

## Behaviour of Hg species in a microtidal deltaic system: The Isonzo River mouth (northern Adriatic Sea)

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### Abstract

Mercury species in the highly stratified water column of the Isonzo River mouth (northern Adriatic Sea) were investigated in February, May and August 2002 (low-normal fluvial discharge). Total, dissolved and particulate mercury (Hg) and methylmercury (MeHg) were measured and their concentrations were related to physico-chemical parameters in terms of temperature, salinity, turbidity, O<sub>2</sub> concentrations and total suspended matter (TSM) as well as particulate organic carbon (POC) content. Particulate Hg and MeHg are well correlated to medium-fine silty suspended sediment and organic matter, respectively. Desorption of Hg from particles in the brackish layer was observed. Due to the presence of a saltwedge, the lower river course seems to be a trap for Hg carried by fluvial waters. MeHg normally decreases approaching the sea but the local increase in the inner zone of the saltwedge could be related to methylation processes in the bottom water layer. Hg export is effective only during medium and high riverine flows acting as an important source of Hg into the northern Adriatic and the adjacent lagoon system.

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### 1. Introduction

The mercury (Hg) biogeochemical cycle in estuaries and river mouths is a topic of great importance in understanding the behaviour of the element in these complex environment. This cycle involves physico-chemical processes (Leermakers et al., 2001; Coquery et al., 1997; Laurier et al., 2003), methylation in the water column (Mason et al., 1993), potential accumu-

lation in bottom sediments (Benoit et al., 1998; Mikac et al., 1999) and bioaccumulation in the aquatic food web (Muhaya et al., 1997; Lawson and Mason, 1998).

Mercury (Hg)-contaminated freshwater inputs from the Isonzo River have affected the Gulf of Trieste and the northern Adriatic Sea for nearly 500 years as a result of the excavation of cinnabar-rich deposits in the Idrija mining district of western Slovenia (Fig. 1a). The Gulf presents then the highest concentrations of Hg (>30 µg g<sup>-1</sup>) in marine sediments observed in the whole Mediterranean area (Covelli et al., 2001). Hg is mostly present in detrital form (cinnabar) in sandy-silty sediments near the river mouth and surrounding beaches (Biester et al., 2000; Covelli et al., 2001).

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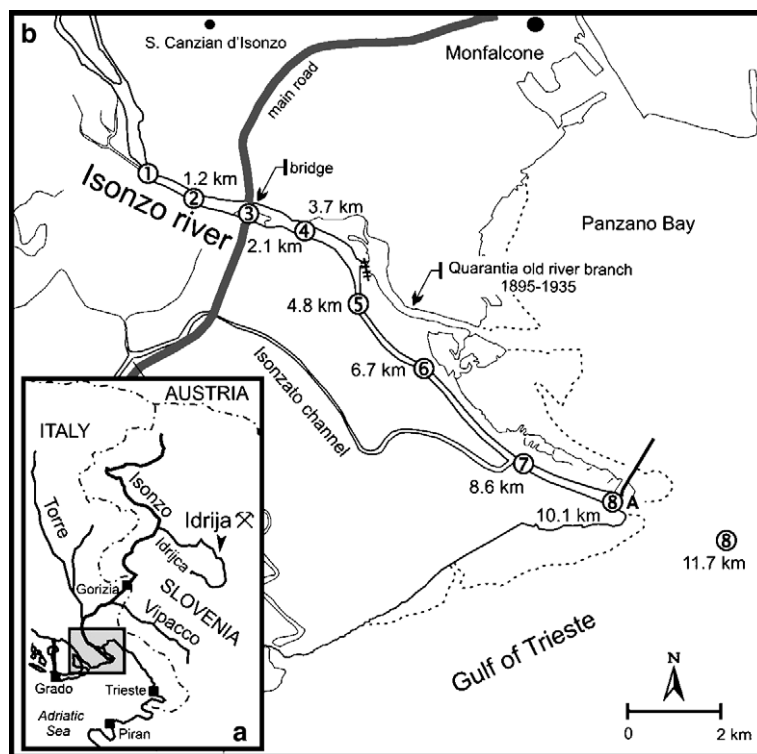


Fig. 1. Index map of the study area (a) and location of sampling stations along the lower river course.

Dispersion of suspended particles is partially due to longshore currents and, more effectively, to interaction between meteo-marine and riverine hydrological conditions.

Although several recent studies have described some aspects of Hg biogeochemistry in the Idrija–Isonzo river system (Hines et al., 2000), in the coastal waters (Faganeli et al., 2003) and in sediments (Covelli et al., 2001) of the Gulf of Trieste, little is known about Hg behaviour at the river mouth. The aims of this study are to identify the relative abundance of Hg species in the lower course of the river during low-normal fluvial discharge, which is mostly prevalent over the entire year, and to understand the effects of physical and biogeochemical factors on the distribution of Hg species within the “estuarine zone” of the river mouth under different seasonal conditions.

## 2. Materials and methods

### 2.1. Field activities

Sampling of the water column along the lower Isonzo River course (Fig. 1b) was performed in three campaigns, under a low hydrodynamic flow regime (Fig. 2a, b and c): in February 2002 ( $56 \text{ m}^3 \text{ s}^{-1}$ ), in

May 2002, during a period of relatively higher water discharge ( $73 \text{ m}^3 \text{ s}^{-1}$ ) after 1 day of heavy rains, and in August 2002 ( $32 \text{ m}^3 \text{ s}^{-1}$ ). Water samples were collected by boat at nine sampling stations along the main axis of the river channel, moving upstream from the sea (station 8), during neap flood–tide conditions. A moderate river flood was intercepted at station 6 in May while sampling was still in progress. Surface samples (i.e. 5-s; s=surface) were taken by hand-dipping 1-L acid pre-cleaned Teflon bottles. Deep water samples were collected by means of a 5-L Teflon-lined Niskin bottle at the bottom (i.e. 5-b; b=bottom) and at variable depths, according to the salinity profiles (i.e. 5-m; m=intermediate), and they were immediately delivered into acid-cleaned 1-L Teflon bottles. To identify the water masses before sampling, temperature, salinity and turbidity were recorded in situ by means of a CTD Hydrolab H<sub>2</sub>O Multiprobe with a 0.1 dbar pressure step.

### 2.2. Analyses

Total mercury (THg) and dissolved mercury (DHg) in water samples were determined by CV AAS after BrCl/UV oxidation and SnCl<sub>2</sub> reduction followed by gold amalgamation and detection (Bloom and Crece-

