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AZIENDA CON SISTEMA DI GESTIONE
 PER LA QUALITÀ CERTIFICATO DA DNV
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REGIONE AUTONOMA
FRIULI-VENEZIA-GIULIA

COMUNE DI
MONFALCONE

PROVINCIA DI
GORIZIA

PROGETTO DEFINITIVO

PER I LAVORI DI APPROFONDIMENTO DEL CANALE DI ACCESSO E DEL BACINO DI
 EVOLUZIONE DEL PORTO DI MONFALCONE

QUOTA DI PROGETTO: -12,50m s.l.m.m.



Tavola ED_14	Titolo PIANO DI MONITORAGGIO AMBIENTALE		
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Ente preposto alla Progettazione



CONSORZIO PER LO
 SVILUPPO INDUSTRIALE
 DEL COMUNE DI
 MONFALCONE

con la Consulenza Ambientale

MONFALCONE AMBIENTE

S.p.A.

a socio unico - Società sottoposta alla direzione e
 coordinamento dello CSIM

Progettista

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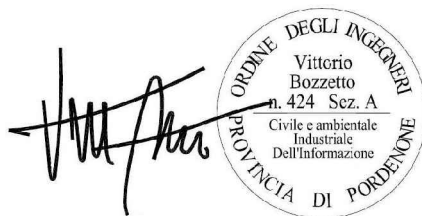
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Il R.U.P.

ing. Sergio SIGNORE

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Progetto definitivo per i lavori di approfondimento del canale di accesso e del bacino di evoluzione del Porto di Monfalcone

Quota di progetto: -12,50 m s.l.m.m.

1. PREMESSA

Il presente documento descrive il Piano di Monitoraggio previsto per i lavori di approfondimento del canale di accesso e del bacino di evoluzione del Porto di Monfalcone che comprende: la bonifica bellica, il dragaggio del canale di accessi e del bacino di evoluzione del Porto di Monfalcone e la messa a dimora dei fanghi nell'esistente Cassa di Colmata del Lisert a Monfalcone, previo rinfianco/innalzamento/impermeabilizzazione degli argini di contenimento, allontanamento dei materiali eccedenti, preparazione del piano di posa, realizzazione di dreni e del sistema di allontanamento delle acque di supero.

L'attività di dragaggio garantirà la profondità di -12,50 m s.l.m.m. su tutto il bacino di evoluzione ed il canale d'accesso al Porto di Monfalcone, per complessivi 885.000 mc di cui circa 385.000 mc all'interno del bacino di evoluzione e 500.000 mc lungo il canale di accesso. Il bacino di evoluzione ha un'estensione di circa 500.000 mq, mentre il canale di accesso ha una lunghezza di circa 5 km e larghezza pari a circa 170 m.

L'intervento dovrà essere eseguito in fasi successive, secondo quando previsto dal cronoprogramma, alcune attività saranno propedeutiche al dragaggio, ovvero la preparazione della Cassa di Colmata per la messa a dimora dei sedimenti.

L'intervento di dragaggio richiederà alcuni accorgimenti di carattere ambientale per garantire che i materiali movimentati non producano migrazione della contaminazione al di fuori dell'area d'intervento, poiché sussiste il rischio potenziale connesso alla movimentazione della frazione sedimentaria più sottile e alla diffusione e dispersione dei contaminanti ad essa associata.

Per quanto riguarda la presenza di elevate concentrazioni di Hg nei sedimenti del Golfo di Trieste, si ricorda che si tratta di una caratteristica geochimica peculiare di quest'area. La mobilità del mercurio dal sedimento alla fase disciolta dipende da numerosi fattori ambientali, la distribuzione di Hg nelle diverse frazioni ottenute dall'estrazione sequenziale selettiva operata in fase sperimentale è fortemente associata alle frazioni meno mobili che entrano in soluzione, ciò induce a ritenere che non sussista un immediato e significativo rischio di trasferimento del Hg dal sedimento alla colonna d'acqua associato ai campioni di sedimento che sono stati esaminati, così come emerso dallo "Studio geochimico sulla speciazione del mercurio nei sedimenti di escavo del Porto di Monfalcone" condotto dal Dip. Matematica e Geoscienze dell'Univ. di Trieste (marzo 2013).

In tal senso un adeguato sistema di controllo e monitoraggio delle attività di movimentazione dei sedimenti risulta di particolare importanza ai fini della tutela dell'ambiente.

Il presente documento descrive la strategia di monitoraggio e di controllo delle attività di dragaggio, movimentazione e refluitamento dei sedimenti nella Cassa di Colmata al fine di minimizzare i possibili impatti negativi che si potrebbero avere sull'ambiente circostante, mettendo in atto apposite azioni di mitigazione. Il sistema di monitoraggio previsto permette di verificare l'efficacia delle eventuali azioni di mitigazione introdotte.

Si riportano di seguito:

- gli obiettivi del piano di monitoraggio e descrizione delle modalità previste per la realizzazione degli obiettivi;
- descrizione delle attività previste di monitoraggio sui diversi comparti ambientali potenzialmente impattanti delle attività previste e la relativa tempistica d'intervento.

In linea generale si evidenzia che comunque, una volta terminate le fasi di cantiere, che saranno gestite con gli opportuni accorgimenti, l'intervento di dragaggio porterà ad un miglioramento dello stato della qualità dell'area di dragaggio, considerata la rimozione di sedimenti aventi concentrazioni di mercurio con concentrazioni superiori a 5mg/kg s.s..

2. STRATEGIE DI MONITORAGGIO

La strategia di monitoraggio scaturisce dal fatto che le attività di movimentazione di sedimenti con elevate concentrazioni di mercurio possono determinare potenziali impatti negativi sull'ambiente e quindi la necessità di salvaguardare lo stesso, prevedendo la contaminazione della colonna d'acqua e qualunque impatto negativo sul comparto biotico.

Nell'eventualità si riscontrino disturbi sull'ambiente, il monitoraggio previsto permetterà di agire attuando gli accorgimenti necessari a minimizzare gli effetti, sia sul comparto abiotico che su quello biotico dovuti soprattutto all'aumento di torbidità per la risospensione dei sedimenti.

In relazione al comparto abiotico, possono verificarsi i seguenti processi chimico-fisici:

- l'aumento della torbidità associata alla risospensione dei sedimenti;
- la mobilizzazione dei contaminanti associati alle particelle in sospensione;
- la solubilizzazione dei contaminanti in seguito al cambiamento delle condizioni chimico-fisiche del sedimento.

Potenziali effetti sul comparto biotico:

- gli impatti diretti di tipo propriamente fisico sugli organismi e su eventuali biocenosi sensibili, causati dall'aumento della torbidità e della concentrazione delle particelle di solidi in sospensione;
- gli effetti dei contaminanti rimessi in circolo, presenti in fase disciolta nella colonna d'acqua o associati alle particelle di solidi in sospensione, su differenti organismi marini;
- il possibile bioaccumulo dei contaminanti nei tessuti degli organismi, con conseguente trasferimento nella catena trofica;
- possibili alterazioni qualitative qualitative sulle biocenosi sensibili presenti esterni all'area di dragaggio.

Un tanto per evidenziare che le aree da sottoporre ad attività di escavo risultano aree antropizzate e pertanto la presenza di biocenosi sensibili che rivestono interesse naturalistico è limitata.

In relazione al comparto biotico potenzialmente sensibile agli effetti delle attività di movimentazione dei sedimenti contaminati delle aree interessate, considerati i tempi stimati per la realizzazione degli interventi e la tipologia delle aree interessate, i potenziali impatti sugli organismi che transitano all'interno dell'area portuale non dovrebbero risultare particolarmente significativi; secondariamente l'attenzione va alla verifica, nel breve così come nel lungo periodo, dell'assenza di fuoriuscita di contaminanti dalla zona propriamente portuale.

In tal senso il sistema di monitoraggio prescelto prevede due diverse scale di controllo ed in particolare:

1. il monitoraggio dell'evento da effettuare durante le operazioni di dragaggio e di refluitamento dei sedimenti allo scopo di individuare, comprendere e delimitare in maniera dettagliata tutti i fenomeni potenzialmente indotti dalla movimentazione dei sedimenti;

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2. monitoraggio dell'intero sistema, da effettuare con cadenza regolare nelle aree interne ed esterne all'area di dragaggio, mediante utilizzo di stazioni fisse e mobili opportunamente distribuite allo scopo di monitorare la variabilità nel tempo dei parametri e delle matrici ambientali di interesse.

Le stazioni di monitoraggio dovranno:

- determinare l'estensione dei potenziali effetti delle attività previste potendo seguirne l'avanzamento spaziale e temporale;
- fornire informazioni per eventuali modifiche delle metodologie di lavoro introducendo opportune misure di mitigazione, qualora si riscontrino effetti ambientali inaccettabili;
- controllare la fuoriuscita di contaminanti (disciolti o associati alla frazione solida sospesa) dalla cassa di colmata, sia nel breve che nel lungo periodo, a seguito dell'attività;
- controllare possibili effetti nel lungo termine sulla qualità ambientale di un'area più vasta di quella direttamente interessata dalle attività.

Le modalità di attuazione della strategia di monitoraggio sono state selezionate sulla base della conoscenza delle condizioni al contorno potenzialmente utili alla comprensione dei processi in atto quali:

- dati di moto ondoso, vento e correntometrici per la caratterizzazione idrodinamica dell'area (si rimanda al quadro di riferimento ambientale del SIA);
- dati relativi al traffico navale;
- caratteristiche chimico fisiche della colonna d'acqua in condizione di relativo fondo naturale;
- variazioni delle caratteristiche chimico fisiche della colonna d'acqua in funzione di modifiche dei fattori non connessi con le attività progettate.

La conoscenza di tali informazioni, sia come dati pregressi che come condizioni di contorno da considerare durante le specifiche attività di lavoro previste è indispensabile non solo per la corretta predisposizione delle attività di monitoraggio, ma anche per la corretta interpretazione della variabilità spaziotemporale dei parametri acquisiti durante le indagini di campo.

