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Distribution and partitioning of mercury in a river catchment impacted by former mercury mining activity

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Abstract Mercury distribution and partitioning was studied in the River Idrijca system, draining the area of the former Idrija mercury mine, Slovenia. Mercury dynamics were assessed by speciation analysis of mercury in water and river bed sediment samples during a 2-year study at locations on the River Idrijca and its major tributaries. Simultaneously, the influence of some major physico-chemical parameters that influence the fate of mercury in the aquatic environment was investigated. The distribution of mercury species in the River Idrijca catchment indicated contamination from mine tailings distributed in the town of Idrija and erosion of contaminated soils. The partitioning between dissolved and particulate mercury phases in river water was found to be mostly controlled by the variable content of suspended solids resulting from changing hydrological conditions and complexation with various ligands present in river water, among which dissolved organic carbon (DOC) seems to be the most important. Overall results indicate that mercury is transported downstream from the mining area mainly as finely suspended material including colloids rather than in the dissolved phase. This riverine transport occurs mostly during short, but extreme hydro-meteorological conditions when remobilization of mercury from the river bed sediments occurs. A significant part of the mercury particulate phase in water corresponds to cinnabar particles. During its transport, important Hg transformation mechanisms that increase the risk of mercury uptake by biota take place, evidenced by the increase in the relative contribution of reactive mercury (Hg_R), dissolved gaseous mercury (DGM) and monomethylmercury (MeHg) downstream from the Idrija mine. However, our data revealed relatively low methylation efficiency in this contaminated river system. We attribute this to the site specific physico-chemical conditions responsible for making inorganic mercury unavailable and limiting the capacity of methylating bacteria.

Keywords Idrija · Mercury · River system · Sediment · Speciation · Water

Introduction

Mercury is considered as one of the most potent toxic substances due to the high toxicity of many of its compounds even at very low concentrations, as well because of the easy uptake of its organic forms by biota and its biomagnification in the food chain, especially in fish. Due to the multitude of natural and anthropogenic mercury sources and its complex cycle in atmospheric, terrestrial and aquatic ecosystems, mercury was recognized as a pollutant of global concern requiring global solutions. One of the

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priorities in addressing the global challenge of reducing risks from releases of mercury is the characterization of existing contaminated sites affecting public and environmental health. Abandoned mercury mines are an important category of contaminated sites which can represent strong sources of mercury for many years, even after active mining has been discontinued. Transport of mercury from such local sources can result in its remobilization, making it available for methylation (Ganguli et al. 2000). Hence, secondary sources of toxic forms of mercury can be produced at great distances from the original source. Rivers draining such sites represent the most important transport mechanism and can carry mercury in dissolved and particulate phases for hundreds of kilometres to estuaries and coastal zones (Horvat et al. 1999). Nevertheless, compared to other environmental compartments, mercury in river systems is less studied, especially in and from contaminated sites. Some recent investigations have focused on the transformation processes of mercury in contaminated rivers (Ganguli et al. 2000; Gray et al. 2000; Hissler and Probst 2006; Ping et al. 2008). However, due to the complex distribution of different mercury species (including dissolved, gaseous and particulate phases) biogeochemical cycling of mercury in rivers is still rather poorly understood. The ratio between mercury in different phases found in aquatic environments is significant for several reasons: the physical state as well as the chemical form of mercury affects its behaviour and its environmental fate, and is controlled by the physical and chemical characteristics of water.

In this context, one such mercury contaminated river system, namely the River Idrijca system impacted by former mercury mining activities in Idrija, was chosen as the study site. In over 500 years of the world's second largest Hg mine, over 12 million tons of mercury ore was excavated, from which 100,000 tons of elemental Hg and 7,618 tons of cinnabar were extracted. During smelting of mercury ore an estimated more than 35,000 tons of mercury was lost to the environment, mostly to the atmosphere as Hg^0 vapour and as particulate phase dumped on the banks or into the River Idrijca as smelting residues (Dizdarevič 2001). Hence, Hg mining activities in Idrija have resulted in significant mercury contamination of surrounding local environments. In the last decades many research studies on mercury in this area were carried out. Mercury cycling in different environmental compartments was investigated in the town of Idrija and its surroundings (Biester et al. 2000; Gnamuš et al. 2000; Horvat et al. 2002; Kocman et al. 2004; Kotnik et al. 2005; Gosar et al. 2006; Žižek et al. 2007), as well as its impact on humans and their health (Kobal et al. 2004, 2008). Moreover, an assessment of the extent of mercury contamination including mathematical modelling in the Gulf of Trieste, the basin into which the Idrijca drains mercury contaminated sediments, was performed (Rajar et al. 2000; Faganeli et al. 2003). The recent study involved the use of stable isotopes of mercury in order to track the transport of Hg from the River Idrijca to the Gulf of Trieste (Foucher et al. 2009).

Although significant advances in our understanding of mercury biogeochemistry in this contaminated site have been made in the last decade, a key issue is not well understood yet: How does the environmental speciation of Hg^{2+} control its bioavailability to methylating bacteria? Toward this end, the main objective of this study was to assess the speciation, reactivity and potential bioavailability of inorganic mercury in the contaminated surface waters of the Idrijca catchment, more than a decade after the end of mining operations in the Idrija mercury mine. Accordingly, we describe the results of a comprehensive 2-year study on mercury speciation and partitioning between dissolved and particulate phases in the Idrijca and its tributaries. The effects of changing hydrological and physicochemical conditions on Hg distribution, including complexation with organic and inorganic ligands, the role of suspended particulate matter and river bed sediment remobilization, were also assessed. The data presented here complement a study of the hydrogeochemical and isotopic characteristics of the River Idrijca reported by Kanduč et al. (2008).

Materials and methods

Study area

The area under investigation, the River Idrijca catchment, covers 624 km^2 of the transitional zone between the Alps, the Dinaric Mountains and the Adriatic Sea. The Idrijca draining this area is approximately 60 km long river with a typical torrential character. Along the valley it flows through the town of Idrija where the area of the former mercury mine is located and merges with the River Soča about 40 km downstream of the town of Idrija (Fig. 1). The Idrijca is supplied by waters from karst springs and several tributaries. The climate is predominately temperate with Mediterranean and Alpine influences. Due to these mixed influences and the mountainous relief, the annual precipitation is very high, from 2,400 to 3,200 mm, with peaks in the spring and autumn. Forests cover almost 80% of the surface, the remaining 20% is mostly natural grassland with some pastures, while urban areas represent less than 1%. The whole area is geomorphologically very heterogeneous, with a wide range of altitudes from 170 to more than 2,000 m a.s.l. Abundant precipitation, steep slopes and highly erodible underlying lithology of this tectonically active region induce severe erosion.

The hydrology of the River Idrijca system is relatively complex due to the many tributaries, the karstic terrain and highly complex system of surface and groundwater flows. The Idrijca and its tributaries are run-off fed streams, where discharge is primarily a function of rainfall. There are typically two

