Svatá, in central Bohemia. Three soil profiles were collected to capture likely high and low impact sites within the mining area at Jedová Hora. Database of thermo-desorption curves of Hg chemical compounds and reference materials was created for the TDA for comparative purposes.

Both mine wastes and soils collected near the Hg mines were highly elevated in total Hg concentrations (up to 120 $\mu g\ g^{-1}$ and 10 $\mu g\ g^{-1}$, respectively). Soils exhibited the highest Hg concentrations mostly in subsurface Ah soil horizons. Higher Hg concentrations in Ah horizons relative to those in O horizons were found in all studied soils. Similar observations were reported by other authors and it is possible that regional decreases in Hg deposition contribute to this contrast in surface and Ah horizon Hg concentrations.

Mine wastes contained mostly cinnabar (HgS) (>80%) and only minor fraction (<14%) of total Hg amount was identified as Hg bound to surfaces of mineral particles, such as Fe-oxyhydroxides or clay minerals. In comparison to waste material the proportion of HgS in soils was smaller (60-80%). High impact soils contained HgS in all horizons and Hg(II) adsorbed onto the mineral surfaces constituted a minor fraction of total Hg. In the low impact soil HgS occurred only in the Ah horizon, which may reflect cinnabar fine particles spread at site during historical mining or ore processing. Deeper mineral horizons of the low impact soil contained only the Hg(II) weakly adsorbed onto mineral particles.

From the environmental point of view cinnabar is relatively stable in the soils. Its dissolution is limited and it is transported mostly in the form of particles. Nevertheless Hg(II) sorbed to

mineral components poses environmental threat due to its mobility and potential formation of highly toxic methyl-Hg.

TDA-ICP-OES seems to be appropriate for differentiation of Hg sulfides, metallic Hg and humic bound Hg. Identification of Hg sorbed onto mineral soil particles is possible, but distinguishing among sorption substrates (e.g. Fe-, Al- or Mn- oxyhydroxides or clay minerals) is limited.

ABSTRAKT

Historické dolování rtuti představuje hrozbu pro životní prostředí díky vysokým koncentracím Hg obsažených v hlušině. Ve středních Čechách byly rudy Hg těženy po více než 150 let, avšak míra kontaminace rtutí v okolí bývalých dolů dosud studována nebyla.

Cílem práce bylo detailně prostudovat materiál hald, představující možný zdroj kontaminace, odhadnout její rozsah v důlní oblasti a odhadnout potenciální mobilitu Hg v materiálu hald a v půdách. Za účelem určení Hg specií v pevných vzorcích byla propracována metoda termální desorpce v kombinaci s ICP-OES (TDA-ICP-OES).

Materiál hald byl vzorkován na dvou těžebních lokalitách, Jedová hora a Svatá. V těžební oblasti Jedová hora byly odebrány tři půdní profily s různou mírou kontaminace (dva půdní profily silně a jeden profil slabě ovlivněný těžbou). Pomocí TDA byla vytvořena databáze termo-desorpčních křivek chemických sloučenin Hg a referenčních materiálů pro srovnávací účely s přírodními vzorky.

Vysoké koncentrace Hg byly naměřeny v materiálu hald i půdách v okolí dolů (> 120 $\mu g.g^{-1}$ resp. 10 $\mu g.g^{-1}$). Nejvyšší koncentrace Hg v půdách byly zjištěny v organo-minerálních horizontech Ah. Vyšší koncentrace Hg v Ah horizontech než v organických byly pozorovány ve všech studovaných půdách a podobné výsledky z oblasti Příbramska uvádějí i další autoři. Zdá se, že pokles Hg depozice v regionálním měřítku by mohl přispívat k rozdílným koncentracím v organických a Ah horizontech.

Materiál hald obsahoval Hg převážně ve formě cinabaritu (> 80%). Menší část z celkové Hg (<14%) byla určena jako Hg vázaná na povrch minerálních částic, jako jsou Fe-oxyhydroxidy nebo jílové minerály. V porovnání s materiálem hald bylo poměrné zastoupení HgS v půdách menší (60-80%). Přesto půdy silně ovlivněné těžbou obsahovaly HgS ve všech půdních horizontech a Hg(II) sorbovaná na povrch minerálních částic tvořila menší část celkové Hg. Půdy slabě ovlivněné těžbou obsahovaly HgS pouze v organo-minerálním horizontu, což pravděpodobně odráží rozšíření částic cinabaritu během těžby nebo zpracování rud. V minerálních horizontech půd slabě ovlivněných těžbou byla Hg přítomna výhradně jako Hg(II) slabě vázaná na minerální částice.

Cinabarit (HgS) je v půdách relativně stabilní, jeho rozpustnost je omezena a je transportován převážně ve formě částic. Naproti tomu Hg(II) sorbovaná na půdní částice je více mobilní,

může být transformována na vysoce toxickou methyl-Hg a představuje tak potenciální riziko pro životní prostředí.

Použití TDA-ICP-OES se zdá být vhodné pro rozlišení Hg sulfidů, kovové Hg a Hg vázané na organickou hmotu. Identifikace Hg vázané na povrchu minerálních částic je možná, ale rozlišení mezi jednotlivými sorpčními substráty (jako jsou Fe-, Al-, Mn- oxidy a jílové minerály) je zatím obtížné.

PREFACE

Pollution of the environment with toxic metals and metalloids represents potential threat for ecosystems and human health. Among them mercury is considered to be one of the most toxic. The ecological and toxicological effects of Hg are strongly dependent on the chemical form present. Organic Hg compounds such as methyl-mercury are generally more toxic than the inorganic ones. Methylated Hg forms are water and lipid soluble and bioaccumulated/ biomagnified through the food chain.

The poisonous properties of Hg have been known since ancient times. Its unique chemical and physical properties led to its widespread use in numerous applications from antiquity until today. Extensive usage has increased human exposure to Hg in most areas of the world, occasionally resulting in adverse health effect, and in some cases death. Serious incidents of mass methyl-mercury poisoning in Japan (Minamata, 1956) and Iraq (1971-1972) initiated growth in Hg research that still continues. Understanding of Hg cycling in the environment and its toxicological effects on humans and wildlife are of worldwide concern.

Mercury in various chemical forms enters the environment from a number of human activities. Mining of Hg ores is one of the most important ones. Mercury mines can impact the environment through the release of Hg from Hg-enriched mine wastes, contaminated soils and mine drainage. Mercury vapor released to the atmosphere during ore processing represents further important Hg source. Environmental concerns related to mining and processing of Hg ores are usually focused on contamination of surrounding terrestrial and aquatic ecosystems. Therefore understanding the processes of Hg release from mining sites is critical to predict its transport and potential bioavailability in natural systems.

Purpose of the dissertation

The Czech Republic has been heavily affected by industrial activities since the 18th century. Border areas on the NW and NE of the country, so-called the Black Triangles, belong to the most polluted areas in Central Europe (Markert et al. 1996). Although the environment of the Czech Republic is bearing several impacts originating in its past, only few studies have dealt with Hg environmental contamination.

The conception of Hg distribution in forest floor humus of the entire country has been presented in the study of Suchara & Sucharová (2002). Few studies dealt with Hg contamination in soils of Příbram region, known for mining and smelting of Pb-Ag ores (Rieuwerts & Farago 1996, Ettler et al. 2007). Recently historical Hg deposition was studied in this region (Ettler et al. 2008).

Although the Hg contamination in areas of historic and active Hg mining is well known phenomenon worldwide (e.g. Biester et al. 1999, Gray et al. 2003, Higueras et al. 2003), the extent of Hg contamination in former Hg mining sites in the Czech Republic has not been yet investigated.

The dissertation attempts to contribute to the present knowledge of Hg contamination in historical mining areas. It focuses on the study of Hg distribution, speciation and potential mobility in mine waste and soils. The method of thermal desorption in combination with ICP-OES (TDA-ICP-OES) has been applied to determine Hg speciation in solid samples.

The aims of individual topics of the dissertation are presented in particular chapters in greater detail, but the principal aim of this work was:

- to prove the application of thermo-desorption analysis (TDA-ICP-OES) on Hg speciation in natural samples such as soils and mine wastes
- to create a thermo-desorption curves database of reference materials (Hg compounds and Hg(II) sorbed on substrates commonly occurring in soils) for comparative reasons with natural samples
- to evaluate the Hg sources in mine wastes and assess the extent of Hg contamination in historical mining area and try to find out the potential environmental impact on surrounding environment
- to estimate potential mobility of Hg in mine waste and soils in terms of Hg species present in the samples

Overview of the contents of the dissertation

A brief overview of mercury behaviour in the environment with emphasis on Hg contamination in mine-impacted regions and methods used for determination of Hg species in solid samples are underlined in Chapters 1 and 2.

Chapter 1 summarizes basic properties of Hg and its compounds, sources (usage) and its impacts on the environment and human health in the first part. Mercury behavior in soils and mine-impacted regions is described in the second part.

Chapter 2 deals with analytical methods of Hg speciation in solid samples. The emphasis is given to thermo-desorption analysis (TDA) applied on studied soils and mine wastes as described in Chapter 3 and 4. Comparison of currently used methods such as sequential extractions (SEA) and extended X-ray absorption fine structure (EXAFS) spectroscopy is included.

Main part of the dissertation is presented as two papers published or submitted to scientific journals – Bulletin of Environmental Contamination and Science of the Total Environment (Chapter 3 and 4, respectively).

Chapter 3 provides initial insight into mercury sources in mine wastes of two abandoned mercury mines, Jedová Hora and Svatá, in central Czech Republic. Mercury concentrations and speciation were determined in mine waste material at both sites.

Chapter 4 focuses on the potential environmental impact of historical mining in terms of Hg soil contamination. The soils surrounding the former Hg mining site Jedová Hora have not been yet investigated, although the speciation and sorption of Hg plays significant role with respect to the fate of Hg in the environment. The vertical distribution of Hg concentrations, Hg speciation and relative abundance of present Hg species in three soil profiles was evaluated.

The last *chapter 5* concludes the obtained results and proposes further research topics in the field of Hg speciation in solid samples.

CHAPTER 1:

MERCURY IN THE ENVIRONMENT

1.1. General properties

Mercury is unique among the other potentially toxic elements due to its liquid state and high volatility under ambient conditions. This unusual behavior results from relativistic contraction of the 6s orbitals (i.e. in Hg atoms, these valence electrons are held very close to the nucleus and do not easily participate in chemical reactions), which leads to weak Hg-Hg bonds, and characteristically low melting (-38.9°C) and boiling points (356.6°C) (Parson & Percival 2005). General properties of Hg and its compounds are described in numerous publications (e.g. von Burg & Greenwood 1991, Mihaljevič 1999, Adriano 2001) in greater detail.

Toxicological potential of Hg has been recognized already in ancient times (Parson & Percival 2005). Nevertheless, Hg has been used by humans for numerous applications (art, science, medicine, agriculture and many industrial processes) throughout human history until today.

The ecological and toxicological effects of Hg are strongly dependent on the chemical form present (Clarkson 1998). Inorganic Hg forms may be transformed to organic, methylated species that are more toxic than the inorganic forms (Boening 2000).

1.2. Sources and global budget of mercury in the environment

Mercury is introduced into the environment by both natural and anthropogenic emissions. Natural sources to the atmosphere are from volcanoes, wind erosion, soil degasification and evasion from the ocean. Man-made releases include burning of fossil fuels, mining and smelting, waste incineration, industrial processes such as cement and chlor-alkali production etc. Estimates of current Hg emissions vary over a broad range, but it is accepted that the antropogenic emissions well exceeded the natural ones (Mason et al. 1994, Figure 1.). Compared to pre-industrial period (circa 1850) the global reservoir of atmospheric mercury has increased two to five times (Fitzgerald et al. 1997). Global Hg budget with current and pre-industrial estimates of Hg emissions is depicted in Figure 1.

Significantly increased atmospheric Hg emissions were observed especially in the northern Hemisphere, in particular in highly industrialized regions of Europe (Pacyna 1996).