In particolare si riscontra, dagli elaborati dello SIA, che nelle condizioni meteo marine più avverse (venti di Scirocco concomitante con i massimi livelli di marea della zona) si raggiungono al massimo altezze d'onda di poco inferiori ai 2m, con periodi di picco dell'ordine di 4-5 s. Con il vento di Ostro, da Sud, le massime onde in grado di raggiungere la zona d'accesso al Porto sono più contenute, non superando mai il metro d'altezza e periodi dell'ordine di 3-4 s.

Le attività di monitoraggio dovranno perdurare, dopo la fine delle attività, per un periodo di tempo sufficiente al ripristino delle condizioni fisico-chimiche iniziali.

Qualora nella fase di monitoraggio in corso d'opera risultassero valori dei parametri rilevati tali da poter rappresentare causa di possibili impatti negativi nei confronti dei comparti biotico e abiotico, sarà valutata l'eventuale attuazione di particolari misure di mitigazione.

3. ATTUAZIONE DELLA STRATEGIA DI MONITORAGGIO

Monitoraggio per la verifica dalla qualità delle acque durante le attività di dragaggio.

Il monitoraggio controllerà le aree da sottoporre a dragaggio per l'eventuale risospensione prodotte dalle attività ed il relativo possibile carico contaminante.

Sono previste fasi di monitoraggio ante opera, in corso d'opera e post opera.

Fase ante-opera:

- identificazione del valore di "bianco" della colonna d'acqua con il posizionamento di stazioni mobili e fisse interne ed esterne alle aree d'intervento con la determinazione del valore di torbidità;
- prelievo di almeno due campioni d'acqua per la determinazione dei solidi in sospensione (TSS) e delle concentrazioni dei contaminanti associati ai TSS.

Fase in corso d'opera: monitoraggio della torbidità attraverso l'utilizzo di stazioni mobili che permettano di eseguire un monitoraggio puntuale durante i lavori con particolare riferimento all'escavazione dei sedimenti con concentrazioni di mercurio superiori a 5 mg/kg s.s.

Modalità: registrazione di un profilo verticale di torbidità prima delle attività di dragaggio, dopo 5 ore dall'avvio delle stesse e in concomitanza della fase conclusiva lungo l'asse dell'area dragata con una spaziatura idonea. Prelievo di campioni d'acqua a profondità ritenute significative sulla base dei profili verticali ottenuti con il torbidimetro per la determinazione della concentrazione dei solidi sospesi e delle concentrazioni dei contaminanti ad essi associati.

Attivazione delle misure di mitigazione: sarà preso come valore soglia oltre il quale attivare misure di mitigazione delle attività di dragaggio il valore di 40mg/l con una persistenza di circa 6 ore (si allega la seguente pubblicazione Covelli et al. 2007 - *Transport and dispersion of particulate Hg associated with a river plume in coastal Northern Adriatic environments*, che riporta la distribuzione areale dei valori di torbidità e del particolato sospeso nell'area davanti la foce dell'Isonzo).

Eventuali azioni correttive da applicare in caso di superamento del valore di torbidità:

- rallentamento o temporanea sospensione delle attività sino al ristabilirsi delle condizioni di torbidità entro i limiti;
- svolgimento delle operazioni in zone distanti dalla zona in cui si è rilevato il superamento;
- eventuale utilizzo di panne galleggianti.

Fase post operam: ulteriore monitoraggio al fine di confrontare i valori di torbidità post operam con i valori di "bianco" rilevati nel corso delle attività di monitoraggio.

Mobilità e biodisponibilità del Mercurio dei sedimenti

Simulazione, in condizioni controllate, in laboratorio e su breve scala temporale, di un evento di risospensione di un sedimento raccolto nell'area interessata ad attività di dragaggio al fine di valutare la mobilità delle specie mercurifere in particolare della componente disciolta e/o metilabile. Tale approccio potrebbe essere applicato in doppio cioè su 2 stazioni nell'area di futuro escavo, che presentino differenti caratteristiche granulometriche.

Campionamento:

- Prelievo, con operatore subacqueo o, in alternativa, tramite box corer, di un campione indisturbato di sedimento dal fondale in corrispondenza di N° 2 punti del canale di accesso al Porto di Monfalcone da scegliersi in base alle caratteristiche chimico-fisiche dei sedimenti. In aggiunta, prelievo di campione superficiale indisturbato di sedimento con benna o carotiere leggero.
- Contestualmente al prelievo del sedimento, raccolta di un volume di acqua superficiale pari a 5 dm³ nel medesimo punto di campionamento per mezzo di una bottiglia tipo Niskin e determinazione di alcuni parametri chimico-fisici (pH, Eh, T e O₂ disciolto).

Fase sperimentale in laboratorio:

- Rimozione dell'acqua surnatante dalla carota e sostituzione con l'acqua superficiale prelevata in situ.
- Risospensione mediante un agitatore meccanico per un tempo definito.
- Prelievo in tempi diversi della risultante "matrice risospesa", costituita sia dalla fase disciolta che da quella particellata.

Analisi:

- Separazione della fase particolata da quella liquida tramite centrifugazione. Analisi dei parametri chimici previsti nella fase disciolta (Mercurio totale e reattivo, Metilmercurio, Ferro, Manganese), misurazione dei parametri ausiliari (pH, Eh, T e O₂ disciolto).
- Analisi chimico-fisica della componente particolata (granulometria e Mercurio) e del sedimento indisturbato di partenza (Mercurio e Metilmercurio).

Risultati attesi:

- Valutazione delle conseguenze di un evento di risospensione limitato nel tempo in termini di mobilità del Mercurio dalla fase particolata alla fase disciolta. Confronto con esperimenti simili eseguiti su sedimenti naturali ricchi in Mercurio.

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Monitoraggio acque scarico durante il consolidamento dei sedimenti nella Cassa di Colmata

Esecuzione di analisi di controllo con cadenza settimanale sui reflui allo scarico, salvo diverse prescrizioni e/o condizioni di esercizio che potranno essere indicate nell'autorizzazione, per tutta la durata delle operazioni di reflui mento dei sedimenti dragati nella Cassa di Colmata.

Controlli analitici meno frequenti saranno eseguiti durante la fase di consolidamento dei sedimenti nella Cassa di Colmata. Durante la fase di consolidamento dei sedimenti si prevede l'esecuzione di analisi di controllo a cadenza mensile per una durata di tre anni. Il campionamento dovrà comunque essere intensificato a seconda delle condizioni in itinere.

I limiti allo scarico dovranno rispettare i valori richiesti dal D.Lgs 152/2006 (Allegato 5 alla Parte III[^], Tabella 3 – Scarico in acque superficiali e in fognatura) fatta eccezione dei cloruri e solfati in quanto gli scarichi sono in ambiente marino.

Parametro	u.m.	Metodo	Valori di emissione in acque superficiali (D. Lgs. 152/06)
pH		APAT CNR IRSA 2060 MAN 29 2003	5,5 – 9,5
Colore		APAT CNR IRSA 2020 29/03	Non percettibile con diluizione 1:20
Odore		RAPPORTI ISTISAN 97/8 PAG. 11	Non deve essere causa di molestie
Materiali grossolani		L-319/76	Assenti
Solidi speciali totali	mg/l	APAT CNR IRSA 2090 B Man 29 2003	≤80
BOD ₅	mg/l	APAT CNR IRSA 5120 MAN 29 2003	≤40
COD (come O ₂)	mg/l	APAT CNR IRSA 5130 MAN 29 2003	≤160
Arsenico	mg/l	EPA-6020A 2007	≤0,5
Bario	mg/l	EPA-6020A 2007	≤20
Cadmio	mg/l	EPA-6020A 2007	≤0,02
Cromo totale	mg/l	EPA-6020A 2007	≤2
Ferro	mg/l	EPA-6020A 2007	≤2
Mercurio	mg/l	EPA-6020A 2007	≤0,005
Nichel	mg/l	EPA-6020A 2007	≤2
Piombo	mg/l	EPA-6020A 2007	≤0,2
Rame	mg/l	EPA-6020A 2007	≤0,1
Stagno	mg/l	EPA-6020A 2007	≤10
Zinco	mg/l	EPA-6020A 2007	≤0,5
Saggio di tossicità acuta (N.B.: Il saggio di tossicità è obbligatorio)		UNI EN ISO 11348-3:2001	Il campione non è accettabile quando dopo 24 ore il numero degli organismi immobili è uguale o maggiore del 50% del totale

Nel caso che il valore della concentrazione dei solidi sospesi superi 80 mg/l sarà ricercato sul particolato anche la concentrazione dei contaminanti ritenuti di maggiore interesse.

Transport and dispersion of particulate Hg associated with a river plume in coastal Northern Adriatic environments

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Abstract

The role of suspended particulate matter (SPM) as an important carrier of mercury (Hg) dispersed into the Gulf of Trieste and in the adjacent Grado lagoon (Northern Adriatic Sea) was studied during a high Isonzo River inflow and the resulting river plume formation. Despite the fact that extreme flood events are rare during the year, they account for most of the PHg influx (37–112 ng L⁻¹) into the Gulf of Trieste. When the river plume is diverted to the SW under the influence of an E–NE wind, the tidal flux acts as a “transport belt” carrying the PHg, mostly inorganic, into the Grado lagoon. A preliminary estimation indicates that the amount of PHg entrapped in the lagoon basin following a tidal semi-cycle accounts for 1.4 kg/12 h, which corresponds to about 49% of the total Hg carried by the tidal flow. These findings should be considered in future remediation strategies in the lagoon environment.

