Acta Adriat.,32(2):753-763(1991)

ISSN:0001-5113
AADRAY

UDC:551.463(262.3)
Conference paper

VERTICAL TRANSPORT OF MERCURY BY SETTLING PARTICLES IN KAŠTELA BAY

VERTIKALNI TRANSPORT ŽIVE TALOŽENJEM ČESTICA U KAŠTELANSKOM ZALJEVU

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The vertical flux of mercury to sediments in the vicinity of a PVC-factory was measured by sediment traps in spring and autumn 1986. The differences in mercury flux between spring and autumn were significant. Depending on the distance from the coast (10-500 m), the flux was 500-50 $\mu gHgm^{-2}d^{-1}$ and 1800-150 $\mu gm^{-2}d^{-1}$, in spring and autumn, respectively.

Total mercury concentrations in sea water were, depending on the distance from the coast, 330-40 $\mu gHgm^{-3}$ for the spring measurement and 380-180 μgm^{-3} for the autumn measurement. Assuming a homogeneous distribution of Hg in the water column overlaying the bottom and first order kinetics of mercury removal by settling particles, the average mercury residence time in water was calculated to be about 20 days.

INTRODUCTION

The beginning of mercury discharges into Kaštela Bay may be traced back to the year 1949 when the PVC-factory, that is its chlor-alkali plant, erected on the northeastern coast of the bay, was set in operation. It has been estimated that by now more than 200 tons of mercury have been discharged to the bay (Vukadin *et al.*, 1984; Mikac and Picer, 1984). This estimate is based on the knowledge of the technology of production of alkali and chlorine (electrolysis of NaCl with mercury electrodes). Even though the results of the most recent researches are considerably more convenient from the standpoint of current mercury input via chlor-alkali effluents /about 60 kg Hg/year

(Tudor *et al.*, 1987)/, an additional permanent input of mercury from two sewage effluent outfalls has been recorded in the eastern part of the bay /assessed load of 10 kg Hg/year (Štambuk-Giljanović *et al.*, 1985)/.

Some of the first published data on total mercury levels in filtered samples of sea water date from 1980 (Mikac *et al.*, 1985). It was reported that samples from the central part of the bay contained 0.09 μg Hg dm^{-3}, those from the eastern part 0.16 μg Hg dm^{-3}, and from the area of the chlor-alkali effluent 0.18 μg Hg dm^{-3}. The first systematic studies of the levels of heavy metals in Kaštela Bay sediments carried out in 1979 (Stegnar *et al.*, 1981) confirmed that this area was heavily loaded with mercury, making it one of the most polluted and threatened areas along the eastern Adriatic coast. Particularly high mercury levels (8.5 mgHg/kg dry sediment) in the vicinity of the PVC factory pointed to the fact that this factory was the main source of mercury pollution in this area. Other studies of mercury and methyl mercury levels in different compartments of the Kaštela Bay ecosystem (sediments, shellfish and fish) (Mikac, 1982; Vukadin *et al.*, 1982; Filipović and Orlov, 1983; Mikac and Picer, 1984; Zvonarić *et al.*, 1987; 1989) came to the same conclusions.

Since earlier researches lacked particularly systematic data on mercury levels in sea water and the rate of its removal to sediment by suspended particle settling, in 1986 we undertook experiments in order to determine the residence time of mercury in the water column of Kaštela Bay.

SAMPLING STATIONS AND METHODS

Measurements of the rate of sedimentation of mercury on suspended particles was performed twice at nine positions in front of the PVC-factory (Fig. 1). Polyethylene bottles, 14.4 cm high, 9 cm in diameter and with an aperture diameter 4.7 cm were used as sediment traps. Traps were fixed by plastic supports to concrete bases on the sea bottom. The height from the sea bottom to the trap top was 70 cm. Traps were exposed from April 24 to June 21 and from November 10 to December 23, 1986. Traps were fixed and collected by a scuba diver. Samples of surface sediments (0-5 cm) under the traps were also taken by scuba diver. Samples were stored frozen until analyzed.

Sea water samples for total mercury were taken in 1 l dark glass bottles, first cleaned by boiling in HNO_3 and then rinsed with double-distilled water, preserved in polyethylene bags until sampling. Samples were preserved by immediate addition of 20 ml HNO_3 (65 % supra-pure) and stored at +4°C until analyzed.

