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Original Research

Mercury in River Sediments, Floodplains and Plants Growing thereon in Drainage Area of Idrija Mine, Slovenia

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Abstract

Half a millennium of mercury production at Idrija is reflected in increased mercury contents in all of its environmental segments. Stream sediments have been monitored along the Idrijca and Soča rivers (70 km) every 5 years since 1991. It has been discovered that there was no decrease in mercury concentration in stream sediments during the last 15 years. Upstream from the town of Idrija, mercury concentrations in active river sediments vary from 1 to 10 mg/kg dry weight (average 3.3 mg/kg). From Idrija to Spodnja Idrija mercury concentrations increase extremely and vary greatly. The average in this area amounts to 603 mg/kg with individual contents up to 4121 mg/kg. From Spodnja Idrija to the Idrijca-Soča confluence the average is 213 mg/kg, while the average in the Soča river sediments is 57 mg/kg.

Floodplain soils and samples of averaged meadow forage and plantain (*Plantago lanceolata*) were collected on river terraces at two localities in the lower course of the Idrijca. It has been determined that floodplains along the Idrijca River are strongly enriched with mercury. The average concentration of Hg in the upper 20 cm of the floodplain at IDB location is 157.7 and at TEM location it is 294.8 mg/kg. Samples of averaged meadow forage and plantain contain from 0.055 to 0.220 mg Hg/kg. In comparison to the plant samples from Idrija in the 1970s, these contents are relatively low. However, regarding mercury contents in plants in non-polluted soils the contents on the Idrijca River terraces are considerably higher than the background.

Keywords: alluvial sediments, floodplain, plants, mercury, Idrija, pollution, geochemistry, Slovenia

Introduction

Mining and processing of mercury ore in one of the largest mercury deposits in the world – the Idrija mercury mine – have caused serious pollution in different environmental compartments. The bulk of roasting residues from the mid-19th century to 1977 was discharged directly into the Idrijca River, and the material was carried at high waters to Soča River and farther into the Adriatic Sea. It has been estimated that 45,500 tons of mercury were emitted into the environment during the operating period of the mine, which ceased production in 1994 [1]. In the lower reaches of the Idrijca the riverine deposits with high mercury contents have been, and will be in the future, a source of mercury-polluted sediment [2-7]. River terraces along Idrijca are rare; the valley is seldom broad enough to develop terraces [8]. They are somewhat more frequent farther downstream, roughly from confluence with the Trebušnica to the narrowing of the valley just before it enters the Soča River. The plains are everywhere carefully cultivated, as farmland is scarce in the

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narrow valley. As the analysis of vegetation on contaminated land or in mining areas may be utilized for identifying the accumulation of heavy metals and to provide insight into their mobilization sequences and availability [9], we estimated the effects of high mercury contents on these river terraces by determining the mercury in plants grown on floodplains.

Mechanisms of Mercury Dispersion in Idrija Mercury Mine Surroundings

Before mining activities in Idrija had started the mercury levels in the environment of Idrija were heightened as a consequence of natural, geogenical conditions. The outcrop is very small (approximately 4,000 m^2). Natural migration of mercury into the wider surroundings of the deposit is limited owing to impermeable Carboniferous clastites and tectonic zones filled with clay [10].

The production of mercury in Idrija started in 1492. In the first decade of mercury mining in Idrija the ore was roasted in piles. Because enormous quantities of timber were required by the mining works, forests in the nearby surroundings of Idrija soon disappeared. Consequently, the miners decided to transport relatively small quantities of rich ore to various places in the woods in the surroundings of Idrija that were suitable for ore roasting. For the first 150 years, until 1652, the ore was roasted in earthen vessels at various sites in the woods around Idrija. Up to now 21 localities of ancient roasting sites have been established on the neighbouring hills (Pront, Pringl) and in more distant localities (Čekovnik, Kanomlja) [11].

It should be emphasized that roasting of ore in piles and in earthen vessels gave a very poor yield and resulted in considerable losses. As a consequence of very high temperatures a third of earthen vessels usually cracked during burning and mercury escaped from the vessels. Large quantities of broken pottery can be found at the localities where old small smelters in woods were situated. The concentrations of Hg in soil at those places are, of course, very high (up to 7,474 mg/kg) [11]. The determined mercury contents in soils at old roasting sites are very high, and they surpass all hitherto described localities at Idrija and in its surroundings [4-6, 12-16]. It is also estimated that there is about 40 tons of mercury still present at all roasting sites in the woods described up to now [11]. Nevertheless, a considerable amount of mercury-rich waste material from these places was transported into the Idrijca River valley.

