CROATICA CHEMICA ACTA CCACAA **70** (1) 271–288 (1997)

ISSN-0011-1643
CCA-2421
Original Scientific Paper

Distribution of Mercury Species in the Water Column of the Stratified Krka River Estuary*

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Received February 15, 1996; accepted October 15, 1996

Investigation of the mercury speciation (total/reactive and dissolved//particular forms) was carried out in waters of the highly stratified Krka River Estuary. The concentrations obtained are in satisfactory agreement with those obtained for other unpolluted aquatic environments (0.5–2.5 ng/L for total mercury, 0.1–0.8 ng/L for dissolved mercury and 0.04–0.75 μg/g for particulate mercury, $\phi \geq 0.45$ μm). Two or three discernible water layers (the upper fresh or brackish water layer, deeper saline layer and the in-between intermediate water layer) revealed different distribution of mercury species. In the upper freshwater layer with low salinity, the fraction of reactive mercury varied considerably with salinity changes (10–100% of the total), both during a single sampling campaign, as well as between particular sampling periods which coincided with different seasons and river regimes. This generally corresponded to the dissolved mercury fraction, confirming the insignificance of the organically bound dissolved mercury. In the bottom saline layer, mercury was mostly reactive (80–100% of the total), and even a part of the particulate mercury behaved as labile toward $SnCl_2$ reduction. In the upper water layer (low-salinity), the largest fraction of mercury was bound to particles, which were mostly of biological origin (plankton), except in the lower part of the estuary, where the particles were of anthropogenic origin (municipal waste discharge from the city of Šibenik). Accumulation of mercury, both in reactive and particulate form, was observed at the halocline, *e.g.* at the fresh/saline water interface (FSI).

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* Dedicated to Marko Branica on the occasion of his 65th birthday.

INTRODUCTION

Mercury is a dangerous ecotoxic pollutant because of its tendency to form even more toxic methylmercury compounds, which can get biomagnified under environmental conditions. A considerable effort is consequently being made to understand the cycling of mercury in the aquatic environment.[1,2] It is shown that mercury speciation in natural waters (the presence of various chemical forms of different behaviour) controls its biogeochemical behaviour and toxicity to aquatic organisms. Operational speciation of metals in water usually includes determination of dissolved/particulate fractions, but in the case of mercury, a proportion of the so-called »reactive mercury« (by definition a fraction of mercury reduced by $SnCl_2$ in acidified sample[3,4]) is also frequently given. It is a measure of the biogeochemically reactive form which represents a substrate for production of both elemental mercury and methylmercury in the water column.[5,6] Different types of water bodies are generally characterized by different mercury speciation in water. In ocean waters, mercury was found to be mostly in the dissolved reactive form,[3,4] whereas a higher proportion of particulate mercury was found in coastal areas, according to the distribution pattern of suspended matter in these waters.[7,8] A completely different mercury distribution was observed in freshwater bodies and estuaries. In lake waters, a proportion of organically bound mercury that could be significant depends on the chemical conditions in the water.[9,10] In estuaries, mercury speciation changes with hydrological and biological conditions, the most important processes taking place at the fresh/saline water mixing boundaries.[11]

The highly stratified Krka River Estuary is a good model for mercury speciation studies in different types of natural waters. Three distinguishable water layers can be observed in the Krka River Estuary: the upper fresh or brackish water layer, deeper saline layer, and the in-between intermediate layer, the width of which depends on the sharpness of the halocline.[12] Hydrological conditions and biological productivity change considerably, depending on the season and the Krka River flow.[13,14] The investigations carried out so far on the mercury concentration levels in different compartments of this ecosystem (water, sediment, mussels, fish and plankton), proved this area to be unpolluted with regard to mercury.[15,16] Preliminary measurements showed that a proportion of reactive mercury varied considerably in the freshwater layer, but remained relatively constant in the saline layer.[15] The accumulation of reactive mercury was observed in the intermediate water layer.[15,17,18]

For a better understanding of the fate of mercury under estuarine conditions, the Krka River Estuary was used as a model for detailed investigations of the distribution of mercury species within the water column.

EXPERIMENTAL

Study Area

The Krka River Estuary is located in the central part of eastern Adriatic coast (Figure 1). It belongs to the type of stratified estuaries characterized by a mean freshwater inflow of 55 $m^3 s^{-1}$ (varying between 10–400 $m^3 s^{-1}$) and a low tidal range (20–50 cm). The surface current is directed seaward, whereas the seawater bottom current has the opposite direction. Owing to the krastic drainage area and travertine barriers located at the mouth of the Krka River Estuary, the estuarine water is characterized by a very low suspended matter concentration (1–10 mg/L). Industrial and municipal discharge from the city of Šibenik (40 000 inhabitants), situated in the lower part of the estuary, is the major anthropogenic source of pollutants.