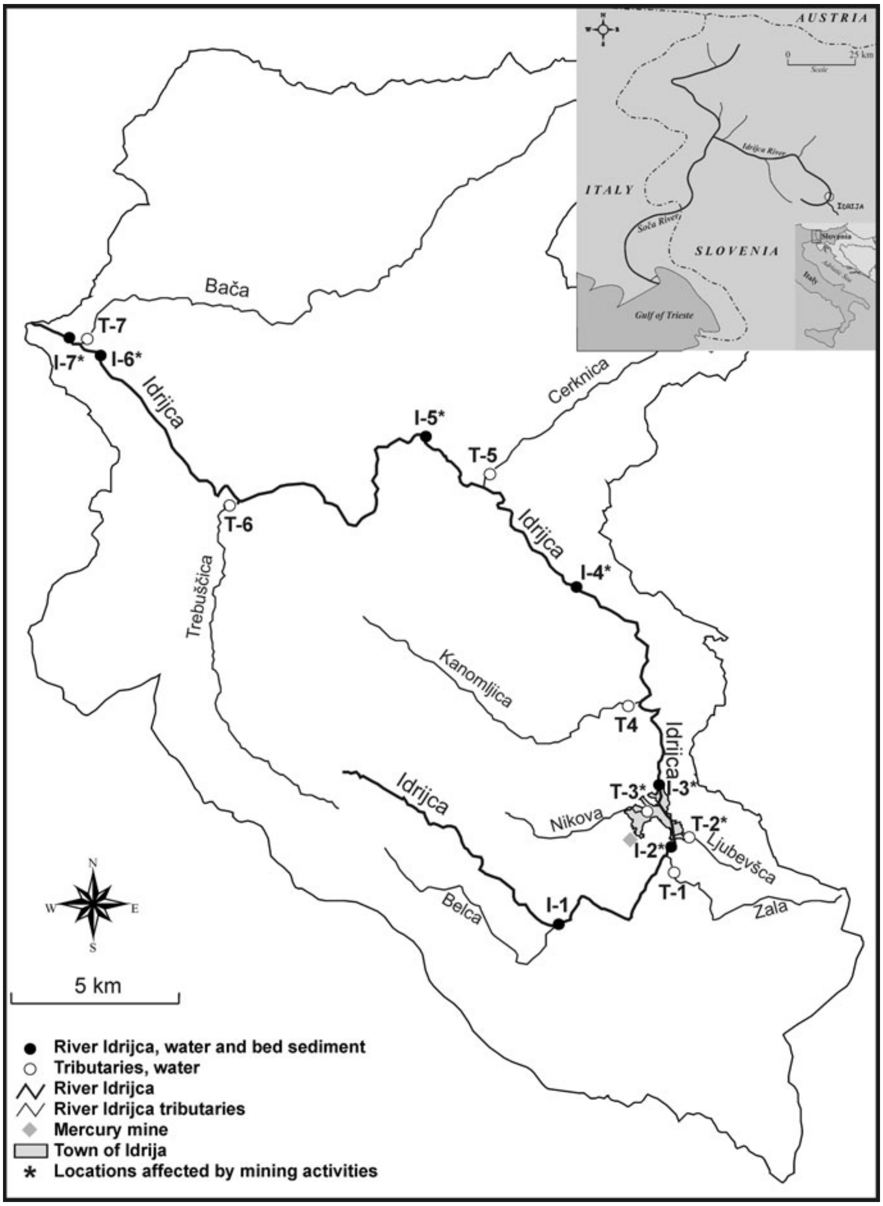

Fig. 1 Geographical location of the River Idrijca catchment and sampling locations (*I* River Idrijca, *T* tributaries)

water-discharge extremes during the year: the longer spring maximum from March to June (due to snowmelt) and the shorter but more intensive autumn maximum in October and November. Characteristic long-term discharge data (1949–2004) from the Environmental Agency of the Republic of Slovenia for the gauging station on the Idrijca at Hotešček (I-6), which is located above the confluence with the River Soča, are as follows: the low long-term discharge varies from 3.4 to 8.5 $m^3 s^{-1}$, the mean long-term discharge varies from 14.3 to 39 $m^3 s^{-1}$, and high long-term discharge varies from 113 to 644 $m^3 s^{-1}$.

Sampling and sample preparation procedures

Surface water sampling locations were selected based on their distance from the Idrija mercury mine area and relationship to the confluences of major and minor streams, at points before and after the confluence. Water samples were obtained from 14 locations altogether, 7 from the River Idrijca (I1-7) and 7 from its major tributaries (T1-7), respectively (Fig. 1). Based on their position, sampling locations can be divided in two groups: locations that were directly affected by the past mining activities (I-2–I-7, T-2 and T-3) and remote locations without direct mine influence (I-1, T-1, T4-7). Sampling was performed during different seasons in autumn-2006 and spring-2007, according to the discharge regimes of the Idrijca and its tributaries. Considering the long-term discharge regime of Idrijca, sampling was performed in low (autumn-2006) and mean (spring-2007) discharges. In January and September 2007, respectively, two additional water samples for mercury analysis were collected at the station of Hotešček (I-6) during higher water discharges to investigate the influence of changed hydrological conditions on mercury speciation and partitioning.

Ultraclean protocols were employed during sampling and sample pre-treatment. Water samples for mercury analysis were collected by hand at the surface of banks of river in 1 l acid-cleaned Teflon© bottles. The samples were stored at 4°C until they were filtered about 4 h later. Water samples were filtered in the laboratory using hydrophilic PVDF 0.45 μm pore size filters (Millipore©). Dissolved mercury species were determined within 24 h of collection.

Sample aliquots collected for major and minor chemical elements analyses were passed through a 0.45 μm nylon filter into polythene/glass bottles and kept refrigerated until analysed. Samples for cationic analyses were acidified with “ultrapure” HNO_3. Samples for dissolved organic carbon (DOC) analyses were acidified and sampled in glass bottles of 30 ml volume. Samples for determining total suspended solids (TSS) and stable carbon isotope analysis of particulate organic carbon ($\delta^{13}C_{POC}$) were collected in 1 l polyethylene bottles and then filtered through a Whatman GF/F (pore size 0.7 μm) glass fibre filter. In our study a 0.7 μm pore size filter was used, which comprises coarse and fine particulate organic material (OM). Filters were ignited before sampling at 480°C with the aim of eliminating organic impurities. Temperature, conductivity, dissolved oxygen (DO), and pH measurements were performed in the field by standardized methods. The precision of DO saturation and conductivity measurements was ±5%. Because pH is sensitive to CO_2 degassing and warming, water samples were collected in large volume, air-tight containers and pH was measured at least twice to verify electrode stability. The field pH was determined on the NBS scale using two buffer calibrations with a reproducibility of ±0.02 pH unit.

River bed sediments were sampled in autumn 2006 at four locations on the River Idrijca (I-1, I-3, I-5 and I-6). A composite stream sediment sample composed of 5–10 sub-samples was taken from each location within a distance of 50 m, stored in a 1 l polyethylene container and transported to the laboratory. After removal of gravel, stones and plant residues, the grain-size distribution was determined by wet sieving and fractions for geochemical analysis were prepared (<0.063 and 0.063–2 mm). Samples were dried at 30°C for 3 days (until constant weight) in the dark, ground and homogenized in an agate mortar, transferred to polypropylene containers and kept until analysis at 4°C in the dark.

Analytical methods

Total mercury in non-filtered (THg) and filtered water (THg_D) was determined by acidification of 100 ml of sample with 0.5 ml suprapur concentrated HCl. The oxidation of all mercury compounds was achieved by adding 1 ml of a solution of BrCl and exposure of the sample to UV light for 3 h. Prior to measurement 60 μl of $NH_2OH{\cdot}HCl$ was added to remove the excess of bromine and chlorine. Oxidized mercury in the sample was then reduced by 10 ml of 5% $SnCl_2$ solution in 0.5 M H_2SO_4 in a reduction cell. Reduced Hg^0 was swept from the sample by N_2, trapped on a gold trap and released by heating to an LDC Milton Roy CV AAS mercury analyzer (Horvat et al. 1987, 1991). The limit of detection was 0.05 ng l^{-1} calculated on the basis of three standard deviations of the reagent blank. Total particulate mercury (THg_P) in water was determined by the subtraction of THg_D from THg.

Total reactive mercury (THg_R) was determined immediately after sampling. An aliquot of 50–100 ml of sample was transferred without addition of any reagent to an acid precleaned reduction vessel containing 5 ml of 5% $SnCl_2$ solution in 0.5 M H_2SO_4 to reduce easily reducible Hg^{2+} to Hg^0. THg_R was then measured in the same way as total mercury. It should be noted, however, that reactive mercury is a method-dependent parameter. Some authors measure it by reduction of acidified water samples, while others use non-acidified samples (Horvat et al. 2003; Kotnik et al. 2007).

Dissolved gaseous mercury (DGM) was determined by transferring 0.1–0.2 l of sample to a glass bubbler immediately after sampling. The sample was purged by a flow of 300–400 ml min^{-1} of N_2. Volatile mercury species were purged for 10 min and collected on a sampling gold trap which was then transferred to a double amalgamation CVAFS analyzer system. Mercury on the sampling gold trap was then released by heating (~500°C) for 1 min in a flow of argon to a permanent gold trap, released again (heating for 1 min, ~500°C) and detected by a CVAFS analyzer (Tekran 2500). The system was calibrated by gas phase mercury (Hg^0) kept at 4°C (Tekran, model 2505 mercury vapour calibration unit). An aliquot of 10–25 μl was transferred with a gas-tight syringe into the measurement train through a septum. The amount of mercury injected was calculated from the Gas Law with a correction for the difference in temperature of the gas phase and the syringe. The detection limit was 0.005 ng l^{-1} based on three standard deviations of the blank. The method is described in more detail in Horvat et al. (2003).

Additionally, dissolved mercury strongly complexed with organic ligands (Hg_D^{org}) was determined as a difference between the total dissolved mercury (THg_D) and the total reactive mercury (THg_R) concentration (Hissler et al. 2006).

Monomethylmercury (MeHg) was determined by transferring the water sample (70 ml) into an acid precleaned Teflon bottle (125 ml) together with 5 ml of concentrated HCl and 30 ml of CH_2Cl_2. MeHgCl was extracted into the organic solvent by shaking overnight and then back-extracted into 40 ml of MilliQ water by evaporation of the CH_2Cl_2. The whole sample was transferred to a Teflon reaction vessel and buffered with acetate buffer to pH 4.9 and 50 μl of 1% $NaBEt_4$ solution was added. After 15 min ethylated MeHg was purged onto a Tenax trap for 15 min with N_2 and thermally desorbed (~200°C) onto an isothermal GC column at 80°C. Hg species were converted into Hg^0 by pyrolitic decomposition (~600°C) under a flow of argon and measured by a cold vapour atomic fluorescence spectrometer (CV AFS) (Brooks Rand) (Horvat et al. 1993, 2003; Liang et al. 1994, 1996). The limit of detection calculated on the basis of three times the standard deviation of the blank was about 0.03 ng l^{-1}. Spike recovery was performed for each batch of analysis and ranged from 80 to 90%. The results were corrected for the recovery factors for each batch. As in the case of total mercury, MeHg was measured in filtered and non-filtered samples. The content of TSS was determined after filtration of a 2 l water sample through a pre-weight 0.45 μm filter, and drying at 110°C and weighing of the filter.