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Keywords: Suspended particulate matter; River plume; Tidal inlet; Mercury; Gulf of Trieste; Northern Adriatic sea; Grado lagoon

1. Introduction

Fluvial suspended particulate matter (SPM) plays the major role in the transport and dispersion of trace metals in estuarine and coastal environments. Several physical, chemical and biological processes contribute to the modification of SPM composition in these ecosystems: hydrodynamics (i.e. water discharge, interaction between freshwater and saltwater, circulation system), particulate-dissolved form interactions (i.e. adsorption, desorption, flocculation, red-ox reactions), sedimentation, erosion, water-bottom sediment (i.e. diffusive and benthic fluxes), and air–water exchanges (i.e. evasion) and biological uptake (e.g., Turner and Millward, 2000; Alliot et al., 2003; Gaston et al., 2006). However, the spatial and seasonal distribution of suspended particulate trace metals is

related to the fluvial flow pattern and, mainly, to the solid suspended load during high flow periods (e.g., van Maren and Hoekstra, 2005). Sedimentation in front of the river mouth seems to be the ultimate fate of fluvial SPM and bottom sediments are often considered as a reservoir for trace metals (i.e. Salomons and Förstner, 1984; Eisma, 1993), although remobilization through natural processes (wave motion, microbial activity and chemical transformations) and anthropogenic activities (dredging and dumping) are always possible, especially in shallow waters.

Studies conducted in the last decade have noted the importance of the Isonzo River as a “passive” source of mercury (Hg) in the Gulf of Trieste (Northern Adriatic sea; Fig. 1) in spite of the closure of the Idrija mine that was active for almost 500 years until it closed 15 years ago (Horvat et al., 1999, 2002; Faganeli et al., 2003). Due to the erosion of the river banks and the floodplain deposits (Gosar et al., 1997; Kocman et al., 2004), fluvial waters have remobilized and transported particle-bound Hg downstream (Biester et al., 1999, 2000) to the estuarine

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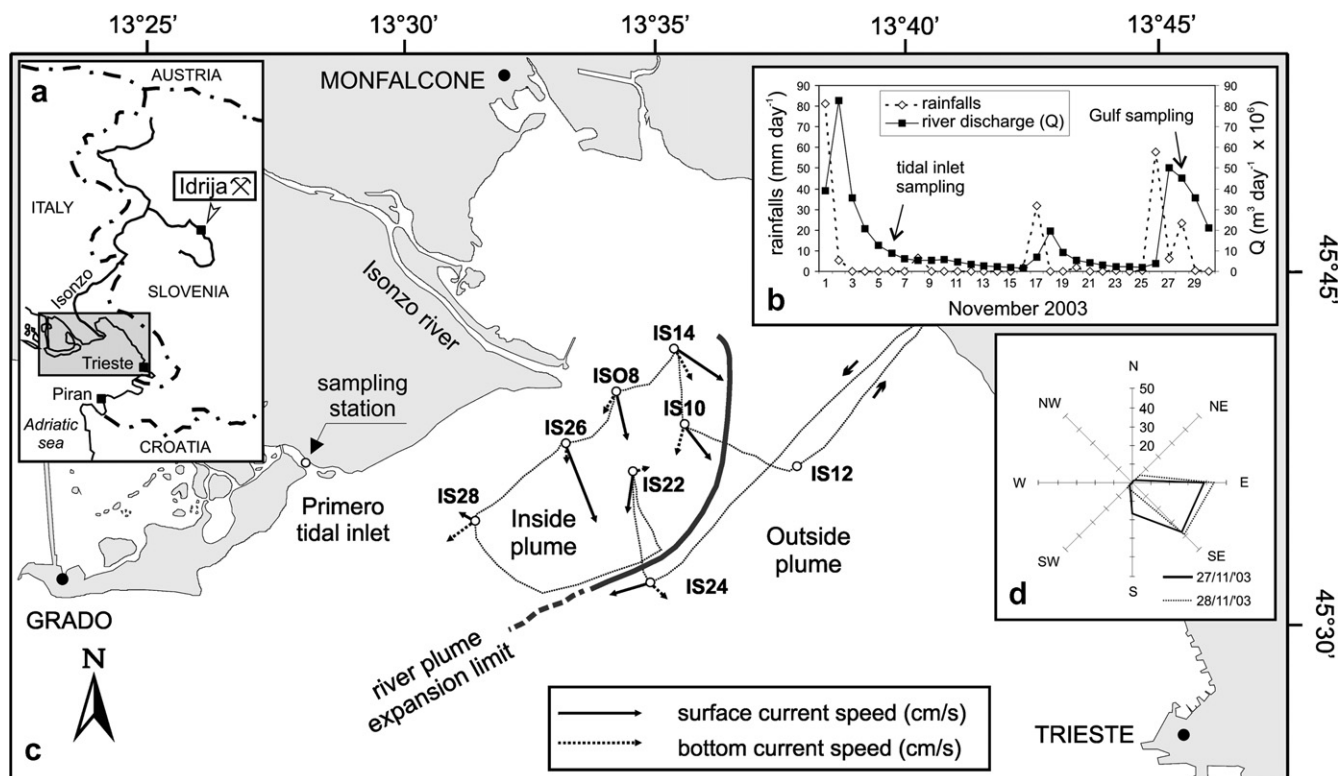


Fig. 1. Location of the Gulf of Trieste (a) and the sampling stations (c) during river plume formation following heavy rainfalls in November, 2003 (b). Direction of winds blowing during sampling and the day before are also reported (d) along with direction and speed of surface and bottom currents. The route followed by the boat (thin line) and the observed expansion limit of the river plume (bold line) are shown in the map.

zone (Covelli et al., 2006b), the marine environment (Covelli et al., 2001, 2006a) and, finally, into the Grado and Marano lagoons (Brambati, 2001; Piani et al., 2005). Seasonal sampling at the Isonzo River mouth has recently showed that dissolved and particulate Hg concentrations are still very high during low and normal river discharge throughout the year (Faganeli et al., 2003; Covelli et al., 2006b). The “estuarine zone” is recognized as an important site for physico-chemical processes such as flocculation, sedimentation and resuspension. Experimental results also demonstrated the occurrence of methylation processes in the inner part of the Isonzo River mouth (Hines et al., 2006), thus suggesting its role as an important “biogeochemical reactor”. However, the export of methyl-Hg (MeHg) into the Gulf waters was low during normal river flow (Covelli et al., 2006b). Conversely, most of the Hg supply occurs during short periods of intensive river discharge (Rajar et al., 2000). The annual mass of particulate Hg (PHg) transported by the Isonzo river in the Gulf of Trieste was estimated to be 1500 kg (Širca et al., 1999b). Simulations using two-dimensional and three-dimensional models have described the importance of physical processes in the transport and dispersion of Hg into the Gulf (Širca et al., 1999a; Rajar et al., 2000). Although a relatively high number of measurements of Hg concentrations in the water column, SPM, plankton and sediments are available for a qualitative comparison with models under normal river

discharge, Hg concentration data are not available for flood events.

The present study determined the contribution of Hg bound to fluvial SPM to the coastal waters of the Gulf of Trieste during peak river discharges and river plume formation. This work also attempts to verify the role of SPM as an important carrier for Hg dispersion into the Northern Adriatic sea and the adjacent Marano and Grado lagoon system. Mercury levels in aquatic plants and organisms from the trophic chains of the lagoon environment (Brambati, 1997) suggest that Hg levels in biological tissues are correlated with bottom sediment Hg concentrations, which show a progressive westward decrease from about 10 mg kg⁻¹ (Grado lagoon) to 1 mg kg⁻¹ (Marano lagoon). Unfortunately, Hg biomagnification increases the total Hg levels in marine species of commercial value, and the magnification process seems to be more intense in the fish farms, where edible fish (e.g., gilt-head bream, *Sparus auratus* and bass, *Dicentrarchus labrax*), at the top of the food chain, showed levels which are far higher (up to about 5 mg kg⁻¹) than in the same species collected in the open sea (0.4 mg kg⁻¹; Brambati, 2001).

It is important to assess the present contribution of tidal fluxes in carrying Hg into the Grado lagoon and, mainly, to the fish farms compared to metal historically “entrapped” in the bottom sediments. At present, there is no evidence of Hg input into the lagoon through fluvial

SPM or particles resuspended by wave motion in the nearby shallow waters, although these processes may be the most significant.

2. Experimental

2.1. Study area

The Gulf of Trieste is a shallow (<25 m depth) semi-enclosed marine basin covering an area of about 500 km² (Fig. 1a). The Isonzo River is the main freshwater inflow. The average annual flow rate at the river mouth is estimated to be about 197 m³ s⁻¹ (ranging between 43 and 666 m³ s⁻¹; INTERREG II, 2001). Most of the year, the highly stratified water column and related hypopycnal flux control the hydrodynamic within the lower reach of the river mouth. This type of circulation, and the consequent buoyancy-dominated depositional pattern, is interrupted during extreme river floods and plume formation that mainly occur in autumn (Covelli et al., 2004). Due to heavy rainfall, the rate of flow can reach 2500 m³ s⁻¹ (RAFGV, 1986). According to Mosetti (1983), the mean annual solid discharge is 150 g m⁻³, with peaks of 1000 g m⁻³ during extreme events. Construction of artificial reservoirs for hydroelectric purposes along the river course is presumed to have reduced the sediment supply to the delta in the last eighty years. Recent assessments of the average sedimentation rate, obtained using Hg as chemostratigraphic marker, are from 1.8 mm yr⁻¹ in the mid-Gulf, to about 6 mm yr⁻¹ in the coastal area in front of the river mouth (Covelli et al., 2006a). Whereas medium to fine sands and silty sands are prevalent along the beaches of the delta front, fine deposits in the prodelta zone are as related to the expansion of the river plume seaward. High concentrations of Hg in bottom sediments (>30 mg kg⁻¹), which exponentially decrease with distance from the riverine source (Faganeli et al., 1991; Covelli et al., 2001), are due to the predominance of cinnabar in the coarser sand-silt fraction (Biester et al., 2000; Covelli et al., 2001). Bound Hg forms, associated with finer particles and low Hg concentrations, are subject to long term transport driven by coastal currents.