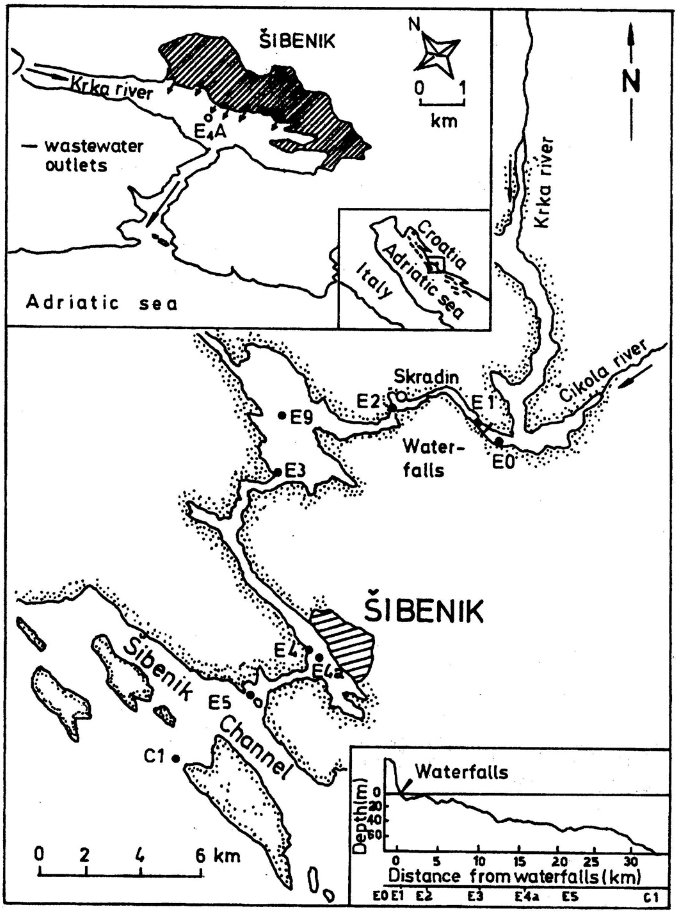

Figure 1. Map of the Krka River Estuary with sampling stations for estuarine water and wastewater.

Sampling and Pretreatment of Samples

Water samples were collected seasonally during 1989, from the surface (0.5 m) and bottom (6 m) water layers along the whole horizontal profile of the Krka River Estuary. Sampling sites (Figure 1) were selected so as to enable monitoring of the key positions in the estuary (E0–E5) and a typical position in the unpolluted coastal area (C1).

In July 1989, the samples from the fresh/seawater interface layer (FSI) were also collected at sites E2–E5. This interface layer is usually very sharp, with a thickness of less than 20 cm and salinity gradient up to $S = 30$. Consequently, it is very difficult to collect properly the interface layer water samples (even to a skillful diver). Therefore, the accuracy of the sampling interface water layer was examined by testing the salinity (which should be about $S = 20$) immediately after sampling. Water samples were taken by a scuba diver[17] in one-liter, acid-cleaned glass bottles. The samples for the determination of reactive and total mercury were immediately acidified with 5 ml of HNO_3 (Merck Suprapur), and analyzed for reactive mercury within a few hours of collection (2–5 h). Unacidified water samples for the determination of dissolved and particulate mercury were filtered through 0.45 μm sartorius filters (previously soaked in 10% HNO_3) under nitrogen pressure, at the day of collection. Reactive and total dissolved mercury were analyzed in filtrate in the same manner as unfiltered water samples.

Analysis

An outline of the analytical procedure used to distinguish mercury operational forms in water samples is given in Figure 2. Reactive mercury in unfiltered (Hg_R) and filtered ($Hg_{D,R}$) water samples was determined by the $SnCl_2$ reduction of HNO_3 – acidified samples (pH about 1). This fraction includes inorganic and organically complexed mercury species which are displaced by protons during acidification of the samples to pH about 1.[3] Total mercury in unfiltered (Hg_T) and filtered (Hg_D) water samples was determined by the $SnCl_2$ reduction following 12 hours of UV-irradiation with a 150 W UV-lamp. Particulate mercury (Hg_P) was determined after acid digestion of filters with concentrated HNO_3 in closed quartz vessels for 2 hours at 150 °C. Organically complexed mercury in unfiltered and filtered water samples, as well as reactive particulate mercury, were calculated by difference.

Mercury was determined using cold vapour atomic absorption spectrometry (CVAAS) after ionic mercury reduction by tin(II) chloride (10% $SnCl_2$ in 20% H_2SO_4) to elemental mercury. Mercury vapour was preconcentrated by amalgamation onto gold wire and nitrogen stripping into a conventional AAS instrument where the mercury peak was recorded.[19] The determination limit of the method is 0.1 ng/L Hg.

RESULTS AND DISCUSSION

Total / Reactive Mercury Concentrations

Reactive and total mercury data obtained from the analysis of water samples collected seasonally during 1989, are presented according to the

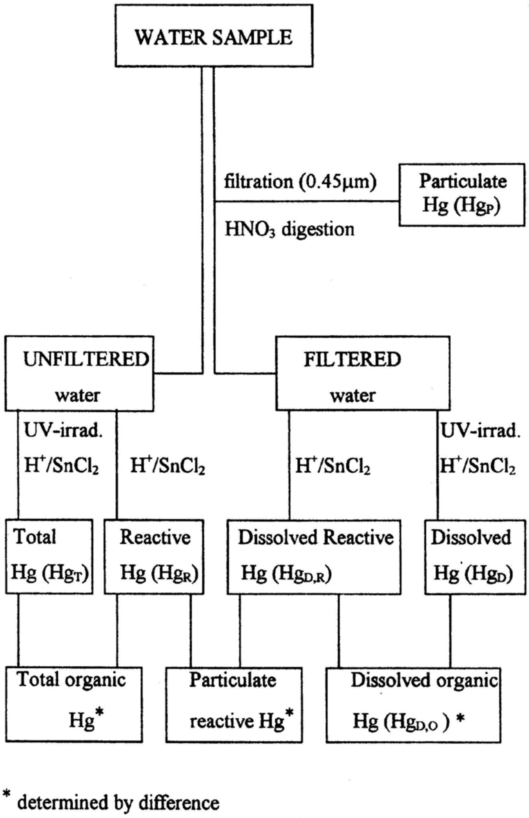

Figure 2. Analytical procedure for the determination of various mercury forms in water.

salinity in the surface water layer (Figure 3a) and according to the distance from the head of the estuary in the saline bottom layer (Figure 3b).