Nevertheless Hg is due to its high volatility easily transported from point sources for long distances. In recent times, remote areas such as polar regions have been adversely affected by the long-range Hg atmospheric transport and Hg is nowadays considered as a global pollutant (Mason & Sheu 2002).
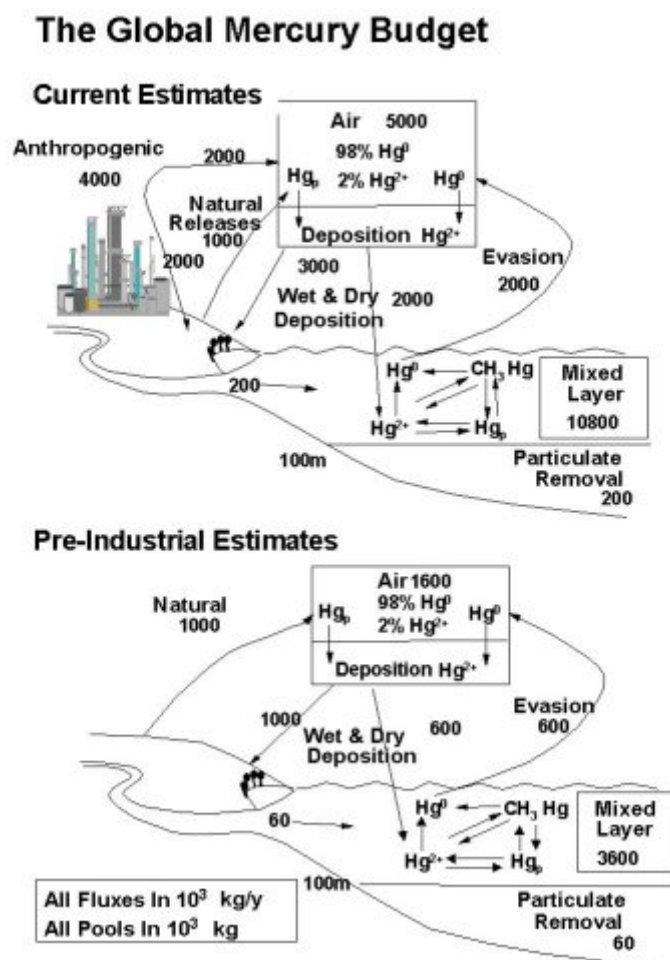
Figure. 1. Global Hg budget with current and pre-industrial estimates of Hg emissions (according to Siegel & Siegel 2005).

1.3. Occurrence and behaviour of mercury in soils

Terrestrial soils represent a very large pool of Hg (Mason et al. 1994), retaining more than 90% of Hg currently deposited on terrestrial landscapes (Fitzgerald 1995). Generally, upland forest soils act as the sinks for atmospheric inputs of total Hg and MeHg (St. Louis et al. 1994, Schwesig & Matzner 2000), because majority of Hg is bound to organic and mineral soil particles.

Background levels of Hg in soils are not easy to estimate due to the widespread Hg contamination. Nevertheless data reported for European arable and forest soils present that the uncontaminated soils typically contain 0.02– 0.15 µg g^{-1} Hg (e.g. Grigal 2003).

The concentrations presently found in the organic horizons reflect accumulated Hg deposition mainly from the last century (Johansson & Iverfeldt 1994) and are usually higher than in the underlying mineral soil horizons (Schwesig & Matzner 2000, Adriano 2001). Schwesig et al. (1999) recorded Hg concentration up to 0.5 µg g^{-1} in the organic horizon, while that of surface mineral soil (0-10 cm depth) was 0.1 µg g^{-1}. The enrichment in the organic horizons is associated with higher soil organic matter (SOM) concentration in these horizons (Yin et al. 1996, Mierle & Ingram 1991).

From a mass balance perspective, the total mass of Hg in mineral soil horizons is generally larger than that in the organic horizons (Krabbenhoft et al. 2005). Schwesig & Matzner (2000) reported Hg mass 17 mg m^{-2} in the organic and 103 mg m^{-2} in mineral horizons in the forest soils of NE Bavaria, Germany. Large pool in mineral horizons is related to higher mass per unit area in these horizons in comparison to surface horizons. Soil bulk density and SOM are inversely related (Grigal et al. 1989). Therefore organic horizons show high Hg concentrations, but the Hg pools are smaller than in mineral horizons.

Sorption, mobilization and transport mechanisms in these two pools is very different, leading to different participation in the Hg biogeochemical cycle that likely places much higher degree of importance on Hg in organic horizons (Krabbenhoft et al. 2005).

1.4. Mercury speciation in soils

1.4.1. Inorganic Hg speciation

The chemical speciation of Hg primarily determines the solubility, mobility, bioavailability and toxicity to biota (Adriano 2001). Inorganic Hg forms may be transformed to organic, methylated species that are generally more toxic than the inorganic forms (Boening 2000).

In soil mercury may occur in various forms: (i) dissolved (solvated or soluble complex), (ii) non-specifically adsorbed (bound mainly by electrostatic forces), (iii) specifically adsorbed (strong binding due to covalent or coordinative forces), (iv) chelated (bound to organic substances) and (v) precipitated (as sulphide, carbonate, hydroxide etc.) (Schuster et al. 1991). Many studies proved that Hg^{2+} is the prevailing form in soils and is associated with organic matter (e.g. Yin et al. 1996, Biester et al. 2002). Therefore the retention and mobility of Hg in

soils is strongly controlled by complexation and solubility of organic matter (Yin et al. 1996, Skyllberg et al. 2003, Mierle & Ingram 1991, Amirbahman et al. 2004). Detailed complexation studies of Hg(II) in soil revealed that Hg is strongly bound to organic matter by reduced sulphur groups, presumably in the form of thiols (Skyllberg et al. 2000, Xia et al. 1999).

1.4.2. Methylated Hg forms

The methylation of inorganic Hg(II) plays significant role in the environmental Hg cycle and takes place in both remote (uncontaminated) areas and impacted environment (Fitzgerald & Mason 1997). Both microbial and abiotic (chemical) methylation mechanisms are known, although the latter is thought to be of only minor importance (Ullrych et al. 2001).

Typical methyl-Hg concentrations in background soils are in the range of 0.01-2 ng g^{-1} (Davis et al. 2007). The production of methyl-Hg seems to be linked with wetlands, lake sediments and saturated upland forest soils (St. Louis et al. 1994, Gilmour et al. 1992, Braunfireun et al. 1999). Primarily sulphate-reducing bacteria are responsible for methyl-Hg formation in aerobic/anaerobic boundaries (Compeau & Bartha 1985, Gilmour et al.1992).

Despite the low concentration of methyl-Hg in soils, these species are at least an order of magnitude more mobile than inorganic Hg compounds, are readily bioaccumulated and biomagnified in the food chain (Bodaly et al. 1997). Consequently MeHg is major concern from an environmental and toxicological perspective.

1.5. Mercury contamination in the mine-impacted environment

1.5.1. Environmental impact of Hg mining

Mercury mining belongs to one of the most important anthropogenic sources releasing Hg into the environment (Mason et al. 1994, Covelli et al. 2001). Extraction of elemental Hg from cinnabar via distillation and the property of amalgamation have been known since approximately the 1st century BC (Parson & Percival 2005).

The primary ore mineral in almost all Hg deposit types is cinnabar (HgS). Elemental Hg is also common, but generally in small amounts (Rytuba 2002). At Hg mines, the ore has been excavated using both underground and open pit methods, crushed and commonly processed in a retort or a rotary furnace at temperatures in excess of 600°C to release Hg into the vapour phase. Elemental Hg vapour was subsequently condensed and collected into flasks (Rytuba

2003). Various ore-processing methods, such as roasting and smelting of ores, may release mercury species to the atmosphere (Ferrara et al. 1998).

Following ore processing, mine wastes, commonly termed calcines, and waste rock are accumulated into tailings piles, generally at the mine site. The extraction process at mines worldwide is not totally efficient and is often incomplete (Gray et al. 2006, Kim et al. 2004a). Gosar et al. (1997) estimated as much as 25% loss of Hg to surrounding environments during processing. As a result of inefficient extraction process, mine wastes are highly elevated in Hg concentrations ranging from 10 to 800 $\mu g\ g^{-1}$ (Rytuba 2003) and represent primary source of Hg contamination. Moreover the release of Hg from mine waste to the environment may continue several decades after mining activities have ceased.

Of additional importance is the mine drainage that is often acidic and can contribute significant amounts of Hg to local waters. Moreover mine drainage provides a favourable environment for Hg methylation due to elevated levels of Hg and high sulphate concentration (Rytuba 2002, Gray et al. 2006).

1.5.2. Major pathways of Hg contamination

Mobilization of Hg from mine waste commonly leads to widespread contamination of terrestrial and aquatic ecosystems and may pose serious hazards to human health (e.g. Biester et al. 1999, Gray et al. 2003, Higueras et al. 2003).

Release, transport and potential bioavailability related to mining wastes are strongly controlled by Hg speciation. Occurrence of Hg phases is influenced by many physical, geological, and anthropogenic factors such as geological origin of the Hg ore and methods of ore processing. Mineral phases such as cinnabar (HgS, hexagonal) and metacinnabar (HgS, cubic) primarily occur in mine waste (Kim et al. 2004a, Gray et al. 2004). Phases such as Hg chlorides, oxides and oxychlorides and elemental Hg(0) comprise the minor fraction, but are water-soluble and can be leached from the mine tailings and enter the surrounding aquatic ecosystems (Kim et al. 2004b, Biester et al. 1999, Kim et al. 2000).

One of the major questions is how Hg gets dispersed from point sources, such as mining sites to sediments and surface waters. Release and transport of Hg from mine waste occurs primarily in the form of Hg-enriched particles and colloids (Rytuba 2003). Sorption of Hg(II) onto mineral particles, which may play significant role in Hg sequestration in mine tailings, were studied by Kim et al. (2004b). It was shown that Hg(II) forms strong, inner-sphere sorption complexes on common mineral particles such as Al- and Fe- oxyhydroxides

(goethite, boehmite and γ-alumina). Coprecipitation of Hg(II) with Fe(III)-hydroxide was also documented (Inoue & Munemori 1979).

Transport of metal(loid) contaminants sorbed to colloids is well documented (Grolimund et al. 1996). Nevertheless laboratory-column leaching experiments of mine wastes showed that most of Hg(II) was not transported as sorbed species, but as colloidal size particles (50-400 nm) of cinnabar or metacinnabar (Lowry et al. 2004, Slowey et al. 2005). Mobilized HgS particles may pose a significant environmental hazard due to dissolving of particles under appropriate conditions (e.g. sub-oxic) and its potential bioavailability (Jay et al. 2000). Moreover transport of colloid-associated Hg may be enhanced by organic acids produced by plants on vegetated mine tailings of inoperative mines (Slowey et al. 2005).

In order to investigate the Hg speciation variety of techniques have been used. The mineralogy of mercury phases in mine tailings has been examined using indirect methods such as sequential extraction (e.g. Bloom et al. 2003). More recently the thermal desorption analysis (e.g. Azzaria & Aftabi 1991, Biester et al. 1999) and X-ray absorption fine structure spectroscopy has been used to directly identify Hg phases (Kim et al. 2000). These methods and their applicability with emphasis on TDA are discussed in Chapter 2.

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CHAPTER 2:

DETERMINATION OF MERCURY SPECIES BY MEANS OF THERMO-DESORPTION ANALYSIS

2.1. Introduction

2.1.1. Mercury speciation in the environment

Since mercury contamination occurs in a wide range of environmental compartments developing methods that help to predict the distribution, mobility and bioavailability of Hg is an important challenge. Mercury occurs in the environment mainly bound to solid materials such as ores, soils, suspended particles, airborne particulate matter etc. Concentrations in these samples vary widely, ranging over several orders of magnitude. Determination of the total Hg concentration in solid samples is performed in most cases by cold vapor atomic absorption spectrometry (CV-AAS) (Hatch & Ott 1968, Morita et al. 1998, Hall 2005). AFS- and ICP-MS-based methods are also commonly employed (e.g. Debrah et al. 1996, Chen et al. 2002, Mann et al. 2003, Hall 2005).

Measurement of chemical speciation of elements is crucial for understanding and predicting their behavior in the environment. This is particularly true for Hg, which exhibits markedly different mobility and toxicity among its species. Mercury in the solid phase can be presented in organic and inorganic forms. Organic Hg species, such as methyl-mercury (MeHg) are more readily bioaccumulated and thus their ecological and toxicological effect is higher than that of inorganic ones (Boening 2000). The extent of MeHg generation is dependent largely on the physicochemical properties of present inorganic Hg species. Soluble inorganic Hg species are easily transported and they typically serve as the precursor for the Hg methylation (Han et al. 2003). Thus chemical speciation of inorganic Hg plays a crucial role in the release, transport and transformation in the environment. Methods used for determination of Hg species in solid samples are described below with the emphasis on the thermal-desorption analysis used in this study.

2.1.2. Current status for mercury speciation in solid samples

Metal speciations are usually carried out through specific single extraction (e.g. Chao 1984) or sequential leaching procedures (Tessier et al. 1979, Zeien & Brümmer 1989, Hall et al. 1996 etc.). In case of the occurrence of volatile elements, like metallic Hg, intensive sample preparation causes considerable losses of the metal throughout the sample preparation (Biester & Nehrke 1997).