Another source of mercury pollution was mineralized rock dumps and especially roasting residues that still contain rather high amounts of mercury. Since 1652, when the first smelter in Idrija was built, the mercury-rich by products of smelting have been deposited along the rivers Nikova and Idrijca. The main reason for complex spatial distribution of roasting tailings in Idrija and its surroundings are threefold: the changes in combustion technology over the centuries, continuously growing quantities of processed ore accompanied by decreasing mercury content and various methods of further treatment of ore residues. The depositories of poor quality ore and remains from smelters are both very important because they contain large quantities of mercury.

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 a larger smelter was needed. In 1867, a modern smelter was built on the right bank of the Idrijca River. New dumps of roasted ore were created on the right bank of the Idrijca River [10]. Since then, until 1977, most roasting remains were dumped directly into the Idrijca River, which carried the material to the Soča River and the Adriatic Sea. For this reason, the river sediments have extremely high mercury contents [4, 13, 17, 18]. High waters deposited mercury-rich material on the floodplains in the lower part of the Idrijca and Soča River valleys, building thus a large accumulation of mercury-enriched sediments.

Mercury was brought far into the Idrija surrounding areas through atmospheric emissions of the new big rotary kiln chimney. The roasting process produced gaseous and particulate matter emissions, which were the major cause behind the huge geochemical halo around the Idrija mercury mine [19, 20]. Total Hg concentrations and Hg speciation were determined in soils and attic dust in 160 km^2 area around the Idrija mercury mine. Spatial mercury distribution in the attic dust shows that the influence of atmospheric emissions caused by the Idrija smelter resulted in impacts on the environment on a regional scale [20].

Materials and Methods

Sediments

The term stream sediment in geochemical prospecting usage normally means active stream sediment collected from stream bed in current contact with stream water. Active the stream sediment is carried by a river in suspension during floods, and by rolling, sliding or saltation under normal flow conditions. However, during normal discharge conditions of a river, only one or at most a few sources of limited area may be exposed to erosion. Consequently clastic stream sediment may reflect only limited parts of the drainage area [21]. Overbank deposites (floodplain sediments) are fine-grained (silty-clay, clayey-silt) alluvial soils of large and small floodplains [22] and are an alternative drainage sample type which is used in geochemical mapping and environmental prospecting [23, 24]. They are produced on floodplains when major floods occur in a river system. During such flood water discharge exceeds the quantity that can pass through an ordinary stream channel. Even in streams of moderate size, the water level can reach several meters above normal, thereby covering large areas. At these times many new sediment sources open up, and the origin of the load suspended in the stream is manifold. Throughout the flood

– and especially during its last phases – some of the load will be deposited on the floodplain at levels well above those of the ordinary stream channel. In this way, nearly horizontal strata of floodplain sediment are built up over long periods of time [25].

Boszke and Kowalski [24] used floodplain soils of the Warta River to identify the effect of Poznań agglomeration as a source of mercury pollution. Study results show that the distribution of mercury in the floodplain soils of the middle part of the Warta River is relatively uniform but the influence of the Poznań urban area on this distribution is observed. It was also observed that the floodplain soils had higher mercury concentrations than the corresponding river sediments. Mercury in the surface and ground water collected from various sites in Poznań is relatively uniform [26]. Much higher differences in mercury concentrations were noted for wet precipitation [27] but they do not exceed acceptable legally admissible values.

The sediment-producing processes are often episodic events. Thus, a sample from the present sediments in the stream channel may be dominated by a source that was particularly active in the time preceding the sampling [28]. In mining areas physical remobilization of abandoned tailings or waste piles and heavy metal-contaminated floodplains alluvium (formed during historic mining activity) provide large amounts of metal contaminants to rivers [29].

Plants

Monitoring the state of environmental pollution with living organisms is one of the major activities of environmental chemistry, and is usually called biomonitoring. The significance of observation of the pollution state of ecosystems with heavy metals by monitoring their contents in living organisms has been in the centre of scientific discussions for at least 30 years [30, 21, 31-33].