In the surface water layer, the concentrations of reactive mercury as well as the percentage of the reactive from the total mercury varied between 40–100% during the low flow in January 1989 (Q = 16 m^3 s^{-1}), and only 10–50% during the medium flow in May (Q = 32 m^3 s^{-1}) and July (Q = 51 m^3 s^{-1}). Variations of the total mercury concentration levels were significantly lower than those of the reactive mercury, both during a single sampling period and between different seasons, as well as for all data in the surface layer (Table I). In the bottom water layer, characterized by constant salinity (Figure 3b), both reactive mercury concentrations and the percentage of the total mercury (60–100%) were fairly constant during all sampling periods.

The ratio of reactive/total mercury in the saline water layer is in good agreement with the literature data, which suggest the predominance of the reactive mercury form in seawater.[3,4] However, the proportion of reactive mercury in waters of low salinity is not as uniform and well-defined as in ocean waters.[20] The concentration of reactive mercury in freshwater could vary due to methodological conditions, and/or redistribution of mercury species by changing physico-chemical parameters in water. It was shown[20] that the determination of reactive mercury in freshwater (probably in brackish

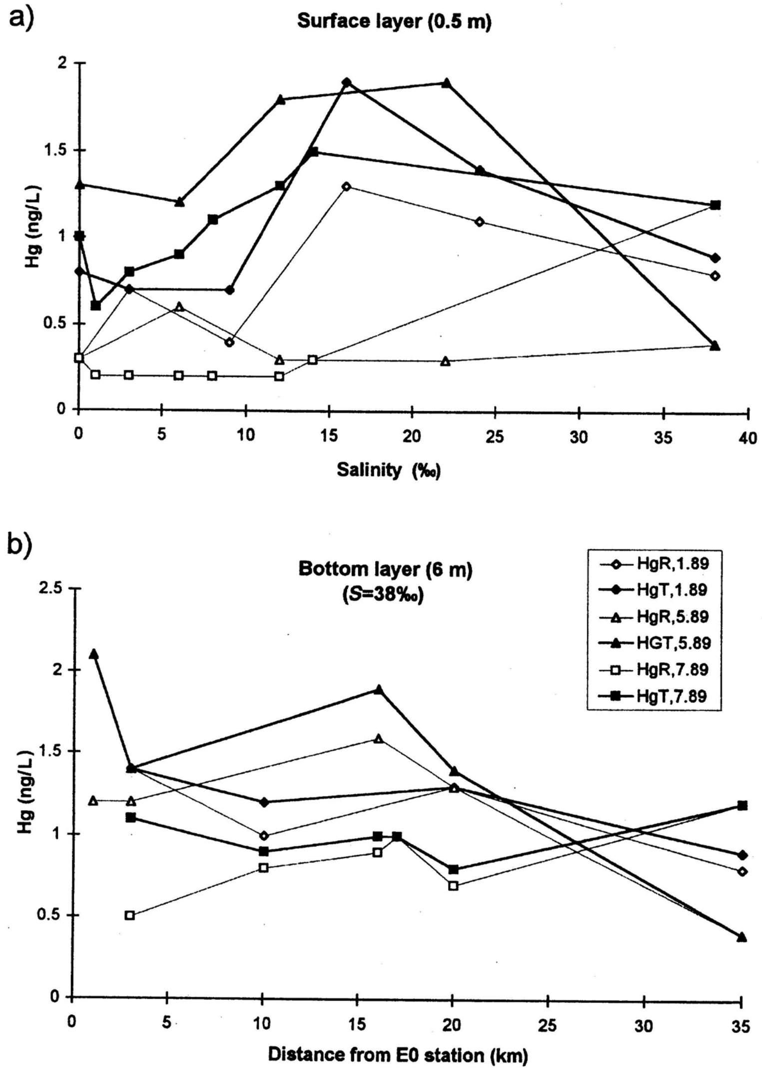

Figure 3. Total and reactive mercury profiles along the surface (a) and bottom (b) water layers of the Krka River Estuary in samples collected during 1989.

TABLE I

Mean concentrations of different mercury species in the waters of the Krka River Estuary sampled in July 1989.

	Mercury concentration (X ± SD, ng/L)				
Water layer	Hg_T	Hg_R	Hg_D	Hg_P	Hg_P[a]
Surface layer(0.5m)	1.0 ± 0.3 93[b]	0.2 ± 0.1 17	0.2 ± 0.2 22	0.8 ± 0.4 77	0.2 ± 0.1 –
Interface layer (1.5 m)	1.6 ± 0.6 85	0.6 ± 0.4 30	0.4 ± 0.1 19	1.5 ± 1.0 81	0.3 ± 0.2 –
Bottom layer (6 m)	1.0 ± 0.1 110	0.9 ± 0.2 98	0.6 ± 0.1 63	0.3 ± 0.2 37	0.3 ± 0.2 –
Overall	1.2 ± 0.4 95	0.5 ± 0.4 42	0.4 ± 0.2 31	0.8 ± 0.7 69	0.3 ± 0.2 –

[a] expressed as μg/g of suspended matter
[b] expressed as percentage of the sum of Hg_D+Hg_P

water as well) depended on the analytical conditions, such as pH of the sample or the duration of sample storage prior to determination.