Therefore several methods have been employed to determine the Hg speciation in solid samples. Generally, the published methods can be classified into two categories. The first, based on sequential selective extraction (SEA), determines the solubility of the Hg compounds present in different leachates (Revis et al. 1989, Bloom et al. 2003, Han et al. 2003, Sladek & Gustin 2003 etc.).

The second category comprises of methods that don't employ separation of the species prior to detection. Extended X-ray absorption fine structure (EXAFS) spectroscopy (Kim et al. 2004, Lowry et al. 2004) and thermal-desorption analysis (TDA) (e.g. Biester & Scholz 1997) are included in this category. These methods require minimal sample preparation, thus allowing the analysis of samples in conditions similar to those observed in their natural state (Kim et al. 2000).

Comparison of SEA, EXAFS and TDA has been made by several authors with emphasis to advantages of individual method (e.g. Biester & Nehrke 1997, Kim et al. 2003, Sladek et al. 2002). It was shown that **sequential extraction procedures** (SEA) often suffer from insufficient selectivity to distinguish Hg binding forms and/or from poor reproducibility of the results (Biester & Scholz 1997). Most of the Hg is extracted in the non-specific residual Hg fraction which can consist of Hg(0), matrix-bound Hg or HgS as well. The effectiveness of the leachants is strongly influenced by the amount of soil organic matter or buffering carbonates (Biester & Scholz 1997). Moreover, Rahman and Kingston (2004) observed that chemical transformation of inorganic mercury to methyl-mercury or vice versa can occur during commonly used extraction procedures.

The **EXAFS** spectroscopy is a non-destructive method which uses high energy synchrotron X-ray radiation to identify specific species based on scattering patterns. Hg species in unknown samples are identified by comparison with Hg model compound spectral database (Kim et al. 2004). Mercury concentration greater than 100 µg g^{-1} are required for the analysis (Kim et al. 2000) and also identification of Hg(0) is difficult using EXAFS (Sladek et al. 2002).

Thermo-desorption analysis (TDA) seems to be preferable to sequential leaching procedures (Biester & Scholz 1997, Sladek et al. 2002). It allows better differentiation of metallic Hg from other Hg compounds like humic bound Hg or Hg sulfides presented in the studied samples (Biester & Scholz 1997).

The advantage of the method is a single measuring without any sample treatment and reagents addition. Thus potential problems of contamination, analyte losses and modification of chemical species present are avoided (Feng et al. 2004). However, data from thermo-desorption measurements reported in the literature provide sometimes hardly comparable results (Lu & Grégorie 2005). This can be explained by the different operating condition used (heating rates, gas flow etc.). Moreover the data were mostly obtained by different self-constructed apparatures.

2.1.3. Principles of TDA

The technique of thermal release of Hg from solid samples has been used since 1904 in cinnabar mines to determine total mercury in ores and in geochemical prospecting (Henry et al. 1972). Nowadays it has been applied for investigations of Hg contaminated sites (Higueras et al. 2003, Palmieri et al. 2006, Biester et al. 1999, Gosar et al. 2006 etc.). More recently, thermal-desorption combined with ICP-MS detection has been reported for analysis of samples like fly ash with low Hg concentration (Feng et al. 2004).

The thermo-desorption analysis (TDA) is an indirect method based on different thermal stability of Hg species present in the solid sample. Mercury species are released by thermal desorption or decomposition. For this purpose a sample containing Hg compounds is continuously heated up to above 500°C and different Hg species will be released at different temperature. The melting points and vapour pressure for some Hg compounds are listed in Table 1. For the detection of Hg released species an atomic absorption spectrometer (AAS) (e.g. Biester & Scholz 1997, Windmöller et al. 1996, do Valle et al. 2006) or IPC-MS (Feng et al. 2004) are used. In contrast to other studies, the ICP-OES detection was used in this study. The method allows to discriminate between various species in which Hg is present in the studied samples, e.g. metallic Hg, humic bound Hg or Hg-sulfides.

Table. 1 Melting points and vapour pressures of some Hg compounds (according to CRC Standard mathematical tables and formulae).

	melting point (°C)	vapour pressure (25°C, mbar)
Hg^0	-39	2.7×10^{-3}
$HgCl_2$	276	1.6×10^{-4}
Hg_2Cl_2	400 sublimation	1.0×10^{-7}
HgS	583 sublimation	--
HgO	500 decompose	3.2×10^{-12}

The results of TDA are presented as Hg thermo-desorption curves (TDC) representing the release of Hg versus temperature. The TDCs enable identification of specific Hg compounds such as Hg(0) or HgS in the sample by comparison with pure Hg standards and distinguishing them from the non-specific matrix-bound compounds (Biester & Scholz 1997). Matrix-bound Hg can be closely specified by comparison with thermo-desorption patterns of prepared reference material. A quantitative determination of specific species can be made by the peak integration (Biester et al. 2000, Feng et al. 2004).

2.3. Experimental

2.3.1. Preparation of reference material and natural samples

Standard Hg compounds were used for the method calibration and to obtain optimal experimental set-up. In particular metallic Hg bearing sand, HgO (Lachema), $HgCl_2$ (Lachema), HgS (red cinnabar, Fluka) and crystalline cinnabar (historical Hg mine Jedová hora) were used as standards. Materials were diluted with quartz powder before speciation analysis and measured with different dilution ratios.

Soils collected in the historical Hg mining area were analysed as natural samples. All soil samples were freeze-dried, sieved (2 mm) and homogenized. Total Hg concentration was determined by a cold vapor-atomic absorption (CV-AAS) Hg analyzer AMA-254 (Altec Co, Czech Republic).

2.3.2. Experimental set-up for the TDA-ICP-OES

The system used in this study for TDA consisted of a custom made temperature-programmable furnace (Clasic, Czech Republic) coupled to ICP-OES (Thermo-Elemental, IRIS Intrepid II) for Hg detection and quantification. Schematic diagram of the analytical setup used in this work is shown in Figure 1.

The temperature inside the furnace can be controlled to provide a linear increase in temperature (from 25 to 900°C). The sample (150 - 200 mg, depending on the total Hg concentration) is loaded onto a nickel boat, placed in quartz tube and heated in the furnace with a temperature gradient 40°C min⁻¹ up to 600°C in the presence of an Ar stream. The released Hg from the sample is carried to the ICP-OES using a stream of Ar gas flowing at a rate of about 2L min⁻¹ and detected at (λ_{Hg}) 184.9 nm in a continuous detection mode.
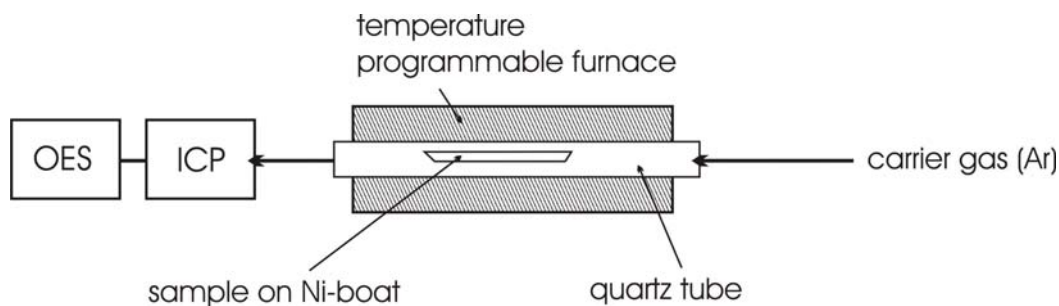
Figure. 1 Schematic diagram of the thermal-desorption apparatus.

2.4. Results and discussion

2.4.1. Standard Hg compounds and reference materials

Standard Hg compounds were analyzed to create a comparative thermo-desorption patterns used by identification of Hg speciation in natural samples. Thermo-desorption curves obtained from the Hg standards are shown in Figure 2. Similar to observations of other authors (Windmöller et al. 1996, Biester & Scholz 1997 etc.) Hg standard compounds were released in following sequence: Hg(0) > HgCl$_2$ >HgO >HgS. Thermo-desorption curve of the standard sample with metallic Hg included double peak (Figure 2.). The first peak represented Hg(0) and the second Hg(II) formed by oxidation of Hg(0) (Windmöller et al. 1996). Conversion of Hg(0) to Hg(II) was observed also by do Valle et al. (2006) in Hg(0) incubated samples and oxidation of the added Hg(0) was calculated in the range of 28-68%. Mercury was released from HgCl$_2$ in the temperature range 230-250°C depending on sample dilution (data not shown). Hg-release temperature from natural crystalline cinnabar ranged from 431 to 456 °C. TDC of red cinnabar (Fluka) showed Hg-release at 460°C. TDC of HgO displayed double peak: 390°C and 605°C, indicating gradual decomposition of the compound.
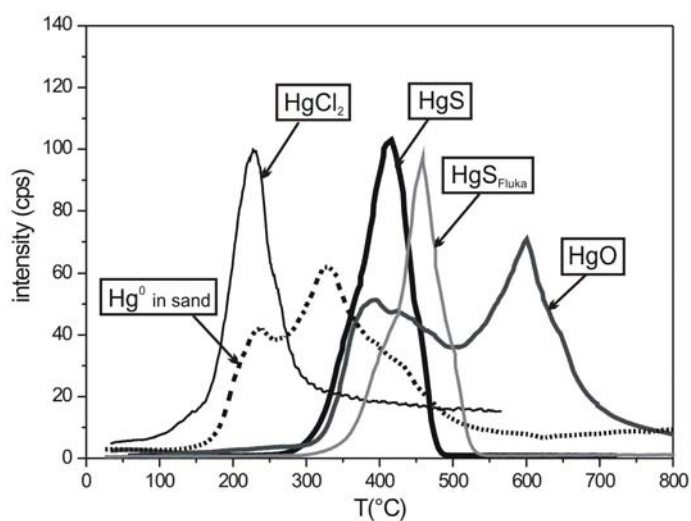
Figure. 2 Hg-TDCs of simple Hg compounds and metallic Hg bearing sand.

There are some differences in the Hg-releasing temperatures of the standard compounds in this study and these obtained by other authors. However it is known, that data from TD measurement reported in the literature are hardly comparable due to different experimental set-up conditions (Lu & Grégorie 2005). Generally, difficulties in comparability of the thermal analysis measurement are known, due to different geometric sample properties (Garay et al. 1987). Appearance temperatures for the release of various Hg species from different matrices and experimental set-up are listed in Table 2. Heating rates from 10 to 50°C min^{-1} and N_2, Ar or air stream as carrier gas with different flow (0.2-0.3 L min^{-1}) were used (e.g. Windmöller et al. 1996, Biester & Scholz 1997, Bombach et al. 1994, Feng et al. 2004). Nevertheless all studies agree that Hg(0) is released at a low temperature, followed by the Hg(II) binding forms (do Valle et al. 2006).

Table 2. The appearance temperatures for release of different Hg species from different matrices and applied operation parameters (adapted from Feng et al. 2004)

mercury species	matrices	appearance temperature (°C)	operating parameters: heating-rate; carrier-gas	references
Hg^0	rock	~ 80	18°C. min^{-1}	Watling et al. (1972)
	soil	~ 150	50°C. min^{-1}	Bombach et al. (1994)
	soil	50	30°C. min^{-1}; N_2 300mL min^{-1}	Biester and Scholz (1997)
	soil	~ 50	10°C. min^{-1}; N_2	Windmöller et al. (1996)
	fly ash	80	50°C. min^{-1}; Ar 1L min^{-1}	Feng et al. (2004)
$HgCl_2$	rock	~ 90	18°C. min^{-1}	Watling et al. (1972)
	soil	80	30°C. min^{-1}; N_2 300mL min^{-1}	Biester and Scholz (1997)
	soil	~ 120	10°C. min^{-1}; N_2	Windmöller et al. (1996)
	fly ash	120	50°C. min^{-1}; Ar 1L min^{-1}	Feng et al. (2004)
HgS	rock	~ 220	18°C. min^{-1}	Watling et al. (1972)
	soil	250	10°C. min^{-1}; N_2	Windmöller et al. (1996)
	soil	200	30°C. min^{-1}; N_2 300mL min^{-1}	Biester et al. (1999)
	soil	220	30°C. min^{-1}; N_2 300mL min^{-1}	Biester and Scholz (1997)
	fly ash	350	50°C. min^{-1}; Ar 1L min^{-1}	Feng et al. (2004)
HgO	rock	100 (multiple peaks)	18°C. min^{-1}	Watling et al. (1972)
	soil	150 (multiple peaks)	10°C. min^{-1}; N_2	Windmöller et al. (1996)
	soil	400 (main peak)	30°C. min^{-1}; N_2 300mL min^{-1}	Biester et al. (1999)
	fly ash	500 (single peak)	50°C. min^{-1}; Ar 1L min^{-1}	Feng et al. (2004)

For the determination of Hg species in natural samples, like soils or sediments, effect of sorbent matrices on Hg release was calibrated with Hg(II) adsorbed onto reference materials such as clay minerals, Fe-oxyhydroxides and humic acid. The releasing characteristics of these soil sorbents are described in methodical part of Chapters 3 and 4.