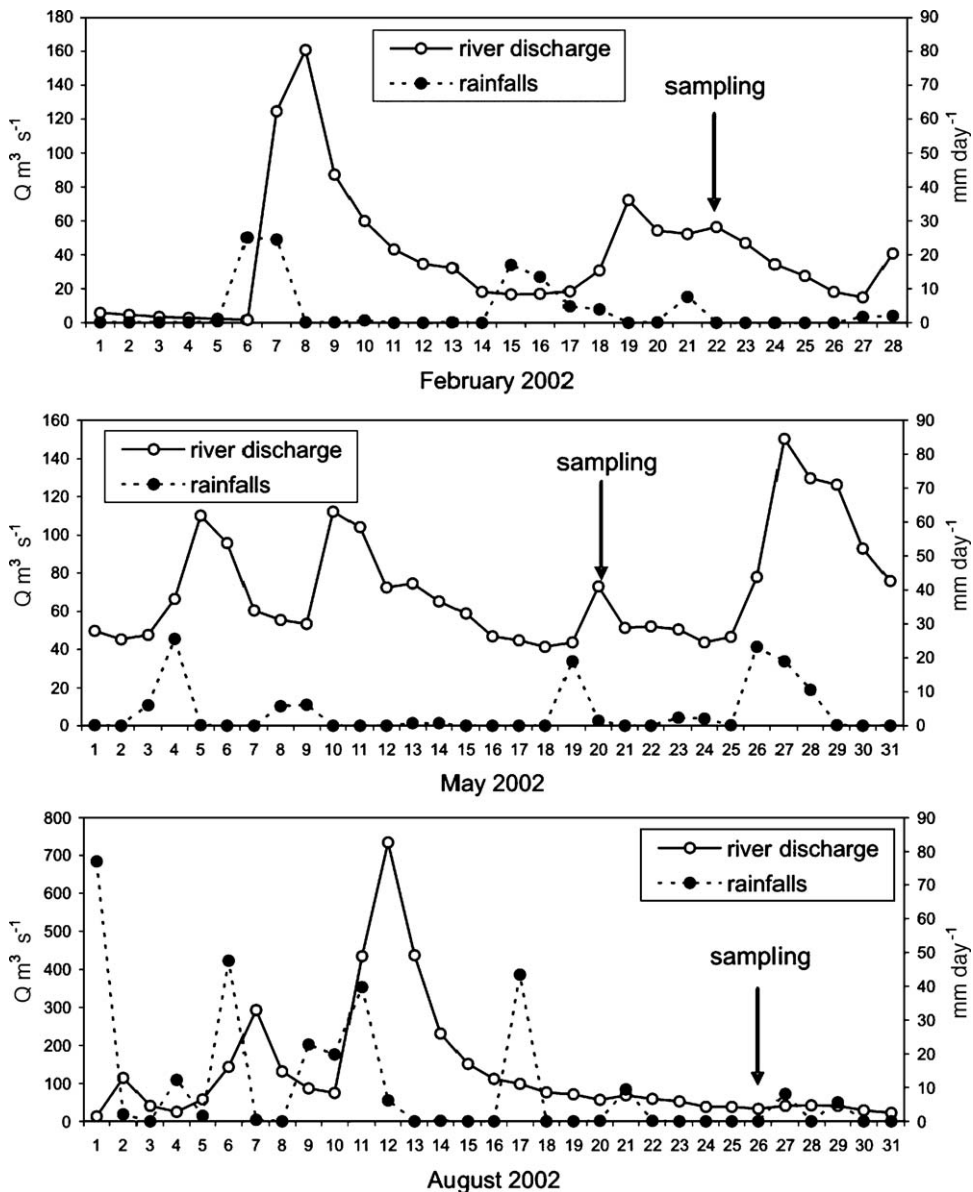


Fig. 2. Daily Isonzo River discharge ( $\text{m}^3 \text{s}^{-1}$ ) and rainfalls ( $\text{mm day}^{-1}$ ) during sampling periods.

lius, 1983). For measuring DHg, the water sample was previously filtered through Nalgene filtration units on Millipore HA (cellulose nitrate) membrane filters with a pore size of  $0.45 \mu\text{m}$ . Filters were pre-cleaned using  $\text{HNO}_3$  and  $\text{HCl}$  baths. Particulate Hg (PHg) was determined after filtering on membrane Millipore HA filters. Filters with particles were lyophilized, weighted and dissolved in Teflon tubes in a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . Samples were then analyzed using the CV AAS technique.

The detection limit of procedure was  $0.1 \text{ ng L}^{-1}$  calculated on the basis of the three standard deviation of

the reagent's blank. The repeatability and reproducibility of the method was 5% and 10%, respectively (Horvat et al., 1991), and total uncertainty for THg (sampling and analyses) was  $\pm 5\%$ .

Reactive Hg (RHg) was determined immediately after sampling by  $\text{SnCl}_2$  reduction in non acidified water samples, followed by gold amalgamation and AAS detection (Horvat et al., 1991). The detection limit of the procedure was  $0.1 \text{ ng L}^{-1}$ , whereas total uncertainty was  $\pm 3\%$ .

Dissolved gaseous mercury (DGHg) was measured immediately after sampling by purging the water sam-

Table 1  
Salinity, temperature (°C), particulate organic carbon (POC,  $\mu\text{g L}^{-1}$ ) and TSM ( $\text{mg L}^{-1}$ ) concentrations in water samples

Station		Salinity			Temperature (°C)			POC ( $\mu\text{g L}^{-1}$ )			TSM ( $\text{mg L}^{-1}$ )		
		Feb	May	Aug	Feb	May	Aug	Feb	May	Aug	Feb	May	Aug
ISO 1	Surface	0.4	0.3	0.3	6.8	15.6	17.7	181	851	174	1.2	29.6	1.3
	Bottom	n.s.	0.3	0.3	n.s.	15.6	17.7	n.s.	833	124	n.s.	30.9	1.1
ISO 2	Surface	0.8	0.3	0.7	6.6	15.7	18.3	206	730	154	3.9	30.2	1.3
	Bottom	0.9	0.4	11.0	6.6	15.7	19.6	208	797	882	3.2	31.9	4.7
ISO 3	Surface	0.8	0.4	1.0	6.6	15.3	18.1	303	577	124	3.5	26.7	1.4
	Intermediate	1.4	0.5	10.9	6.6	15.2	20.4	251	587	446	2.4	27.6	2.9
	Bottom	17.0	0.6	22.3	8.0	15.0	23.4	345	589	368	14.4	26.4	4.3
ISO 4	Surface	1.4	0.9	1.0	6.6	14.8	20.0	272	589	161	2.3	23.9	1.5
	Intermediate	16.3	3.8	23.1	7.7	14.6	21.9	210	606	701	12.7	24.4	4.7
	Bottom	34.9	33.3	30.4	7.3	16.1	24.6	137	229	427	13.6	5.6	4.3
ISO 5	Surface	2.2	1.4	2.5	6.5	14.5	19.8	293	643	256	2.9	27.3	1.9
	Intermediate	2.4	3.0	17.9	7.1	14.6	22.1	263	655	633	3.3	28.0	8.1
	Bottom	37.4	33.8	30.6	7.1	16.2	24.7	177	201	394	11.5	4.4	6.2
ISO 6	Surface	1.8	1.8	3.1	6.7	14.4	19.6	242	518	216	3.6	19.1	2.0
	Intermediate	3.9	21.8	21.4	7.3	16.7	23.0	255	1170	463	6.1	9.9	5.4
	Bottom	37.8	35.2	30.7	7.3	16.7	24.6	153	234	361	16.4	15.5	6.4
ISO 7	Surface	1.8	2.5	3.3	6.8	14.6	19.8	327	424	199	2.7	6.4	2.1
	Intermediate	16.0	14.5	22.1	7.5	14.8	23.2	199	549	405	8.6	13.5	14.3
	Bottom	38.4	34.5	31.9	7.4	17.6	24.5	140	219	390	18.8	12.9	9.8
ISO 8A	Surface	2.4	3.4	3.2	7.6	14.8	19.5	269	467	240	2.8	4.2	2.6
	Intermediate	16.4	18.2	23.9	7.9	15.3	22.8	250	563	507	10.4	11.1	6.5
	Bottom	32.4	30.3	29.9	7.3	19.2	23.9	232	390	496	22.5	26.3	8.0
ISO 8	Surface	18.6	30.1	31.7	7.3	18.5	24.1	206	393	444	4.9	24.4	4.3
	Bottom	38.2	35.6	34.8	7.4	18.6	24.7	159	295	536	11.0	25.8	5.9

ples for 10 min using Hg free nitrogen with a flow rate of  $0.5 \text{ L min}^{-1}$  for removing volatile Hg species ( $\text{Hg}^0$  and dimethyl Hg) and trapping them onto a gold-coated silica trap kept at room temperature. The gold sampling trap was then transferred, through thermal desorption, to a double amalgamation CV AFS analyzer system. The detection limit of the procedure was  $5 \text{ pg L}^{-1}$  calculated on the basis of the three standard deviations of the system and bubbler blank. The repeatability of the method was 4%, whereas total uncertainty was  $\pm 3\%$ .