Because of high pH values of the calcareous Krka River Estuary, the pH at the surface and bottom water layers was similar (about 8).

All measurements of reactive mercury were performed in the same way by acidification of water samples (HNO_3, 5 ml/L) to approximately pH 1, immediately after sampling. Analyses of reactive mercury were performed within a few hours of sampling. This means that the methodological conditions were not responsible for the differences obtained for mercury concentrations. Acidification of water samples is a well-recognized method for the determination of reactive mercury concentrations in saline and brackish water samples. This method was used in the case of such a stratified estuary in oder to obtain comparable data for both saline and fresh/brackish water samples.

Variability of reactive mercury in estuarine samples could be influenced by pH, salinity and/or organic matter content.[21] In the surface water layer of the Krka River Estuary, salinity gradually increases towards the mouth of the estuary, due to entrainment of the bottom seawater into the upper freshwater layer.[13] pH values could not be responsible for mercury redistribution, since these values are similar in the saline and freshwater layers and do not change during the mixing of the surface and bottom waters.

The spatial distribution of reactive mercury generally demonstrates an increase between salinity $S = 0$ and $S = 38$ (Figure 3a). However, the same difference (almost 10 times) was obtained in the water samples of the same salinity values during different sampling periods. Seasonal changes in the water column of both salinity and biological activity, obviously influence the concentration level of reactive mercury.

Maximum concentrations of total mercury, as well as considerable differences in reactive mercury concentrations were observed at sites E4a and E5 (the Šibenik Bay and the Šibenik Channel, respectively (Figure 1); (in Figure 3a they correspond to salinities S = 10–30, depending on the river flow). The highest total mercury level could be explained by certain anthropogenic influence. The Šibenik Bay is under the influence of municipal sewage rich in mercury. The measurements performed during the period 1989–1991 (Table II) showed that wastewater contained between 0.15 to 1.5 µg/L of mercury. Although an efficient dilution by harbour waters rapidly decreases mercury concentration in the vicinity of wastewater outlets (Table II), the anthropogenic influence can be observed in the centre of the Šibenik Bay (stations E4a), and frequently in the Šibenik Channel (location E5). Anthropogenic influence on the mercury level in water is less evident in the bottom layer (Figure 3b), due to inefficient mixing of the surface and bottom layers. It has already been shown for some other pollutants originating from wastewaters (alkylphenol polyethoxylates surfactants) that the wastewater plume spread into the estuary entirely into the upper water layer, while the underlying bottom layer remained more or less unaffected.[22]

Considerable differences between the reactive and total mercury concentration levels obtained in the Šibenik Bay could be attributed to seasonal

TABLE II

Mercury concentration in the municipal wastewaters (the city of Šibenik) collected from the sewage channels (1–4) and the harbour, in the immediate vicinity of the corresponding sewage outlets (1a–4a).

Sampling site	Mercury concentrations (ng/L)				
	July 1989		Sep 1990	Nov 1990	March 1991
	Hg_T	HgP	HgT	HgT	HgT
1	–	–	1550	200	875
1a	265	182	320	–	345
2	–	–	611	788	509
2a	146	78	80	–	88
3	–	–	875	–	215
3a	93	51	165	–	56
4	–	–	190	329	147
4a	450	292	–	–	166

variations of biological activity. In January, when the biological activity was low, the reactive and total mercury levels differed slightly, whereas in May and July, when the aquatic production was more pronounced, the differences were considerable. Such differences were particularly noticeable in the Šibenik Bay during the summer period[14,23] when local plankton blooms appeared due to nutrient input. The correlation between reactive mercury and parameters such as DOC, POC and algal pigments should be established in due course in the waters of the Krka River Estuary.

Dissolved/Particulate Mercury

For a better understanding of the nature of reactive mercury, a more detailed operational speciation study, which included separation of dissolved and particulate mercury ($\phi \geq 0.45$), was carried out in July 1989. In the upper and intermediate water layers, dissolved mercury accounted for only a small fraction (about 20%) of the total mercury concentrations (Table I). It was mainly in the reactive form (Figure 4), except in the river water (site E0), where a significant part of dissolved mercury was in the form of organically bound complexes unavailable for $SnCl_2$ reduction. In the bottom saline water layer, mercury was mostly in dissolved form (about 60%, Table I) and entirely reactive. The low level of dissolved organically complexed mercury coincided with the low level of dissolved organic carbon (about 1 mg/L), typical of the waters of the Krka River Estuary.[24] Only in estuaries characterized by a high and variable level of dissolved organic carbon (DOC), the proportion of organically bound mercury strongly depends on the DOC concentration.[25]