2.4.2. Mercury speciation in natural samples

Thermo-desorption analysis has been successfully applied in several studies to specify Hg-binding forms in mine waste (e.g. Biester et al. 1999), soils and sediments (Azzaria & Aftabi 1991, Bombach et al. 1994, Biester et al. 2000, Gosar et al. 2006, Navarro et al. 2006, Piani et al. 2005 etc.). Recently, Feng et al. (2004) used this method for identification of Hg forms in atmospheric particulate matter.

We applied TDA for the identification of Hg species and binding forms in soils contaminated by Hg mining. Mean concentration of total Hg in selected sample was 9.9 μg g^{-1}. TDA was carried out in triplicates to obtain analytical accuracy. The TDCs obtained from three sample replicates are depicted in Figure 3A, illustrating the reproducibility of the results. Two major signals appeared at each TDC, indicating the presence of two different Hg forms. The

appearance temperatures of the individual peaks are summarized in Table 3. The first peak is comparable with reference material of Hg adsorbed weakly onto the surface of clay minerals or Fe-oxyhydroxides. The second peak fits with thermo-desorption pattern obtained for HgS standards (see Figure 2).
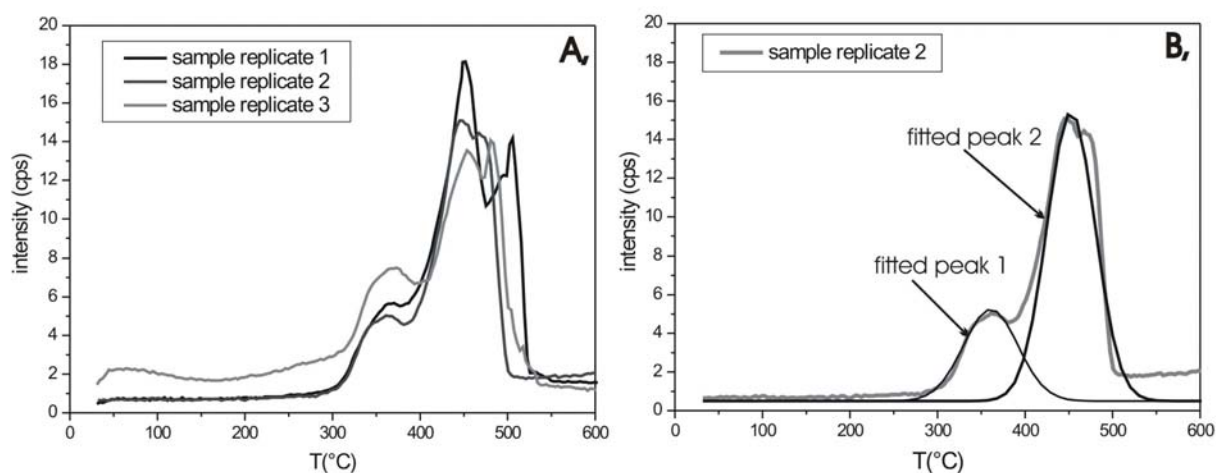
Figure 3. Hg-TDCs of three sample replicates of soil contaminated by Hg mining (A) and TDC of sample replicate 2 smoothed with Gaussian curves (B).

Table 3. Hg releasing temperatures and relative abundance of Hg forms in three replicates of soil contaminated by Hg mining.

	Hg releasing temperature (°C)		relative abundance of Hg forms (%)	
	signal 1	signal 2	signal 1	signal 2
sample replicate 1	362	451	26.3	73.7
sample replicate 2	361	453	26.5	73.5
sample replicate 3	364	458	28.6	71.4

Intensities of the signals were variable depending on the sample amount and Hg total concentration. The releasing temperatures of individual detected Hg forms varied in the range ± 5°C. Higher RSD in contaminated samples may be caused by heterogeneous distribution of Hg compounds like Hg(0) or HgS, which occur in soils or sediments without binding to matrix components (Biester & Nehrke 1997).

Relative abundance of Hg forms in natural samples was calculated according to peak areas of TDC using Peak Fitting Module of OriginPro software (ver. 7.03). The TDC of sample replicate 2 separated into individual peaks is depicted in Figure 3B as an example. The TDCs

of all replicates were smoothed with two Gaussian curves. Relative abundance of Hg forms computed from the area under the TDCs is summarized in Table 3.

2.6. Conclusion

Beside the knowledge of total Hg levels, the determination of Hg chemical forms in the environment is essential for predicting its solubility, transport and potential bioavailability. By combining thermal-desorption and ICP-OES Hg species in solid samples can be analyzed. The advantage of TDA is a single measurement with minimal sample treatment, thus allowing the analysis of samples under conditions similar to those observed in their natural state without losses of volatile Hg-compounds. Moreover no addition of reagents is required, so there exist no threats on modification of chemical species present in the sample. In comparison with other methods such as sequential extraction, TDA allows better differentiation of metallic Hg from other Hg compounds like humic bound Hg or Hg sulfides presented in the studied samples.

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CHAPTER 3:

DISTRIBUTION AND SPECIATION OF MERCURY IN MINE WASTE DUMPS

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Abstract

Historic mercury mines represent an environmental threat due to high Hg concentration in waste material. In the central Czech Republic, Hg ores were mined at two sites for more than 150 years. Mine wastes collected near the Hg mines were highly elevated in total Hg concentrations (up to 120 $\mu g.g^{-1}$). Studied waste material contained mostly cinnabar (HgS), that is relatively stable in soils and thus resistant to formation of highly toxic methyl-Hg. Nevertheless minor part (<14%) of total Hg was identified as mineral surface bound Hg, which might undergo methylation processes and thus it represents potential long-term environmental risk.

Keywords: mercury, mine waste, mercury speciation, thermo-desorption analysis

3.1. Introduction

Mercury is a ubiquitous pollutant, which enters the environment from both natural and anthropogenic sources. Among anthropogenic sources, Hg mining and smelting represent important sources of Hg pollution (Ebinghaus et al. 1998). The ecosystems surrounding Hg mining sites are usually highly contaminated (Biester et al. 1999, Loredo et al. 2005). Historical mining activities leave behind a legacy of contaminated mine dumps, which may serve as a permanent source of Hg for the environment. Therefore, the precise knowledge of Hg content and its forms in the waste material is essential to (1) evaluate the environmental risks, and (2) assess the potentials for future Hg migration.

In the central Czech Republic (CR), Hg ores were mined at two sites at Jedová Hora ("Poison Mountain") and Svatá ("Saint"). These mines produced considerably less Hg ore compared to well-known mines in Europe, such as Almaden (Spain) and Idrija (Slovenia). The mining wastes at these sites were piled at mine dumps without any precautions to avoid its spreading and, former mine dumps of different age and composition still remain at original locations. According to previous studies (e.g., Loredo et al. 2005) chemical and physical dispersion of Hg to the environment surrounding the mine dumps might occur in future and may cause local contamination problems.

The region of central CR was evaluated as the most Hg contaminated area according to the litter horizon studied in the entire country (Suchara and Sucharová 2002). Reported Hg concentrations in the litter horizons of the coniferous forest sites ranged from 0.9 to 1.25 µg g^{-1} in central CR. Another study in central CR reported Hg concentrations up to 6.5 µg g^{-1} in soils directly affected by Pb smelting (Ettler et al. 2007). Available data on Hg concentrations in Czech soils are rather scarce, but up to date, no information is available concerning Hg in Czech mine wastes.

The aim of this study was to provide initial insight into mercury sources in mine wastes of two abandoned mercury mines in central Czech Republic.

3.2. Materials and methods

Mine waste samples were taken at dumps of two historical Hg mines, Jedová Hora and Svatá. The sampling sites are approximately 50 km SW of Prague, the capital of CR (Figure 1). Mercury ore at both sites was cinnabar (HgS) that was produced as a byproduct of Ordovician iron ore mining. At Svatá, Hg mining was conducted from the second half of the 16th century till 1760. At Jedová Hora, Hg mining started in the 18th century and continued till 1870 (Sattran et al. 1978). The annual production of cinnabar at Svatá ranged from 100 to 500 kg. In total, the production during the mine operation (about 90 yr) was estimated to be 10-20 tons of HgS (Velebil 2004). Amount of HgS mined at Jedová Hora was reportedly much greater than at Svatá (Sattran et al. 1978), but there is no exact information available on the total production. Velebil (2003) estimated the total production of 7.8 tons of HgS in the period from 1778 to 1779.

Mine waste material was sampled on two mine dumps at Svatá (S1 and S2) and on two dumps at Jedová Hora (J1 and J2) (Figure 1). Areas of dumps at both sites with developed soils are recently covered with mixed forests (mostly European beech and Norway spruce). Mine waste material was sampled from the top 10 cm, and at the bottom of 1 m deep pits at each sampling site. All samples were freeze-dried, sieved (2 mm) and homogenized.
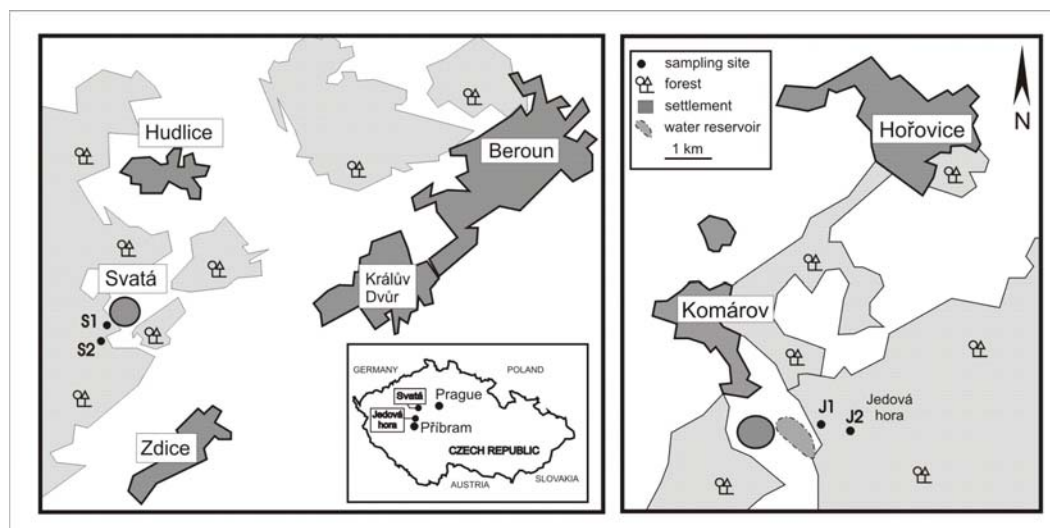
Figure 1. Locations of studied mine waste dumps in the Czech Republic and detailed positions of each sampling site (S1, S2, J1, J2).

Concentration of total Hg was determined by a cold vapor-atomic absorption (CV-AAS) Hg analyzer AMA-254 (Altec Co, Czech Republic). Quality control was ensured using the commercially available standard reference material "river stream sediment 1" (Analytika Co). Triplicate measurements of this material yielded 1.58 ± 0.04 $\mu g\,g^{-1}$, corresponding well with the certified values 1.55 ± 0.07 $\mu g\,g^{-1}$.

Mercury speciation analysis was carried out using a thermo-desorption (TD) method, which has been successfully applied to specify Hg-binding forms in solid material (e.g. Windmöller et al. 1996, Biester et al. 1999). The analysis was performed using a custom-made device that combines a programmable oven (Clasic, Czech Republic) placed into the Ar path of an ICP-OES (Thermo-Elemental IRIS Intrepid II). The samples (150 - 200 mg, depending on the total Hg concentration) were heated in the oven with a temperature gradient 40°C min^{-1} up to 800°C in the presence of an Ar stream. The volatilized Hg was detected at 184.9 nm in a continuous detection mode. The results of TD analysis are presented as Hg thermo-desorption curves (TDC) representing the release of Hg versus temperature. Peak areas of TDC from natural samples were evaluated using Peak Fitting Module of OriginPro software (ver. 7.03).