Total methylmercury (TMeHg) determination in water was performed using solvent extraction, aqueous phase ethylation, gas chromatographic separation, pyrolysis, and CV AFS detection (Horvat et al., 1993a,b; Liang et al., 1994). Dissolved methylmercury (DMeHg) was determined using the same procedure as TMeHg with an added filtration step. Samples were filtered on Nalgene filtration units through Millipore HA (cellulose nitrate) membrane filters with a pore size of  $0.45 \mu\text{m}$ . Particulate methylmercury (PMeHg) was calculated from the difference between the total and dissolved phases. The limit of detection calculated based on three times the standard deviation of blanks was about  $3 \text{ pg L}^{-1}$ . The repeatability and reproducibility was 5% and 10%, respectively, whereas total uncertainty was  $\pm 7\%$ . The quality of analytical measurements for Hg analysis

and speciation was checked by the regular use of certified reference materials (CRMs) such as IAEA 405 (trace and major elements in estuarine sediments) and NIST SRM 2976 (trace elements and MeHg in mussel tissue). As for water samples, CRMs for total, reactive and methylmercury are not extant and methods were continuously validated by the US EPA protocol (EPA Method 1631).

Salinity of the Niskin bottle samples was also measured using the Mohr–Knudsen titrimetric method (Strickland and Parsons, 1972). Oxygen concentrations in the water samples were determined using the Winkler method (Grasshoff et al., 1983). Total suspended matter

Table 2  
Salinity ranges for freshwater, brackish and saltwater samples in the three sampling

		Freshwater	Brackish	Saltwater
February	Min–max	0.4–3.9	16.0–18.6	32.4–38.4
	Average	$1.7 \pm 1.0$ $n=12$	$16.8 \pm 1.0$ $n=5$	$36.1 \pm 2.5$ $n=7$
May	Min–max	0.3–3.8	14.5–21.8	30.1–35.6
	Average	$1.4 \pm 1.3$ $n=14$	$18.1 \pm 3.7$ $n=3$	$33.3 \pm 2.2$ $n=7$
August	Min–max	0.3–3.3	10.9–23.9	29.9–34.8
	Average	$1.7 \pm 1.3$ $n=9$	$19.1 \pm 5.3$ $n=8$	$31.4 \pm 1.6$ $n=7$

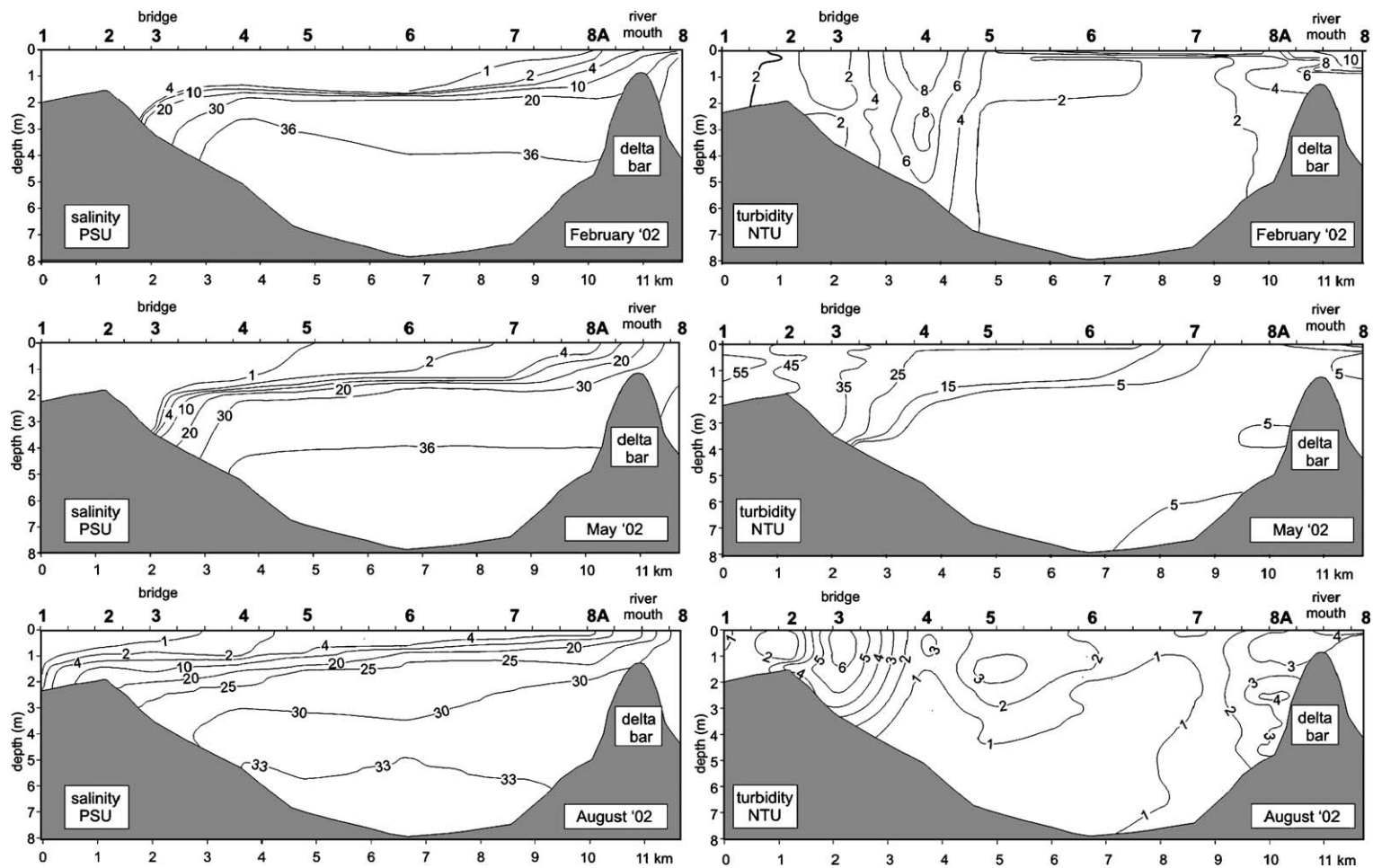


Fig. 3. Schematic cross section of the river mouth and spatial variability of salinity (PSU) and turbidity (NTU).



(TSM) was measured using vacuum filtration through Whatman fibreglass GF/F (diameter=47 mm, pore size=0.8  $\mu\text{m}$ ) filters, ignited at 450  $^{\circ}\text{C}$  (Strickland and Parsons, 1972). Particulate organic carbon (POC) content, expressed as a percentage of total solid and concentration ( $\text{mg L}^{-1}$ ) in filtered water samples, was determined after acidification with 1 M HCl (Hedges and Stern, 1984), using a Perkin Elmer CHN Elemental Analyser. Particle size analysis in the range 9–4  $\phi$  (1.95–62.5  $\mu\text{m}$ ) was performed by using a Coulter Multisizer II (Coulter Electronics Ltd., 1972). The Accucomp programme was used to acquire and process grain-size spectra.

### 3. Results and discussion

#### 3.1. Hydrological setting

The Isonzo River (average annual flow rate of 197  $\text{m}^3 \text{s}^{-1}$ , INTERREG II, 2001) is affected by long periods of low–medium discharge and short peaks of intense riverine flow (up to 2500  $\text{m}^3 \text{s}^{-1}$ , RAFVG (Regione Autonoma Friuli-Venezia Giulia), 1986), associated with a high suspended sediment load (up to 1000  $\text{g m}^{-3}$ ), following heavy rainfalls that normally occur in the autumn season. Results of the ancillary parameters (salinity, temperature, dissolved oxygen and TSM concentrations) are reported in Table 1. Three types of water (freshwater, brackish water and saltwater) were recognized during each sampling based on defined salinity ranges (Table 2). In our early contribution (Covelli et al., 2004), it was pointed out that, for most of the year, the highly stratified water column and related hypopycnal flux are prevalent in the dynamic regime within the lower reach of the distributary mouth where the saltwedge shifts its position landward according to the tidal range (Fig. 3). The circulation pattern in the last sampling (August) was quite similar to that of February although the very low summer discharge allowed higher mixing at interface between the two water masses along the river channel. The saltwedge tip was located more upstream in summer and the riverine flow hardly overpasses the delta bar. The high turbidity zone (HTZ) was always recognizable at the saltwedge tip (stations 3, 4 and 5), but high values of turbidity were also recorded at the river mouth, near the delta bar, due to higher turbulence caused by friction between the two water masses and the river bed at very shallow depth (1.5 m). As a consequence, TSM concentrations in the river were very low in comparison to the underlying saltwater where TSM increased downstream. The saltwedge was present in May and a partially thermally stratified water column

appeared (warmer layer at the top). Although the arriving moderate river flood was pushing seawards, the saltwedge tip and the interaction between the two water masses determined higher turbulence in this area. The very high turbidity values were clearly related to the moderate flood event as confirmed by high TSM concentrations. The residence time of the highly saline bottom waters can be quite long during part of the year as proved by oxygen depletion (up to 25% of saturation) found in May and August, although less evident in the latter sampling (Fig. 4). Water renewal of the saltwedge may occur following intense river discharge events. The saltwedge is pushed out of the river mouth, fluvial water empties the channel, and the outflow spreads as a plume above the underlying marine waters in the Gulf of Trieste transporting fine riverborne material into the prodelta zone and even outside the Gulf. When the flood has ceased and the current has slowed down, saltwater again enter the river mouth. The Isonzo River mouth may hence be defined as a microtidal, low energy and fine-grained deltaic system.