2.2. Sampling strategy

Field activities were performed in two campaigns, both of them during a distinct flood event and consequent river plume formation (Fig. 1b). The first one was conducted at the Primero tidal inlet on the 6 November, 2003, five days after the highest river discharge (82 × 10⁶ m³ day⁻¹ or 950 m³ s⁻¹) of the season was recorded. The second one was conducted in front of the river mouth on the 28 November, 2003, following a minor flood event (50 × 10⁶ m³ day⁻¹ or 580 m³ s⁻¹), due to one day of moderate rain. The Isonzo River discharge data were acquired from the gauging station of Pieris (Gorizia) located about 15 km upstream from the river mouth. Meteorological conditions

in the Gulf did not allow us to sample the plume in front of the river mouth following the first flood event.

Water samples at the Primero tidal inlet were collected using a rubber boat at a fixed point to the right bank of the channel, and followed the tidal cycle; i.e. during flood–tide (h 7.30 and 16.00) and ebb–tide (h 11.00 and 13.30) in spring tide conditions. Temperature, salinity, and turbidity profiles were recorded using a CTD HydroLab H₂O Multiprobe, with a 0.1 dbar pressure step. Current velocity and prevalent flow direction of the tidal fluxes were also measured at one meter intervals along a vertical profile using a currentmeter (Anderaa RCM9). Water samples were collected using a Niskin bottle (5 l) in the surface and bottom layers, and they were immediately transferred to borosilicate glass bottles, which were subjected to a hot acid precleaning step to avoid contamination as reported in EPA Standard Methods (EPA, 2001).

Sampling in the Gulf was carried out using a boat at eight previously selected stations (Fig. 1c) during flood tide (neap tide conditions). The stations were located along transects radially expanding from the river mouth and intercepting the extent of the river plume. At each station, continuous water column profiles by CTD as well as current speed and direction were recorded and water samples were collected at surface and bottom depths following the same procedure adopted for the tidal inlet. Surface sediments (0–2 cm) were also sampled using a stainless steel Van Veen grab.

One aliquot of the water samples was used for the determination of the grain-size spectra, a second one for salinity, SPM concentrations, particulate organic carbon (POC) and particulate total nitrogen (PN) determinations. The third aliquot was processed for total particulate mercury (PHg) and particulate methyl-Hg (PMeHg) analyses. Two aliquots of the sediments were freeze-dried and used for grain-size determination and organic C, total N and Hg analyses.

2.3. Analyses

Samples for SPM size determinations (range of 9–4 phi; 1.95–62.5 μm) were processed immediately after collection using a Coulter Multisizer II (Coulter Electronics Ltd.) equipped with an Accucomp programme to acquire and process grain-size spectra. Grab samples were treated for 24 hours with H₂O₂ to remove organic matter and subsequently wet sieved (53 μm) to separate sand from the muddy fraction. The obtained sandy fraction was analyzed using a Macrogranometer (Brezina, 1979). The fraction <53 μm was collected, filtered through 50 grade Whatman cellulose filters (R 185 mm) and dried at 40 °C. In this fraction, grain-size distribution was determined on the basis of the suspension of sample in distilled water to which was added of 0.5 g dm⁻³ Na-hexametaphosphate antiflocculant solution and then analyzed by a Micrometrics Sedigraph 5100 Particle Size Analyzer.

SPM concentrations were determined by filtering a known amount volume of water through glass fiber filters (Whatman GF/F; diameter 47 mm) previously precombusted at 450 °C (Strickland and Parsons, 1972). All filters were frozen at –20 °C and stored until analysis.

Organic carbon (POC) and total nitrogen (PN) in particulate suspended matter were determined after acidification of samples with HCl 1N (Hedges and Stern, 1984) using a CHNS Elemental Analyzer (Perkin Elmer).

Particulate Hg (PHg) was determined after filtering on cellulose nitrate membranes (Millipore HA, 0.45 µm pore size). Filters were subsequently lyophilized (Lyphlock, Labconco), accurately weighed, and a complete dissolution (HF + *aqua regia*) procedure was conducted in a closed microwave system equipped with a P/T sensor unit in PTFE vessels (Multiwave 3000, Anton Paar). Analytical determination of Hg was performed by CVAFS (Tekran mod. 2500), after a reduction step using SnCl₂ (10%), coupled with a gold trap preconcentration system (Ferrara et al., 1986). The detection limit calculated on the basis of three standard deviations of the reagent blank was <0.1 pg. Triplicate analyses were performed on each sample. Reproducibility was <3%. The accuracy for Hg determination in solid phase was controlled using a certified reference material (PACS-2, mean value 3.04 ± 0.2 mg kg⁻¹, National Research Council Canada). Results obtained on the basis of three replicates (2.92 ± 0.09) were in good agreement with the certified material value.

Sediment samples were sieved through 2 mm screen to eliminate coarse material and shell debris. Digestion procedures followed EPA method 3052 (EPA, 1996), whereas analytical determinations were performed with CVAAS (MHS-15, Perkin Elmer 5100 PC; reductant agent NaBH₄ 3% in NaOH 1%). Quality control was achieved using certified reference materials (PACS-2 harbour sediment, NCR-CNR, Canada). Recoveries of Hg was 97 ± 5% (*n* = 3 replicates). The detection limit calculated on the basis of three standard deviations of the reagent blank was 0.25 µg g⁻¹ on the basis of 0.3 g dry sediment.

Particulate methyl-Hg (PMeHg) was determined by acid leaching, solvent extraction, distillation, followed by aqueous phase ethylation, precollection on Carbotrap, isothermal gas chromatography separation and CVAFS detection. Detection limits as low as 0.001 ng MeHg g⁻¹ as Hg for 100 mg sample weight were obtained (Horvat et al., 1993).

3. Results and discussion

3.1. Physico-chemical characteristics of the water column during river plume formation in the Gulf of Trieste (28 November, 2003)

In front of the Isonzo River mouth, hydrodynamic conditions were characterized by the presence of two distinct layers due to the high input of freshwaters during sampling (Fig. 2). The low salinity (5.9–14.5 or 1.7–32.0 PSU) and

low temperature (11.5–13.0 °C) surface layer varied from 1 m (ISO8) to 3 m (IS28) thick depending on the dilution effect. The thermocline was well developed and, in the lower layer, salinity reached values higher than 34 (36 PSU), typical of Gulf water, whereas temperatures were slightly higher and almost constant (13.3–13.7 °C).

The current velocity measured in the surface layer, varied between 15 and 38 cm s⁻¹ and showed a dominant circulation pattern in the SE direction (Fig. 1c). Surface currents flowed SW and W, but only in the outer stations (IS24 and IS28). The simplest form of a buoyant surface plume in coastal waters is the radial spreading from a continuous source (Garvine, 1984). The resulting apparent rotation of the river plume was due to meteorological conditions and, especially, to wind blowing during and after river floods. The limited and asymmetrical expansion of the plume into the mid-Gulf was then a consequence of E and SE winds that were prevalent on the sampling day (43% and 39%, respectively) and the day before (Fig. 1d). The plume spread up to 6 km seawards, partially covering the SW sector of the Gulf. When the strong Bora wind periodically blows from E to NE in association with river flood events, this mechanism is always enhanced and the river plume is diverted and stretched NE–SW carrying SPM south-westwards along the coastline.

The first visible evidence of the spreading of the river plume was a sharp chromatic edge between the Gulf water and the high turbidity region (Fig. 1c). At the time of sampling operations, only the outer stations (IS12 and IS24) were not reached by the fluvial suspended load yet, although surface waters showed salinity values between 30.5 and 32.5 (30 and 37 PSU), thus testifying to an initial mixing between the two water types (Fig. 2). Here, the lowest surface turbidity values were detected (3 NTU), whereas less than 0.5 NTU were measured in the lower layer. On the contrary, the sampling point IS28, located at the same linear distance from the river mouth as the previous mentioned stations, showed higher surface turbidity values (avg. 12, max. 43 NTU). Since the highest turbidity values in the surface layer (avg. 46 NTU) as well as in the lower one (avg. 38 NTU) were recorded at station IS26, and not in front of the river mouth (avg. 30 and 6 NTU at the surface and in the bottom layer, respectively, at ISO8), it was evident that most of the suspended load flowed southwards. The slight difference in turbidity between surface and bottom layers of the station IS26 was a consequence of the mixing between riverine and marine waters due to the shallowness of the sea bottom. The main flow direction is facilitated by the occurrence of a submarine channel between the distributary mouth and the delta bar (Covelli et al., 2004).

3.1.1. Suspended particulate matter: distribution, grain-size and origin

The SPM values at the surface ranged from 8.2 to 44.2 mg L⁻¹ and were more concentrated at the nearshore stations ISO8 and IS26 following the extension of the