Thermo-desorption properties of standard Hg compounds (such as Hg0, HgO, $HgCl_2$ and HgS) were evaluated in order to obtain optimal experimental setup. Effect of sorbent matrices on Hg release was calibrated with Hg(II) adsorbed onto standard materials such as clay minerals, Fe-oxyhydroxides and humic acid. In particular we used kaolinite and montmorillonite (Sigma Aldrich) and Fe oxyhydroxides, goethite (α-FeOOH) and

lepidocrocite (γ-FeOOH), that commonly occur in soils, prepared according to Cornell and Schwertmann (1996). Hg(II) adsorption to the mineral samples was performed as follows: 1 g of the solid material was suspended in a 5 ml solution of 40-800 μg Hg mL^{-1} (prepared from a stock solution of 1000 μg mL^{-1} of HgCl$_2$). The suspension pH was not adjusted. The suspension was vigorously shaken at room temperature for 1 h, then left intact for 24 h. After supernatant removal by centrifugation, the obtained solid material was rinsed with distilled water and dried at 60°C. Adsorption of Hg(II) to humic acid (Sigma Aldrich) was prepared according to Arias et al. (2004).

Mine waste pH was determined using a 1:2 (v/v) ratio of waste material and deionized water suspension. Oxidizable carbon (Cox) was determined by the sulfochromic oxidation method (ISO 14235). Total sulfur (Stot) was determined as BaSO4 by gravimetric method. The X-ray diffraction analyses (XRD) were carried out using a PANalytical X`Pert Pro diffractometer with CuKα radiation at 40 kV and 30 mA, and step scanning at 0.05°/300 s in the range 3-80° 2θ.

3.3. Results and discussion

Selected physicochemical properties of mine waste samples are given in Table 1. The mine wastes from Jedová Hora were in the neutral to basic range, but the samples from Svatá were acidic (Table 1). Higher waste pH at Jedová Hora was probably caused by the presence of siderite (FeCO$_3$) and other carbonates in the mine waste material. Top layers of mine dumps were generally rich with organic matter at both sites (Cox up to 15.72 %). Higher Stot concentrations (Table 1) in selected samples were probably related to the presence of ore minerals such as pyrite (FeS$_2$), chalcopyrite (CuFeS$_2$) and baryte (BaSO$_4$) in mine dumps (Velebil 2003).

The XRD analysis revealed that the sampled waste material from Jedová Hora consisted mainly of goethite, hematite (α-Fe$_2$O$_3$), siderite and kaolinite. In waste material from Svatá, Fe-oxyhydroxides (goethite, hematite), clay minerals (kaolinite, illite) and quartz were identified. Presence of clay minerals and Fe-oxyhydroxides suggested relatively favorable conditions for Hg adsorption to the mineral surfaces.

**Table.1**. Hg concentrations and physicochemical properties of mine waste.

	Hg (μg g^{-1})	pH$_{H20}$	C_{ox} (%)	S_{tot} (mg kg^{-1})	CEC (mol kg^{-1})
Svatá					
S1	1.2 ± 0.03	5.11	3.74	80	30.3
S2 (10 cm)	0.8 ± 0.04	4.88	15.72	1380	62.6
S2 (1 m)	0.7 ± 0.02	5.51	3.53	<50	33.9
Jedová Hora					
J1 (10 cm)	50 ± 4.1	6.67	12.06	1740	22.7
J1 (1 m)	120 ± 14.7	7.73	2.07	1040	51.9
J2 (10 cm)	86 ± 14.7	6.76	7.55	1140	43.6
J2 (1 m)	101 ± 8.9	8.09	2.36	730	24.4

Mercury concentrations in the mine waste samples were highly variable (Table 1). Mercury concentrations in mine waste at Svatá were relatively low (0.7-1.2 μg g^{-1}), and at both sampling sites (S1 and S2) Hg concentrations did not exceed the limit defined by Czech legislation for soils (0.8 μg g^{-1}, Czech Regulation 13/1994). The highest Hg concentrations were found at Jedová Hora in the samples from the bottom of 1 m deep pits (up to 120 μg g^{-1}). Such high concentrations may be attributed to vertical migration of Hg from the upper layer of the dump.

In general, mine waste materials are reported to be very heterogeneous as they may contain Hg in the form of HgS, metallic Hg0 or as Hg(II) bound to mineral or organic components (Biester et al. 1999). Prepared standard samples were analyzed at first to identify thermo-desorption properties of different Hg forms and binding environments. Thermo-desorption curves obtained from the analysis of standard Hg compounds were similar to these obtained by other authors (e.g.; Biester and Scholz 1997, Feng et. al 2004).

In Figure 2a, the first peak for the standard metallic Hg-bearing sand represents Hg0 and the second peak represents Hg(II) formed by oxidation of Hg0 (Windmöller et al. 1996). TDC obtained from the standard samples indicate that the Hg release temperature from clay minerals range from 336 to 347°C (Figure 2b). TDC of the Fe-oxyhydroxides included two peaks (Figure 2b), with the first peak (300 to 330°C) being more intensive than the second peak (450 to 520°C). The two peaks perhaps represent the weakly- and strongly-bound Hg, respectively. Peak areas of the double peak TDC depended on the total Hg concentration used for saturation of Fe-oxyhydroxides (50-800 μg mL^{-1}, data not shown). Similar to other studies

(e.g.; Biester et al. 1999), Hg bound to humic acid (HA) was released at higher temperatures than weakly-bound Hg to mineral components (Figure 2b).
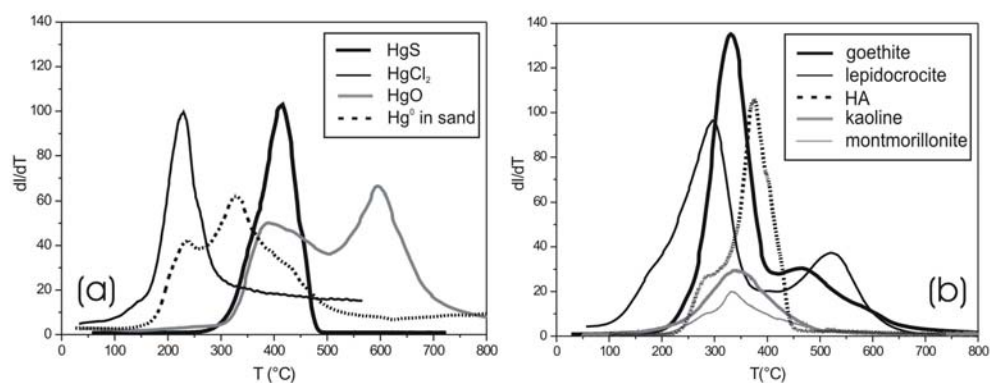
Figure 2. TDC of Hg for (a) known Hg compounds and metallic Hg-bearing sand, and (b) clay minerals, Fe- oxyhydroxides and humic acid saturated by $HgCl_2$.

The TD analysis of Jedová Hora samples showed two major peaks in the temperature range from 25 to 800 °C (Figure 3a, 3b). We propose that the first peak at 320 °C (J1) and 336 °C (J2) corresponds to the release of weakly-bound Hg, either from clay minerals or Fe-oxyhydroxides (Figure 1b). The second peak at 438°C (J1) and 450°C (J2) suggests the presence of HgS, due to the correspondence of this peak with that of the HgS standard (Figure 2a).

The samples taken at the top of mine dumps and those taken at the bottom of the 1 m pits showed similar TDC patterns. Higher peak intensities of bottom samples J1 and J2 in comparison to top sample at the same locations (Figure 3a, b) correspond to differences of total Hg concentrations in these samples (Table 1). TDC for samples from Svatá showed similar pattern with two major peaks (Figure 3c, d). The major fraction of Hg in mine waste was released at 456°C, with only a minor fraction released at 340°C. The TDC for the S2 samples (Figure 3d) correspond to significantly lower Hg concentrations (Table 1). Peak area analysis suggests that in most samples studied here, 80 - 90% of total Hg is present as HgS, and only 12-14% of total Hg is weakly adsorbed to the mineral components.
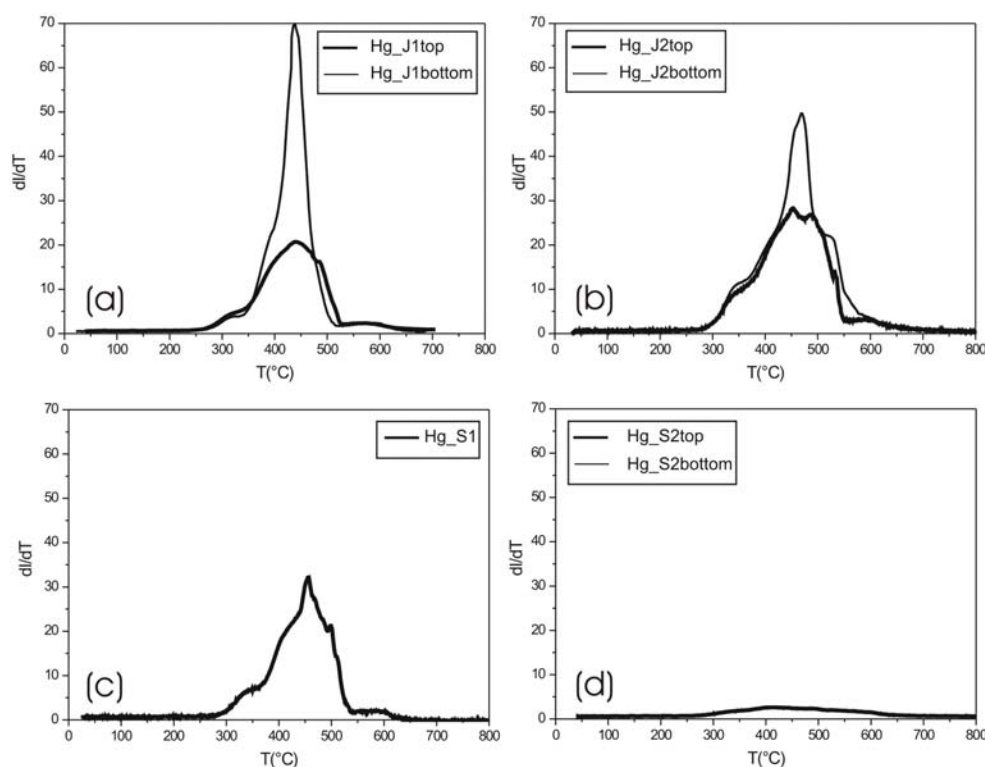
Figure 3. TDC of Hg in mine waste samples from Jedová Hora (a and b) and Svatá (c and d).

Cinnabar is a solid with limited solubility and a slow oxidation kinetics (Ravichandran et al. 1998). HgS dissolution has been reported in the presence of high sulfide concentrations and at pH > 6 (Wang and Driscoll 1995). We propose that Hg detected as adsorbed to mineral surface of clays or Fe-oxyhydroxides in this study originated most probably from leaching or weathering of HgS. Comparing the standards elemental Hg was not detected by TD analysis in any of the samples.

Samples containing mostly HgS, which is relatively stable in the subsurface environment of the mine waste dumps, are not subject to any significant methylation that results in the formation of highly toxic methyl-Hg (Gray et al. 2003). However, Hg associated with mineral surfacesmay undergo methylation processes, and thus, may represent a potential long-term environmental risk.

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CHAPTER 4:

MERCURY DISTRIBUTION AND SPECIATION IN SOILS AFFECTED BY HISTORIC MERCURY MINING IN THE CZECH REPUBLIC

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Abstract

Vertical distribution and mercury speciation in soil profiles were studied to evaluate the extent of contamination and potential Hg mobility in a historical Hg mining area. Three sites were chosen for a case study of Hg contamination. One site was considered a low impact site located 400 m uphill from the mining activities, and two sites were located in a presumably more highly impacted area. Soils profiles were sampled at each site. Mercury speciation and binding forms were determined by thermo-desorption analysis.

High impact soils in a close vicinity of the mine shaft exhibited relatively high Hg concentrations ranging from 8 to 10 $\mu g\ g^{-1}$ in the surface (Ah) horizons and from 3 to 9 $\mu g\ g^{-1}$ in the underlying mineral soils. Approximately 50-80% of total Hg in all soil horizons of high impact soils was present as relatively insoluble HgS. The remaining 20-50% of total Hg was attributed to adsorbed phases on mineral surfaces.

