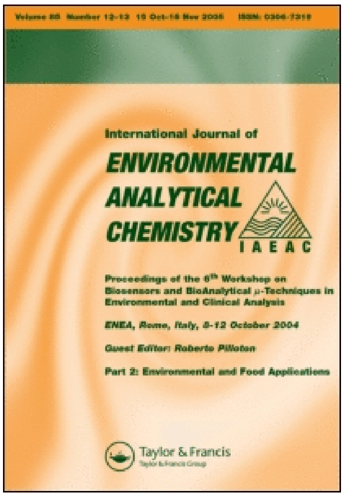

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Vertical distribution of mercury in the Krka river estuary

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The concentrations of reactive and total mercury (in the UV-irradiated samples) were measured in unfiltered and acidified samples by atomic absorption. The samples were collected in the vertical profile on one selected station in the Krka river estuary (Croatia) during 1997–2000. The estuary is permanently stratified and characterized by the subsurface temperature maxima. The maximum concentrations of reactive and total mercury range from 0.9 to $3.3\,\mathrm{ng\,L^{-1}}$, and from 1.3 to $6.0\,\mathrm{ng\,L^{-1}}$, respectively. The vertical transport of mercury across the picnocline is enhanced under the influence of a north wind.

Keywords: Mercury; Estuary; Atomic absorption; Environmental analysis

1. Introduction

Mercury is one of the rarest elements in the earth's crust [1, 2]. However, in a small number of places, it occurs in higher quantities, mainly as the mineral cinnabar [3–7]. The environmental cycle of mercury is complex and involves chemical, biological, and physical processes [8–11]. Natural sources of mercury in the environment include weathering of rocks, degassing of soil, and volcanic activities, while anthropogenic sources include burning of fossil fuels, cement, pesticide and steel productions and incineration of wastes [12]. The concentration of mercury in ocean water varies from 0.05 to $2\,\mathrm{ng\,L^{-1}}$ [13–16]. In surface waters, a significant fraction of total mercury is in the elemental form [9, 10, 15]. In deep waters, mercury is adsorbed on the surface of suspended mineral particles and dead phytoplankton cells [17–19].

In this short communication, the distribution of mercury species in the water column of the stratified Krka river estuary is reported. The estuary is a fish farm and a shellfish cultivation area, but it is also burdened by the heavy traffic of touristic boats. Therefore, the monitoring of heavy metals in the estuary was established. Our previous measurements indicated significantly increasing concentrations of mercury in the halocline [20–24]. The objective of this work is to analyze the influence of weather conditions on the maximum concentration of mercury.

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2. Experimental

Water samples were collected in precleaned 1 L Teflon FEP bottles (Nalge Nunc International, Rochester, NY) by scuba diving [20]. Prior to sampling, the bottles were removed from the plastic bags and rinsed several times with the subsurface water. Sampling depths were controlled by a marked weighted line suspended from a boat. The diver was facing the direction of the current, opening and closing the sampling bottle with outstretched hands. The analyses were performed in unfiltered samples, without any preconcentration step, in order to avoid contamination.

The temperature was measured *in situ*. Salinity was immediately determined in each sample using a refractometer (Atago, Japan). The pH was measured using a Mettler Toledo model MP 120 pH-meter. Dissolved silicate was determined by the standard colorimetric procedure [25]. The complexing capacity for copper(II) ions was determined by anodic stripping voltammetry [26, 27]. Sea-water density was calculated using the equation given by Millero and Kremling [28], and verified by Whitfield and Turner [29].

For the determination of mercury, $5\,\mathrm{mL\,L^{-1}}$ of concentrated suprapur HNO_3 was added to each sample immediately after it was collected. The concentration of mercury was measured by cold vapour atomic absorption spectrometry using the 253.7 nm absorbance peak, as described previously [30–32]. A Perkin-Elmer model 410 atomic absorption spectrometer was used. The samples were collected in a mercury reduction vessel containing a 10% $SnCl_2$ and 20% H_2SO_4 solution. The vessel was purged with extra-pure nitrogen, so that the mercury vapour was passed over gold wool in a silica-glass tube, which acted as an amalgamation trap. Then, the gold was electrically heated to 800°C, and the deposited mercury was re-evaporated and allowed to pass through a silica-glass cuvette where the concentration of mercury was measured. A known amount of standard solution was then added and analysed for calibration purposes. The blank of used reactants was determined and subtracted. The determination limit was $0.01\,\mathrm{ng\,L^{-1}}$ in 300 mL sample. The precision of measurement of $1\,\mathrm{ng\,L^{-1}}$ standard solution, using the atomic absorption Hg standard, was 1%. All reagents were of analytical grade (Merck).