The scientific base for utilization of the plants for detecting environmental pollution is found primarily in the works of Russian researchers from the field of biogeochemical mineral prospecting. They started using plant samples for prospecting, especially the copper and nickel deposits in the Ural Mountains and in Siberia. Kovalevsky, the principal author from this field, published more than 460 biogeochemical studies. He found the plants to be a good sampling material. In many instances he established a close relationship between metal contents in plants and those in mineralized areas. Even the comparison with soils showed in many cases that the plants indicated mineralization better than the soils. Kovalevsky laid in his works the theoretical foundations of biogeochemistry as a prospecting method. He found that various plant species possess various abilities for fixing chemical elements.

In the last decade plants are also used to clean soils contaminated with potentially toxic metals and make them safe and usable for humans. This is designated in different publications as phytoremediation or bioremediation [21, 33]. It is an outgrowth of principles and processes that have been used in biogeochemistry applied to mineral prospecting mentioned above. Phytoremediation is also used for the restoration of the environment in the world's largest mercury mining district (Almadén) [34, 35].

Sampling

Stream sediments were collected from the moving bottom load of fine sediments. They were collected as far away from the banks as possible, with special care not to sample collapsed bank material of the local origin. The stream sediments were monitored systematically since 1991, every 5 years on 20 locations in the Idrijca and Soča River. Timing of sampling is a factor to be considered in the environmental studies in which seasonal dynamics can affect analytical results [21]. A composite stream sediment sample was taken in similar summer low water conditions from 5 sublocations within a distance of 50 m, every 5 kilometres. In the vicinity of the Idrija mine each kilometre was sampled. The sampling locations are presented in Fig. 1.

Floodplain sediments, or better to say floodplain soils, were sampled in 1999 at two localities in the lower course of Idrijca, downstream from the Trebušnica confluence. Near the village Idrija pri Bači (IDB) on river terraces two profiles were sampled (Idrija pri Bači 4 and 5 – IDB4, IDB5), and on river terraces near the Temnikar farm (TEM) three additional ones were taken (Temnikar 1, 2 and 3 – TEM1, TEM2, TEM3) (Fig. 1). The data about the profiles are listed in Table 1.

The IDB4, IDB5, TEM1 and TEM2 profiles were sampled with a drilling set mounted on a field vehicle. The sediment profiles were sampled in 5 to 6 centimeter intervals. The TEM3 profile is situated at the edge of a terrace that has been formed by erosion of high waters. Samples were collected as follows. The river cut was cleaned on the surface (about 20 cm of surficial material were removed), and then channel-sampled.

At the locations of the terrace profiles the samples of averaged meadow forage and plantain (*Plantago lanceolata*) were collected within a 50 meter radius. Of the collected plants only the parts above the ground, stems and leaves, were used for analysis.

Sample Preparation and Analytical Methods

The samples of stream and floodplain sediments were air-dried. Two grain size fractions (<0.04 and <0.125 mm) of stream sediments were prepared for chemical analyses by dry sieving. Floodplain soils were gently crushed in a ceramic mortar, sieved and analyzed in a fraction below 0.063 mm. The air dry plant material was ground to analytical grain size (<0.063 mm). In all samples mercury was determined using Cold Vapour Atomic Absorption