Total mercury concentrations in samples were determined by LDC Milton Roy CV AAS mercury analyzer, after acidic decomposition with nitric, perchloric and sulphuric acid at 250°C. Quality control included reagent blanks to assess contamination and replicate samples to check precision. One certified reference material (CRM) and one reference material (RM) were also used to assess accuracy, using CRM BCR 580, Estuarine sediment, obtained from the Institute for Reference Materials and Measurements (IRMM) and RM IAEA 405, Trace elements and methylmercury in estuarine sediment, obtained from the International Atomic Energy Agency (IAEA). The agreement with certified values was within the certified range. The results obtained were continuously recorded in quality control charts to control the accuracy and precision over the whole period of the study.

Major and minor cations in water samples were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Jobin Yvon Horiba instrument. The precision of the method was ±5%. Analyses of major and minor anions were performed on a Dionex ICS-2500 IC (ion chromatograph) apparatus with an analytical precision of ±2%. DOC concentrations were measured using high-temperature platinum-catalyzed combustion followed by infrared detection of CO_2 (Shimadzu TOC-5000A) with a precision of ±2%. The measurements of cations, anions and DOC were performed at University of Michigan, Ann Arbor, USA.

The stable carbon isotope composition of particulate organic carbon ($\delta^{13}C_{POC}$) was determined with a Europa Scientific 20–20 continuous flow isotope ratio mass spectrometer (IRMS) with ANCA—SL preparation module for solid and liquid samples at the Department of Environmental Sciences at the Jožef Stefan Institute. Samples were first pre-treated with 1 M HCl to remove carbonates. Filters coated with suspended matter were then washed with distilled water before stable isotope analysis. Approximately 1 mg of particulate matter was scraped from the filter for analysis, put into a tin capsules and analysed. NBS 22 (oil) reference material was used to relate the analytical results to the VPDB. Sample reproducibility was ±0.2‰.

Samples of river water suspended matter were also examined to determine their qualitative and quantitative composition using a JEOL JSM 5800 with an electron micro analyser scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDXS) at the Department of Ceramics at the Jožef Stefan Institute. Water samples were first filtered through a Whatman GF/F (pore size 0.7 μm) glass fibre filter. The filters were then dried at 105°C for 24 h and impregnated with graphite before analysis.

For statistical analysis of the data, the Windows statistical software package SPSS (Ver. 12.01; SPSS, Chicago, IL, USA) was used.

Results and discussion

Chemical evolution of river water

The Idrijca and its tributaries are rivers with torrential character, having a high specific discharge, and therefore, a high weathering intensity. The concentration of TSS varied enormously over time and space, from less than 1 to more than 400 mg l^{-1} during flooding (Table 1). The pH of these waters is neutral to basic (7.7–8.8), with dominant dissolved ions of HCO_3^-, Ca^{2+} and Mg^{2+}. Major chemistry data of the River Idrijca are presented in Kanduč et al. (2008). In this study we focus only on iron, sulphate, chloride and DOC data in order to explain the behaviour of different mercury species in riverine system. DOC concentrations ranged from 1.1 to 22 mg l^{-1} during both sampling seasons, which is typical of unpolluted rivers (Shu 1998). Higher DOC concentrations were observed in some tributaries of the Idrijca. This can be related to a higher organic matter input from decomposition in the terrestrial environment, which increases DOC leached from soils, especially during the spring sampling season. As most of the catchment is covered by forest and due to the absence of significant anthropogenic sources, concentrations of chloride and sulphate were low in both the Idrijca and its tributaries. Measured concentrations are in the range typical of unpolluted rivers (Roy et al. 1999). Concentrations of iron in the dissolved phase ranged from 0.5 to 34 μg l^{-1}. In the Idrija region, the main sources of iron are the mine pit water and combusted Hg ore residues. The increased iron content is a consequence of leaching the oxidation products of pyrite and metallic iron present in the ore. The oxidation process was primarily the consequence of combusting ore in the smelter, from where the ignited wastes were returned to the pit as backfilling material or dumped along the river banks.

The isotopic composition of particulate organic carbon ($\delta^{13}C_{POC}$) revealed the terrestrial origin of suspended organic matter in river as a result of degraded soil OM and plant litter, respectively. $\delta^{13}C_{POC}$ values in the Idrijca catchment have an average value of −27.6‰ and are similar to local soils (−26.6‰), indicating that POC is mostly derived from soil OM (Kanduč et al. 2008).

Mercury in river water

Total mercury in river water

The results for mercury speciation in water samples from the River Idrijca and its tributaries determined in autumn-2006 and spring-2007 are presented graphically in Fig. 2. Total mercury concentrations (THg) in

Table 1 Results for Hg speciation and physicochemical characterization of water samples collected from the River Idrijca and its tributaries between 2006 and 2007

Sampling date	Location	THg (ng l^{-1})	THg$_D$ (ng l^{-1})	THg$_P$ (ng l^{-1})	THg$_R$ (ng l^{-1})	DGM (ng l^{-1})	Hg_D^{org} (ng l^{-1})	MeHg$_T$ (ng l^{-1})	MeHg$_D$ (ng l^{-1})	T (°C)	Condut. (μS/cm)	pH	TSS (mg l^{-1})	DOC (mg l^{-1})	Cl (mg l^{-1})	SO$_4$ (mg l^{-1})	Fe (μg l^{-1})	$\delta^{13}C_{POC}$ (‰)
17.11.06	I-1	0.81	0.30	0.51	0.28	0.15	0.02	–	–	8.8	338	8.17	0.78	7.92	1.29	6.36	3.12	−26.7
	I-2[a]	1.68	0.96	0.72	0.50	0.18	0.46	–	–	8.0	327	7.96	0.18	2.94	2.50	6.20	0.52	−25.7
	I-3[a]	54.8	31.7	23.0	10.7	1.73	21.0	–	–	6.5	364	7.73	2.70	6.20	2.50	7.28	2.12	–
	I-4[a]	47.6	34.6	12.9	11.6	2.69	23.0	–	–	8.5	375	8.34	1.85	1.12	2.83	13.1	4.12	−27.9
	I-5[a]	28.8	24.0	4.77	7.59	1.35	16.5	–	–	9.0	409	8.06	1.10	–	4.03	33.6	3.82	−27.8
	I-6[a]	10.8	8.68	2.12	4.17	1.16	4.51	–	–	9.5	410	8.30	1.70	2.07	2.78	36.0	33.9	–
	I-7[a]	11.3	8.68	2.65	2.38	1.09	6.30	–	–	9.6	412	8.26	2.10	5.87	3.64	36.4	13.7	–
	T-2[a]	26.0	19.5	6.47	9.82	1.62	9.70	–	–	8.3	465	8.29	0.75	2.82	11.0	16.5	6.32	−27.6
	T-3[a]	49.7	41.8	7.91	11.6	1.56	30.2	–	–	8.4	434	8.23	1.52	3.64	6.74	13.2	4.32	−27.5
	T-4	41.1	3.69	37.4	1.07	0.36	2.62	–	–	8.2	378	8.34	0.82	18.8	2.15	20.5	10.8	−26.7
	T-5	4.60	1.26	3.34	0.15	0.15	1.11	–	–	9.5	378	8.19	3.85	4.38	8.19	27.8	0.82	−26.6
	T-6	0.34	0.20	0.14	–	–	–	–	–	8.6	348	7.77	0.15	6.36	1.05	6.72	4.02	−27.3
	T-7	0.20	0.05	0.15	–	–	–	–	–	9.2	282	8.27	0.56	13.5	1.51	9.51	3.12	−26.8
23.01.07	I-6	26.0	10.7	15.3	3.05	–	7.65	–	–	–	–	–	23.1	–	–	–	–	–
17.05.07	I-1	0.76	0.26	0.49	0.20	0.18	0.06	0.13	0.10	9.0	333	8.43	1.24	4.83	1.01	3.69	0.60	−27.8
	I-2[a]	0.69	0.25	0.43	0.15	0.13	0.10	0.14	0.12	7.3	353	7.92	0.23	4.87	2.45	4.34	0.60	−28.0
	I-3[a]	283	143	140	33.1	23.7	110	0.27	0.24	11	367	8.43	4.31	7.98	3.60	10.8	5.70	−26.9
	I-4[a]	44.2	19.7	24.5	5.23	3.24	14.5	0.53	0.27	11	485	8.44	2.45	13.3	3.66	68.9	12.5	−28.1
	I-5[a]	32.3	16.7	15.6	2.96	2.16	13.8	0.52	0.20	12	416	8.29	1.75	3.90	4.06	34.7	7.50	−27.1
	I-6[a]	22.3	7.67	14.7	1.72	1.60	5.95	–	–	13	383	8.82	4.00	18.0	3.17	14.8	2.60	−27.3
	I-7[a]	14.3	9.38	4.95	2.00	1.60	7.38	0.20	0.20	13	356	8.77	3.58	5.09	2.55	15.1	3.20	−28.1
	T-1	32.8	3.51	29.3	1.90	0.94	1.61	–	–	11	420	8.09	1.30	2.85	5.29	7.14	2.60	−31.3
	T-2[a]	12.0	7.69	4.33	2.96	1.48	4.73	–	–	10	444	8.54	1.17	8.39	10.3	9.94	4.30	−27.6
	T-3[a]	49.8	27.0	22.9	5.16	1.49	21.8	–	–	10	418	8.67	2.52	4.24	4.52	9.92	5.70	−27.5
	T-4	3.53	1.09	2.44	0.52	0.70	0.57	–	–	11	368	8.29	0.70	3.12	1.90	14.5	1.80	−26.7
	T-5	3.87	0.25	3.62	0.20	0.19	0.05	–	–	12	349	8.35	6.59	2.35	4.35	18.2	14.1	−26.6
	T-6	0.43	0.21	0.22	–	–	–	–	–	12	181	8.37	0.20	1.56	1.01	4.87	1.90	−27.3
	T-7	0.23	0.14	0.10	–	–	–	–	–	12	282	8.40	1.04	6.32	1.31	7.49	1.60	−26.8
28.05.07	I-2[a]	3.49	0.91	2.58	0.62	0.37	0.30	–	–	–	–	–	0.30	22.0	2.78	4.42	0.50	–
	I-3[a]	125	69.8	55.1	13.1	5.77	56.7	–	–	–	–	–	3.90	3.98	2.82	7.75	3.10	–
	I-5[a]	98.6	34.7	63.9	5.55	2.25	29.1	–	–	–	–	–	6.20	15.5	3.01	26.2	–	–
	I-6[a]	51.7	9.97	41.7	4.10	1.91	5.87	–	–	–	–	–	10.3	16.8	2.51	38.1	–	–
19.09.07	I-6[a]	708	6.75	702	3.78	1.10	2.97	–	–	–	–	–	433	–	–	–	–	–