Reactive mercury represents the fraction available for reduction with $SnCl_2$ after acidification of the sample [33] and includes all labile ionic forms of mercury. Total mercury was measured in the same sample after UV irradiation for 24 h using a 150 W lamp (Hanau, Germany) and includes stable organic complexes of mercury [34].

3. Study area

The Krka river estuary is located in the central part of the eastern Adriatic coast, in Croatia. It is cut into the limestone erosional plane, starting below 46 m high waterfalls and ending at the mouth of the Šibenik channel, along a total length of 22 km (see figure 1). Its depth increases from 2 m at the falls to 42 m in the channel. The Krka is the main freshwater supply of the estuary and has a mean annual discharge of $55\,\mathrm{m^3\,s^{-1}}$, with large seasonal and monthly variations ranging from 10 to $400\,\mathrm{m^3\,s^{-1}}$ [35]. The estuary is stratified, and the brackish surface current flows seaword over a seawater countercurrent [36]. This is caused by the sheltered geography and a low

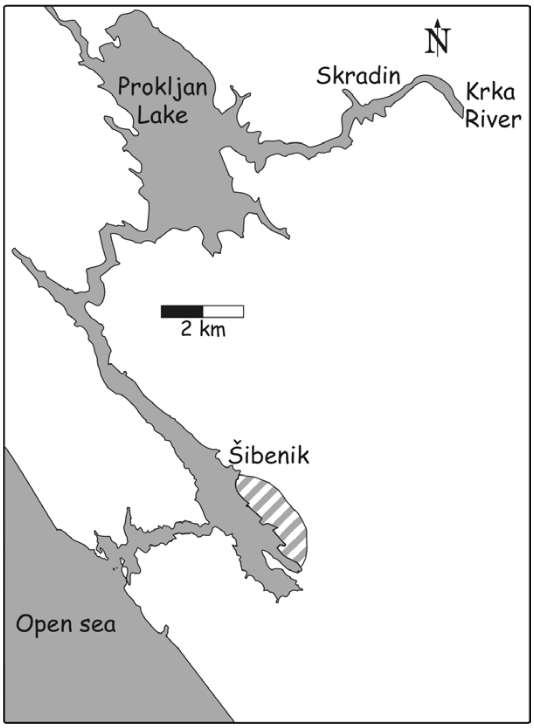

Figure 1. Krka river estuary (Adriatic coast).

tidal range of 20–50 cm. Above waterfalls, the lakes are formed which limit the input of particulate material into the estuary [22, 37]. Anthropogenic sources of pollution are industrial and municipal waste discharge from the town of Šibenik (40,000 inhabitants), which is situated in the lowest part of the estuary [21].

4. Results and discussion

Figures 2–5 show that the main characteristics of the estuary are well-defined picnocline and halocline which appear at various depths, depending on the position in the estuary and the freshwater inflow. The samples were collected at small depth intervals, paying special attention to the freshwater–seawater interface (FSI). This is a layer within which the salinity increases for about 25%, or more. Its thickness depends on the weather conditions and ranges from 50 cm to 2 m. For a diver, it is usually of a veil-like appearance because of the change in refraction index with the increasing salinity. Figure 2 shows that the estuary is stratified throughout the year and that subsurface temperature maxima appear within the FSI. Data reported in figure 2a were measured on a hot summer afternoon, when the air temperature was 35°C. In the freshwater layer the temperature was 30°C, while in the FSI it increased to 34°C. These are the highest temperatures recorded in the Adriatic sea [38]. A few days later, under the influence of the west wind, the surface and the maximum temperatures decreased to 29°C, and 32.5°C, respectively (not shown). The temperature maxima were detected in the