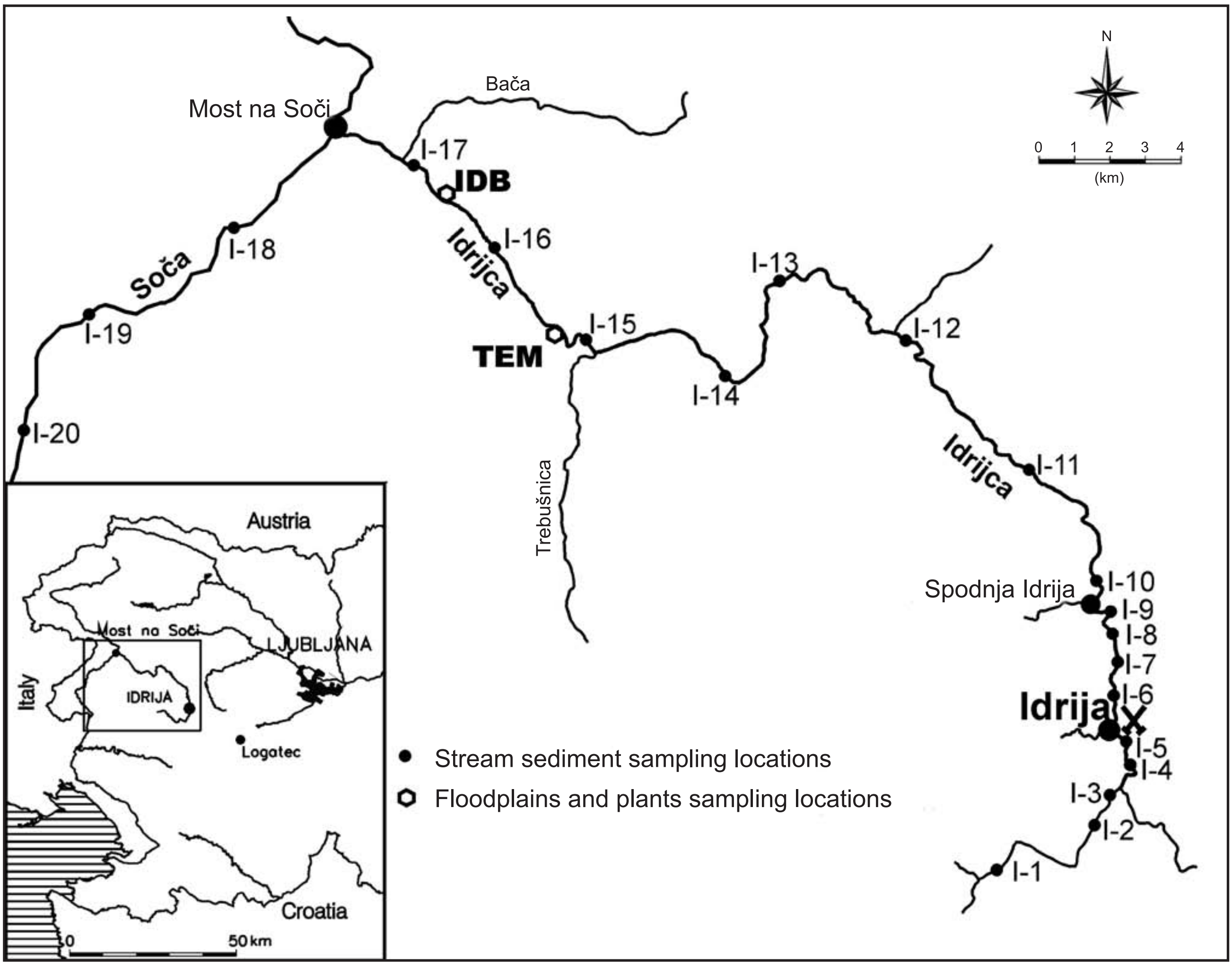

Fig. 1. Stream sediment, floodplain and plant sampling locations.

Table 1. Characteristics of sampled soil profiles.

Profile	Above normal river level	Sampled material	Distance from river	Soil type
Idrija pri Bači 4 IDB4	2.9 m	flood-plain	25 m	alluvial soils
Idrija pri Bači 5 IDB5	4.2 m	1st terrace	63 m	eutric brown soils
Temnikar 3 TEM3	3.0 m	flood-plain	20 m	alluvial soils
Temnikar 2 TEM2	3.7 m	1st ter-race	100 m	alluvial soils
Temnikar 1 TEM1	8.3 m	2 nd ter-race	140 m	eutric brown soils

Spectrometry (CVAAS) following the aqua regia extraction (1 hour, 95°C).

Quality was assured by shipping samples to the laboratory in a random succession to distribute any errors due to laboratory performance, while the objectivity was assured through the use of neutral laboratory numbers. Moreover, accuracy was estimated by blind determinations of Standard Reference Material San Joaquin Soil (SJS-1). The values for total mercury in SJS1 in 1991 and 1995 (0.097±0.015 mg/kg, n=9), 2001 (0.10±0.024 mg/kg, n=3) and 2005 (0.113±0.005 mg/kg, n=3) were in agreement with the certified concentrations of 0.1±0.02 mg/kg. Procedural blanks were run with each set of sample analyses. The reliability of determinations was assessed as very satisfactory. It was established that the means of Hg concentration in the standard differ by less than 20% of the recommended values.