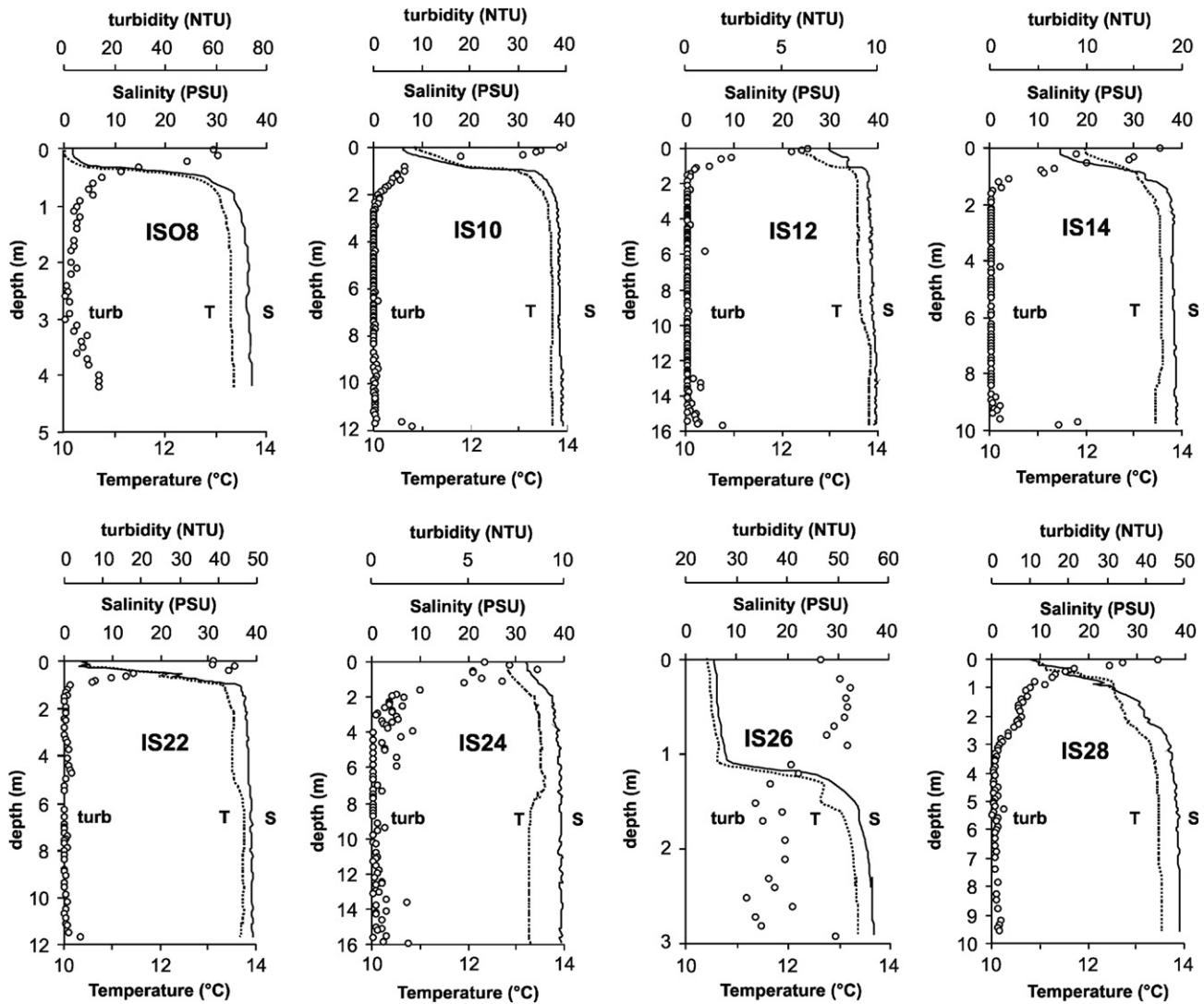


Fig. 2. Vertical profiles of turbidity (turb, NTU, Nephelometric Turbidity Unit), Salinity (*S*, PSU, Practical Salinity Unit) and Temperature (*T*, °C) in the sampling stations in the Gulf of Trieste (28 November, 2003). Note change in scale for turbidity to emphasize vertical variability.

freshwater plume. SPM varied between 4.2 and 35.3 mg L⁻¹ in the bottom saline layer. Surface-bottom SPM ratios ranged from 4 to 7. When the marked differences in surface water properties with seawater is high, the flow dynamics is dominated by the gravitational spreading of the thin layer of the buoyant water (Garvine, 1984). A distinct visual boundary forms the leading edge of the spreading motion. The lowest SPM values, as already shown by turbidity, were observed in the stations IS12 and IS24, outside the plume, where surface concentrations were only twice that in the bottom layer.

The grain size spectra in the surface layer changed from the Isonzo River mouth seawards according to the mentioned consecutive plume fronts (Fig. 4). Surface SPM samples near the mouth (ISO8 and IS26) are skewed and sorted, with the mode size of 5.29 and 7.38 μm, respectively. Positively skewed spectra with finer mode size (4.24 μm) appeared in the surface samples of the more external river plume front (IS14, IS10, IS22 and IS28).

On the contrary, in the bottom layer samples, with the exception of the shallow water stations ISO8 and IS26 where surface spectra are similar to the bottom ones, the size distribution is poorly sorted, thus confirming the marine origin of the particles (Covelli et al., 2004, 2006b). The outer stations IS12 and IS24, that were not reached by the fluvial suspended load at the sampling time, showed identical mode size (8.25 μm) for the surface grain-size distributions and similar mode size (5.29 and 5.91 μm) for the bottom samples. The sharp peak revealed by the surface sample at IS12 station could be due to phytoplankton predominance and, particularly, to the aggregation of diatom cells influenced by low salinities, water column stratification and nutrient availability as already noted in brackish waters during low river discharge conditions (Covelli et al., 2004).

The surface concentrations of POC and PN were higher at the surface (527–222 and 82–29 μg L⁻¹, respectively) than at the bottom (82–39 and 82–14 μg L⁻¹, respectively),

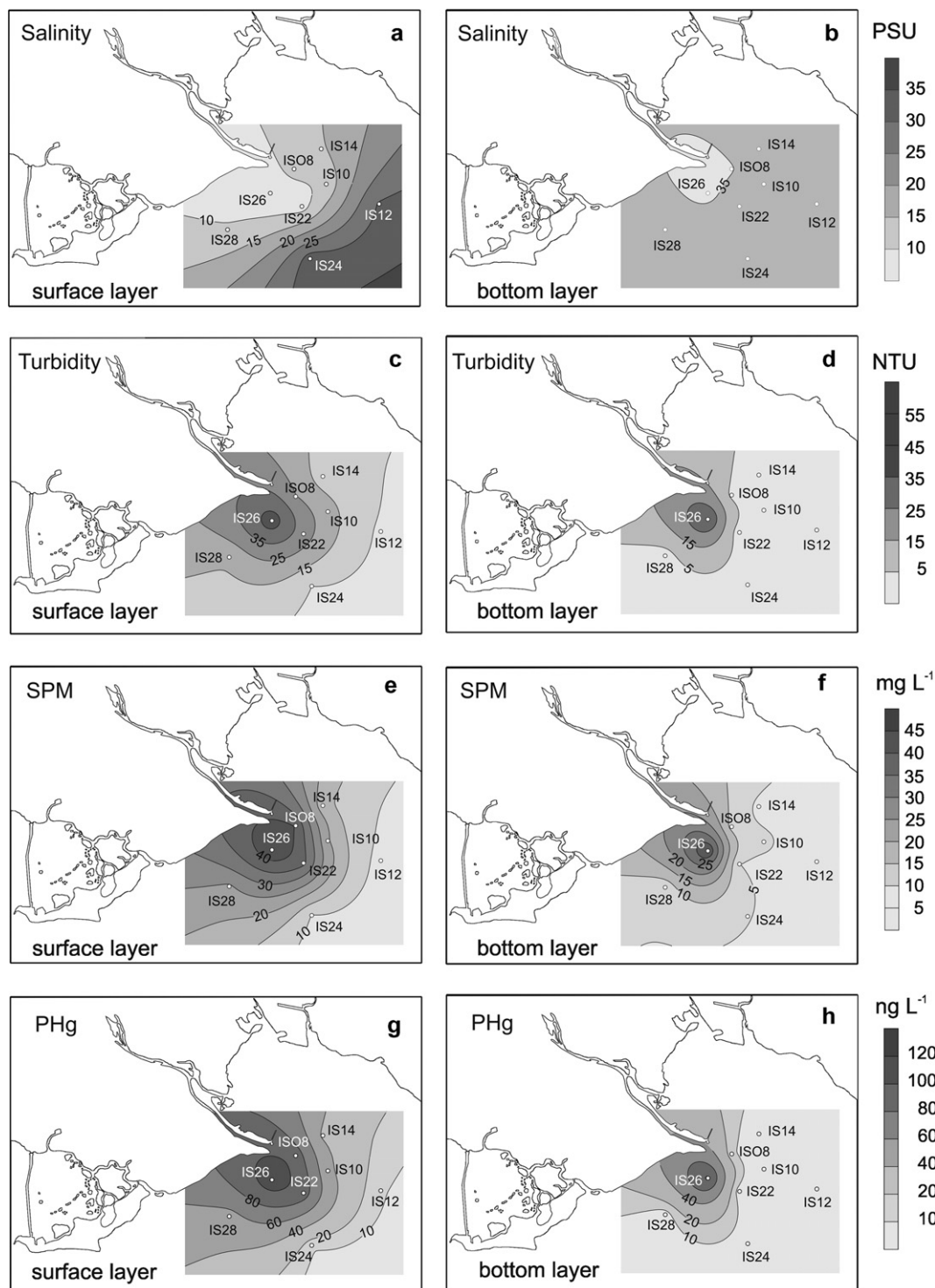


Fig. 3. Areal distribution of principal parameters measured in the surface and bottom layers of the water column in the Gulf of Trieste: Salinity (a–b), turbidity (c–d), suspended particulate matter (SPM, e–f) and particulate mercury (PHg, g–h).

with maxima at IS26 station, showing decreasing values seaward due to dilution effects as observed for SPM. An opposite trend was observed for POC and PN with surface values varying between 0.78–1.33% for POC and 0.15–0.25% for PN, respectively, which were usually lower than the related bottom samples (0.35–2.33% for POC and 0.07–0.50% for PN). In spite of higher surface SPM concentra-

tions associated with the buoyant plume in November, 2003, the particulate organic component was comparatively lower than that previously observed in surface waters (salinity <22) during the winter (avg. POC 7.1%) and spring (avg. POC 4.0%) seasons with low-normal river discharge (Covelli et al., 2004). Significant inverse relationships between percentage values of POC and PN and