Total mercury was determined by cold vapour atomic absorption spectrophotometry with amalgamation pre-treatment, as described in detail by Horvat *et al.*(1986; 1986a); Zvonarić *et al.*(1987) and Horvat *et al.*(1987).

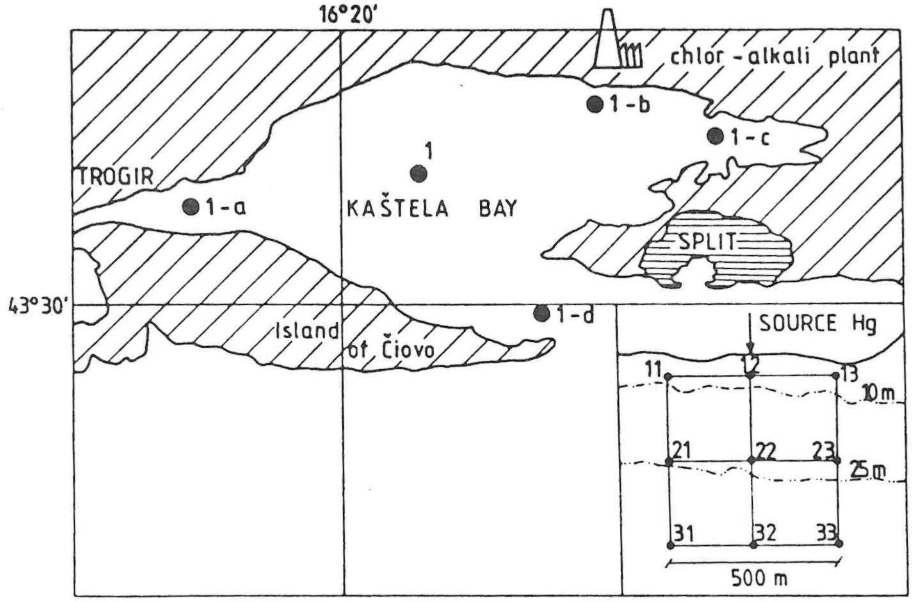

Fig. 1. Study area with sampling stations for sediments (●) and mercury flux measurement locations by sediment traps (on the inset map)

The accuracy of the results obtained was checked using SRMs from the National Institute of Standards and Technology (NIST, formerly NBS), Washington, and inter laboratory comparisons.

RESULTS AND DISCUSSION

The measurements of the vertical flux of settling suspended particles (Fs),organic material in sedimented particles (OM), mercury contained in particles settled in sediment traps $(Hg)_p$ and total mercury in the sea water (dissolved + particulate) $(Hg)_w$ carried out between April 24 and June 21 and between November 10 and December 23, 1986 are presented in Table 1.

The sedimentation rate (or the vertical flux of suspended particles) was the highest closest to the coast, while 250 m (position 21-23) and 500 m offshore (positions 31-33) the values were equal. Close to the coast a considerable quantity of sedimentary suspended matter occurs in organic form (about 40%), while further offshore the proportion of organic matter in the flux of suspended particles is reduced to 6-13 % .

Table 1. Results of measurements of the sedimentation rate of suspended particles (FS), proportion of organic fraction of sedimented matter (OM), mercury contained in sedimented particles (Hg)p, mercury flux (FHg) and mercury levels in sea water (Hg)w

POSITION	DEPTH (m)	Fs ($gm^{-2}d^{-1}$)	OM (%)	$(Hg)_p$ (mgg^{-1})	F_{Hg} ($mgm^{-2}d^{-1}$)	$(Hg)_w$ (mgm^{-3})
APRIL - MAY						
11	9	53.8	37.3	10.48	564.2	317
12	9	-	-	-	-	535
13	9	-	-	-	-	135
21	25	77.8	5.9	4.69	364.6	52
22	24	16.0	8.2	7.29	116.6	44
23	20	5.7	10.8	4.50	25.7	55
31	30	11.0	11.4	5.31	58.2	37
32	28	2.2	12.9	6.78	14.7	46
33	30	9.5	6.5	6.15	58.4	45
NOVEMBER - DECEMBER						
11	9	62.2	31.7	16.64	1035.8	442
12	9	138.2	48.3	12.87	1778.0	249
13	9	170.6	10.6	14.87	2536.7	444
21	25	40.8	6.4	6.38	260.0	439
22	24	-	-	-	-	113
23	20	32.1	10.5	8.10	259.7	210
31	30	22.9	7.1	5.27	120.7	117
32	28	37.5	6.4	-	-	354
33	30	38.3	8.5	4.77	182.7	60