In the upper water layer, dissolved mercury generally corresponded to reactive mercury, whereas in the intermediate water layer, and especially in the saline water layer, reactive mercury (measured in unfiltered samples) was sometimes higher than dissolved mercury (Table I). This indicated that a fraction of particulate mercury in these samples was available for $SnCl_2$ reduction (so-called particulate reactive mercury). This could be mercury that was adsorbed on different minerals (calcite, quartz, some manganese minerals) found in the waters of the Krka River Estuary, and suggested to be efficient scavengers for different trace metals.[18,26,27]

A plot of the total dissolved mercury concentrations against salinity found in the water samples collected in July 1989 is presented in Figure 5a. In the surface water layer (line connected dots), a decrease in dissolved mercury concentrations between the river site and the first estaurine site, and furthermore an increase towards the sea, could be observed. Removal of mercury from the dissolved phase could be a result of flocculation of organic mercury colloids,[28] but in the case of the Krka River Estuary, this should be verified by establishing a relationship between mercury and organic matter. A significant role of colloidal mercury fraction has recently been proved for mixed, turbide estuaries;[29] but the significance of such a fraction in low-turbidity stratified estuaries is doubtful. Further increase of dissolved mercury concentrations with salinity along the estuary is comparable with the distribution pattern of other dissolved metals (especially cadmium) in the Krka River Estuary.[30]

Most of the mercury in fresh and brackish water is bound to particles (about 80%, Table I). Particulate mercury is well-correlated with a difference between total and reactive mercury (Figure 5b; $r = 0.843$, $n = 17$), which proves that unreactive mercury is bound mostly to particulate organic matter. It may originate from the mineral (terrigenous), organic (biological) and/or anthropogenic components of the suspended matter. The origin of

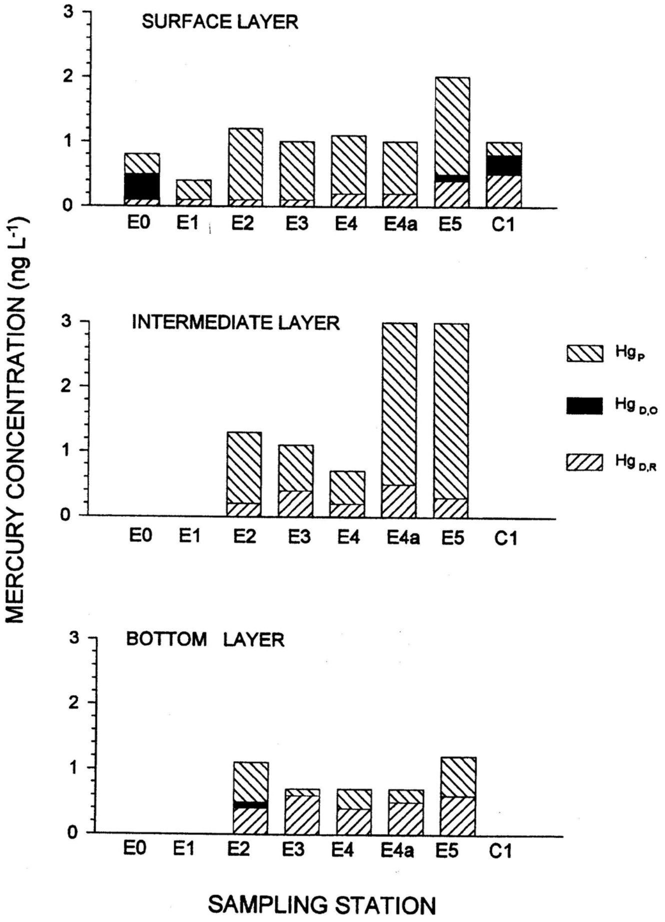

Figure 4. Dissolved and particulate mercury profiles along the surface, intermediate and bottom water layers of the Krka River Estuary in samples collected in July 1989.

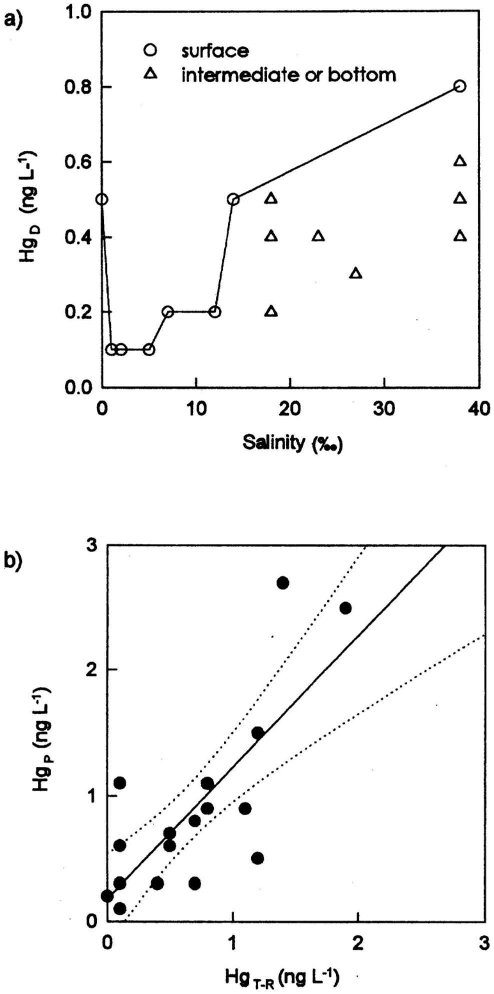

Figure 5. Plot of (a) dissolved mercury against salinity, and (b) particulate mercury versus the difference between total and reactive mercury in samples collected in July 1989.