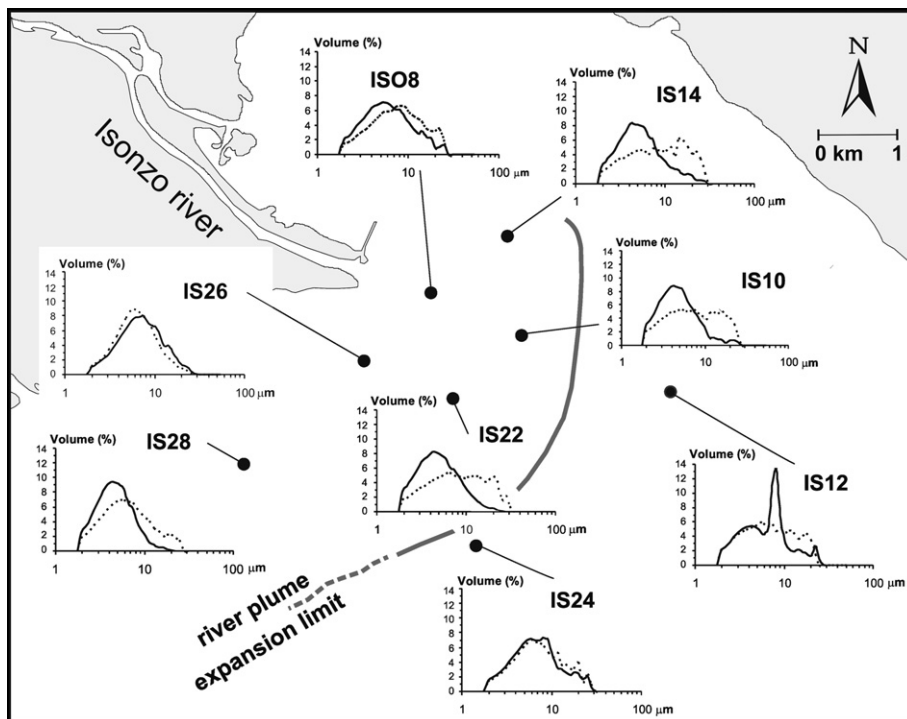


Fig. 4. Grain-size spectra (Volume %) of suspended particulate matter in surface (—) and bottom (...) water samples of the Gulf of Trieste during Isonzo river plume formation (28 November, 2003).

suspended matter load (Fig. 5) were observed for the Po river (Pettine et al., 1998; Boldrin et al., 2005) as well as several rivers in the world (Mybeck, 1982). According to the latter author, autochthonous particulate matter would be mixed with land-derived organic poor particles. The high correlation between POC and PN values (Fig. 5) and low C/N ratios confirm that nitrogen is prevalently organically bound in riverine suspended matter and not dependent on the fluvial discharge. It also suggests that the particulate organic matter is, even during high riverine discharge, mostly of planktonic origin.

3.2. Particulate Hg (PHg) distribution in the water column of Gulf of Trieste and its relationship with grain-size and organic matter

Particulate Hg concentrations measured in the surface layer of the water column emphasizes the importance of these flood events in carrying significant amounts of this metal in particulate form into the Gulf. In fact, the PHg concentrations in front of the river outflow (ISO8) were from 5 to more than 40 times higher in comparison with results obtained during low river discharge (Fig. 6a; data from Covelli et al., 2006b). However, the highest PHg values, at the surface (112 ng L^{-1}) as well as at the bottom (84 ng L^{-1}), were observed further south, at station IS26 (Fig. 3g–h). Here, the lowest difference in terms of PHg concentrations between the two water layers indicates the area where the highest transport, turbulence and friction with the sea-bottom occurred. PHg values were generally higher than 37 ng L^{-1} within the buoyant river plume,

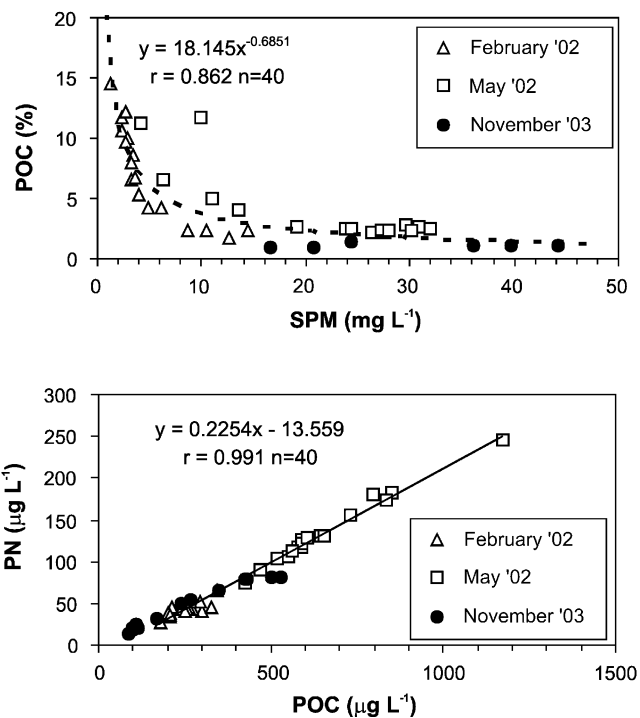


Fig. 5. Relationship between POC (Particulate Organic Carbon) and SPM (Suspended Particulate Matter) (above), and POC and PN (Particulate Nitrogen) (below), in the surface layer of the Isonzo River plume during high river discharge (28 November, 2003). Results obtained from two previous sampling (February and May, 2002) at low-normal river discharge (data from Covelli et al., 2004) have been included.

whereas they reached only 6 and 12 ng L^{-1} offshore (IS12 and IS24, respectively). Apart from the already mentioned

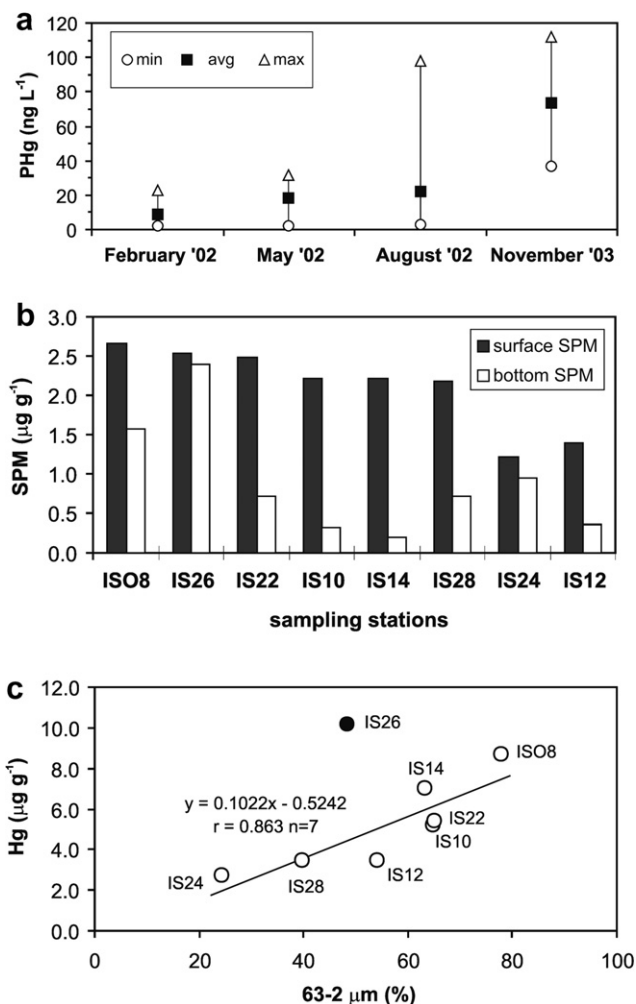


Fig. 6. (a) Particulate mercury concentrations (PHg) in the surface layer of the Isonzo River plume during high river discharge (28 November, 2003) compared to previous sampling (February, May and August, 2002) performed at low-normal river discharge (from Covelli et al., 2006b); (b) PHg contents, expressed as dry weight, in the river plume of early November, 2003 and (c) relationship between Hg concentration and silty fraction in bottom sediments of the Gulf of Trieste.

results for IS26 station, PHg in the bottom water layer was usually less than 13 ng L⁻¹ (IS08) with the lowest value recorded at IS14 (<1 ng L⁻¹). In terms of dry weight (μg Hg per g of SPM), surface PHg values varied between 1.2 and 2.7 μg g⁻¹ (avg. 2.3 μg g⁻¹), whereas bottom values ranged between 0.2–2.4 μg g⁻¹ (avg. 0.9 μg g⁻¹). PHg dry weight concentrations (Fig. 6b) in the plume were similar to previous results obtained during low-normal Isonzo River discharge (Covelli et al., 2006b). It seems that higher amounts of Hg bound to suspended particles do not correspond to higher SPM concentrations in the fluvial waters and dilution was the main factor affecting its distribution.

PHg in the surface waters show the best positive correlation ($P < 0.01$) with particles ranging between 8 and 16 μm either in terms of volume (Fig. 7a) or expressed as dry weight (Fig. 7c), confirming the high affinity of Hg for the fine silty component of the SPM (Covelli et al., 2006b) as also observed for bottom sediments (Covelli

et al., 2001 and Fig. 6c). The bottom SPM sample of the IS26 station was similar due to the high mixing of the water column at shallow depths. The only exceptions are those samples collected beyond the external limit of the river plume (IS12 and IS24) which were not affected by the incoming river SPM at the time of sampling. They were similar to bottom samples in terms of very low and uniform PHg concentrations and higher percentage of silt (25–35%) showing no relationship between the two parameters.