The rate of sediment accumulation may be measured by entrapping settling suspended particles in sediment traps (Gardner, 1980; 1980a; Simpson, 1982). After Gardner (1980) the measured flux of new particles in a sediment trap need not necessarily be equal to the net sedimentation and to the sediment accumulation rate in a given environment. This kind of sedimentation may also include resuspension of sediment transported horizontally from some other site. In any active area the deposition rate of resuspended sediment may considerably exceed the deposition of new particles (Gardner, 1980). Therefore, in measuring the flux in the present study, this fact should also be considered.

Results of mercury sedimentation rate measurements also depend on the accuracy of the measurements of the rate of suspended particle settling. The efficiency of sediment traps is defined by their geometry and current speed. Optimum efficiency is attained when the ratio of the depth to breadth of the trap aperture is between 2 and 3. However, in bottles with a narrower aperture and wider body increased efficiency is quite possible (Gardner, 1980; 1980a).

Tsunogai *et al.*,(1986) showed that in winter the obtained flux of suspended particles in the sediment trap (gross) ordinarily exceeded the "net" flux measured by ^{234}Th, while in spring these two fluxes were equal. A higher flux was generally obtained in winter. These differences were attributed to spring stratification and winter water convection respectively, and not to the efficiency of traps. It is well known that vertical stratification is present in the Kaštela Bay in April, May and June, while in December the water column is well mixed (Zore-Armanda, 1980), so that partial sediment resuspension is quite possible. Mercury flux is also reduced with the distance from the coast, that is with the distance from the chlor-alkali plant effluents. Here the effect of depth increase is also superimposed, since it is well known that the mercury sedimentation rate may rapidly decrease with increase in depth (Smith and Loring, 1981).

Sedimentation is the most important process of mercury removal from the water column. Mercury adsorption on suspended particles is a rather rapid process which, for example, takes not more than four hours in the case of clay particles (Frenet-Robin and Ottman, 1978). The quantity of adsorbed mercury is inversely proportional to particle size (Renzoni *et al.*, 1973). The presence of organic matter enhances the adsorption process. However, we obtained a very poor positive correlation between sedimented mercury (Hg)p and the quantity of organic matter in the traps (OM).

For the Scheldt Estuary it was established (Zafiropoulos, 1986) that 165 μmgHg m^{-2}d^{-1} was deposited on the sea bottom by sedimentation of suspended particles, while Pheiffer-Madsen (1981) reported a mercury flux of 2 μg m^{-2}d^{-1} at a sediment accumulation rate of 4.5 gm^{-2}d^{-1} for Ho Bay (Denmark). Smith and Loring (1981) applied geochronological analysis by which they assigned the mercury concentrations of 4-14 μg g^{-1} of sediment, recorded in the vicinity of a chlor-alkali plant, to a flux of 400 - 1500 μg Hgm^{-2}d^{-1}. These values refer to the period of intensive discharge of mercury, while upon reduction of effluent inputs the flux was reduced to 50 μgHg m^{-2}d^{-1}.

Mercury residence time on the settling particles in the water column may be easily calculated, assuming a well mixed column, by the kinetic equation of the first order:

$$h \times \frac{d(Hg)_w}{dt} = -k_T \times (Hg)_w \times h = F_s \times (Hg)p = F_{Hg}$$

where $(Hg)_w$ - the concentration of total (dissolved + particulate) mercury in sea water

($\mu g\ m^{-3}$), Fs - sedimentation rate of suspended particles ($g\ m^{-2}d^{-1}$), $(Hg)_w$ - concentration of particulate mercury in the trap ($\mu g\ g^{-1}$), h - depth of the sea water column overlying the trap (m), F_{Hg} - mercury flux ($\mu g\ m^{-2}d^{-1}$) and k_T - the coefficient of mercury sedimentation rate by suspended particles. The reciprocal value k_T gives the residence time τ_T ($1/k_T$). The coefficients of mercury sedimentation rate by suspended particles offshore of the chlor-alkali plant are given in Table 2.