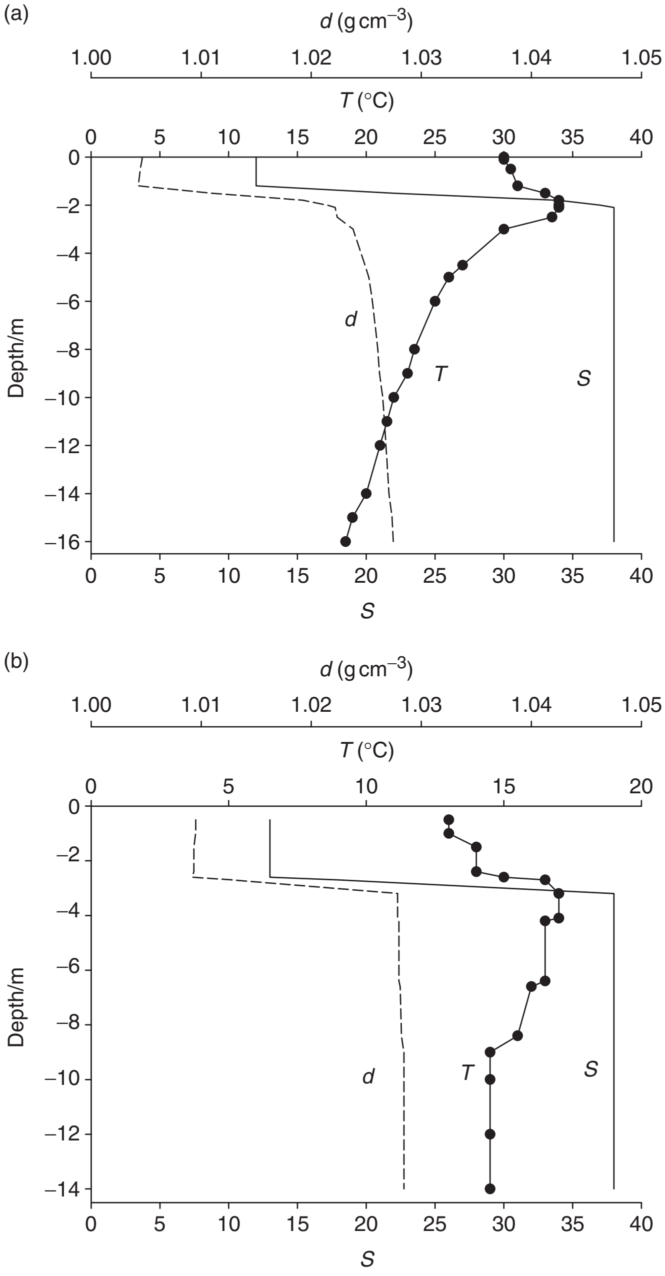

Figure 2. Vertical profiles of salinity (S), density (d) and temperature (T) on (a) 27 July 1998 and (b) 31 March 1999. The air temperatures were (a) 35°C and (b) 17°C.

FSI from March, as can be seen in figure 2b, until November. In winter, the maximum appears at depths between 5 and 7 m, which are just below the FSI. In this season, the difference between the maximum and the surface temperatures can be higher than 10°C.