#### 3.2. Total, particulate, dissolved, reactive, and dissolved gaseous Hg

A summary of the results is reported in Table 3. Total Hg (THg) concentrations in freshwater increased

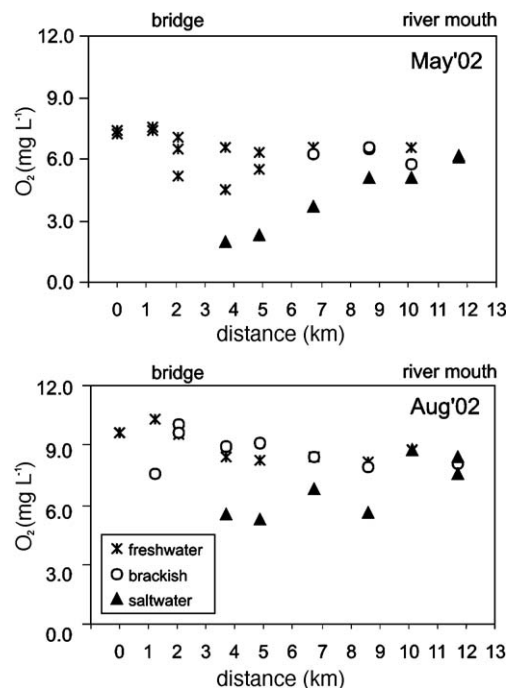


Fig. 4. Longitudinal profiles of dissolved oxygen concentrations in the river mouth in the three types of water.

Table 3  
Summary of concentrations of total Hg (THg, ng L<sup>-1</sup>), dissolved Hg (DHg, ng L<sup>-1</sup>), particulate Hg (PHg, ng L<sup>-1</sup>), total MeHg (TMeHg, pg L<sup>-1</sup>), dissolved MeHg (DMeHg, pg L<sup>-1</sup>), particulate MeHg (PMeHg, pg L<sup>-1</sup>), dissolved gaseous Hg (DGHg, ng L<sup>-1</sup>) reactive Hg=(RHg, ng L<sup>-1</sup>) in water samples

		Station																								
		ISO 1		ISO 2		ISO 3		ISO 4			ISO 5			ISO 6			ISO 7			ISO 8A			ISO 8			
		Surface	Bottom	Surface	Bottom	Surface	Intermediate	Bottom	Surface	Intermediate	Bottom	Surface	Intermediate	Bottom	Surface	Intermediate	Bottom	Surface	Intermediate	Bottom	Surface	Intermediate	Bottom	Surface	Bottom	
RHg	Feb	ng L <sup>-1</sup>	0.87	n.s.	0.51	0.33	0.49	2.23	2.78	0.88	0.75	0.51	0.38	0.72	0.85	0.85	0.71	0.38	0.41	0.89	0.48	–	–	–	1.99	0.31
	May	ng L <sup>-1</sup>	0.15	0.41	0.18	0.77	0.32	1.62	0.53	0.44	0.84	–	–	–	–	–	–	–	1.46	0.77	0.49	0.65	0.82	0.77	2.42	0.49
	Aug	ng L <sup>-1</sup>	0.58	0.59	0.69	1.09	0.94	1.54	1.69	0.68	0.95	0.79	1.05	1.16	0.68	0.87	1.17	0.85	0.82	1.12	0.70	0.37	0.86	0.64	0.54	0.87
THg	Feb	ng L <sup>-1</sup>	7.22	n.s.	16.22	19.19	14.23	13.21	13.54	9.21	7.10	5.43	12.53	14.76	15.10	31.57	36.44	16.61	25.54	20.58	15.53	–	–	–	9.25	40.29
	May	ng L <sup>-1</sup>	33.25	29.29	21.08	21.43	4.73	14.91	14.17	19.26	10.08	7.43	28.28	9.02	7.19	31.57	<DL	<DL	23.92	24.78	110.75	<DL	38.26	173.99	28.14	53.61
	Aug	ng L <sup>-1</sup>	27.14	5.59	10.45	21.43	12.49	13.41	39.56	14.34	9.51	13.58	16.97	30.76	20.79	24.12	35.99	71.53	16.96	28.51	33.41	103.51	25.80	57.53	4.47	17.61
DHg	Feb	ng L <sup>-1</sup>	4.71	n.s.	3.13	5.93	9.49	7.47	5.65	3.98	3.33	1.84	7.72	6.34	5.14	17.01	13.85	7.42	15.38	10.43	5.59	–	–	–	7.12	13.11
	May	ng L <sup>-1</sup>	2.16	1.97	0.46	2.82	2.32	2.81	2.45	1.06	1.52	1.38	1.43	0.93	n.a.	1.38	1.71	–	12.32	12.27	41.11	12.37	6.66	81.26	10.76	23.85
	Aug	ng L <sup>-1</sup>	6.33	–	–	8.06	5.77	10.28	12.54	5.58	4.25	9.34	3.48	11.97	8.97	5.02	7.65	6.15	5.96	7.84	8.52	5.96	6.71	2.76	–	7.74
PHg	Feb	ng L <sup>-1</sup>	2.51	n.s.	13.09	13.26	4.74	5.74	7.89	5.23	3.77	3.59	4.81	8.42	9.96	14.56	22.59	9.19	10.16	10.15	9.94	–	–	–	2.13	27.18
	May	ng L <sup>-1</sup>	31.09	27.32	20.62	18.61	2.41	12.10	11.72	18.20	8.56	6.05	26.85	8.09	7.19	30.19	<DL	<DL	11.60	12.51	69.64	<DL	31.60	92.73	17.38	29.76
	Aug	ng L <sup>-1</sup>	20.81	–	–	13.37	6.72	3.13	27.02	8.76	5.26	4.24	13.49	18.79	11.82	19.10	28.34	65.38	11.00	20.67	24.89	97.55	19.09	54.77	–	9.87
TMeHg	Feb	pg L <sup>-1</sup>	125	n.s.	173	117	203	66	234	142	185	229	158	174	76	119	115	n.a.	100	77	95	–	–	–	69	110
	May	pg L <sup>-1</sup>	76	60	51	61	<DL	36	75	94	<DL	<DL	38	<DL	<DL	43	<DL	<DL	<DL	<DL	57	82	87	94	<DL	<DL
	Aug	pg L <sup>-1</sup>	1252	1350	169	247	180	286	234	218	69	262	135	237	142	85	106	68	673	112	120	96	88	152	56	56
DMeHg	Feb	pg L <sup>-1</sup>	103	n.s.	147	72	173	33	199	130	92	168	130	134	55	74	87	<DL	70	55	66	–	–	–	52	97
	May	pg L <sup>-1</sup>	36	36	12	19	DL	14	52	52	<DL	<DL	16	<DL	<DL	20	<DL	<DL	<DL	<DL	43	73	70	81	<DL	46
	Aug	pg L <sup>-1</sup>	1232	1323	150	200	162	269	223	209	40	243	131	210	133	72	82	57	670	98	111	91	74	145	51	49
PMeHg	Feb	pg L <sup>-1</sup>	22	n.s.	26	45	30	33	35	12	93	61	28	40	21	45	28	17	30	22	29	–	–	–	17	13
	May	pg L <sup>-1</sup>	40	24	39	42	15	22	23	43	14	12	22	10	11	23	12	11	23	13	15	9	17	13	10	<DL
	Aug	pg L <sup>-1</sup>	20	27	19	47	18	17	11	9	29	19	4	27	9	13	24	11	3	14	9	5	14	7	5	7
DGHg	Feb	ng L <sup>-1</sup>	0.16	n.s.	0.22	0.56	0.64	2.04	2.65	0.24	0.39	0.94	0.45	1.08	0.75	0.56	1.05	0.75	0.50	1.13	1.12	–	–	–	0.44	0.91
	May	ng L <sup>-1</sup>	0.23	0.08	0.07	0.10	0.10	0.13	0.31	0.24	0.29	0.13	0.07	0.16	0.23	0.33	0.21	0.13	0.09	0.15	0.07	0.13	0.34	0.18	0.23	0.16
	Aug	ng L <sup>-1</sup>	0.06	0.07	0.17	0.18	0.07	0.20	0.22	0.07	0.16	1.78	0.16	0.15	0.05	0.03	0.16	0.09	0.10	0.17	0.08	0.06	0.10	0.06	0.06	0.09