I Idrijca River

T tributaries

[a] Locations affected by mining activities

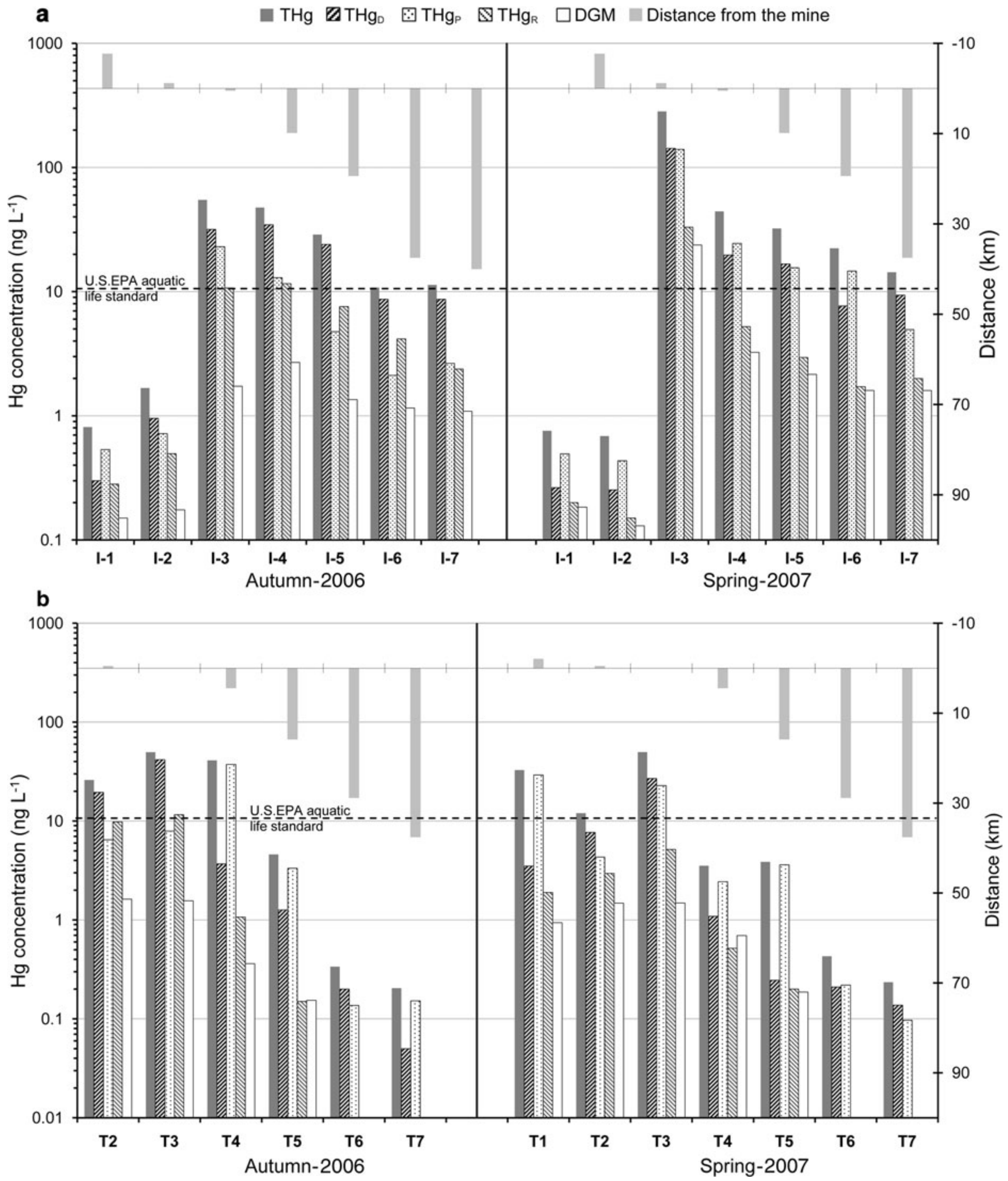

Fig. 2 Distribution of inorganic mercury species in the River Idrijca (**a**) and its tributaries (**b**) versus distance from the Idrija mine in autumn-2006 and spring-2007. Negative distances are those upstream of the Idrija mine. The U.S. Environmental Protection Agency (U.S.EPA 1992) Hg standard for protection against adverse chronic effects on aquatic life (12 ng l^{-1}) is shown for reference

the Idrijca increased over 300-fold just downstream of the mining and metallurgical area (I-3) and remained elevated by a factor of more than 10 until the confluence with the River Soča (I-7), compared to values obtained in the upper part of the Idrijca (I1-2). The highest THg concentrations were observed in the town of Idrija (I-3) at the site where water draining from the mine is collected and released into the River Idrijca (up to 283 ng l^{-1}). This is also the reason for the large difference in mercury concentrations observed at location I-3 in both sampling campaigns. In autumn-2006 at this location the sample was taken just before the mine drainage release, while in spring-2007 the sample was taken after the release. Afterwards, mercury concentrations gradually decreased downstream reaching 10–15 ng l^{-1} of THg just before the confluence with the River Soča (I-7). This is still high and close to 12 ng l^{-1}, a concentration that according to the U.S.EPA (1992) may result in chronic effects to aquatic life. These data are comparable to those measured in 1998 and 2000 (Hines et al. 2000; Bonzongo et al. 2002; Horvat et al. 2002), indicating that even more than a decade after the closing of the Idrija mine, the Idrijca continues to supply mercury to the downstream aquatic systems. The distribution of mercury in the tributaries of the River Idrijca indicates contamination from mine tailings distributed in the town of Idrija and erosion of contaminated soils which are a result of atmospheric deposition over the centuries of Hg ore processing. During both sampling campaigns the highest concentrations were measured in the tributary Nikova (T-3), a stream draining the town of Idrija and the Pront hill where native mercury-bearing carboniferous clastic rocks can be found. There was a clear decrease of Hg concentrations observed with increasing distance of the tributaries drainage area from the town of Idrija (Fig. 2). Hence, the lowest THg concentrations (<0.5 ng l^{-1}) were measured in the samples collected at locations T6 and T7. Hg concentrations at these two remote sites are comparable to concentrations measured in water from non-polluted sites (Peckenham et al. 2003).