The POC values expressed as volume were very well correlated to PHg ($P < 0.001$, Fig. 7b), and to fine silt (Fig. 7d) in surface waters suggesting an important role of the organic component as metal carrier. However, this hypothesis is only partially true since no relationship exists between POC (% dry weight) and the silty fraction (Fig. 7e) and between POC and PHg (Fig. 7f). The organic matter seems then to be associated with the suspended particles on the whole and not dependent on particle sizes. In addition, the organic matter does not play an important role as a Hg carrier in freshwaters at high river discharge as observed at low river flow (Covelli et al., 2006b). Conversely, PHg is definitely more affected by the specific size ranges of suspended particles that are mostly inorganic, particularly at high river stage. Mercury in SPM and bed load enters the Gulf of Trieste as cinnabar (HgS) or non-cinnabar, mainly organically bound Hg(II) (Biester et al., 2000). Cinnabar is the predominant Hg species in tailings of different age in variable percentages depending on the efficiency (50–90%) of the roasting technique during past activity, whereas atmospheric-derived Hg is mainly bound to humic acids in soils near Idrija (Biester et al., 1999). Furthermore, the cinnabar component predominates in the coarse sandy fraction of the bottom sediments near the Isonzo River mouth (Covelli et al., 2001), whereas in the fine grained material (<63 μm) of the Gulf, speciation analysis suggested that microcrystalline red cinnabar coexists with metacinnabar (black HgS) and organo-mercury-sulphides (Biester et al., 2000). Although SPM has not been analyzed for Hg species, it can be assumed that the finest particles (<16 μm) in the river plume contain a significant amount of microcrystalline cinnabar.

In spite of the Idrija mine closure about twelve years ago, the present inputs of PHg observed during Isonzo River plume formation confirm that a large amount of the metal in particulate form must be still stored in alluvial deposits of the river drainage basin. Recent assessments of Hg stored in the Idrija River valley accounts for 2029 tons (Žibret and Gosar, 2006) whereas about 900 tons should be buried in bottom sediments of the Gulf of Trieste (Covelli et al., 2006a). These are only small amounts compared to the overall 40,000 tons of Hg that was dissipated into the environment during the five-century-long mining history (Miklavčič, 1999).

Mercury contents in surface bottom sediments ranged from 2.76 to 10.19 μg g⁻¹. They are related to the silty fraction of the sediments rather than to the distance from the Isonzo River mouth (Fig. 6c). The positive linear

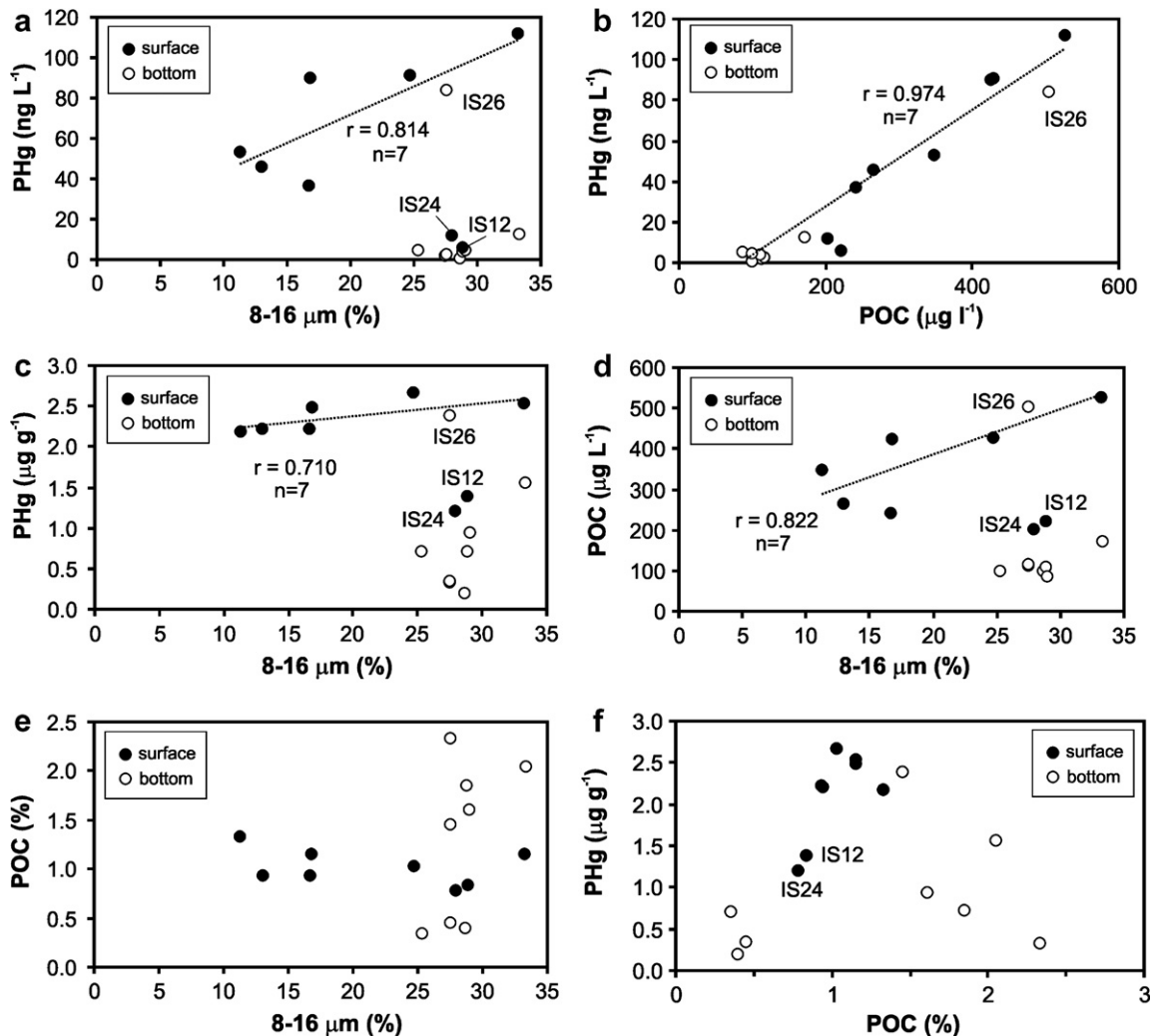


Fig. 7. Relationships between particulate mercury concentration (PHg), particulate organic Carbon (POC) and fine silt fraction (8–16 μm) in the water samples of the Gulf of Trieste (28 November, 2003). IS12 and IS24 surface water samples were not affected by the river plume at the time of sampling. Conversely, IS26 bottom water sample belongs to the surface samples group due to the high mixing of the water column (see (c), for example) at shallow depth.

correlation ($P < 0.5$) between the two variables supports this hypothesis. The only exception is the station IS26 falling outside the linear trend. A partial Hg contribution from the fine sandy fraction in the sample can explain the anomaly. The measured concentrations are slightly lower than previously assessments (Covelli et al., 2001), especially in front of the river mouth ($\sim 9 \mu\text{g g}^{-1}$), thus indicating a possible decrease in the most recent Hg inputs as already seen in the long core GT2 from the prodelta area of the Isonzo River (Covelli et al., 2006a) or, at least, of Hg bound to the coarse sandy fraction of the nearshore zone.

3.3. Physico-chemical characteristics of the water column and SPM at the Primero tidal inlet (6 November, 2003)

The river plume formation in the Gulf at the beginning of November, 2003 (Fig. 1b) was dispersed by the strong E–NE Bora wind (Fig. 8a). Sampling at the Primero tidal inlet (Fig. 1c) was aimed to investigate the dynamics of riv-

erborne SPM transported by tidal fluxes into the lagoon during a tidal semi-cycle.

Salinity, temperature and turbidity profiles, which were conducted at four stages of the tidal semi-cycle (Fig. 9), provided clear evidence of thermohaline stratification during at least three of the four samplings. The brackish surface layer was characterized by progressive increases of these parametric values down to 2–3 m depth, where they became almost constant and typically marine.

In the first sampling (h 7.30) in flood–tide (Fig. 8b), salinity in the surface layer ranged between 20.3 and 32.4 PSU, temperature between 10.0 and 12.7 °C, whereas turbidity values were in the range 79–259 NTU (Fig. 9). In the bottom layer, the water column was more homogenous: salinity ranged between 32.7 and 34.1 PSU, temperature was slightly higher (12.8–13.1 °C), whereas turbidity (44–80 NTU) and SPM concentration (81.0 mg L^{-1}) were lower than in the surface layer. Conversely, the SPM concentration (234.3 mg L^{-1}) measured at the surface in early

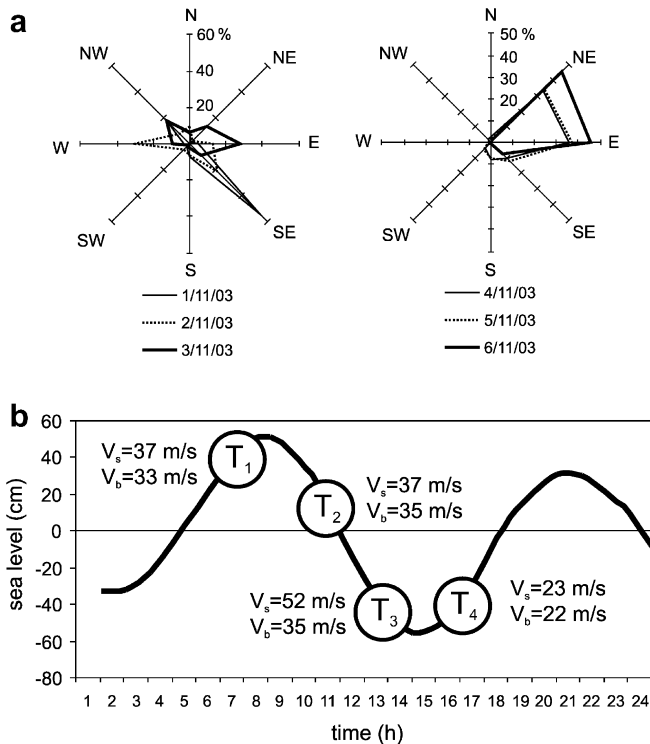


Fig. 8. (a) Wind frequency (%) measured at Trieste (ARPA FVG OSMER) from the 1st to the 6th November, 2003 at the time of river plume formation; (b) tidal curve (a time lag of about 30 min were applied to real data recorded at Trieste) and related sampling time at the Primero inlet on the 6th November, 2003; average current velocities are reported for the surface (V_s) and bottom (V_b) water layers.