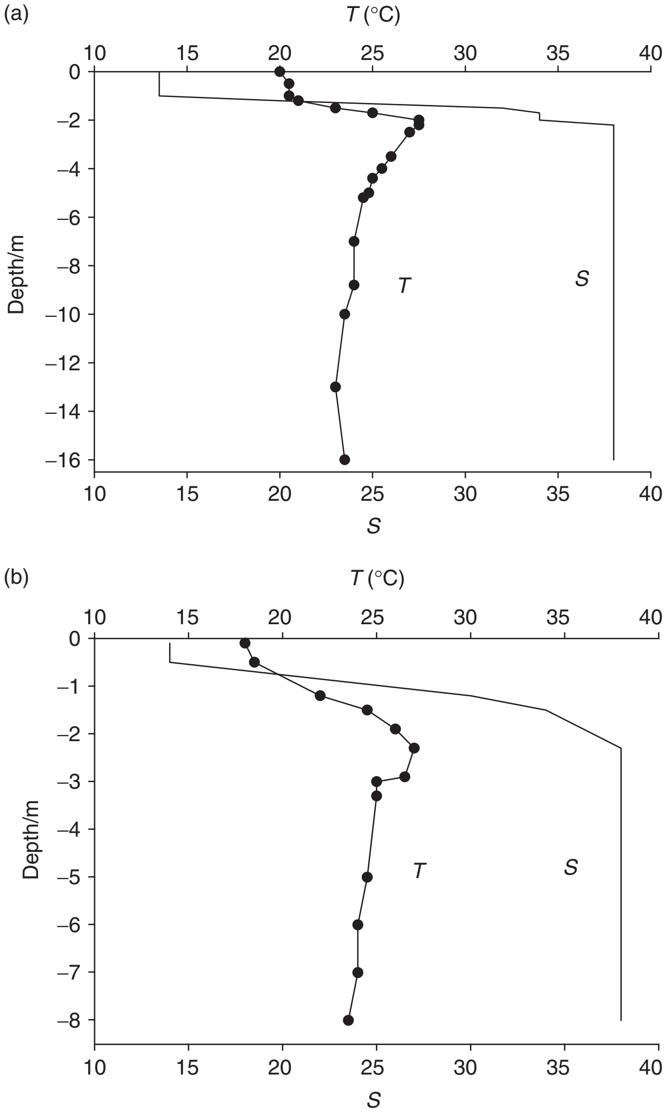

Figure 3. Vertical profiles of salinity (*S*) and temperature (*T*) at (a) 3:30 pm, 15 October 1999 and (b) 7:30 am, 16 October 1999. The air temperatures were (a) 20°C and (b) 11°C.

Figure 3 shows that the diurnal variation of surface temperature (±2°C) has minimal influence on the temperature maximum in the FSI. During the night, the maximum changed from 27.5 to 27°C.

Figure 4 shows that the concentration of dissolved silicate decreases, while the pH increases in the FSI. The complexing capacity for copper(II) ions is at a maximum within FSI (see figure 5). The maximum can be connected to the accumulation of dissolved organic compounds, insoluble liquid organic aggregates and suspended mineral particles, as observed in the FSI [22, 24, 37]. The organic matter accumulated

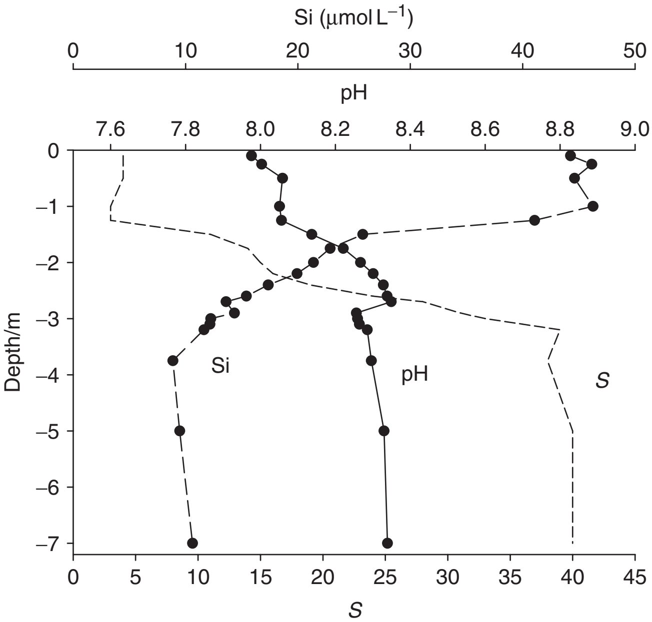

Figure 4. Vertical profiles of salinity (*S*), dissolved silicate (Si) and pH on 14 April 1999, at 11:30 am.