Dissolved and particulate mercury phases in river water

In order to understand inorganic mercury distribution in river water according to the different hydrological and physico-chemical conditions, we divided it into its three most important forms: total reactive mercury ($\mathrm{THg_R}$), dissolved mercury strongly complexed to organic matter ($\mathrm{Hg_D^{org}}$) and total particulate mercury ($\mathrm{THg_P}$). We obtained the $\mathrm{Hg_D^{org}}$ concentration by difference between the total dissolved mercury concentration ($\mathrm{THg_D}$) and the total reactive mercury concentration ($\mathrm{THg_R}$). These three mercury forms were found to be distributed differently at locations that were directly affected by the past mining activities (I-2–I-7, T-2 and T-3) compared to more remote locations (Fig. 3). During the low water period (autumn-2006), at locations under the direct influence of the mine, the three Hg forms were distributed rather evenly. The relatively high share of dissolved Hg forms at these sites is attributed to mercury leaching from ore residues and calcines, desorption from the particulate phase and complexation with different organic and inorganic ligands present in water. During the higher water period (spring-2007) at these sites water was more enriched in $\mathrm{THg_P}$ (>50% of total mercury measured in water), mostly due to resuspension of contaminated riverbed sediments. On the other hand, during both seasons, at locations without direct mine influence (I-1, T-1, T4-7) the majority of mercury (>60%) was associated with the particulate phase. These results suggest that at those sites where atmospheric deposition is the dominant source of mercury, mercury is firmly bound

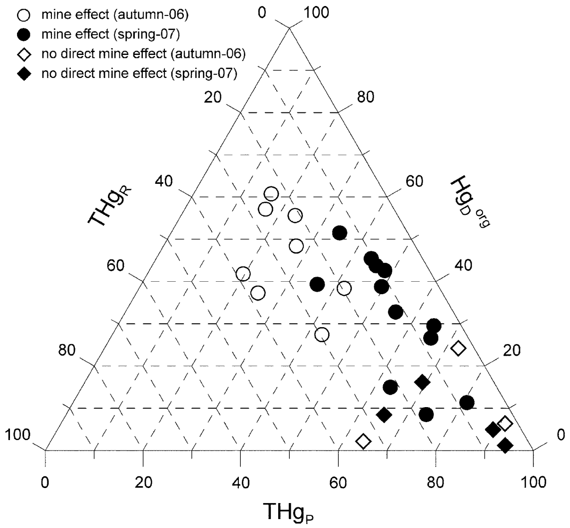

Fig. 3 Distribution of three mercury forms in waters of the River Idrijca catchment. $\mathrm{THg_P}$: total particulate mercury; $\mathrm{THg_R}$: total reactive mercury; $\mathrm{Hg_D^{org}}$: dissolved mercury strongly associated with organic ligands

in/on soils and is transported to local streams mostly in the particulate phase.

Suspended particulate matter (SPM) provides a large surface area for chemical reactions that are important for mercury cycling. $\mathrm{THg_P}$ in river water is mostly the result of weathering and contaminated soil erosion processes and is known to have a strong affinity for adsorption on coatings of Fe- and Al-(hydr)oxides (Kim et al. 2004) or to bind to OM on suspended inorganic constituents. The results obtained by the SEM/EDXS microscopy of the riverine suspended material support this assumption. As it can be seen in Fig. 4, a relatively low content of suspended matter is observed, with material of organic origin dominating (dark coloured parts). The inorganic component is composed of terrigenous components like silica, alumosilicate minerals (clay minerals), Fe- and Al- oxides, hydroxides and carbonates as remnants of carbonate and clastic rock weathering products in the Idrijca catchment. Moreover, the $\delta^{13}\mathrm{C_{POC}}$ values (Table 1) revealed the dominance of soils in the suspended matter where humic substances as the major organic constituents of soil are most likely present. Humic substances are known to have a large ion-exchange capacity and have an affinity to strongly bind mercury. However, at mercury mine polluted sites such as the Idrija region, a significant part of the mercury particulate phase in water can be due to cinnabar particles present. Results of the SEM/EDXS microscopy of suspended matter confirmed this assumption. In Fig. 4 a grain of a cinnabar on the filter from location I-7 on the River Idrijca can be seen. Although almost 40 km downstream from the mercury mine, erosion of soils and the resuspension of riverbed sediments containing cinnabar obviously still effects the composition and partitioning of mercury in water.

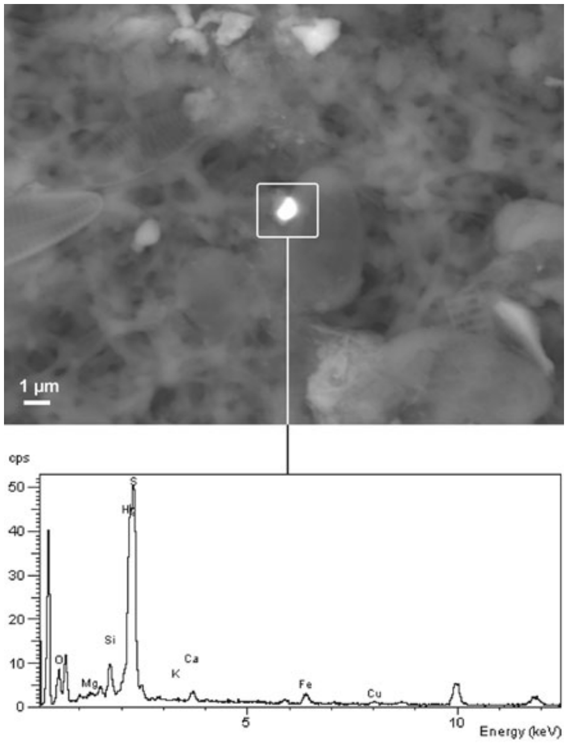

Fig. 4 SEM/EDXS microscopy of suspended matter in the River Idrijca from location I-6 (Hotešček). The *marked grain* displays a qualitative spectrum (belonging *graph*) of a cinnabar particle

By definition, $\mathrm{Hg_D^{org}}$ chemical forms are strongly associated with dissolved organic ligands, through covalent binding to thiol-type functional groups (Ravichandran 2004). Consistent with this, an increasing trend was observed, although not statistically significant, between the relative contribution of $\mathrm{Hg_D^{org}}$ to the total dissolved mercury fraction ($\mathrm{THg_D}$) and to DOC. However, it should be noted that the operationally defined dissolved mercury fraction measured in this study (<0.45 μm) can contain a substantial portion of the unfiltered mercury concentration. Using the nominal 0.45 μm cut-off to distinguish the particulate from the dissolved phase can overestimate the truly dissolved pool. The nominal filtrate may contain colloids in addition to "truly dissolved" species and bias the results (Babiarz et al. 2000). A positive relationship between $\mathrm{Hg_D^{org}}$ and mercury in the particulate phase ($\mathrm{THg_P}$) was observed, which suggests that measured dissolved mercury is partly stabilized in solution by complexation and/or sorption on colloidal humic-hydrous oxides. This assumption is further supported by the increase of the percentage of $\mathrm{Hg_D^{org}}$ (relative to the total dissolved Hg phase) with the increase of iron, observed in water samples taken in spring-2007, which indicates sorption of mercury by Fe-hydroxides as a result of their strong binding capacity and affinity for trace metals such as mercury.

Reactive mercury in river water

Reactive mercury is a methodologically defined parameter, but it can be useful in interpretation of data. The methods used to measure reactive mercury are not standardized (or agreed), and therefore variations may occur in various studies due to differences in the protocols employed. In this study, reactive mercury is defined as all mercury species that are readily available for reduction with $SnCl_2$ solution and volatile mercury species. The measured total reactive mercury (THg_R), therefore, represents the portion of mercury that consists of DGM and fraction weakly bound to inorganic (e.g. $Hg(OH)_2$, $HgCl_2$) and organic complexes (Horvat et al. 2002). The results discussed here refer to reactive mercury (Hg_R) corrected for the presence of DGM by subtracting its value from the total reactive mercury (THg_R) measured by the analytical procedure described. Hg_R concentrations increased from <0.05 ng l^{-1} in the River Idrijca upstream of the mining area and in the remote tributaries to a maximum of 10 ng l^{-1} within the town of Idrija. In the River Idrijca, Hg_R then decreased downstream reaching concentrations around 1 ng l^{-1} just before the outflow into the River Soča. The concentrations of Hg_R are in a good correlation with the concentrations of THg_D ($r = 0.71$, $P < 0.001$), although the concentrations of Hg_R are lower on average by about a factor of 10. This may suggest that a part of dissolved mercury is responsible for its further transformations in water. The somewhat weaker but still significant correlation ($r = 0.40$, $P < 0.05$) between Hg_R and THg_P indicates the weaker reactivity of mercury bound to particles. Moreover, significantly higher Hg_R concentrations were measured during low water discharges in both the Idrijca and its tributaries, suggesting that Hg_R is formed within the water column under such conditions. Consistent with the assumption of the potential bioavailability of Hg_R under such environmental conditions, an enhanced uptake of mercury by organisms, resulting in higher MeHg concentrations in the abiotic and biotic compartments of the River Idrijca, has already been observed (Žižek et al. 2007).

Dissolved gaseous mercury in river water

Dissolved gaseous mercury concentrations measured in this study represent all volatile mercury species in water samples. As dimethyl mercury in surface waters is usually under the limit of detection, it is assumed that the values for DGM represent only dissolved Hg^0. Knowledge of DGM concentrations is important, as the formation and volatilization of DGM is an important mechanism by which freshwaters may naturally reduce their mercury burden. DGM concentrations in the River Idrijca vary from concentrations below 0.15 ng l^{-1} in the upstream parts of the catchment up to 23.7 ng l^{-1} near the mine drainage, while in the tributaries DGM concentrations are below 1.62 ng l^{-1}. DGM concentrations measured upstream from the mine and in the Idrijca tributaries are comparable with those reported for mercury impacted rivers (O'Driscoll et al. 2003) and estuaries (Cardona-Marek et al. 2007), while DGM concentrations in the River Idrijca are up to 20 fold higher. In the Idrija mercury mine region, a large part of DGM can originate from native mercury bearing rocks, mine drainage and mine residues. For example, one of the highest DGM concentrations in the tributaries was measured in the Nikova stream (location T-3) which drains the Pront hill area, where the outcropping bedrocks contain native mercury. On the other hand, DGM in surface water may also result from the reduction of divalent mercury either photolytically and/or microbiologically. DGM may also be oxidized to divalent mercury in surface waters, particularly in the presence of chloride ions (Yamamoto 1996), which would result in an increase of Hg_R. In the Idrijca downstream from the mine, a general decrease was observed in the percentage of mercury as Hg_R (relative to THg_D) with an increase of DGM concentration, although this was not statistically significant. Assuming this relationship, it can be postulated that reduction of divalent mercury prevails in this specific well aerated aquatic environment.