particulate mercury could be established by comparing data along the estuary. Horizontal distribution of suspended matter (SM) and particulate mercury (expressed on the weight of SM) is presented in Figure 6. Particulate mercury concentrations do not follow the pattern of suspended matter, which indicates different sources of mercury at different sampling sites. For example, the interface water layer samples at sites E4 and E4a in the Šibenik Bay, both containing a high amount of suspended matter (11.2 and 6.2 mg/L, respectively), showed very different particulate mercury levels (0.04 and 0.4 μg/g,

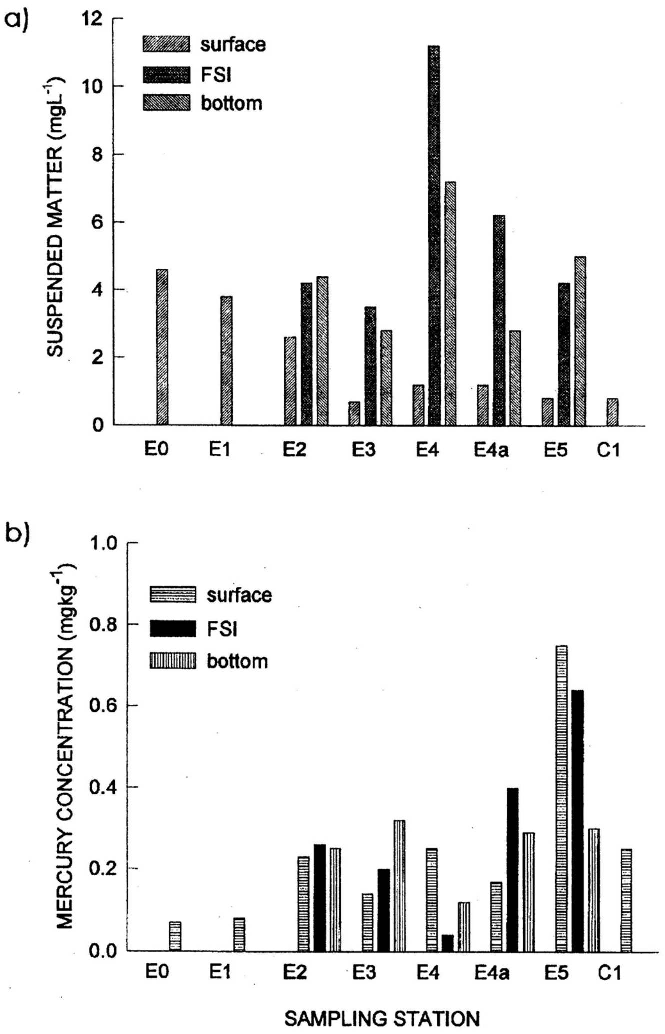

Figure 6. Suspended matter (a) and particulate mercury (b) profiles along the water layers of the Krka River Estuary in samples collected in July 1989.

respectively). The influence of municipal wastewater is much more pronounced at site E4a, situated in the vicinity of the Šibenik harbour (especially in the interface water layer where the particles are accumulated), than at station E4, situated at the opposite end of the Bay, as shown for some organic pollutants originating from wastewater.[22] Therefore, much higher concentrations of mercury at site E4a could be explained by the presence of sewage particles highly enriched with mercury (Table II). In contrast, the mercury content in plankton (collected with a 20 mm net mesh size) of the Krka River Estuary (0.064–0.083 μg/g d.w. in freshwater layer and 0.074–0.129 μg/g d.w. in seawater layer, unpublished results) is significantly lower than that found in suspended matter (similar to some Mediterranean areas[31]).

July 1989 was characterized by a high productivity (plankton bloom), especially in the central part of the estuary (highly eutrophic zone off the city of Šibenik). This was demonstrated by a very low transparency in the water column (Secchi depth of 2/0.8 m on site E4a in comparison with 3/1.5 m on site E5 and 22/13 m on site C1). A bloom developed at the surface, but not in the bottom water layer (which was observed visually by the diver), typical of this stratified estuary.[14,22] A low mercury level at site E4 could be influenced by the higher percentage of low mercury biological particles during the plankton bloom. This is in a good agreement with the assumed origin of particulate organic matter, based on the results of the analysis of organic biomarkers (sterols).[32] Three source inputs are recognized: a) terrigenous (predominating in the bottom saline water layer, b) aquo-biological (predominating in the upper and interface water layers, and c) sewage (dominant in the particles accumulated at the halocline in the central part of the estuary, reflecting input from the sewage outfall of the city of Šibenik).

Mercury Accumulation at the FSI

One of the characteristics of this stratified estuary is a very pronounced halocline and a well-defined interface between fresh and saline water layers. Stable organic films form at this interface and it has been suggested that trace metals could accumulate in this organic film.[12] Enrichment by various metals (Hg, Cu, Cd, Pb and Zn) at the halocilne at site E3 was reported by Branica *et al.*[33] In that study, only reactive mercury and DPASV-avalilable fraction of metals in unfiltered samples were measured, so that the nature of the maximums obtained was ambiguous. It was reported[30] that some dissolved metals (Cd, Cu, Ni) did not accumulate at the interface of site E2, whereas others (Fe and Pb) accumulated only slightly, which can be attributed to the adsorption of colloidal fraction. The appearance of pronounced peaks of reactive mercury in the interface water layer in the estuary was reported elsewhere.[15,17,18] From a more detailed study carried out in the upper part of the estuary (site E2), which also included measurements of the total mercury,[18] it was concluded that mercury speciation in the freshwater and interface layer should also be connected with organic matter. Neither of these studies, however, explained the nature of the metals accumulated at the fresh/saline water boundary. Also, most of these studies were carried out in the upper part of the estuary.