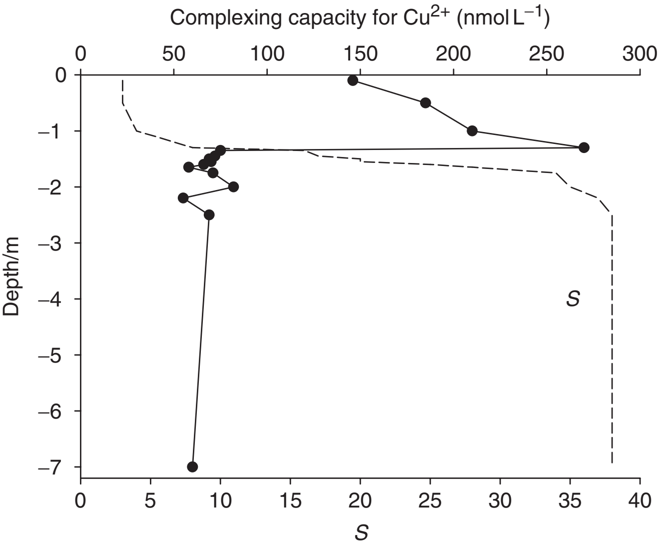

Figure 5. Vertical profiles of salinity (*S*) and the complexing capacity for copper(II) ions on 13 May 1999.

in the FSI originates primarily from the decomposition of the freshwater phytoplankton [39]. It seems that this material increases the thermal capacity of the FSI, which could explain the observed temperature maxima.

A typical vertical distribution of concentrations of reactive and total mercury is shown in figure 6. In the brackish water ($S \leq 5$), the concentrations of total and reactive

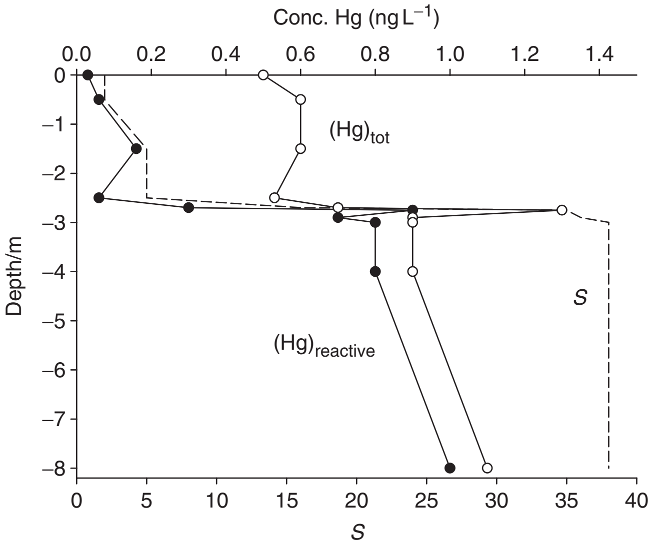

Figure 6. Vertical profiles of salinity (S) and total and reactive mercury on 14 January 1998.

mercury are between 0.5 and 0.6 ng L^{-1}, and between 0.03 and 0.16 ng L^{-1}, respectively, while in the sea water ($S = 38$), these concentrations are between 0.9 and 1.1 ng L^{-1}, and between 0.8 and 1 ng L^{-1}, respectively. These values are comparable with the concentrations of mercury in the open waters of the Mediterranean Sea [40, 41]. The difference between the total and reactive mercury, which was operationally defined as a total organic mercury [30], changes from about 0.4 ng L^{-1}, in the freshwater, to 0.1 ng L^{-1} in the seawater. Considering the previous measurements of methyl mercury in the estuary (ca 0.1 ng L^{-1} above and ca 0.06 ng L^{-1} below the FSI) [23], this difference can be only partly ascribed to the presence of methyl mercury. Both forms of mercury are at a maximum within the FSI. This phenomenon can be explained by the association of mercury with dissolved organic compounds and mineral particles accumulated in the FSI [18, 24]. However, an additional maximum of mercury concentration may appear below the FSI, as can be seen in figures 7 and 8. These measurements were performed after the periods in which a north wind was blowing. Under the influence of this wind, a vertical gyre within the marine layer is formed, which has a direction from the FSI toward the sediment [42]. This process enhances the transport of mercury from the FSI into the sea water.

A different distribution is shown in figure 9. These data were collected after the south-wind period. The maximum mercury concentration appears in the freshwater layer, above the FSI. A similar distribution was observed after heavy rain, with the maximum appearing at the surface [22]. This indicates that there is an atmospheric input of mercury, which is occasional and followed by a slow vertical transport of mercury from the surface towards the FSI. The south wind causes the decrease in outflow of brackish water and diminishing vertical gyres in both freshwater and seawater layers.