n.s.=not sampled; <DL=under detection limit; (–)=missing sample.

slightly from February (avg.  $18.19 \pm 9.25 \text{ ng L}^{-1}$ ) to August (avg.  $25.73 \pm 29.90 \text{ ng L}^{-1}$ ) showing similar fluvial contributions in different seasons under a low regime. Conversely, the highest contents of THg were found in saltwater in late spring (avg.  $63.52 \pm 66.49 \text{ ng L}^{-1}$ ) and summer (avg.  $31.27 \pm 24.64 \text{ ng L}^{-1}$ ). In freshwater, most of the Hg transported by the fluvial current was associated with suspended particles (PHg). The average relative abundance of PHg to THg in freshwater varied between 51% (February) and 84% (May). PHg concentrations in freshwater in February and August (avg.  $9.56 \pm 5.93$  and  $25.35 \pm 32.25 \text{ ng L}^{-1}$ , respectively) as well as in saltwater (avg.  $10.54 \pm 8.71$  and  $28.50 \pm 25.60 \text{ ng L}^{-1}$ , respectively) were normally higher than the brackish water indicating that at intermediate salinity a removal process of Hg from some components of fluvial particles is operative. In the saltwedge, the highest PHg concentrations were found in the lower section of the river channel (between 7 and 10 km) before the delta bar in May and, partially, in August (Fig. 5b, c). This evidence could be explained by resuspension affecting the silty bottom sediments as a consequence of bed friction due to flood tide currents ( $15 \text{ cm s}^{-1}$  at station 8a, unpublished data) flowing upstream. However, flocculation and sedimentation of Hg-rich particles as a consequence of flow deceleration and increasing of saltwater entrainment in the freshwater due to breaking of internal waves before and near the bar crest cannot be excluded (Wright and Coleman, 1974). PHg concentrations in freshwater, normalized for suspended load,

were very low in May ( $0.1\text{--}1.8$ , avg.  $0.8 \pm 0.5 \mu\text{g g}^{-1}$ ), although the moderate flood waters were one order of magnitude richer ( $\sim 30 \text{ mg L}^{-1}$ ) in TSM than the winter and summer samplings. Higher PHg values were observed in February ( $1.4\text{--}4.0$ , avg.  $2.8 \pm 1.0 \mu\text{g g}^{-1}$ ) and in August ( $4.9\text{--}37.3$ , avg.  $12.3 \pm 11.7 \mu\text{g g}^{-1}$ ). PHg concentration variability in freshwater was as much as three orders of magnitude higher than those reported for uncontaminated European rivers (Table 4) and also significantly higher than those found in the contaminated Seine, Loire and Scheldt rivers (Coquery et al., 1997; Leermakers et al., 1995), thus confirming the Isonzo River to be one of major sources of Hg in particulate form in the European coastal waters.

PHg showed a linear relationship with particles ranging between 16 and  $32 \mu\text{m}$  (medium silt) for freshwater ( $r=0.848$ ;  $n=11$ ;  $P<0.001$ ) and also independent of water type ( $r=0.728$ ;  $n=21$ ;  $P<0.001$ ) in February (Fig. 5d), whereas no significant correlation was found between PHg and grain-size in May (Fig. 5e) and August (Fig. 5f). PHg in saltwater decreases as the saltwedge tip is approached since the coarse fraction transported by tidal currents may progressively accumulate at the river bottom and TSM becomes enriched in fine particles as reported in Fig. 6 for samples collected in February.

POC values were almost constant in February along the river course and in the different water masses (Fig. 7a). High variability of the organic component was observed in May, due to the moderate flood event in the upper river mouth (Fig. 7b), and in August (Fig. 7c) when

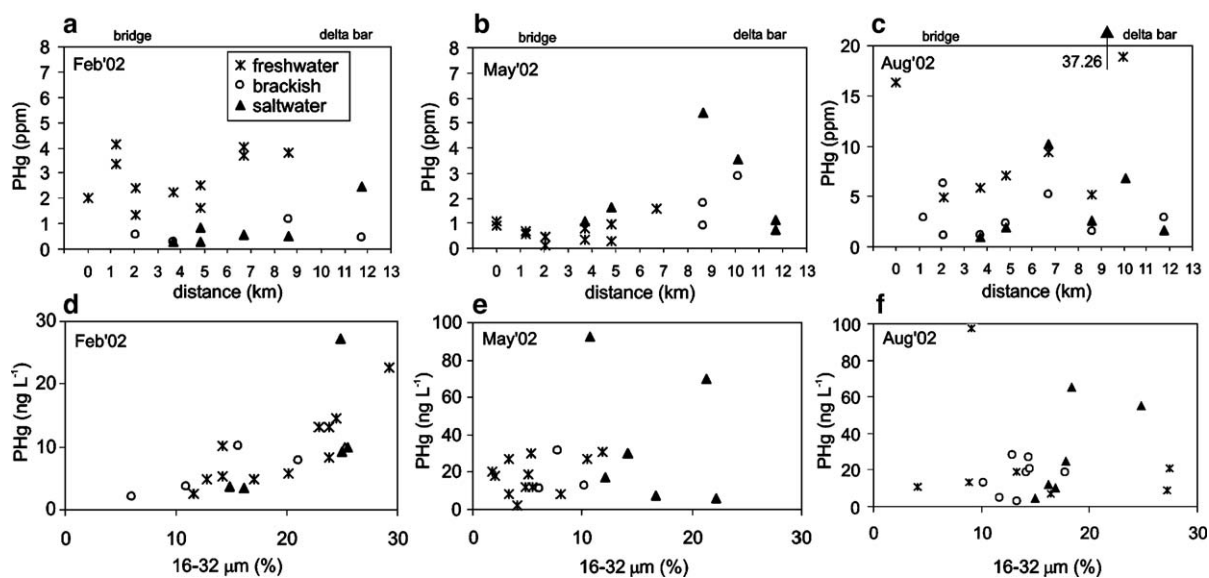


Fig. 5. Longitudinal profiles of particulate Hg (PHg) concentrations ( $\mu\text{g g}^{-1}$ ) in the river mouth in different sampling periods (a, b and c) and its relationships with grain-size fractions (d, e and f).