The aim of this study was to determine the operational form (organic/inorganic; dissolved/particulate and reactive/total) in which mercury is accu-

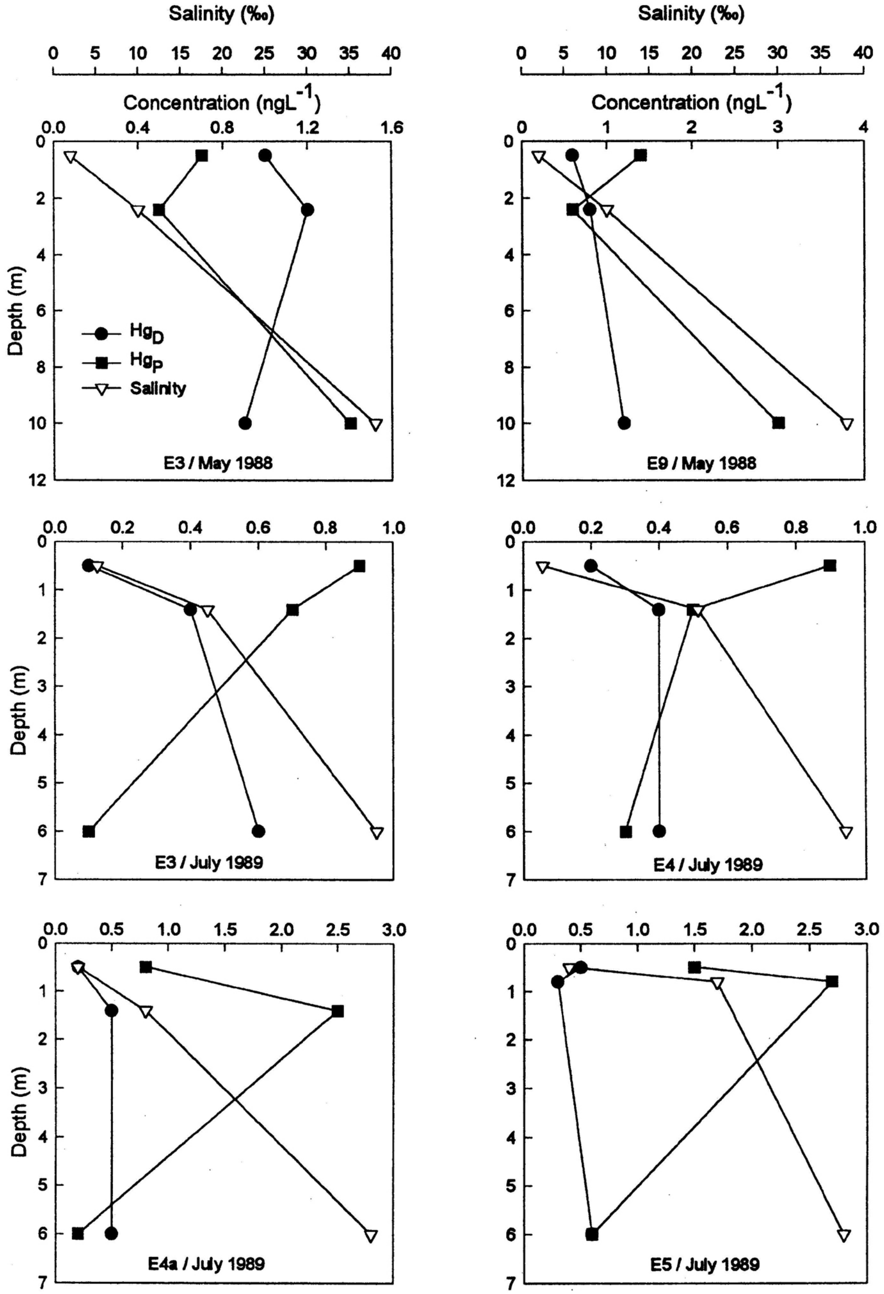

Figure 7. Vertical profiles of dissolved and particulate mercury in the water column of the Krka River Estuary obtained in May 1988 (sites E3 and E9) and July 1989 (sites E3, E4, E4a and E5).

mulated at the water interface. Operational speciation of mercury was investigated along the vertical water profile in May 1988 and July 1989.

In May 1988, dissolved and particulate mercury profiles were measured at sites E3 and E9 (Figure 7). In spite of a well-defined halocline, mercury maximum was not observed at the interface. The values of dissolved mercury increased slightly at the interface at both sites. However, the concentrations of particulate mercury were lower at the interface than in the surface water layer. These results indicate that the particles accumulated at the interface released mercury under the influence of increased salinity (complexation by chlorides, competition of macrocations and agglomeration and condensation of organic matter). Due to the lower residence time of mercury in dissolved than in particulate phase at the interface water layer, the peak of dissolved (or reactive) mercury is practically undetectable.