Table 2. The coefficients of removal of mercury (kT) from the sea water column by particle sedimentation (residence time t = 1/kT is given in brackets)

Position	Trap depth (m)	k_T (day^{-1})	
		MAY - JUNE	NOVEMBER-DECEMBER
11	9	0.198 (5.05)	0.260 (3.84)
12	9	-	0.793 (1.26)
13	9	-	0.635 (1.57)
21	25	0.280 (3.57)	0.024 (41.60)
22	24	0.110 (9.09)	-
23	20	0.023 (43.50)	0.062 (16.10)
31	30	0.052 (19.20)	0.034 (29.40)
32	28	0.011 (90.00)	-
33	30	0.043 (23.20)	0.102 (9.80)

Sedimentation rate coefficients are highest closest to the coast, showing that about 20-80 % of the mercury in the sea water column will settle on the sea bottom daily. About 2-10 % of total mercury is daily removed to sediment 250 and 500 m offshore (off the outfall). The geometric mean of the sedimentation rate coefficients of mercury is 0.05 d^{-1}.

The mercury sedimentation rate coefficient k_T may be expressed according to the equation (Santschi, 1984):

$$k_T = \frac{F_s \times (Hg)_p}{h \times (Hg)_w} = \frac{Fs \times K_D}{h \times (1 + S \times K_D)}$$

where: S - the concentration of suspended particles ($mg\ dm^{-3}$), K_D - coefficient of distribution of mercury between the liquid and solid state (dm^3kg^{-1}). If S $K_D << 1$ then $kT = K_D\ Fs/h$, and the residence time of mercury (τ_T) may be expressed as a function of Fs/h:

$$\log \tau_T = -\log k_T = -\log K_D - \log (Fs/h)$$

The ratio of $\log \tau_T$ to $\log$ (Fs/h) is depicted in Fig. 2. The regression coefficient from equation (3) for the data collected during the exposure of traps in November and December is equal to one, just as required by equation (3), and $\log K_D = 4.57$. For the trap exposed in May-June, the coefficient of linear regression is lower than theoretically required (-1) suggesting that $\log [\![(Hg)_p/(Hg)_w]\!]$ is also a function of the mercury residence time (Santschi, 1984).

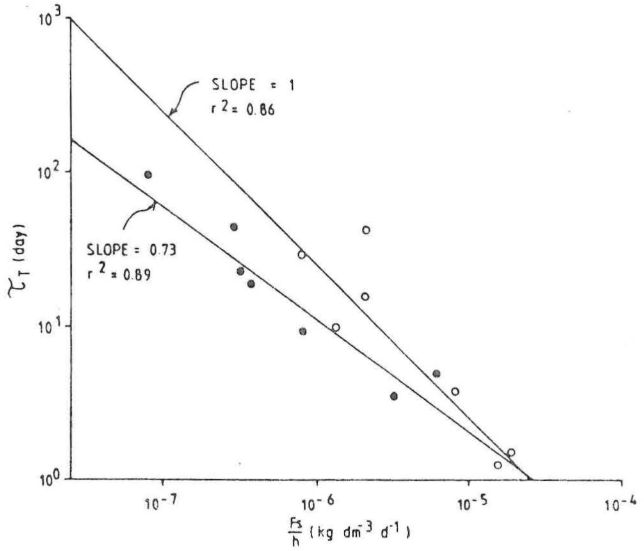

Fig 2. Mercury residence time in the water (τ_T) in relation to the rate of suspended matter flux (Fs) and to the depth of the water column (h) overlying the sediment traps: May-June (●); November-December (○)

According to measurements in coastal waters, estuaries and the laboratory the values of $\log K_D$ for mercury range from 4.7 to 6.0 (Balls, 1989). The values of the coefficient of distribution between the particulate and dissolved states of mercury may be reduced with an increase in the suspended particle concentration (Balls, 1989). The K_D "in situ" values depend on both the particle residence time and the unbalanced distribution of metals between the solid and dissolved state (Honeyman *et al.*, 1988).

