Mercury Speciation in Water of the Krka River Estuary

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Research studies concerning the mercury cycle in the Krka River Estuary have been carried out since 1983. Preliminary results showed relatively low mercury levels in sediments and mussels *Mytilus galloprovincialis* from this area (1). The mercury levels in estuarine water and seawater are comparable with the values found recently in unpolluted coastal areas and open ocean waters (1). The vertical distribution of mercury concentraction in this highly stratified estuary indicates the mercury accumulation at the fresh/saline water interface (1,2). A proportion of organic mercury in various samples has also been measured. The methylmercury was found in sediments, mussels and fish, but not in water (1). Further investigations will be focused on the study of mercury speciation in water, especially at the fresh/saline water interface.

During 1988 and 1989 distributions of reactive and total as well as dissolved and particulate mercury in estuarine waters were investigated. Reactive mercury-$(Hg)_R$ concentration measurements represent those Hg species that are readily reducible by $SnCl_2$ in acidified water. It is composed of dissolved inorganic Hg species; certain mercury associations with organic ligands and in unfiltered water sample the mercury which is easily leached from particulate matter. Total mercury-$(Hg)_T$ refers to the amount of Hg measured after UV-photochemical destruction of samples and will also include stable organomercury associations. It was found that the reactive mercury in unfiltered water generally corresponds to the values of the dissolved mercury fraction. This is in accordance with the fact that the dissolved mercury was mostly inorganic, both in fresh and saline water. A positive correlation between the difference of total and reactive mercury concentrations and quantity of suspended matter, as well as with the concentration of particulate mercury has been found in unfiltered estuarine water. From this it can be concluded that particulate mercury is predominatly bound in organic complexes.

In the deeper saline water layer, over 80 % of the total mercury is reactive Hg. However, this percentage changed in the upper layer, depending on hydrological and/or biological conditions. For example, the portion of reactive mercury in unfiltered samples from the upper layer at the low river discharge

Table 1. Concentrations of reactive and total mercury (ng dm^{-3}) in unfiltered samples from the upper water layer (0.5 m) of the Krka River Estuary

	January 1989 ($Q = 16\ m^3\ s^{-1}$)				July 1989 ($Q = 51\ m^3\ s^{-1}$)			
L(km)[a]	S(‰)	$(Hg)_R$	$(Hg)_T$	$\%(Hg)_R$	S(‰)	$(Hg)_R$	$(Hg)_T$	$\%(Hg)_R$
0	0	0.3	0.8	38	0	0.3	1.0	30
1	-	-	-	-	1	0.1	0.5	20
4	3	0.7	0.7	100	2	0.1	0.9	11
10	10	0.4	0.7	57	5	0.2	1.0	20
17	16	1.3	1.9	68	7	0.1	1.2	8
22	25	1.1	1.4	79	14	0.3	1.5	20
32	38	0.8	0.9	90	38	1.2	1.2	100

[a] Distance from the begining of the estuary in seaward direction

(January 1989) was significantly greater than at the high river flow in July 1989 (Table 1), reflecting the influence of hydrological conditions.

Speciation of mercury along the vertical water profile showed a minimum of the particulate mercury at the interface of fresh and saline layers. This finding is in accordance with the presumption that particles accumulated at the interface (3) release mercury owing to dissolution as a result of increased salinity (aglomeration of organic matter, competition of macrocations and complexation by chloride).

Further investigations on the mercury speciation in water will contribute to a better understanding of the biogeochemical cycle of mercury in stratified estuaries as well as of mechanisms regulating mercury behaviour at the boundary conditions which are prevailing at the fresh/saline water interface.

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3. Žutić,V. and Legović,T. Nature 328 (1987) 612.