Table 4

Range of dissolved (DHg) and particulate Hg (PHg) concentrations measured in freshwaters of different rivers

	DHg (ng L <sup>-1</sup> )	PHg (μg g <sup>-1</sup> )	
Isonzo River mouth (Feb)	3.13–5.38	1.36–4.17	This study
Isonzo River mouth (May)	0.46–2.82	0.09–1.58	This study
Isonzo River mouth (Aug)	3.48–6.33	4.93–37.26	This study
Scheldt estuary (Belgium)	0.5–5.2	0.4–1.7	Leemakers et al., 1995
Loire estuary (France)	0.40–1.20	0.10–1.00	Coquery et al., 1997
Seine estuary (France)	0.20–0.60	0.5–2.0	Coquery et al., 1997
St. Lawrence River (Canada)	0.08–2.05	0.04–0.52	Quemerais et al., 1998
St. Lawrence estuary (Canada)	0.36–1.56		Cossa and Gobeil, 2000
Patuxent River (USA)	0.2–1.5		Benoit et al., 1998
Lena River (Russia)	0.90–1.08	0.04–0.22	Coquery et al., 1995
Ob River (Russia)	0.48–0.64	0.04–0.06	Coquery et al., 1995
Yenisey River (Russia)	0.16–0.42	0.04–0.06	Coquery et al., 1995

suspended particles in brackish water and saltwater were richer in the organic fraction than the fluvial waters. POC showed no significant correlation with PHg except in freshwater in May, thus suggesting that the organic component plays a minor role as a metal carrier in freshwater as well as in saltwater at low river flow.

The very high fine/coarse ratio and the higher (>500 μg L<sup>-1</sup>) POC values of the riverborne suspended matter in May (Fig. 7b) are in parallel with the low Hg concentrations (Fig. 5b). This evidence suggests that the fluvial particles could be due to erosion from the uppermost part of the soil by quick runoff due to local rainfalls along the lower part of the drainage river basin, rather than from the upper (Slovenian) river course where most of the Hg lost during roasting processes accumulated in the riverbanks (Hines et al., 2000; Horvat et al., 2003).

DHg concentrations in freshwater are consistent with those reported for the Scheldt river (Leermakers et al., 1995) and higher than those found in the Seine and Loire rivers (Coquery et al., 1997). DHg values appeared in the same order of magnitude in February (avg. from 6.06 ± 3.96, in saltwater, to 8.64 ± 4.75 ng L<sup>-1</sup> in freshwater) (Fig. 8a) and August (avg. from 5.44 ± 0.96 ng L<sup>-1</sup>, in freshwater, to 8.66 ± 2.78 ng L<sup>-1</sup> in brackish water) (Fig. 8c) along the water column. In May, DHg showed very low concentrations in freshwater (avg. 3.29 ± 3.90 ng L<sup>-1</sup>) in the upper part of the river course whereas high values were found in saltwater (avg. 31.67 ± 31.48 ng L<sup>-1</sup>) (Fig. 8b). In terms of percentage of THg, brackish water showed a higher value of DHg (avg. 39–54%) compared to surface and saltwater probably due to the partial desorption of Hg from suspended matter and possible formation of electrochemically charged complexes at low salinity. The relative affinity of Hg for the particulate phase in freshwater expressed as log  $K_d$  (= [PHg]/[DHg], L

kg<sup>-1</sup>) was confirmed by higher average values (5.5–6.2) compared to brackish water (4.9–5.5) and saltwater (4.9–5.6). Freshwater  $K_d$  values are quite in agreement with those reported for some European estuaries (Coquery et al., 1995, 1997).

Reactive Hg (RHg) concentrations in the water samples were usually lower than 1 ng L<sup>-1</sup>. Taking into account data from the three sampling campaigns, RHg, as a percentage of THg, was always slightly higher in brackish water (avg. 3.8–4.0%) when compared to freshwater (avg. 3.2–5.5%) and saltwater (avg. 1.7–4.8%). In February (Fig. 8d) as well as in August (Fig. 8f), the percentage of RHg also showed high values in the HTZ and at low salinity (brackish water and freshwater), sharply decreasing downstream. This fact would suggest that labile Hg is preferentially available in the upper river mouth and it can be involved in various transformations including methylation. In May (Fig. 8e), the adsorption effect of dissolved Hg on particles would also have limited the percentage of RHg in freshwater showing lower values than in February.

The highest dissolved gaseous Hg (DGHg) values were detected in winter predominantly in brackish water (avg. 0.68 ± 0.54 ng L<sup>-1</sup>) as much as in the O<sub>2</sub> depleted zone of the saltwedge (avg. 0.94 ± 0.18 ng L<sup>-1</sup>), probably due to higher heterotrophic activity and lower evaporation to atmosphere. On the other hand, low values with insignificant differences between water bodies were observed in spring (avg. from 0.16 ± 0.06 ng L<sup>-1</sup>, in saltwater, to 0.23 ± 0.10 ng L<sup>-1</sup>, in brackish water) and summer (avg. from 0.09 ± 0.05 ng L<sup>-1</sup>, in freshwater, to 0.31 ± 0.64 ng L<sup>-1</sup> in saltwater).

### 3.3. Total, particulate and dissolved MeHg

The percentage of TMeHg to THg, considering all the samples, are lower in May (<0.5%) than in Febru-

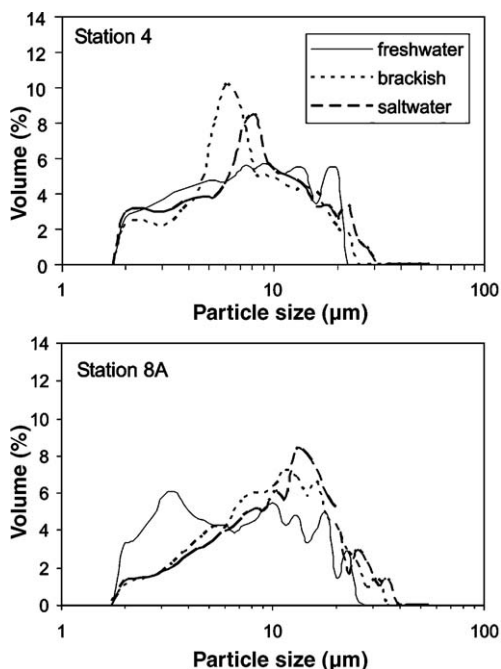


Fig. 6. Grain-size distributions of TSM in the upper (station 4) and lower (station 8A) river mouth in February.

ary (0.3–4.2%) and in August (0.1–24.1%). In the last sampling, the maximum TMeHg concentrations ( $1252\text{--}1350\text{ pg L}^{-1}$ ) were recorded in the freshwaters of the upper river mouth, showing a prevalent amount of the dissolved phase with respect to the particulate one (85–99%). This amount was lower in winter (50–92%) and in spring (24–70%).

Particulate methylmercury (PMeHg) showed the highest values in February (avg. from  $31 \pm 10\text{ pg L}^{-1}$ , in freshwater, to  $42 \pm 35\text{ pg L}^{-1}$  in brackish water) compared to May (avg. from  $12 \pm 2\text{ pg L}^{-1}$ , in saltwater, to  $25 \pm 12\text{ pg L}^{-1}$  in freshwater) and August (avg. from  $10 \pm 5\text{ pg L}^{-1}$ , in saltwater, to  $23 \pm 12\text{ pg L}^{-1}$  in brackish water). There was a decrease of PMeHg from the upper river mouth seawards, especially in the freshwater layer, in August. This tendency was not observed in February and May. Contribution of PMeHg from riverine particles reported based on weight are higher in August ( $25.1\text{--}0.6$ , avg.  $9.6 \pm 8.2\text{ ng g}^{-1}$ ) and in February ( $14.0\text{--}4.6\text{ ng g}^{-1}$ , avg.  $10.6 \pm 4.1\text{ ng g}^{-1}$ ) than in May ( $0.4\text{--}3.5\text{ ng g}^{-1}$ , avg.  $1.2 \pm 0.8\text{ ng g}^{-1}$ ) in spite of higher suspended load in this season. Peaks of PMeHg on a volume basis were recorded at those sampling points (stations 4 and 5) corresponding to the HTZ in February (Fig. 9a) at as high level as in August (Fig. 9c) due to the similarity of the hydrological regimes. In the same sampling, percentage of PMeHg to PHg was also observed from

twice to three times as high as the general trend in brackish and saltwater nearby the saltwedge tip (Fig. 9d and f).