The mercury balance in the bay water may be described by the equation:

$$\mathrm{v \ x} \frac{d(\mathrm{Hg})_w}{dt} = \mathrm{I - (kt + k_b) \ x \ (Hg)w \ x \ V}$$

where: $(\mathrm{Hg})_w$ - mercury concentration in the sea water (μg m^{-3}), V - volume of the bay (m^{-3}), $\mathrm{k_T}$ - total mercury sedimentation rate coefficient (d^{-1}), $\mathrm{k_b}$ - coefficient of the bay water exchange rate (d^{-1}), I - total mercury input to the bay water (μg d^{-1}). Under stationary conditions $[\![d(\mathrm{Hg})_w/dt=0]\!]$

$$\mathrm{I = (k_T + k_b) \ x \ (Hg)_w \ x \ V}$$

The renewal time of Kaštela Bay water is 30 days (Zore-Armanda, 1979) or $\mathrm{k_b} = 1/30 = 0.033$ d^{-1} and the geometric mean of $\mathrm{k_T}$ from Table 2 is 0.05 d^{-1}. The mean residence time of mercury (τ_{Hg}) in the bay water is

$$\mathrm{k_{Hg}} = 1/\tau_{\mathrm{Hg}} = \mathrm{k_T + k_b} = 0.05 + 0.033 = 0.083$$

that is τ_{Hg} is 12 days.

The ratio of the sedimentation rate coefficient to the total coefficient of mercury removal from the bay water gives the fraction (f) of the total mercury input which is removed from the water to the sediment of the bay

$$\mathrm{f = k_T / (k_T + k_b)}$$

whereas the fraction that is removed by the water is (1-f).

Since the mean time of Kaštela Bay water exchange is 30 days ($\mathrm{k_b} = 0.033$ d^{-1}) and the mean mercury sedimentation rate coefficient $\mathrm{k_T} = 0.05$ d^{-1}, a value for f is obtained of f = 0.6; that is, about 60 % of the mercury mass is removed to sediment and the remaining 40 % is removed by water transport. If only the eastern part of Kaštela Bay (τ = 14 days), where the mercury pollution sources are located, is taken into consideration, 40 % of the mercury input is removed to sediment and 60 % is transported to the central part of the bay. It follows, therefore, that the quantity of mercury deposited on the sea bed of the eastern part is twice that in the central part. In fact, mercury concentrations in the sediment of these two parts do show this same ratio (Stegnar *et al.*, 1981; Zvonarić *et al.*, 1989).

CONCLUSIONS

The mean mercury sedimentation rate by the first order kinetics from the water column of the Kaštela Bay is 0.05 d^{-1}. With the flushing period of the Kaštela Bay of 30 days, the mean residence time of mercury is 12 days. Under stationary conditions about 60% of the total mercury input is removed to sediment and the remaining 40% is removed out of the bay by advection.

From the data on the mercury and suspended matter sedimentation rate the coefficient of distribution of mercury between the liquid and solid state (K_D) was obtained to be 3.72×10^4 dm^3kg^{-1}.

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Accepted: November 9, 1990

VERTIKALNI TRANSPORT ŽIVE TALOŽENJEM ČESTICA U KAŠTELANSKOM ZALJEVU

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KRATKI SADRŽAJ

U blizini PVC-tvornice mjerena je brzina taloženja žive na česticama pomoću taložnica ("sediment trap") smještenih 70 cm iznad morskog dna. Izmjereni fluks žive ovisno o udaljenosti od obale (10-500 m) bio je 500-50 μgHgm^{-2}d^{-1} tijekom proljeća i 1800-150 μgHgm^{-2}d^{-1} tijekom jeseni. Pretpostavljajući homogeni stupac morske vode iznad dna i kinetiku prvog reda za odstranjivanje žive taloženjem čestica, izračunat je srednji koeficijent brzine taloženja žive od 0,05 dan^{-1}. Uzimajući da se koeficijent brzine taloženja žive (k_T) može iskazati kao funkcija omjera fluksa suspendiranih čestica (F_s) i dubine (h) tj. $k_T = K_D F_s / h$, tada je koeficijent proporcionalnosti K_D koeficijent distribucije žive između čvrste i otopljene faze u morskoj vodi. Za Kaštelanski zaljev je dobivena vrijednost 3.72 x 10^4 dm^{3}kg^{-1}.

Uz vrijeme izmjene vode Kaštelanskog zaljeva od 30 dana, vrijeme zadržavanja žive u morskoj vodi zaljeva je tada 12 dana. U stacionarnim uvjetima oko 60% ukupnog ulaza žive u vodu zaljeva se taloži na morsko dno, dok se preostalih 40% advekcijom vode odnosi van Kaštelanskog zaljeva.