Results

Stream Sediments

At the first two sampling locations in the upper part of the Idrijca River, upstream of the Idrijca and Zala confluence, the mercury concentrations were on average

3.3 mg/kg (from 0.9 to 10.2 mg/kg, Table 2). In the Idrija town before the smelter higher mercury contents were determined, from 5 to 643 mg/kg, while the average is 87 mg/kg. In this part of the river the contents at the same locations vary greatly between the sampling years. It is evident that the influence of the mining waste material deposited at the river site is significant. Between the smelter location in Idrija and Spodnja Idrija the stream sediments contain a rather high mercury content: on average 603 mg/kg. The maximum concentration (1,777 mg/kg in fraction <0.04 mm and 4,121 mg/kg in fraction <0.125 mm) was determined in the closest vicinity of the smelter in 2001. Further downstream, from Spodnja Idrija onwards, the sediments contained lower mercury concentrations. The mercury mean in this area is 213 mg/kg, whereas downwards in the Soča river it is 57 mg/kg. Mercury contents in the analyzed sediments are presented in Figs. 2 and 3 and basic statistical data in Table 2.

There is a strong correlation between mercury contents in the two analyzed fractions (r=0.91). Mercury is enriched in the coarser-grained fraction (<0.125 mm; Fig. 2). There was no decrease in mercury concentration determined during the last 15 years, although mercury production in Idrija stopped in 1995. That is most likely because unknown amounts of tailings containing high concentration of mercury are still deposited along the banks of the river and significant amounts of this material are transported downstream during every high-water event.

Soil

Mercury contents in the profiles on the river terraces have also been described in paper by Biester et al. [4]. Since mercury contents in plants are controlled by mercury contents in soil at the depth of the roots, only the upper soil horizons (0–20 cm depth) in the traverses will be considered here.

In the Idrija pri Bači 4 profile (IDB4) the mercury contents in the upper 20 cm vary between 130 and 196 mg/kg, the average is 157.7 mg/kg (Fig. 4). It is interesting to note that the contents of this profile are the highest in the topmost segment (0-6 cm) – 196 mg/kg. The sampled material consisted of relatively unweathered sandy-silty sediment deposited on the floodplain overgrown with grass. The grain size is rather coarse, prevalence in medium grained sand, in contrast to fine grained sand in other samples.

In the Idrija pri Bači 5 profile (IDB5), located at a higher position on the first terrace, 4.2 m above the normal Idrijca water level, Hg contents vary between 40 and 46 mg/kg (average is 41.6 mg/kg) in the upper part of the profile (Fig. 4).

In the Temikar 1 profile (TEM1), located on the third river terrace 8.3 m above the Idrijca level, the contents of Hg distinctly decrease with depth. The highest content was determined in the upper 6 cm (7.5 mg/kg), then mercury contents decrease and are on average 5.4 mg/kg in the 0-20 cm in depth (Fig. 5).

In the lower situated Temikar 2 profile (TEM2) on the second river terrace (3.7 m above the normal Idrijca level), in the upper part 60.5 mg Hg/kg appear with continuous decrease of Hg to 20 cm depth, where 47.5 mg/kg Hg were recorded. The average is 53.6 mg/kg.

In the upper 5 cm of Temnikar 3 profile (TEM3), situated 3 m above the river level, at the edge of the river terrace, a high value of 447 mg Hg/kg was determined. In the proceeding deeper samples the contents are about half of that, so the average in the upper 20 cm is 294.8 mg/kg (Fig. 5).

Plants

At the Idrija pri Bači 4 (IDB4) location the average forage sample contains 0.145 mg Hg/kg dry weight, and plantain 0.22 mg Hg/kg. At the higher situated Idrija pri Bači 5 (IDB5) locality 0.24 mg Hg/kg dry weight in average forage and 0.055 mg Hg/kg dry weight in plantain were determined (Fig. 4). The illogical difference between the mercury concentration in these two plant samples taken at the same locality was most probably caused by contamination during sampling. The sampling form contains a remark saying that the collector did not wash his hands after sampling the high mercury sediment at IDB4, and collecting the forage material at IDB5. Since the mercury content in the corresponding plantain (*Plantago lanceolata*) sample is relatively low, we presume that the real Hg content of the forage sample on the same location also contains a relatively low amount of metal. Therefore, the determination of the forage at IDB5 location will not be considered further.

Table 2. Basic statistics for mercury content in stream sediments.