Methyl mercury in river water

The conversion of inorganic mercury to methylmercury (MeHg) is important because its greater toxicity and especially its bioavailability. The net amount of methylmercury produced in the aquatic environment, however, is dependent on concomitant processes of methylation and demethylation. Therefore, measured methylmercury concentration alone does not reveal much information about these simultaneous processes. Toward this end, here results for MeHg measured in water samples of the Idrijca at only six locations during the spring 2007 sampling campaign are presented in order to investigate its trend in spatial distribution and to make comparison with previously published results obtained in the last decade from the same sites. Usually, a great deal of attention is paid to factors governing the production of MeHg from the inorganic mercury species. In the absence of data on rates of mercury methylation and MeHg demethylation, observational field data were used to examine the fate of Hg and assess the potential effects on environmental levels and transport of MeHg.

In a river system with a known point source of mercury contamination such as Idrijca, one should expect downstream exponential decrease in mercury concentrations away from the source. This was the case for the inorganic Hg forms, while MeHg concentrations in both filtered ($MeHg_D$) and non-filtered samples ($MeHg_T$) revealed a slightly different distribution. Compared to both upstream locations, concentrations of MeHg in the Idrijca increased by a factor of 2–4 below the mine and reached their maximum ca. 10 km downstream of the mine at location I-4 (0.53 ng l^{-1}) and therefore did not coincide with the highest observed THg levels (Fig. 5). Concentrations then decreased downstream and reached 0.21 ng l^{-1} at location I-7. The MeHg/Hg ratio which is considered to be a useful estimate of the net production of MeHg normalized to the total mercury concentration (Gilmour et al. 1998) varied widely among sites. Upstream of the mine, $MeHg_T$ was nearly 20% of THg while it remained less than 1.5% along the Idrijca downstream from the mine, indicating relatively lower methylation efficiency at downstream locations. Dissolved methylmercury ($MeHg_D$) accounted from 40 up to 98% of total methylmercury ($MeHg_T$). The percentage of $MeHg_D$ was the lowest at the two most MeHg abundant sites (I-4 and I-5) where suspended particulate matter accounted for a major fraction of MeHg. However, the distribution coefficient (K_d) for MeHg was in the range of 10^3–10^5, which is significantly lower compared to inorganic mercury (10^5–10^7) and indicates weaker binding of MeHg to suspended solids.

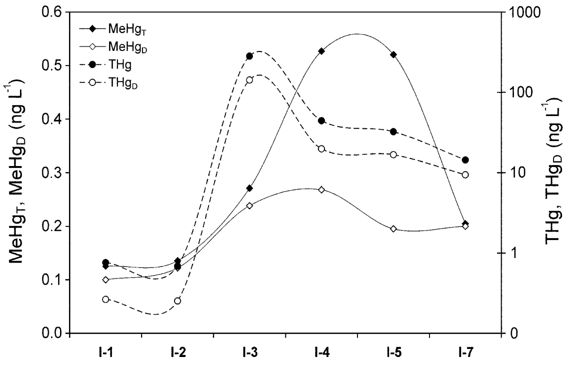

Fig. 5 $MeHg_T$ and $MeHg_D$ concentrations and comparison with THg and THg_D concentrations in the River Idrijca

These trends observed are in a good agreement with the work done since 1998 in the River Idrijca (Hines et al. 2000; Bonzongo et al. 2002; Horvat et al. 2002; Žižek et al. 2007) and clearly show that although the production of mercury at the Idrija mercury mine stopped in 1994, the area remains a permanent source of mercury for the riverine system. There, important transformation mechanisms that convert inorganic mercury to MeHg take place and in this way make it biologically available. However, considering very high levels of inorganic mercury in this river system, relatively low MeHg abundance is observed. This could be explained by site-specific conditions that drive microbial mercury transformations. Idrijca and its tributaries are typical HCO_3^-–Ca^{2+}–Mg^{2+} rivers (Kanduč et al. 2008), as a result of mineral components leached from carbonate rocks in the catchment. In addition, these waters are very well aerated and have neutral to alkaline pH. Such conditions may be responsible for making inorganic mercury unavailable and limiting the capacity of methylating bacteria (Morel et al. 1998). Methylmercury transformation will only take place if divalent mercury is in a form available for uptake by microorganisms, which in turn, depends on the nature of inorganic mercury complexes. As shown by the results of inorganic mercury analysis, in Idrijca majority of mercury is associated with finely suspended particulate matter including colloids rather than with the dissolved phase. Consequently, mercury firmly bound in the particulate phase may be less bioavailable than in the dissolved phase. In support of this assumption, a general increase in MeHg levels with the relative increase of Hg_R, fraction of weakly bound mercury which is readily available for reactions, was observed. On the other hand, downstream from the mine, the dissolved fraction of MeHg showed a general increase with increasing DOC concentrations (Fig. 6a). In microbial methylation, complexation with DOC generally limits the amount of inorganic mercury available for uptake by methylating bacteria because DOC molecules are generally too large to cross the cell membranes of the bacteria (Ullrich et al. 2001). However, in sulphate-limited

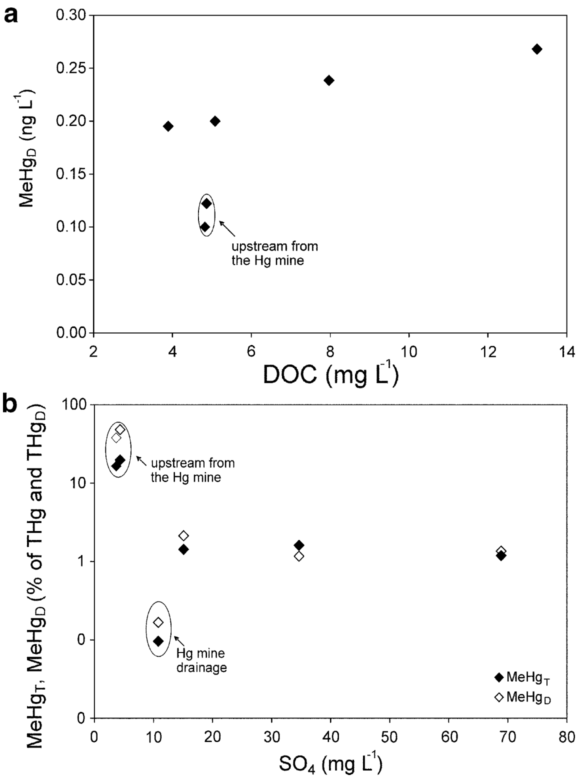

Fig. 6 Relationship between (**a**) MeHg$_D$ and DOC and (**b**) MeHg/THg ratios and sulphate concentrations in the River Idrijca

environments (such as the River Idrijca) where microbes may utilize organic matter as an energy source, DOC may have a stimulating effect on microbial growth and thus enhance methylation rates in the water column and sediments (Ravichandran 2004). Moreover, it was shown recently by Dong et al. (2010) that in contaminated ecosystem, natural dissolved organic matter controls the mercury speciation by forming strong complexes with ionic Hg^{2+} and MeHg, thereby influencing biological uptake and methylation of Hg in aquatic environments. This applies also to Idrijca, where calculation of carbon mass balance revealed degradation of organic matter as one of the most important biogeochemical processes in the catchment (Kanduč et al. 2008). Furthermore, as observed before by Bonzongo et al. (2002), investigation of the relationship between the percentage of MeHg and sulphate concentrations revealed that with the exception of the most Hg polluted site in Idrija, the percentage of MeHg decreases with increasing sulphate concentration (Fig. 6b). This trend supports the assumption of sulphate-reducing bacteria (SRB) as principal mercury methylators. On the other hand, in oxic conditions and environments with high mercury concentrations such as in the Idrijca, reductive demethylation can be favoured (Barkay et al. 2005). In such systems, mercury-resistant bacteria that produce organomercurial lyase enzymes to degrade MeHg could be present. In fact, Hines et al. (2000) detected *merA* genes throughout the freshwater system downstream of the Idrija mine as well as *merB* genes just downstream the site where water draining from the mine is released into the river (location I-3). This response of bacteria to mercury stress can then further explain the relatively low MeHg concentrations in the Idrijca.

Mercury partitioning between dissolved and particulate phases in river water

When the distance between polluted sites in the town of Idrija and downstream sampling sites increases, the possibility of exchange between the dissolved and particulate phases increases. This is most obvious in the case of reactive (Hg$_R$) and DGM for which relative percentages increase downstream from the Idrija mine. The partitioning is known to be controlled by the physico-chemical conditions of the river water such as pH, redox conditions, temperature and complexation with a variety of organic and inorganic ligands (Boszke et al. 2002). In this study, the influence of TSS, water pH, DOC and inorganic (Cl) ligands on the variations in distribution coefficient (K_d) was investigated (Fig. 7).