The highest Hg concentration in the low impact soil was detected in the Ah horizon (7 $\mu g\ g^{-1}$). Mineral soil horizons contained relatively low Hg concentrations ($\leq 0.6\ \mu g\ g^{-1}$). Over 40% of total Hg in the Ah horizon of the low impact soils was HgS, likely deposited as fine particles derived from past mining activities. The Hg in mineral horizons of low impact soils was exclusively Hg(II) weakly-bound to mineral particles.

Our study indicated that HgS contamination in the vicinity of a former mining area occurs in most Ah horizons of the area, but contamination of mineral soil horizons appears to be limited to the sites downhill from the mine shaft.

Key Words: mercury, soils, mercury speciation, thermo-desorption analysis, mercury mining

4.1. Introduction

Mercury contamination in areas of historic and active Hg mining is a well known phenomenon (e.g. Loredo 2003, Biester et al. 1999, Gray et al. 2003, Higueras et al. 2003). Elevated Hg concentrations found in mine wastes commonly lead to widespread contamination of the mining site and surrounding environment. Release and transport of Hg from mine waste occurs primarily in the form of Hg-enriched particles and colloids (Rytuba 2003). In contrast to other potentially toxic elements, which mostly attach to colloids such as Fe oxides, colloidal HgS was identified as the dominant form of Hg transported from mine waste material (Lowry et al. 2004).

Mercury speciation in soils contaminated by Hg mining depends on many factors such as geological origin of Hg ore, methods of ore processing and physico-chemical properties of receiving soils (Davis & Bloom 1997). Cinnabar (HgS), metacinnabar and metallic Hg were identified as predominant species in soils from Hg mine-impacted regions (Navarro et al. 2006, Loredo et al. 2005). The species presented in soils determines Hg solubility, mobility and potential bioavailability in terrestrial and aquatic ecosystems. Therefore the identification of Hg species and retention mechanisms is essential in assessing the environmental risks posed by contaminated soils.

Suchara & Sucharová (2002) studied mercury contamination of the forest floor humus in the entire Czech Republic and found that the central CR was one of the most contaminated regions. Reported Hg concentrations in coniferous forest floor humus (H-layer) ranged from 0.9 to 1.25 μg g^{-1}. The Příbram region located in the central CR has been known for its historical mining of Ag, Pb, Fe and Hg ores and associated ore processing. Rieuwerts and Farago (1996) found Hg concentrations up to 2.3 μg g^{-1} in the topsoil (0-5 cm) close to a Pb smelter and 1.6 μg g^{-1} in the Pb-Ag mining area. Ettler et al. (2007) more recently reported Hg soil contamination in the Příbram region up to 6.5 μg g^{-1} in Ah horizon of forest soils.

Mercury ore mining in the central CR was carried out over 130 years until its decline at the end of the 19th century (Sattran et al., 1978; Velebil, 2003). The rates of production for Hg ore was much smaller in the central CR compared to some other mines in Europe and only reached on the order of tons per year (Velebil 2003). The mine wastes, however, still remain at their original locations without precautions to avoid environmental dispersion of these materials.

The soils surrounding the former Hg mining site at Jedová Hora have not been yet investigated. In addition, we have imperfect knowledge of the speciation and sorption mechanisms that determine the fate of Hg in the environment. In this study, we evaluate the vertical distribution of Hg concentrations, Hg speciation and relative abundance of present Hg species in three soil profiles at Jedová Hora. This study provides important information about the potential environmental impact of historical mining as it relates to soil Hg soil contamination.

4. 2. Materials and Methods

4.2.1. Site description

This study focused on an abandoned Hg mining area located approximately 50 km SW of Prague, the capital of the Czech Republic (Fig. 1). The study site is aptly named Jedová Hora (which translates to English to "Poison Mountain"). The Hg ore was cinnabar (HgS) and it was mined as a by-product of Ordovician iron ore mining, mostly containing hematite (Fe_2O_3) and siderite ($FeCO_3$). The area where mining of Fe-ores and HgS occurred, with the preserved main mine shaft centrally located, is depicted in Fig. 1. The mine was in operation from the 18th century until 1870 (Sattran et al. 1978). Accurate information on total Hg production is not available, but Velebil (2003) estimated production at this site was on the order of tons per year. The only available detailed data on Hg production cover periods 1778-1779 and 1854-1858 with 7.8 and 3.4 tons of HgS, respectively (Velebil 2003). Initially Hg ore was probably processed directly on-site, later ore processing was moved to the village of Komárov (Fig. 1). The mining area has been covered with mixed forests in the last 50 years, primarily European beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*). The soils were classified as Haplic or Dystric Cambisols (FAO, 2006).
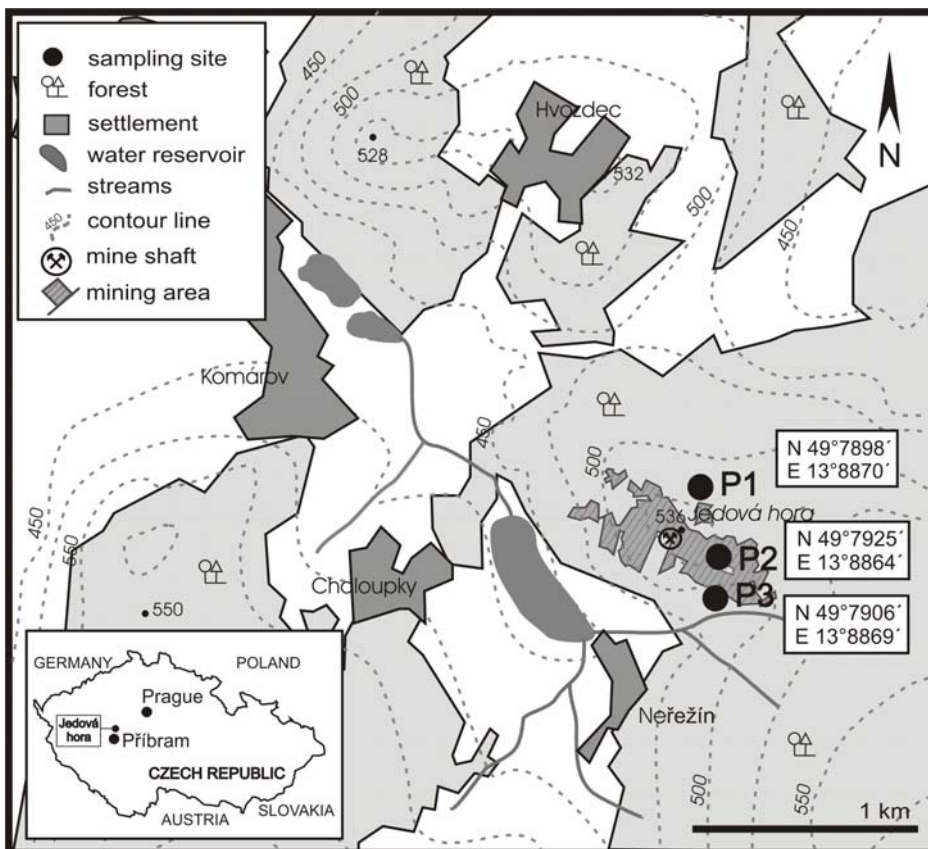
Figure.1 Location and map of the mining site and studied soil profiles (P1, P2, P3).

4.2.2. Sampling and sample preparation

Three soil sampling sites (P1, P2, P3) were selected to capture likely high and low impact sites within the mining area (see Fig. 1). The low impact soil profile P1 was located (400 m) uphill from the main mine shaft (Fig. 1). It was considered to be relatively unaffected by direct contamination by coarse solid materials from mining operations or down-slope solute transport. Soil profiles P2 and P3 were located down-slope from the mine shaft in an area directly affected by mining (see Fig. 1). Soil pits were excavated to a depth of 0.8 m and samples were taken from the major morphological horizons. Bedrock samples were defined as boulders >5cm in diameter taken from the bottom of the C horizon at each excavated soil pit. All samples were freeze-dried, sieved (2 mm) and homogenized.

4.2.3. Analytical procedures

Concentrations of total Hg were determined on a cold vapor-atomic absorption (CV-AAS) Hg analyzer AMA-254 (Altec Co, Czech Republic). The determinations were performed in triplicate with a relative standard deviation (RSD) < 5%. The quality control of Hg measurements was assured by the analysis of standard reference material 'river stream sediment 1', produced by Analytika Co. (Czech Republic). Triplicate measurements of the certified reference material yielded 1.58 ± 0.04 $\mu g\ g^{-1}$, corresponding well with the certified value 1.55 ± 0.07 $\mu g\ g^{-1}$.

Mercury speciation analysis was carried out using a thermo-desorption (TD) method, which has successfully been applied to estimate Hg speciation in solid materials (e.g. Windmöller et al., 1996; Biester et al., 1999). The analyses were performed using a custom-made apparatus consisting of a programmable oven (Clasic, Czech Republic) placed into the Ar path of an ICP-OES (Thermo-Elemental IRIS Intrepid II).

The soil samples (150 - 200 mg, depending on the total Hg concentration) were heated in the oven with a temperature gradient of $40°C\ min^{-1}$ to a maximum 600°C in the presence of an Ar stream. The volatilized Hg was detected at 184.9 nm in a continuous detection mode. The results of TD analyses are presented as Hg thermo-desorption curves (TDC) representing the release of Hg versus temperature. Peak areas of TDC from natural soil samples were evaluated using Peak Fitting Module of OriginPro software (ver. 7.03).

Thermo-desorption properties of standard Hg compounds (Hg^0, HgO, $HgCl_2$ and HgS) were evaluated in order to optimize the experimental apparatus. In particular, metallic Hg bearing

sand, HgO (Lachema[TM]), HgCl$_2$ (Lachema[TM]) and HgS (red cinnabar, Fluka[TM]) and crystalline cinnabar from the studied mining site were used as standards. All compounds were diluted with quartz powder before the speciation analysis. The effect of sorbent matrices on Hg release was calibrated with Hg(II) adsorbed onto the following reference substrates: clay minerals, Fe-oxyhydroxides and humic acid. In particular, we used kaolinite and montmorillonite (Sigma Aldrich[TM]) and Fe-oxyhydroxides goethite (α-FeOOH) and lepidocrocite (γ-FeOOH), prepared according to Cornell & Schwertmann (1996).

Hg(II) adsorption onto the mineral substrates was performed as follows: 1 g of the solid material was suspended in a 5 ml solution of 40-800 μg Hg mL^{-1} (prepared from a stock solution of 1000 μg mL^{-1} of HgCl$_2$). The suspension pH was not adjusted. The suspension was vigorously shaken at room temperature for 1 h and then left intact for 24 h. After supernatant removal by centrifugation, the solid material was rinsed with distilled water and dried at 60°C.

Soil pH was determined using a 1:2.5 (v/v) ratio of soil and deionized water suspension (Pansu & Gautheyrou, 2006). Total organic carbon (TOC) and total sulphur (S_{tot}) were determined using an Eltra Metalyt CS1000S elemental analyzer. Cation exchange capacity (CEC) was calculated as the sum of exchangeable cations extracted with 0.1M BaCl$_2$ buffered at pH 8.1 (ISO 13536). To obtain the upper estimate of the CEC fraction attributable to expandable clay minerals (ECM) we used [Cu(trien)]$^{2+}$ analysis. The mass of 100-200 mg of sample was suspended in 5 ml of water before the addition of 5 ml of 9 mM solution of [Cu(trien)]SO$_4$ (trien=1,4,7,10-tetraazadecane). The suspension was then stirred for 10 min and filtered into 50 ml flasks. Remaining Cu in solution was determined by AAS (Zeiss 3, Jena, Germany). This method has been used previously for determination of clay CEC (e.g. Meier and Kahr 1999, Czímerová et al. 2006) and recently of soils (Hernández-Soriano et al. 2007).

Total Fe (Fe$_{tot}$), Mn (Mn$_{tot}$) and Al (Al$_{tot}$) concentrations were determined after sample digestion in a microwave oven in a PTFE crucible with a mixture of HF and HNO$_3$ acids (Merck[TM], Suprapur). To dissolve fluorides, HClO$_4$ was added (Šulcek & Povondra 1989). Fe, Mn and Al concentrations in solutions were measured using ICP-OES (Thermo-Elemental IRIS Intrepid II). Oxalate extraction (0.2M ammonium oxalate at pH 3) was performed according to Pansu & Gautheyrou (2006).