Region	n	mean (mg/kg)	median (mg/kg)	min (mg/kg)	max (mg/kg)	S.D.
Upsteam Idrijca – Zala confluence	16	3	2	0.9	10.2	2.6
Idrija town upstream smelter	24	87	22	5.4	643.1	172.5
Idrija smelter – Spodnja Idrija	40	603	410	32.0	4121.0	720.5
Spodnja Idrija -Soča river	56	213	174	3.2	878.5	176.2
Soča river	24	57	42	16.4	183.0	45.3

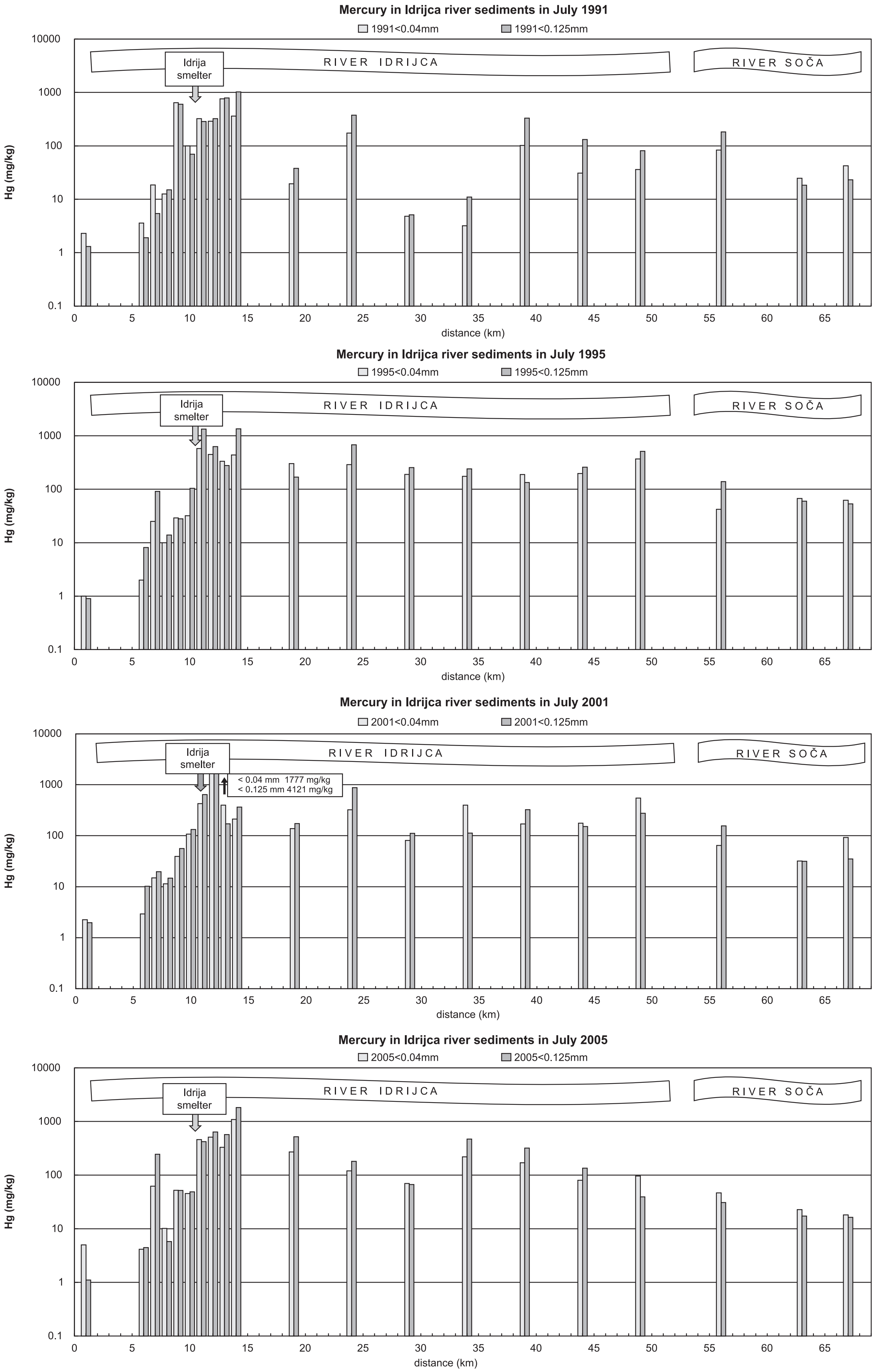

Fig. 2. Mercury in Idrijca river sediments in 1991, 1995, 2001 and 2005.