Log K_d values ranged from 4.6 to 7.2, showing that the bulk of mercury is associated with the particulate phase. It must be noted that in calculation of the distribution coefficient, dissolved mercury was corrected for DGM. The K_d values tend to decrease as concentrations of suspended particulate matter increase (Fig. 7a), particularly in the parts of the catchment that were not directly influenced by the mercury mine. At these sites K_d seems to be controlled by dissolved mercury phases, while at sites directly influenced by the mine, K_d is more affected by particulate bound mercury. On the other hand, the evolution of K_d observed may also reflect the particle concentration effect, according to which the concentration of colloids in the fraction passing through the filter increases as particulate matter

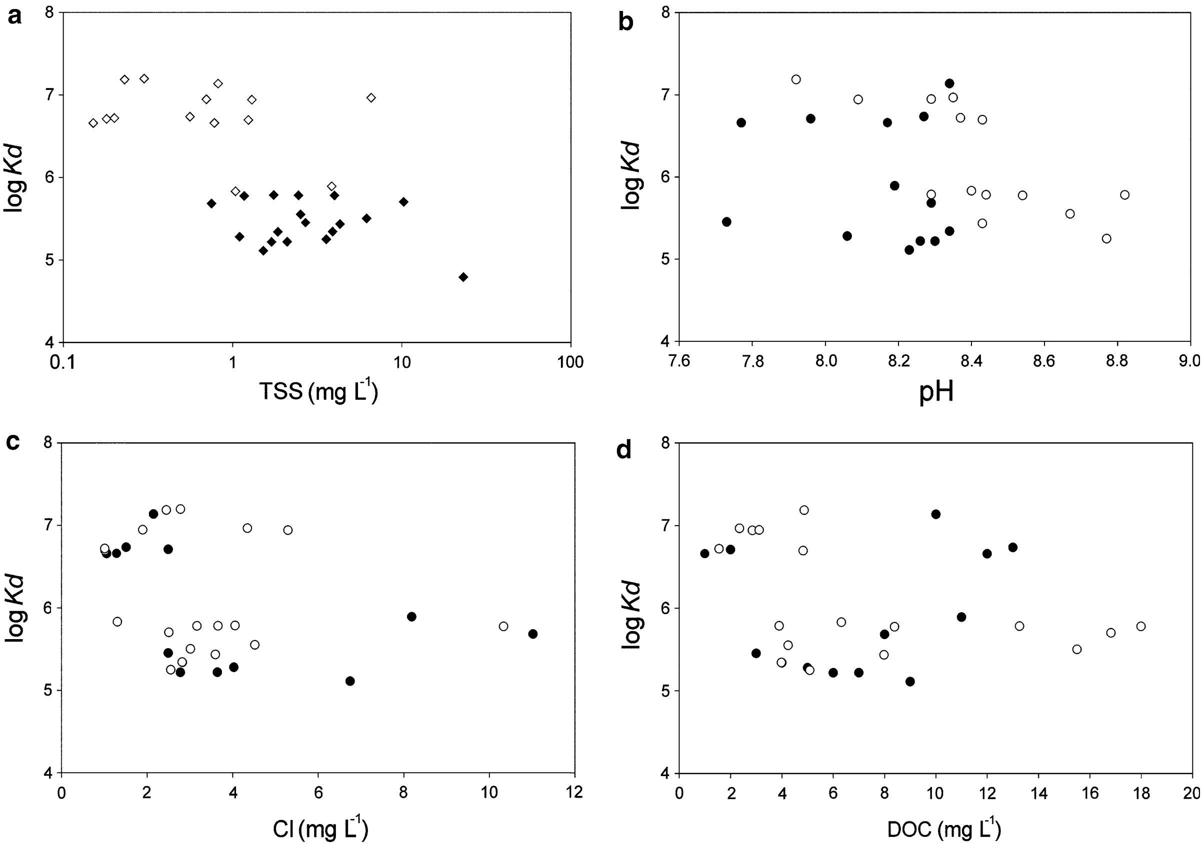

Fig. 7 Relationships between the mercury partitioning coefficient (log K_d) and **a** total suspended sediment concentration (TSS), **b** pH, **c** chloride concentration and **d** DOC concentration in waters from the Idrijca catchment. *Open squares* represent the samples collected at locations that were not under direct mine influence and *black squares* the samples collected at locations directly affected by the mine downstream from the plant. *Open circles* correspond to low water levels (autumn-2006) and *black circles* to higher water levels (spring-2007)

increases (Berzas Nevado et al. 2009). However, the pattern observed is consistent with previous studies in the River Idrijca (Hines et al. 2000; Bonzongo et al. 2002; Horvat et al. 2002) and other studies performed in stream waters impacted by mercury pollution (Gray et al. 2000; Hissler and Probst 2006). Moreover, in the Idrijca catchment, the partitioning is also influenced by the pH of the water. The pH of water determines the solubility and biological availability of chemical constituents in water including mercury. In general, an increase of pH leads to cation adsorption and anion desorption that increases the quantity of inorganic and organic ligands in solution. In the presence of a wide range of anionic ligands, Hg^{2+} can produce charged and neutral chemical compounds, the nature of which would then control mercury bioavailability (Bonzongo et al. 2002). K_d tends to decrease when pH increases, particularly for pH values higher than 8 (Fig. 7b). This trend is more evident during higher water levels (spring-2007), when the pH is higher due to weathering and erosion of the carbonate-rich bedrock. Under such conditions, complexation of dissolved mercury by organic and inorganic ligands is increased. The relative importance of each ligand for mercury complexation depends on the concentration of mercury and the ligand, and the binding strength for the Hg–ligand complex (Ravichandran 2004). Among inorganic ligands, hydroxide, chloride, and sulfide are considered to be the most important in controlling the speciation of mercury in aquatic environments (Schuster 1991; Ravichandran 2004). Among the inorganic anions, Hg^{2+} forms the strongest covalent compounds with chloride ions. Hg^{2+} can also hydrolyse to $Hg(OH)_2$. Well-aerated waters containing traces of stable organic ligands speciate mercury between different chloro- and hydroxy-mercury complexes as a function of pH and Cl concentrations (Boszke et al. 2002). A decreasing trend in Hg adsorption on aqueous particulates was observed with increasing Cl concentration (Fig. 7c). However, at pH conditions between 7.5 and 8.5 and the chloride concentration range observed (<12 mg l^{-1}), Cl is unlikely to compete with hydroxide. Mercury–chloride complexes are thought to be important at low pH and/or high chloride concentrations. Moreover, the stability constants for Hg-chloride and Hg–hydroxide complexes reported in the literature are much lower than those for Hg–DOC complexes (Lamborg et al. 2003; Ravichandran 2004). Therefore, DOC would most probably constitute the main ligand for Hg complexation, especially during higher water discharges due to the increased input of terrestrial organic matter (Fig. 7d). Similar trends were observed in the Thur River, impacted by Hg releases from the chlor-alkali industry (Hissler and Probst 2006).

Hydrological conditions and Hg speciation/partitioning in river water

During different hydrological conditions the observed differences in mercury concentration are mostly due to variation of mercury associated with the particulate phase (THg_P). For example, at location I-6, variation in the relative contribution of THg_P from less than 20 up to more than 99% was observed. On the other hand, concentrations of other inorganic Hg forms at this site remained more constant and were within the same order of magnitude (RSD up to 30%). In the Idrijca catchment, the most important hydrological events are rainstorms, which can produce extreme discharges of short duration. During such events, mercury is mobilised from contaminated soils in the catchment in to the river system in both the particulate and dissolved phase. Consequently, under such conditions the total amount of both mercury phases transported downstream is increasing. However, at higher discharges also resuspension of the river bed sediments occurs, resulting in the significant increase of mercury associated with the particulate phase observed. As there is no correlation between the mercury bound to particulates and other mercury forms, the differences in THg_D, Hg_R and DGM observed under different hydrological conditions are most probably related to the variable physico-chemical conditions discussed in the previous section. These results indicate the importance of resuspension of Hg from the river bed sediment and transport of Hg-contaminated particles in the mass flow and mass budget of mercury on the catchment scale. In an average hydrological year, more than 85% of the annual suspended sediment transport along the Idrijca is caused by a few flood waves regularly occurring during autumn due to rainfall and during spring due to snow melting (Žagar et al. 2006). During these events, suspended matter with elevated mercury content is partly deposited on the floodplains. Consequently, the floodplains along the Idrijca are found to be strongly enriched with mercury and are some of the most contaminated sites in the catchment (Žibret and Gosar 2006).