These results suggest complex dynamics of mercury species in the water column. The vertical distribution of mercury concentration describes the situation in the

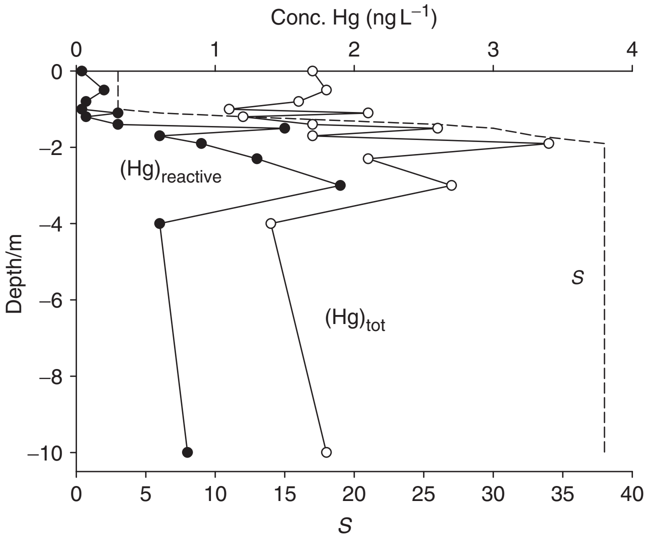

Figure 7. Vertical profiles of salinity (S) and total and reactive mercury on 18 July 2000.

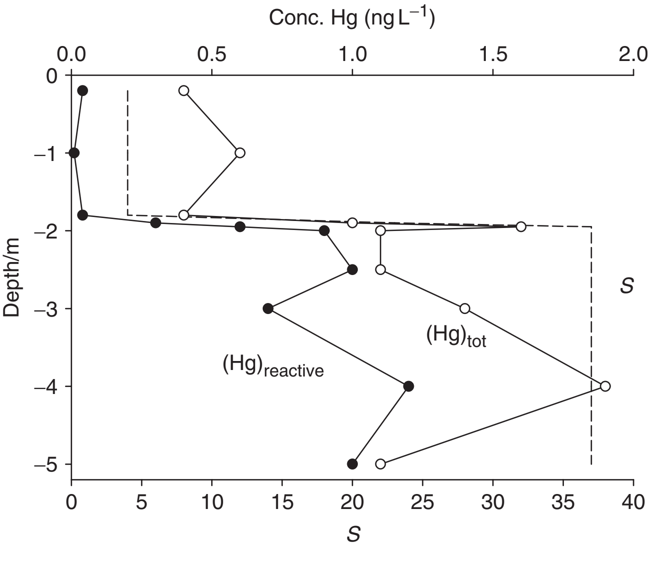

Figure 8. Vertical profiles of salinity (S) and total and reactive mercury on 11 February 1997.

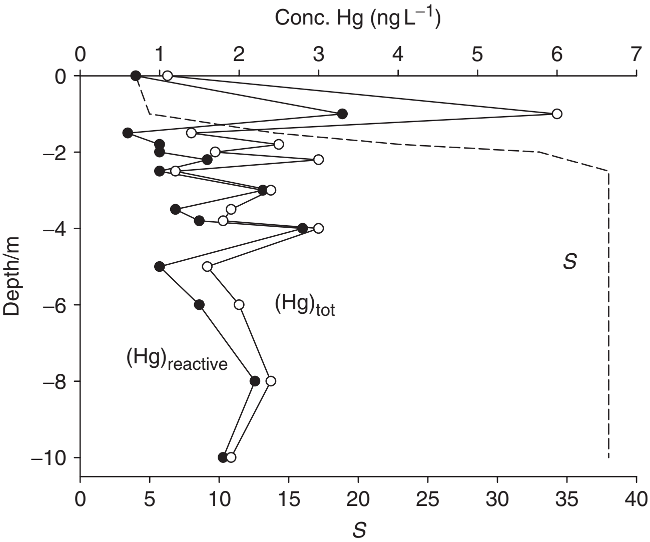

Figure 9. Vertical profiles of salinity (S) and total and reactive mercury on 14 July 2000.

particular moment and depends on the weather conditions. The mercury cycle probably starts with atmospheric input, which is followed by the association of mercury with organic material and suspended mineral particles. The transport of mercury across the FSI is enhanced by a wind-induced vertical gyre within the marine layer.

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