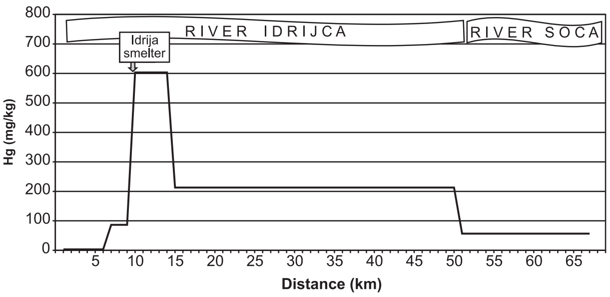

Fig. 3. Average mercury contents in Idrijca and Soča sediments.

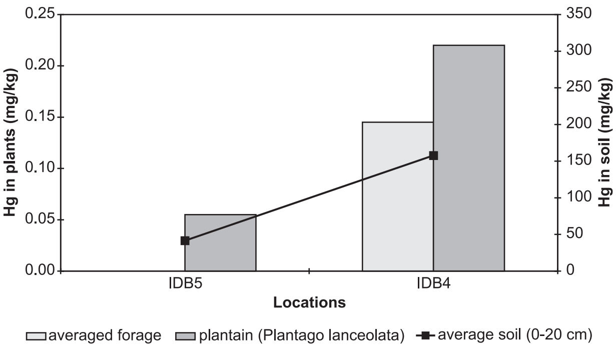

Fig. 4. Mercury in floodplain soils and plants growing at Idrijca pri Bači (IDB).

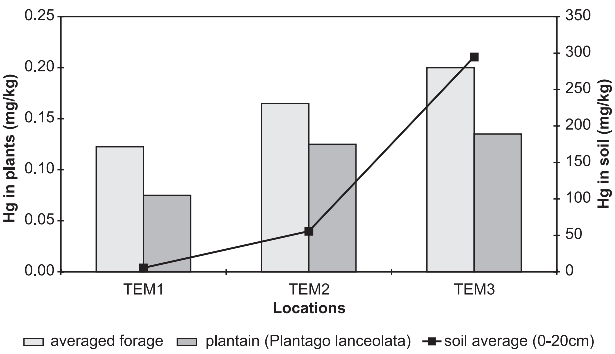

Fig. 5. Mercury in floodplain soils and plants growing at Temnikar (TEM).

The lowest mercury concentration at the Temnikar farm was determined in the samples from the highest terrace (TEM1): in the sample of average forage 0.123 and in the plantain 0.075 mg Hg/kg dry weight (Fig. 5). On the second terrace (TEM2) the contents in the two plant samples are somewhat higher (in average forage 0.165 and in plantain 0.125 mg Hg/kg dry weight). On the first river terrace (TEM3) with extremely high contents in soil/sediment, very high mercury contents also in plants were determined: in forage 0.2 and in plantain 0.135 mg Hg/kg dry weight (Fig. 4). All three locations at the Temnikar farm are characterized by somewhat higher Hg in the forage versus the plantain.

Discussion and Conclusions

Determination of Hg content in the stream and floodplain sediments confirmed that the Idrijca River mercury load is very high. The concentration of mercury in the river sediments varies greatly and does not depend simply on the distance from pollution sources but also on hydrological conditions. The Idrijca is a fast-flowing river which, at higher water levels, partially erodes its own river bed. In this way, a large part of the polluted sediments is swept away and carried downstream towards the Soča River before it is finally accumulated in the sediments of the Adriatic Sea. Another accumulation of mercury-loaded material occurs in the floodplains along the Idrijca and Soča Rivers, which are flooded during high waters. Floodplain soils on the first Idrijca river terrace have somewhat higher total mercury content at the Teminkar 3 (TEM3) location (mean 295 mg/kg, range 231-447) than the corresponding river sediments (mean 217, range 102–331). A similar situation, when the floodplain soils had higher mercury concentrations than the river sediments, was observed by other authors in floodplain soils of the Elbe River [36] and the Warta River [24]. At the location Idrija pri Bači 4 (IDB4) the situation is quite the opposite: floodplain soils with the mean 157 mg/kg (range 130 – 196) have some lower mercury content than the corresponding river sediments (mean 274, range 36–547). This again proves that the mercury contents in sediments of the Idrijca River are not uniformly distributed but are highly dependent upon waterflow and erosion conditions in the catchment area.