Due to the changing hydrological conditions, the longitudinal profiles of the evolution of K_d between different sampling locations were quite different during different hydrological periods (Fig. 8). During low water discharge, K_d progressively decreased from upstream to downstream, whereas during moderate and high water discharges, K_d increased after the town of Idrija. Very high and constant K_d values upstream from the mine (location I-2) during different hydrological conditions indicate the strong affinity of Hg for particulate phase at this site. During low flow, the decrease in K_d downstream from the mine is attributed to the increase of dissolved Hg due to Hg complexation by dissolved organic and inorganic ligands, which increase downstream. The increase of

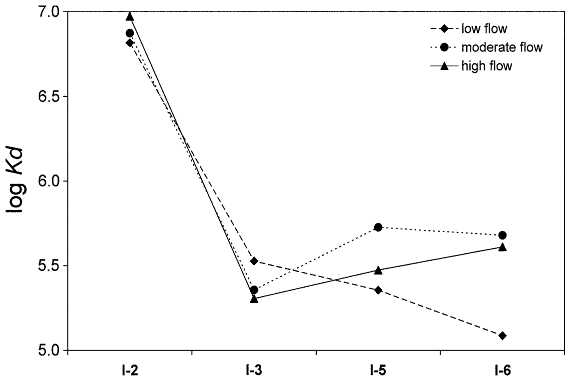

Fig. 8 Spatial evolution of Hg distribution coefficient (log K_d) along the Idrijca River

K_d downstream from the mine during the higher water flows could be attributed to remobilization of particulate Hg from river bed sediment. At the Idrija station (I-3), K_d was comparable during all three periods, demonstrating that at this station the distribution of Hg is greatly influenced by drainage from the mining sites.

Total particulate mercury in the river bottom sediment

The concentration of mercury in river sediments is a good indicator of water pollution with mercury. On one hand, river sediments are compartments where mercury accumulates as a result of simple sedimentation and transport processes, and on the other, mercury can be released from the sediments, becoming available for further biogeochemical transformations (Boszke et al. 2003). Previous studies in the Idrija region (Hines et al. 2000; Horvat et al. 2002) showed that river sediments represent the major source of methylmercury for the aquatic environment. However, there are still many gaps in our understanding of the mechanisms that govern methylation processes. Recently, much work was carried out towards better understanding of these processes in the River Idrijca. For example, new methodologies for determination of the mercury methylation and demethylation potential by the use of radiotracer-techniques were used (Hines et al. 2006; Žižek et al. 2008). Due to the complexity of the problem, a detailed study of the methylation processes was beyond the scope of the present work. Here, only total concentrations of mercury in sediments are reported in order to determine their amount, spatial distribution and consequently, the pool available for further transport and transformation processes.

Analysis of both the silt/clay and coarser fraction in the River Idrijca revealed mercury concentrations from less than 0.1 μg g^{-1} in the upper part of the catchment (I-1) to more than 4,000 μg g^{-1} just downstream of the mercury mine (I-3) (Fig. 9). This maximum was followed by a rapid decrease downstream until it reached rather constant but still high concentrations of approximately 30–50 μg g^{-1} before the confluence with the River Soča. The distribution of Hg between the two size fractions is not uniform along the Idrijca. With the exception of the most polluted site in Idrija, fine particles (<63 μm) had up to 12 times higher Hg concentrations than coarse ones (63 μm–2 mm), where total mercury concentrations ranged from 0.2 to 54 and 0.03 to 33 μg g^{-1}, respectively. However, the abundance of the coarse fraction indicates that 60–98% of the total Hg is bound to coarse grained particles. Therefore, the coarse fraction could represent the principal reservoir for Hg trapping in the riverbed. In terms of riverine transport, mercury transport associated with the finer particles is dominant during average hydrological conditions, while mercury concentrated in coarse ones is remobilized during extreme hydrological events. Hence, the concentration of mercury in river sediments does not depend simply on the distance from pollution sources but also on the hydrological conditions. At higher water levels, the Idrijca erodes its own river bed and the flood plains along the stream channel. This indicates that the sources and transport of Hg are strongly

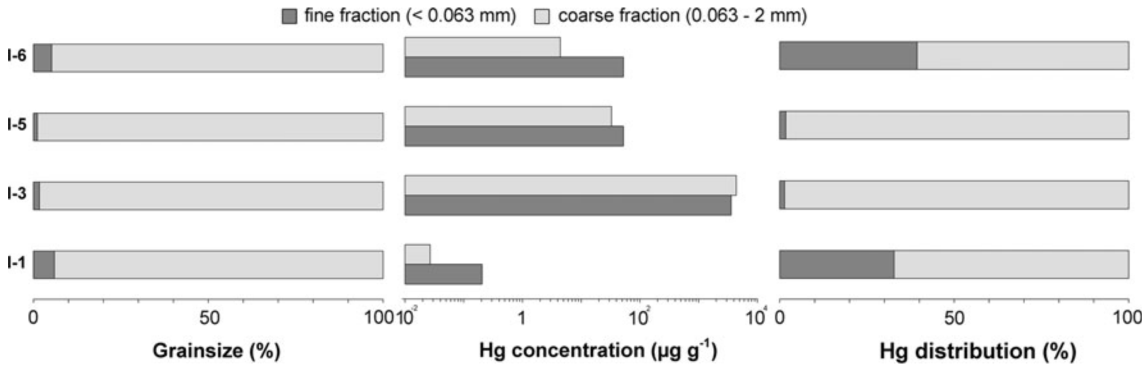

Fig. 9 Percentages of fine and coarse sediment fractions, THg concentrations and abundance of Hg in each fraction at four sampling stations of the Idrijca River

influenced by inhomogeneities along the river system that include particles of cinnabar originating from the mine. During sample preparation and their characterization, cinnabar coatings were observed on some opaque minerals. Similar observations were made by others (Gosar et al. 1997) who reported 1% of cinnabar grains resulting in 10% of the Hg content in some of the Idrijca sediments. The dominance of the cinnabar Hg fraction (more than 80%) in coarse grained flood plain samples was confirmed before by the results of a sequential extraction procedure, while non-cinnabar fractions were found to be enriched in areas where fine grained material is deposited (Kocman et al. 2004). The results of mercury analysis of Idrijca sediments indicate that more than a decade after the end of mining operations, terrestrial sources of mercury such as natural rocks containing mercury, deposits of combustion residues, as well as remobilization of contaminated river bed sediments, remain the major Hg input to the aquatic environment.

Conclusions

The results of the analyses of mercury in water and river bed sediments of the Idrijca catchment revealed that the Idrija mining district continues to supply high levels of mercury into the river system, despite the fact that the mine has been closed since 1995. The results presented in this article were obtained under very good quality control system that guarantees comparability of the measurement results with those measured previously. In terms of concentration values and mass flows, it can be concluded that mercury loads and concentrations in the river remain similar to those observed 10 years ago. In addition, the results re-confirmed the importance of the water compartment in mercury transformation processes (methylation, demethylation and reduction). The distribution of mercury in both the River Idrijca and its tributaries was found to be greatly influenced by the distance from the mining sites in the town of Idrija. A decrease in mercury concentrations and the evidence of the ore mineral cinnabar even 40 km downstream from the mining area indicates that contaminated soils, Hg-laden material and tailings deposited near the Idrija mine represent the main source of mercury for this aquatic environment. The results of mercury speciation in water samples suggest that suspended material transports most of the mercury downstream, mostly during short, but extreme hydro-meteorological conditions when remobilization of Hg from the river bed sediments occurs. During its transport, important Hg transformation mechanisms take place, as evidenced by the changed partitioning of Hg between the dissolved and particulate phases. When the distance between polluted sites in the town of Idrija and downstream sampling sites increased, an increase in the relative contribution of potentially bioavailable mercury species was observed which increases the risk of mercury uptake by biota. The partitioning was mostly controlled by the variable content of suspended solids as a result of changing hydrological conditions and complexation with various ligands present in river water, among which DOC seems to be the most important. In the River Idrijca, a relatively high share of the reactive Hg was measured. Our data suggest that reduction of reactive Hg prevails in this specific aquatic environment. In this way, these waters naturally reduce part of their mercury burden. The results for MeHg distribution in the Idrijca support the assumption of other authors that methylation is mainly a microbially mediated process. The methylation efficiency in this specific contaminated system depends on different biogeochemical controls. Our data revealed relatively low methylation efficiency in Idrijca. We attribute this to the fact the chemical composition of these waters is predominantly influenced by weathering of carbonate bedrocks, waters have high pH and are well aerated. Such conditions may be responsible for making inorganic mercury unavailable and limiting the capacity of methylating bacteria.

An important outcome of this work is also an indication of analytical problems related to mercury speciation and fractionation analysis in aqueous samples. For example, when standard protocols are employed and a 0.45 μm filter is used as the division between the particulate and the dissolved phase, the filtered fraction may overestimate the truly dissolved phase if colloids are present. However, our data suggest that a significant part of mercury in water can be associated with the colloidal phase which is extremely important for an understanding of its environmental function and fate. Moreover, at the mercury mine contaminated site, highly insoluble cinnabar particles are present. Furthermore, the methods available to measure reactive mercury are not standardized (or agreed), and therefore difference may occur in various studies due to differences in the protocols employed. These analytical issues increase the uncertainties in data interpretation and make comparisons between studies difficult. Therefore, further improvements and harmonization of methods for mercury analysis and speciation are needed, with a special focus on contaminated sites.

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