The X-ray diffraction analyses (XRD) were carried out using a PANalytical X`Pert Pro diffractometer under the following conditions: CuKα radiation, 40 kV, 30 mA, step scanning

at 0.05°/300 s in the range 3-80° 2θ. UV–Vis diffuse reflectance spectroscopy (DRS) and voltammetry of microparticles (VMP) were determined in the presence of Fe and Mn oxides. DRS was performed according to methodology described in Grygar et al. (2003) using a Perkin Elmer Lambda 35 spectrometer equipped with an integrating sphere (Labsphere[TM]). Semiquantitative estimates were obtained by comparison of the areas of the electron-pair transition bands of samples with a set of calibration mixtures of synthetic goethite in a mineral matrix. VMP was performed with μAutolab potentionstat (EcoChemie, the Netherlands) with a paraffin-impregnated graphite working electrode. Reference potentials of the Fe- and Mn-oxide phases previously reported by Bakardjieva et al. (2000) and Grygar & van Oorschot (2002) were used.

4. 3. Results and Discussion

4.3.1. Soil Properties

Selected physicochemical properties of the study soils are given in Table 1. Soils were mostly acidic with pH values ranging from 3.2 to 5.8 in the individual horizons. The Oe and Oa horizons of forest soils (Oe and Oa) were rich in organic C (up to 48 wt. %) and also showed the highest S_{tot} concentrations (up to 1.7 g kg^{-1}) of the soil horizons. The cation exchange capacity (CEC_{BaCl2}) varied from 78 to 133 cmol kg^{-1} in organic and from 14 to 32 cmol kg^{-1} in mineral horizons. The fraction of CEC_{BaCl2} attributable to expandable clay minerals (ECM) was estimated to range from 9.0 to 19.5% of the total CEC_{BaCl2} in the O horizons, according to results of the $[Cu(trien)]^{2+}$ method (Table 1). The percentage of ECM contributions to the total CEC_{BaCl2} was comparable in mineral horizon, with the exception of C horizons in profile P2 and P3, where it reached 29.6 and 34.8%, respectively.

Clay fraction accounted for 14-22% of the total particle size distribution in the fine earth fraction for most samples (Table 1). A notably higher content of clays were observed in C horizons at profiles P1 and P3 (41 and 44%).

Individual soil horizons from low impact profile P1 located outside the mining area contained 7-27 g kg^{-1} of Fe_{tot}. All soil horizons at profiles P2 and P3 contained higher Fe_{tot} concentrations ranging from 40.6 to 154.8 g kg^{-1}. Higher concentrations of Fe_{tot} in P2 and P3 are interpreted as being due to the location of these soils down-slope in the mining area. This is strong evidence for the direct contamination of P2 and P3 soils with mined Fe ores or waste materials and suggests P1 was minimally impacted by mining contamination (Table 1).

Oxalate extractable Fe concentrations, thought to represent the presence of poorly crystalline Fe phases, e.g. ferrihydrite, were similar in all profiles (Table 1). However, the relative importance of Feox (expressed as Feox/Fetot ratio) was higher in profile P1 (up to 67% of Fe_{tot}) due to the lower Fetot mass. In P2 and P3, only 2-13% of Fe_{tot} was extracted by oxalate solution (Table 1). Similar Feox concentrations in high and low impacted soil may indicate slow rate of mine waste weathering. Therefore formation of poorly crystalline Fe-oxyhydroxides, representing effective sorption substrates for Hg, is limited.

The combination of DRS and VMP methods revealed the presence of well-crystalline goethite (α-FeOOH) in all samples. Trace amounts of hematite (α-Fe_2O_3) were identified in the Ah horizon of P1. The results of semiquantitative estimates of Fe(III) oxides by DRS indicated presence of ca. 2% of crystalline goethite in P1, while P2 and P3 contained 5-10% goethite. In addition, MnOOH was identified in Oa, Ah and Bw horizons of profile P3 using VMP.

The XRD analysis revealed that the major mineral components of these soils were quartz, clay minerals (kaolinite, illite and mixed-layer illite-montmorillonite) and goethite (α-FeOOH). Hematite (α-Fe_2O_3) and siderite ($FeCO_3$), commonly occurring in waste material at this mining site (Hojdová et al. 2008), were not detected in these soils by XRD. The presence of clay minerals and Fe-oxyhydroxides represents relatively favourable conditions for Hg adsorption to the mineral surfaces.

Table 1. Selected physicochemical parameters of the studied soil profiles.

soil profile	horizons (depth, cm)	pH_{H2O}	TOC (%)	CEC_{BaCl2} (cmol kg^{-1})	$CEC_{CuTrien}$ (cmol kg^{-1})	$CEC_{CuTrien}/CEC_{BaCl2}$ (%)	Stot (g kg^{-1})	Fetot (g kg^{-1})	Mntot (g kg^{-1})	Altot (g kg^{-1})	oxalate extractable (g kg^{-1}) Fe_{ox}	Mn_{ox}	Al_{ox}	Fe_{ox}/Fe_{tot} (%)	particle size distribution (%) clay	silt	sand
P1	Oe	3.50	39.2	133	15	11.0	1.5	7.3	0.3	7.3	2.4	0.16	1.10	32.6	n.d.	n.d.	n.d.
	Oa	3.42	47.9	133	12	9.0	1.7	17.4	0.2	6.6	5.4	0.04	2.45	31.1	n.d.	n.d.	n.d.
	Ah (0-2)	3.22	7.2	32	4	13.0	0.8	24.5	0.1	6.1	7.0	0.04	1.37	38.6	20	58	22
	Bw (2-19)	3.35	2.4	17	3	16.4	0.8	10.1	0.1	9.5	6.8	0.07	1.12	67.2	22	57	21
	C (19-36)	3.59	0.9	16	3	21.7	1.0	26.8	0.1	84.3	6.6	0.02	1.48	24.5	41	46	13
P2	Oe (1cm)	5.88	30.4	79	15	19.0	0.8	40.8	4.3	28.2	2.4	0.02	1.37	5.9	n.d.	n.d.	n.d.
	Ah (0-10)	5.25	4.8	27	5	20.1	<0.2	43.7	6.2	25.5	5.6	3.75	2.64	12.9	14	53	33
	Bw (10-36)	4.43	1.5	19	3	16.4	<0.2	48.9	5.5	28.2	5.3	2.87	2.66	10.8	17	51	32
	C (36-85)	4.92	0.4	14	4	29.6	<0.2	154.8	2.2	84.3	2.5	0.97	1.23	1.6	20	34	46
P3	Oe (1cm)	5.33	26.6	78	15	19.5	0.7	40.6	5.2	22.5	1.4	0.02	0.87	3.5	n.d.	n.d.	n.d.
	Ah (0-14)	4.58	2.8	20	3	16.6	<0.2	106.6	5.0	63.3	5.3	2.88	2.28	4.9	15	48	37
	Bw (14-42)	4.66	1.0	16	3	17.8	<0.2	61.2	4.2	26.7	5.0	2.55	2.06	8.2	19	43	38
	C (42-60)	4.71	0.4	19	7	34.8	<0.2	92.8	1.6	99.1	2.6	1.40	1.35	2.8	44	26	30

n.d.: not determined

4.3.2. Total Hg concentrations

Figure 2 shows the vertical distribution of Hg concentrations in the three soil profiles. All samples of soil from the Jedová hora site contained elevated total Hg concentration in comparison to average values for unpolluted soils (0.01-0.5 μg g^{-1}; Alloway 1995).

The P1 soil sampled above the mining area (P1) only contained elevated Hg concentration only in the upper Oa and Ah horizons (Figure 2A). Relatively high Hg concentrations in both organic and mineral soil horizons of profiles P2 and P3 (Figure 2B, C) reflect contamination from mining and smelting operations at the site.

Higher Hg concentrations in Ah horizons relative to those in O horizons were found in all studied soils. Similar observations of higher Hg concentrations in O versus A horizons were reported for forest soil profiles in the Příbram region by Ettler et al. (2007). It is possible that regional decreases in Hg contribute to this contrast in surface and Ah horizon Hg concentrations. It is difficult to draw conclusions from the limited sample size in this study, and in light of the differences in the matrix properties of O versus Ah horizon that could affect adsorption dynamics. Decreases in accumulation rates of Hg in peat cores from the Příbram region (Ettler et al. 2008) support the concept of decreases in Hg emissions leading to declines in Hg input to ecosystems.

In profile P2, the Hg concentration in individual mineral horizons decreased with depth following the typical Hg depth distribution in soils (Navarro et al. 2006). Mercury distribution in profile P3 was more variable with the highest Hg content in the mineral horizon C (Figure 2C). Bedrock underlying profile P3 also contained higher Hg concentrations, compared to P1 and P2, probably due to presence of ore minerals.

The relatively low Hg concentrations in mineral horizons of profile P1 did not exceed the limit defined by the Czech legislation for soils (0.8 μg g^{-1}; Czech Regulation 13/1994).

4.3.3. Mercury speciation

4.3.3.1. Standard materials

Chemical speciation of Hg in soils affected by mining was characterized by means of thermo-desorption analysis (TDA). The method of TDA relies on comparing thermo-desorption curves (TDCs) of standard materials with TDC of soil samples.

We noted some differences in the Hg-releasing temperatures of the standard compounds in this study in comparison to those reported by other authors. Difficulties in the comparability of TD measurements are reported in the literature and attributed to differences in the

experimental conditions used (Lu & Grégorie 2005, Windmöller et al. 1996). Heating rates from 10 to 50°C min^{-1} and N_2, Ar or air stream as carrier gas with different flow (0.2-0.3 L min^{-1}) have been reported (e.g. Windmöller et al. 1996, Biester & Scholz 1997, Bombach et al. 1994, Feng et al. 2004). In our experiments we used heating rates of 40°C min^{-1} under an Ar stream (2 L min^{-1}).
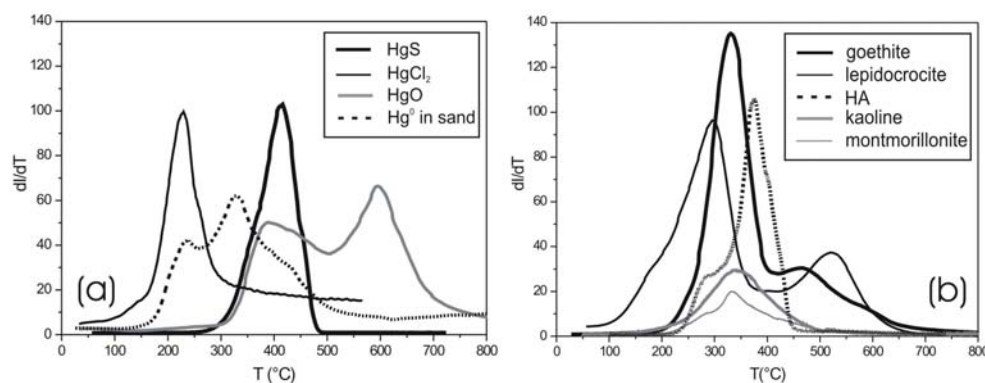
Figure. 3 TDC of Hg for (a) simple Hg compounds and metallic Hg bearing sand, (b) clay minerals, Fe- oxyhydroxides and humic acid (HA) saturated by $HgCl_2$.

TDC of the standard samples with metallic Hg had a double peak (Figure 3a), where the first peak represented Hg^0 and the second peak Hg(II) ions formed by oxidation of Hg^0 (Windmöller et al., 1996). TDC of Hg released from clay minerals reached its maximum values in the range from 336 to 347°C (Figure 3b). TDCs of both standard Fe-oxyhydroxides goethite and lepidocrocite included two peaks (Figure 3b). The first most intensive peak on both curves had its maximum a in range from 300 to 330°C and the second in a range from 450 to 520°C. We infer that the first peak could represent Hg weakly-bound onto the surfaces of Fe-oxyhydroxides. The second peak could correspond to either re-crystallization of the highly porous structure of the corresponding ferric oxides and evolution of the residual surface Hg and/or escape of Hg from the inside the Fe oxide particles. Similar to the findings of other authors (e.g. Biester et al. 1999) we found that Hg bound to humic acid (HA) was released at higher temperatures than Hg weakly bound to mineral components (Figure 3b).

4.3.3.2. Low impact soil profile P1

The TDCs of individual horizons of all three soil profiles studied are shown in Figure 4. TDCs of organic horizons were not determined due to problems with epirheumatic compounds, which tend to settle on the walls of the pyrolitic device causing serious artifacts.

The TDC of the Ah horizon from soil P1 showed two major peaks in the temperature range from 25 to 600 °C. We propose that the first peak at 350°C corresponds to Hg weakly-bound onto surfaces of mineral particles, probably either clay minerals or Fe-oxyhydroxides. The releasing temperatures from clay minerals and Fe-oxyhydroxides were quite similar (see Figure 3b). Therefore, we did not manage to distinguish these two sorption substrates.