It is likely that lower oxygen concentrations typical of HTZ at the saltwedge tip are favourable for methylation activity as suggested by Mason et al. (1993) for a strongly stratified estuary. Decreasing values downstream, not only for PMeHg but also for DMeHg (Fig. 9g and h), would suggest that MeHg produced in the upper part of the river mouth or carried in suspension by fluvial waters is diluted and partially demethylated but not exported to the coastal waters of the Gulf. Previous results for the surface layer of the water column in the Gulf of Trieste showed DMeHg concentrations between 47 and  $<0.5\text{ pg L}^{-1}$  depending on the river flow (Faganeli et al., 2003). Freshwater concentrations of DMeHg were

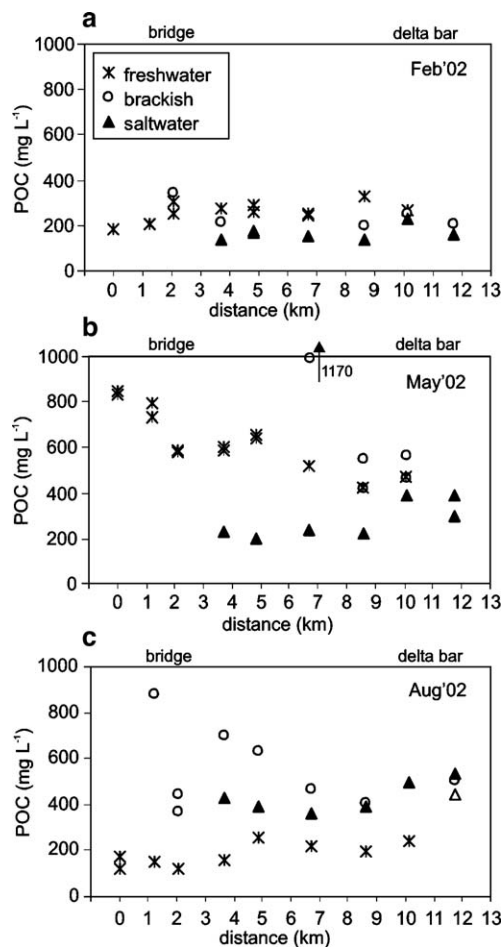


Fig. 7. Longitudinal profiles of particulate organic carbon (POC) concentrations ( $\text{mg L}^{-1}$ ) in the river mouth in the three types of water during different sampling periods.

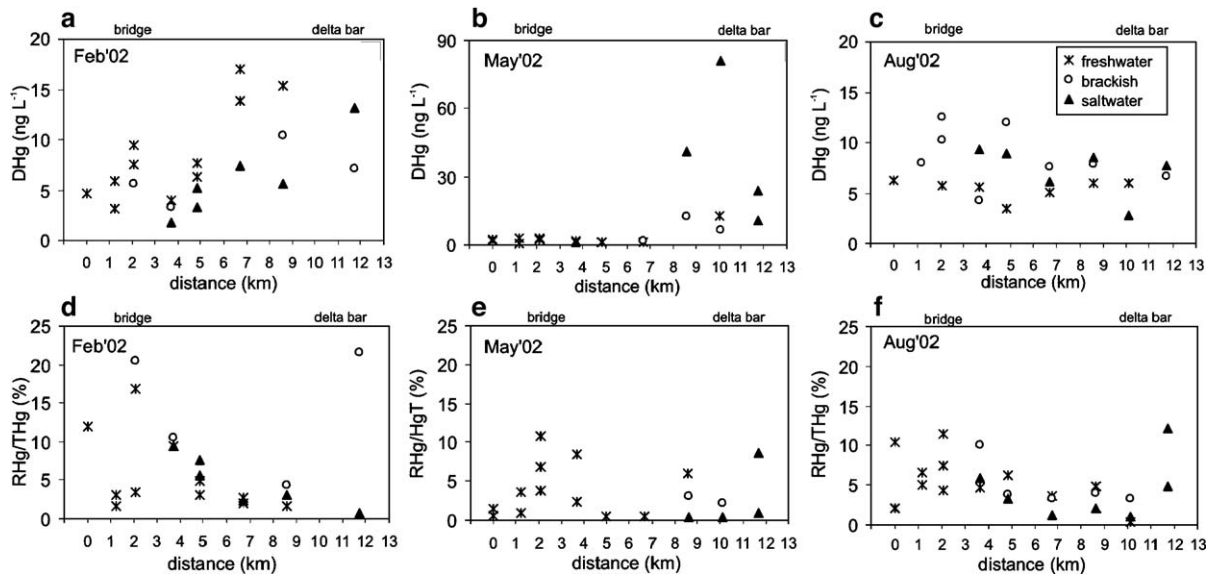


Fig. 8. Longitudinal profiles of dissolved Hg (DHg) concentrations ( $\text{ng L}^{-1}$ ) in different sampling periods (a, b and c) and related percentage of reactive Hg (RHg) (d, e and f).

highest in August (up to  $1323 \text{ pg L}^{-1}$ ) in comparison to February (up to  $147 \text{ pg L}^{-1}$ ) and especially to the moderate flood event of May, when surface waters

generally showed very low DMeHg values ( $12\text{--}73 \text{ pg L}^{-1}$ ). It seems evident that the more elevated summer temperatures and the higher biological activity in that

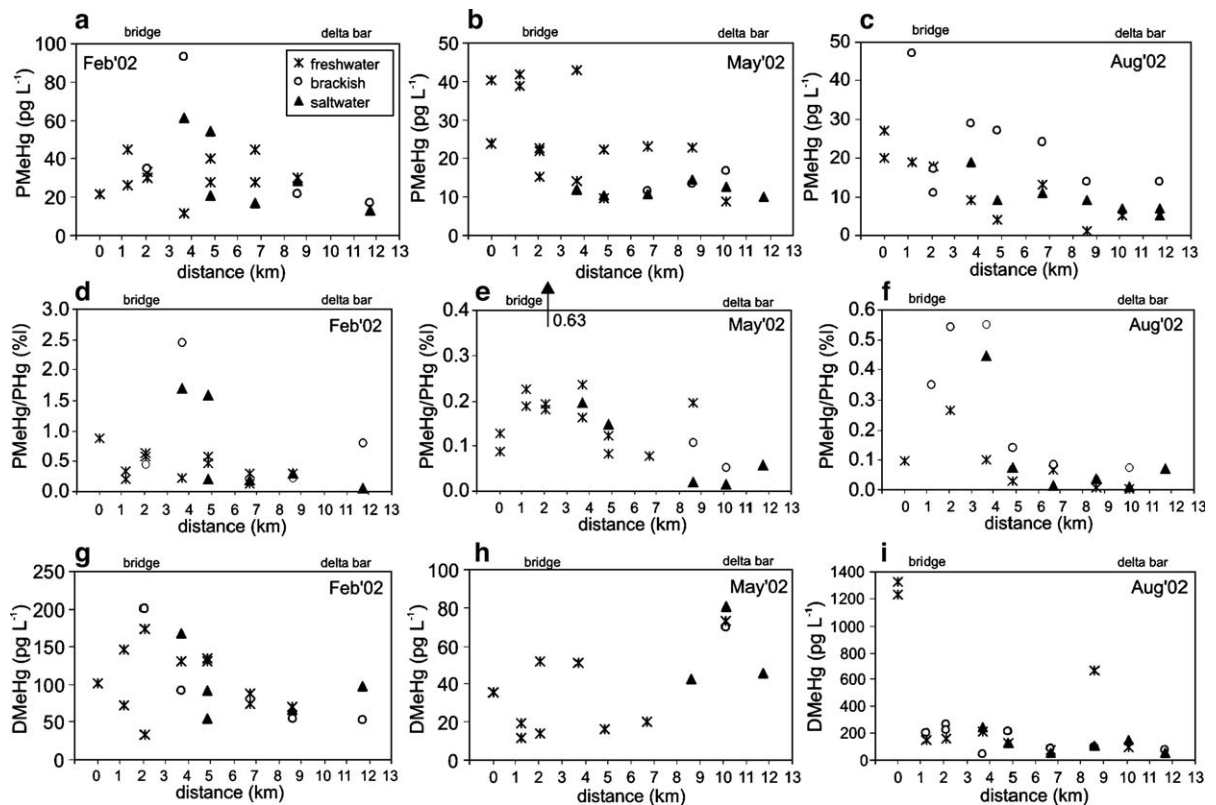


Fig. 9. Particulate MeHg (PMeHg,  $\text{pg L}^{-1}$ ; a, b and c), PMeHg/PHg ratio (%; c, d and f) and dissolved MeHg (DMeHg,  $\text{pg L}^{-1}$ ; g, h and i) profiles in the river mouth in different seasons.

period play an important role in MeHg availability in fluvial waters.