The distribution of Hg in plants has recently received attention in most studies because of the Hg pathway into the food chain. Therefore, most information is at present related to the Hg content of plant foodstuffs [37].

In the Almadén mercury mining area the behaviour of mercury in the soil-plant system was studied and the mercury absorption capacity of the different plant species was determined [33]. Special attention was given to the easily available forms of mercury in the analyzed soils and used as the transfer factor for the Hg-availability index that relates to the amount of mercury in a plant with the total amount of mercury in soil and with easily available forms [35].

Samples of the average forage and plantain in the present study contain from 0.055 to 0.220 mg Hg/kg dry weight. The Slovenian regulations [37] set the highest permitted contents of Hg in forage at 0.2 mg/kg. This limit is exceeded in two samples:

– plantain (0.22 mg Hg/kg) on the first river terrace at Idrija near Bača (IDB4 locality),
– average forage (0.20 mg Hg/kg) on the first terrace at the Temnikar farm (TEM3 locality).

Kosta and coauthors [39] and Stegnar [40] determined

Hg in the stems and leaves of various plant species at two locations in Idrija: close to the chimney of the roasting facility, and at Pront, in the outcropping area of native mercury-containing rocks. At the roasting plant they determined from 0.91 to 12.14 mg Hg/kg non-dried sample and at Pront from 0.06 to 0.77 mg Hg/kg non dried sample. They also investigated the plants at Podljubelj near the abandoned mercury mine, where they found from 0.02 to 0.25 mg Hg/kg in non dried material. For comparison, we recalculated our data to non dry material. We obtained contents from 0.026 to 0.05 mg Hg/kg non dried forage material and from 0.012 to 0.041 mg Hg/kg of non dried material of plantain. These values are relatively low compared to the Idrija soil samples from the 1970's. They are of the order of magnitude of values determined in the surroundings of the Podljubelj abandoned mercury mine.

Gnamuš [41] and Gnamuš and coauthors [14] determined mercury contents in samples of mixed deer plant food at several localities in the surroundings of Idrija and in a reference site at the Ljubljana Zoo. Close to the roasting plant chimney he found an average of 52 mg Hg/kg, near the roasting installations an average of 33 mg Hg/kg dry weight, and at three localities in Idrija from 0.5 to 1.3 mg Hg/kg dry weight, at Srednja Kanomlja 0.3 mg Hg/kg and at the Ljubljana Zoo about 0.1 mg Hg/kg dry weight [41]. Moreover, the comparison with the presented contents confirms a comparably low mercury plant intake on the Idrijca river terraces.

Referring to the mercury contents in the plants on unpolluted soil (background) that have been estimated at 0.013 to 0.085 mg Hg/kg dry weight in grasses [42], it can be concluded that the values of mercury on the Idrijca terraces are well above the background level.

Several authors have made an attempt to estimate a permissible limit for Hg in food plants and proposed 0.05 mg Hg/kg non-dried weight. The allowable limit of Hg in plant stuffs should always be calculated on the basis of daily Hg intake by a given population group [37].

Of interest is the comparison of soil contents (upper horizons on river terraces) with those of plants on them (Figs. 4 and 5). The contents of total mercury in soils evidently influence the contents in plants to a certain degree. The comparison of the samples from river terraces at the Temnikar farm shows abrupt increases of soil contents from the first toward the third river terrace. In plants, however, the differences are small, possibly owing to the presence of a large part of mercury in the cinnabar [4], where it is inaccessible to plants. On the first river terrace (TEM3 locality), where the soil mercury contents are no less than 55 times higher than on the third terrace, the average forage sample contains 1.6 times more Hg and plantain sample 1.8 times more Hg than the comparable samples on the third terrace. This observation is consistent with the observations of authors [37] who state that the contents in the plants from mining areas are not closely associated with high contents in soils. They presume the existence of a barrier that prevents the plants to uptake larger amounts of mercury from soils that contain it at very high levels. This is conforming to Kovalevsky's hypothesis of the absorption barrier [43]. The uptake of mercury from soils by plants also depends upon mercury speciation and numerous factors in the soils, e.g. soil type, pH, and amounts of organic substances, ionic exchange capacity and various biological factors such as microbial activity and specific properties of plant species. An additional reason for relatively low uptake by plants can be a strong bonding of mercury with the soil components.

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