In July 1989, vertical mercury profiles were measured at several estuarine sites (Figure 7). In the upper part of the estuary (site E3), mercury maximum was not observed at the interface water layer. However, in the lower part of the estuary (stations E4a and E5), pronounced mercury maxima were obtained. Only a small percentage (<20%) of this mercury was dissolved and reactive, while the main part was particulate and organic. It was suggested that these mercury-rich particles were of the sewage origin. This example together with previously observed peaks of reactive mercury indicate that mercury maxima, which appear at the interface of fresh and saline water layers, do not necessarily have the same operational speciation of mercury. In the upper part of the estuary, mercury maximum can be composed of dissolved or reactive particulate mercury (mercury adsorbed on mineral surfaces, as suggested by Bilinski *et al.*[18]). In the lower part of the estuary, with significant mercury input from sewage, it can be composed of particulate organic mercury.

The importance of the mercury input from sewage is obvious from a quantitative comparison of possible mercury sources in this water body (Table III).

TABLE III

Source of mercury input in the Krka River Estuary

Source	Input data	Average conc. (ng/L)	Annual input of Hg (kg/yr)
Krka river (E0)	Average flow: 50 $m^3\ s^{-1}$	0.8	1
Rainwater	Annual deposition: 840 mm/yr	30	0.5
Wastewater	Average flow: 0.3 $m^3\ s^{-1}$	600	5

The amount introduced annually by wastewater is by the order of magnitude higher than the mercury deposited by rain. However, due to permanent stratification and efficient transport in seaward direction, the influence of this source on the upper part of the estuary could hardly be expected. For this part of the estuary, an input from the atmosphere (after heavy rains) could be significant, as suggested for mercury[18] and cadmium and lead.[30]

CONCLUSIONS

Mercury concentration levels in the waters of the Krka River Estuary are comparable with those obtained for other unpolluted estuarine and ocean waters. A small amount of mercury of anthropogenic origin was observed in the Šibenik Bay, but it only affected overlying waters of the lower part of the estuary. Two distinguishable water layers in the estuary reveal different mercury speciation. In the upper fresh or brackish water layer, variable proportion of reactive to total mercury was found, depending both on salinity and seasonal changes, whereas reactive mercury prevailed in the bottom saline water layer. The dissolved part of mercury is mainly inorganic, which is in agreement with the low level of dissolved organic carbon. Most part of the mercury in water of low salinity is particulate, presumably of biological origin, but in the lower part of the estuary it can be ascribed to anthropogenic influence. In the central part of the estuary, mercury maxima composed of particulate mercury were observed at the fresh/saline water interface (FSI). Taking into account the previously observed maxima of reactive mercury at FSI in the upper part of the estuary, it is obvious that such an accumulation of mercury throughout the entire estuary is not always of a unique nature.

Mercury speciation is important for predicting the mercury methylation. In the water column of the Krka River Estuary, a slow methylation rate should be expected because of low concentrations of dissolved organic mercury and DOC, as well as relatively high pH values. Preliminary estimates[34] (using a bioassay technique) and measurements[35] indicated low concentration levels of methylmercury in waters of the Krka River Estuary. However, it would be interesting to find out whether the microconditions at the intermediate water layer, (which is characterized by a high biological activity), favour biomethylation of mercury and cause the accumulation ion of monomethyl mercury. Further investigations of these two processes should be carried out in due course.

Acknowledgements. – The authors wish to thank Dr. Marko Branica for his outstanding expertise in the long-standing scientific environmental research in the Krka River Estuary, his enthusiasm and perseverance in maintaining the marine station Martinska, and for critical reading of the manuscript. The work was supported by the Ministry of Science and Technology of the Republic of Croatia. Financial support from the UNEP/FAO contract and the International Bureau of KFA Juelich, within the bilateral agreement, is gratefully acknowledged.

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SAŽETAK

Raspodjela živinih vrsta u stupcu vode u raslojenom ušću Krke

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U vodi ušća rijeke Krke ispitivana je raspodjela vrsta žive (specijacija), te njihova zastupljenost u otopljenoj fazi odnosno vezanje na krutim česticama. Izmjerene koncentracije žive odgovaraju nezagađenim vodenim sustavima i kreću se u rasponu 0.5–2.5 ng/L za ukupnu živu, 0.1–0.8 ng/L za otopljenu živu odnosno 0.04–0.75 μg/g za živu vezanu na čestice, ϕ = 0.45 μm). Dva dobro odvojena sloja (gornji slatkovodni ili bočati, a donji slani) toga raslojenog ušća pokazala su različitu raspodjelu vrsta žive. U gornjem sloju udjel reaktivne žive (anorganske ili vezane u labilne organske komplekse) znatno se mijenja (između 10–100% od ukupne) s promjenom saliniteta u okviru pojedinih uzorkovanja i između različitih uzorkovanja u pojedinim sezonama. Reaktivna živa pretežno odgovara otopljenoj, što upućuje na malu zastupljenost organski vezane otopljene žive. U donjem sloju živa je pretežno otopljena i reaktivna (80–100% od ukupne). U vodi niskog saliniteta (gornji sloj vodenog stupca) živa je većim dijelom vezana na čestice koje su uglavnom planktonskog porijekla, osim u donjem dijelu estuarija koji je pod utjecajem otpadnih voda grada Šibenika. Povišene koncentracije žive na granici slatkog i slanog sloja, nađene su u obliku reaktivne odnosno partikularne žive.