PMeHg in freshwater was normally associated with the 16–32  $\mu\text{m}$  fraction of TSM in February and August (Fig. 10a and b) whereas organic Hg in riverine flood samples rich in TSM was predominantly bound to very fine particles, mostly the 4–8  $\mu\text{m}$  fraction of TSM (Fig. 10c) and POC (Fig. 10d), thus testifying to its recent origin from surficial soil erosion as was observed for total PHg. The lower log  $K_d$  ( $=[\text{PMeHg}]/[\text{DMeHg}]$ ,  $\text{L kg}^{-1}$ ) values for MeHg (4.0–5.5) in all waters seem to indicate a weaker binding of organic Hg on particulate matter compared to PHg.

PMeHg concentrations in the summer season are higher in the brackish water samples showing a very significant positive linear correlation with POC ( $r=0.944$ ;  $n=8$ ;  $P<0.001$ ; Fig. 10e) and also with the 8–16  $\mu\text{m}$  fraction of TSM ( $r=0.884$ ;  $n=8$ ;  $P<0.005$ ; Fig. 10f) that was not observed in the previous samplings. Investigation of the grain-size distribution of TSM revealed that freshwater samples are usually skewed, poorly sorted and dominated by fine particles, with the mode size ranging from 6.6 to 14.7  $\mu\text{m}$  as reported in Covelli et al. (2004). On the contrary, in the marine bottom layer samples, the size distribution is positively skewed with the coarser modal class between 12.8 and 16.0  $\mu\text{m}$ . This particle size distribution is also evident in front of the river mouth (station 8), thus confirming that the seawater intruding into the lower river course at the bottom is the main source of selected size range of particles. In

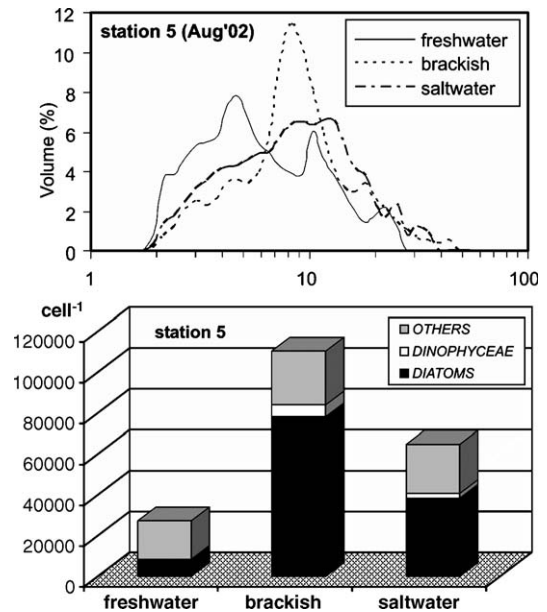


Fig. 11. Grain-size distribution of TSM (a) and related abundances of phytoplankton (b) in station 5 in the summer season.

brackish water, particle size distributions show a typical sharp peak in the fine fraction when compared to surface samples (Fig. 11). Microscopic analyses revealed an abundance of phytoplankton (mainly *Thalassionema nitzschoides*, *Pseudo-nitzschia seriata*, *Chaetoceros affinis*) in brackish water, four times higher than at the surface and twice as high as in bottom saltwater, respectively (Cabrini, personal communication). The aggregation of diatom cells should

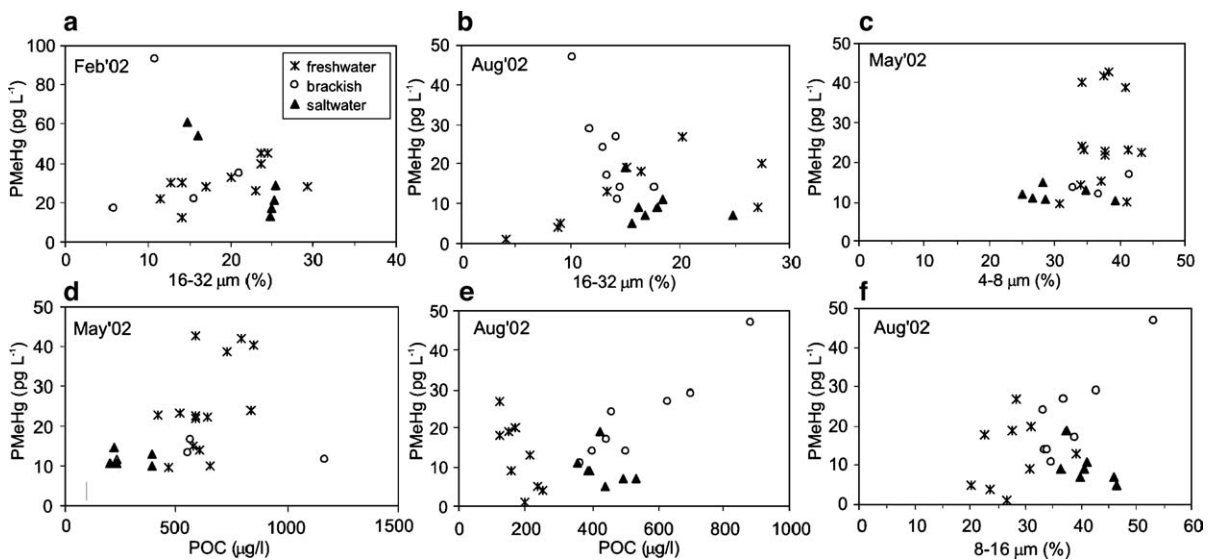


Fig. 10. Relationships between particulate MeHg (PMeHg,  $\text{pg L}^{-1}$ ) and grain-size fractions (a, b, c and f) and particulate organic carbon (POC,  $\mu\text{g L}^{-1}$ ; d and e).



be influenced by low salinities (Eisma, 1993), water column stratification, low rainfall and nutrient availability (Jones et al., 1998; Orive et al., 1998). The increase of oxygen and organic carbon in the brackish layer is also due to phytoplankton activity rather than mixing with the underlying saltwater. The relative abundance of MeHg, especially in particulate form, in brackish water would indicate a microbiological origin of MeHg at this depth or, alternatively, MeHg could be controlled by redox conditions such as precipitation/dissolution (adsorption/desorption) involving Fe and Mn hydroxides (Quemerais et al., 1998). Methylation under aerobic conditions has been observed in marine and freshwater environments, most likely caused by aerobic organism (Mason et al., 1993). Although no data about phytoplankton biomass (Chlorophyll a) are available to support this hypothesis, it is possible that MeHg produced by bacteria in situ would have eventually been accumulated by the phytoplankton community.

#### 4. Conclusions

Most of Hg in the riverine water is in particulate form predominantly associated with medium silt during low discharge and with fine silt during moderate flood events. Higher concentrations observed in brackish and saltwater are a consequence of flocculation processes and bottom resuspension, respectively.

Dissolved MeHg and particulate MeHg show high concentrations in the high turbidity zone (HTZ) probably due to an intense methylation process, flocculation and sedimentation. At higher temperatures (August sampling), dissolved MeHg contents are higher probably due to higher methylation rates. The majority of MeHg is not exported to the marine zone. The important biogeochemical activity of the HTZ is confirmed by higher percentages of reactive Hg. Particulate MeHg during low riverine flow is mostly bound to fine particles and POC and the highest contents were found at the saltwedge tip.

During low riverine flow, the Isonzo River mouth acts as an important “biogeochemical reactor” involving processes such as Hg methylation, flocculation, sedimentation and resuspension.

Exporting of Hg is effective only during medium and high riverine flows. Suspended matter is spread as a plume in the coastal waters of the Gulf and it is eventually driven by surficial currents, mostly anticlockwise alongshore. This can be an important way of Hg dispersion into the northern Adriatic Sea and the adjacent lagoon system.

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