The estimated proportion of the total CEC_{BaCl2} attributable to expandable clay minerals (ECM) constituted only 9-22% (Table 1), which suggests that Hg might not have been dominantly adsorbed to ECM. In addition, relatively high concentrations of Feox indicate that Fe-oxyhydroxides could be the dominant sorption substrates.

No corresponding peak for organically bound Hg was detected on the TDCs for the Ah from soil P1. Binding of Hg to organic matter (e.g. HA standard) is much stronger leading to a higher Hg-releasing temperature of 400° (Figure 3b).

The second maximum at 453°C indicated the existence of HgS, determined by the correspondence of this peak with that of the HgS standard (Figure 3a). Cinnabar is a mineral with limited solubility and a kinetic resistance to oxidation (Ravichandran et al. 1998, Alloway 1995). Therefore, we infer that cinnabar enters the soil mainly as mechanically degraded particulate material (Palmieri et al. 2006). At the study site, HgS was probably introduced to soils in the form of HgS particles derived from the erosion of historical mine dumps and mechanically dispersed to the surrounding environment. Evidence for the downward migration of HgS particles from the topsoil was not detected (Figure 4a). In deeper mineral horizons (Bw, C), only one peak at 370 °C was observed (Figure 4a), suggesting the presence of Hg weakly adsorbed onto soil mineral particles.

4.3.3.3. High impact soil profiles P2 and P3

TDC of the samples from profiles P2 and P3 displayed similar patterns to one another, defined by two different peaks at 360°C and 470°C in P2, and 355°C and 440 °C in P3 (Figure 4b, c). The first maximum corresponded to the Hg released from mineral surfaces of either clay minerals or Fe-oxyhydroxides (Figure 3b). The second peak at 453°C was evidence of Hg in the form of HgS (see TDC of HgS standard in Figure 3a). The presence of

HgS in P2 and P3 mineral horizons was probably caused by erosion of mine wastes and anthropogenic dispersion during the mining activities.

Signal intensity expressed in dI/dT on the y-axis (Figure 4) for soil horizons corresponded well with their total Hg concentrations. Relatively high dI/dT values were recorded in the horizons with elevated Hg concentrations (compare Figures 3 and 4).

4.3.3.4. Relative distribution of Hg species in studied soil profiles

An evaluation of the distribution of Hg forms showed that 60% of total Hg amount in the Ah horizon of P1 was adsorbed onto mineral surfaces and 40% of Hg was present as HgS (Figure 4a). The HgS in the Ah horizon of P1 might reflect fine particles spread at site during historical mining or ore processing activities. The presence of a single peak in the case of Bw and C horizons for P1 suggested the presence of Hg adsorbed onto mineral surfaces was the dominant Hg phase in this soil.

In soils P2 and P3 that were intensively impacted by mining, cinnabar (HgS) was identified in all soil horizons. The proportion of Hg present as HgS (the second peak on the TDC) was higher than the proportion of Hg bound to Fe-oxyhydroxides or clay minerals (Figures 4b, c). The relative abundance of HgS compared to total Hg was 68% in P2 and 50% in P3. The relative abundance of HgS compared to total Hg ranged from 60-80% in mineral Bw and C horizons of P2 and P3 soils.

The highest total Hg concentration detected in bedrock and C horizon samples came from soil P3, with the majority of Hg attributable to HgS. This suggests that the profile has developed from substrates containing significant amounts of cinnabar. It is interesting to note that more than 80% of total Hg in mine waste materials located at nearby heaps occurred as HgS (Hojdová et al. 2008).
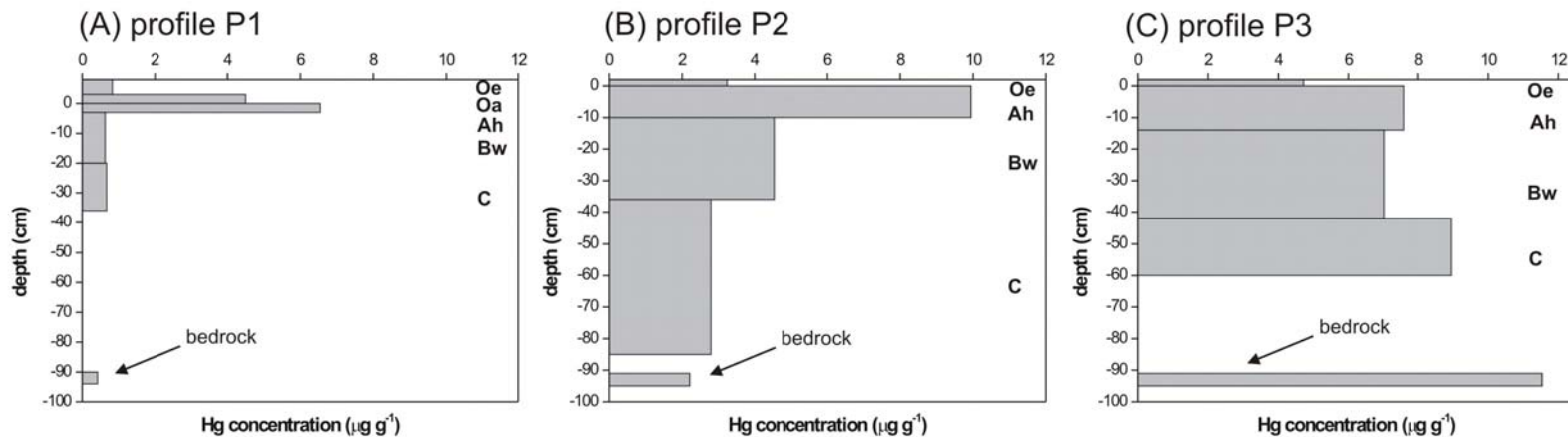
Figure 2. Vertical distribution of Hg in soil profiles
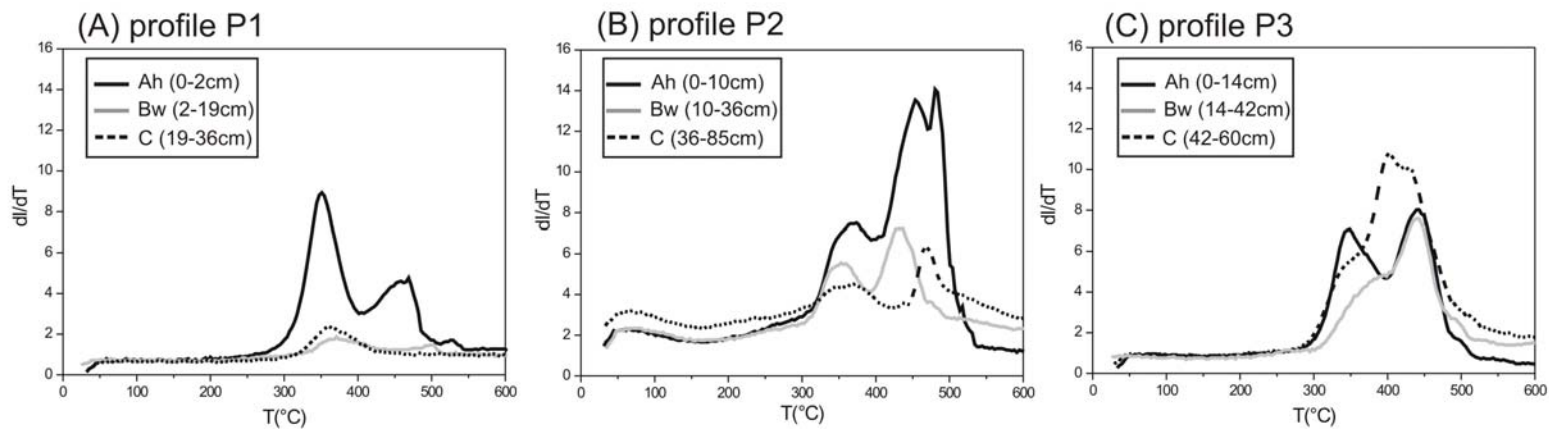

Figure 4. Hg-TDC of soil samples from individual soil horizons.

4. 4. Conclusions

The results of this study showed that mineral soils were most contaminated by the mining activites at Jedová Hora when located downhill from the main shaft in the area of former mining. We detected higher Hg concentrations in Ah horizons compared to O horizons that could be evidence for recent declines in Hg deposition, although other matrix effects could contribute to these results. Therefore, some of the Hg burden and possible changes over time for these soils could reflect trends for declining Hg deposition in the Příbram region, and not just local processes at the study site associated with mining. The Bw and C horizons of soils believed to be most heavily impacted by the mining operations had higher Hg concentrations than the soil studied located uphill of the mining operations and considered less impacted.

Thermo-desorption analysis revealed the presence of Hg in the form of HgS and Hg(II) weakly-bound to soil particles. Soil profiles sampled in the mining area that were most intensively impacted contained sparingly soluble and kinetically stable HgS in all horizons. Hg(II) adsorbed onto the mineral surfaces constituted a smaller fraction of total Hg in these samples.

In the low impact soil uphill from the former mining area, HgS was found only in the Ah horizon, suggesting only surficial evidence for the transport of Hg in the form of HgS particles originating from past mining activities. The dominant form of Hg in mineral horizons from low impact site was Hg(II) weakly-bound to mineral particles. Mercury sorbed to mineral components has been shown to be more mobile and poses a long-term environmental risk at this site.

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CHAPTER 5:

GENERAL CONCLUSIONS AND FUTURE ENVIRONMENTAL ISSUES

In this thesis following environmental issues were investigated:

(i) mercury sources in mine wastes and the extent of Hg contamination and its potential environmental impact on surrounding environment in historical mining area in the central Czech Republic, (ii) potential mobility of Hg in mine waste and soils in terms of Hg species present in the samples, (iii) the application of thermo-desorption analysis (TDA-ICP-OES) on determination of Hg speciation in natural samples such as soils and mine wastes. The following main conclusions were reached.

(i) mercury sources in mine wastes and the extent of Hg contamination in the vicinity of the mining area

Both mine wastes and soils collected near the Hg mines were highly elevated in total Hg concentrations. Soils exhibited the highest Hg concentrations mostly in subsurface Ah soil horizons. Higher Hg concentrations in Ah horizons relative to those in O horizons were found in all studied soils. Similar observations were reported by other authors and it is possible that regional decreases in Hg deposition contribute to this contrast in surface and Ah horizon Hg concentrations. Information on changes in Hg deposition in the Czech Republic are rare, although it is situated in the industrial part of Europe and it is bearing several environmental loads from the past.

(ii) potential mobility of Hg in mine waste and soils in terms of Hg species present in the samples

Mine wastes contained mostly cinnabar (HgS) and only minor fraction of total Hg amount was identified as Hg bound onto surfaces of mineral particles, such as Fe-oxyhydroxides or clay minerals. In comparison to waste material the proportion of HgS in soils was smaller. Nevertheless high impact soils contained HgS in all horizons and Hg(II) adsorbed onto the mineral surfaces constituted a minor fraction of total Hg. In the low impact soil HgS occurred only in the Ah soil horizon, which may reflect cinnabar fine particles spread at site during

historical mining or ore processing. Deeper mineral horizons of the low impact soil contained only the Hg(II) weakly adsorbed onto mineral particles.

From the environmental point of view cinnabar (HgS) is relatively stable in soils. Its dissolution is limited and it is transported mostly in the form of particles. Despite Hg sorbed to mineral components comprised the minor fraction of total Hg, it poses environmental threat due to its mobility and potential formation of highly toxic methyl-Hg. Potential sources of methyl-Hg to the aquatic environment have not been studied yet in the Czech Republic. The only available data are the methyl-Hg concentration in vertebrates, especially in fish.

(iii) the application of thermo-desorption analysis (TDA-ICP-OES) on Hg speciation in soils and mine wastes

Beside the knowledge of total Hg levels, determination of Hg chemical forms in the environment is essential for predicting its solubility, transport and potential bioavailability. In the thesis thermal-desorption combining with ICP-OES was used to identify Hg species in waste material and soils contaminated by Hg mining. The advantage of TDA is a single measurement with minimal sample treatment, no addition of reagent, so there exist no threats on modification of chemical species present in the sample. TDA-ICP-OES seems to be appropriate for differentiation of Hg sulfides, metallic Hg and humic bound Hg. Identification of Hg sorbed to mineral soil particles is possible, but distinguishing among sorption substrates (e.g. Fe-, Al- or Mn- oxyhydroxides or clay minerals) is limited. Therefore application of TDA in combination with other methods e.g. electron microprobe analyses will be necessary. Moreover the creation of broader termo-desorption curves database of reference materials such as Hg adsorbed onto Mn oxides would be reasonable.

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