November was significantly higher than Gulf samples collected in late November (Fig. 3e–f). This seems quite reasonable considering that increased SPM concentrations depend on riverborne particles supplied by Isonzo River flood events of different magnitude (Fig. 1b). In addition, an unidentifiable contribution of bottom sediment resuspension caused by the strong E–NE wind in the shallow waters near the tidal inlet cannot be excluded. Rajar et al. (2000) simulated a transport–dispersion model for suspended particles within two days of 13 m s^{-1} E–NE wind blowing in the Gulf. The same authors reported that this situation could produce a maximum flow velocity of up to 35 cm s^{-1} in the nearshore area between the river mouth and the tidal inlet, which could resuspend up to 9 mm of bottom sediments. However, we can reasonably exclude this hypothesis on the basis of the grain-size distribution of our samples reported in Fig. 10, showing modal sizes $<10 \mu\text{m}$, which is significantly finer than the coarser sandy silty sediments recovered from the nearshore area (i.e. ISO8, IS26 and IS28 stations).

The thermohaline stratification was still present in the second sampling (h 11.00), which was during ebb–tide conditions. The opposite situation to the flood tide occurred regarding SPM, which was transported by tidal currents flowing seawards, leading to turbidity. Both showed higher values in the bottom layer (95.3 mg L^{-1} and 21–97 NTU) than at the surface (18.5 mg L^{-1} and 20–38 NTU, Fig. 9).

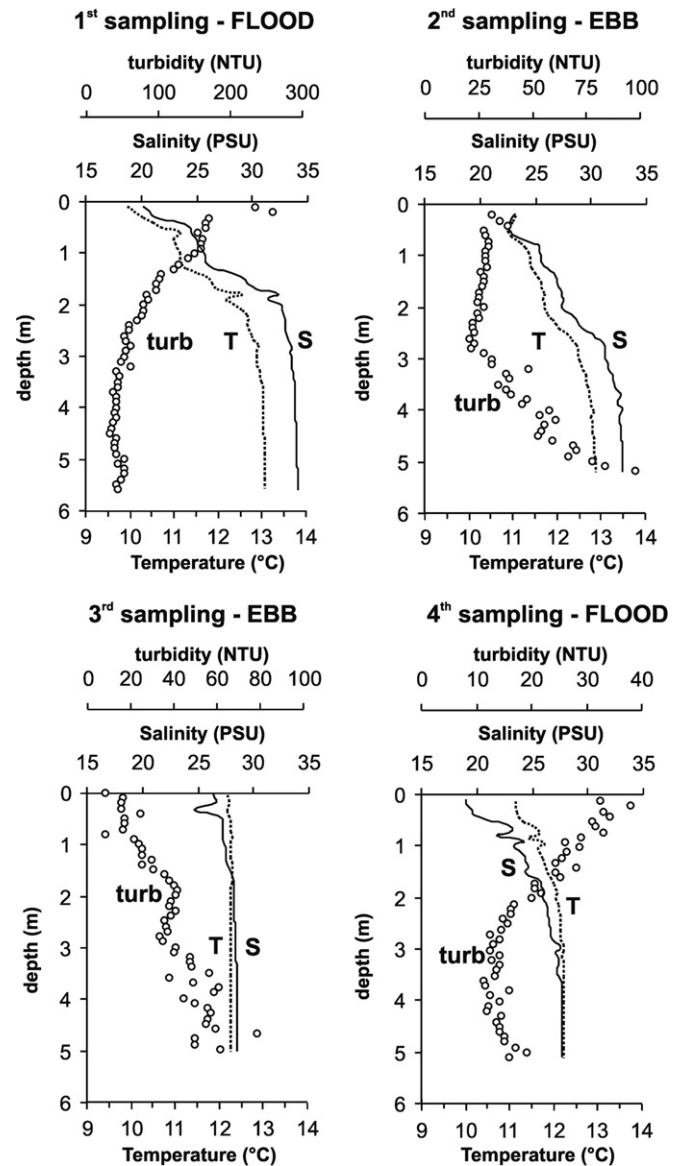


Fig. 9. Vertical profiles of turbidity (turb, NTU, Nephelometric Turbidity Unit), Salinity (S, PSU, Practical Salinity Unit) and Temperature (T , °C) in the four sampling stages at the Primero lagoon inlet (6 November, 2003). Note change in scale for turbidity to emphasize vertical variability.

These results can be explained by considering processes, such as transport and sedimentation of fine-grained particles regulated by tidal flows in the estuarine and lagoon environments (Pethick, 1984). Maximum velocity is reached by the rising tide when half of the mudflats are covered at mid-tide. Thereafter, the velocity drops to zero approaching slack water when the whole of the mudflats are submerged. Reducing current velocity allows fine sediments to settle out of the water column, but not all of the suspended particles can reach the bottom and accumulate on the mudflats. Part of the suspended load is carried by the reversed tidal flow towards the inlet with particles more concentrated near the bottom than at the surface of the water column.

This behaviour is also suggested by the grain-size spectra of the SPM (Fig. 10). Particle size distribution and mode

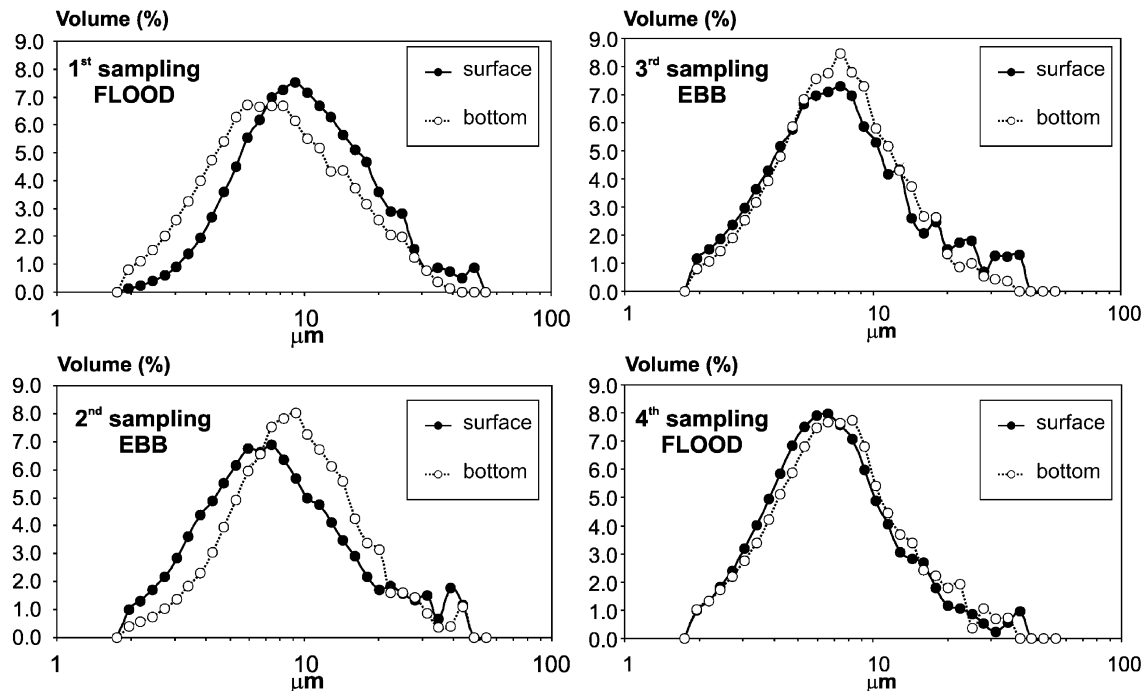


Fig. 10. Comparison of grain-size spectra of suspended matter at the tidal inlet during different tidal phases (flood and ebb) on the 6th November, 2003.

(9.2 μm) of SPM in the bottom layer from the second sampling were nearly the same as those obtained from the surface sample previously collected during flood-tide. Unlikely, identical grain-size spectra and mode (7.4 μm) for both surface and bottom layers in the third sampling (h 13.30) that was still in ebb-tide were observed. The water column appeared homogeneous both for temperature (12.2–12.4 $^{\circ}\text{C}$) and salinity (26.2–28.5 PSU). A possible explanation is that water flowing out of the lagoon during the final stage of the ebb tide was not affected by freshwaters belonging to the river plume as in the previous two samplings. Conversely, turbidity (Fig. 9) showed a slight increasing trend with depth from 15.5 to 49.7 NTU, which are related to SPM concentrations measured at the surface (15.8 mg L^{-1}) and at the bottom (49.5 mg L^{-1}).

Thermohaline stratification occurred again in the last sampling during flood conditions (Fig. 9). Low salinity and temperature (19.1–27.0 PSU and 11.1–12.1 $^{\circ}\text{C}$, respectively) values were recorded in the surface layer where the suspended load was more concentrated (34.7 mg L^{-1}) compared to the bottom (14.3 mg L^{-1}) and more saline waters. Turbidity constantly decreased with depth from a maximum of 38 to about 14 NTU demonstrating that a new ingress of brackish waters and riverborne SPM in the inlet driven by tidal flow.

3.4. Particulate mercury (PHg) and methyl-Hg (PMeHg) associated with SPM during a tidal semi-cycle at the Primero tidal inlet

Mercury bound to suspended sediments transported by tidal fluxes flowing through the Primero inlet followed the trend already observed for SPM and turbidity. In the

first sampling (h 7.30), PHg as well as PMeHg showed the highest concentrations (1647 ng L^{-1} and 0.497 ng L^{-1} , respectively) at the surface, whereas, at the bottom, PHg was four times (403 ng L^{-1}) and PMeHg almost ten times (0.041 ng L^{-1}) lower (Fig. 11). During ebb-tide, in the second sampling (h 11.30), PHg at the surface was noticeably lower (105 ng L^{-1}) compared even to the bottom waters (729 ng L^{-1}) affected by the partial settling of suspended particles from the surface layer as described in the previous paragraph. PMeHg was only 0.025 ng L^{-1} in the same layer, but was lower than the detection limit (<LOD) at the bottom. No data were available for PMeHg in the third sampling (h 13.30) when PHg contents were shown to have significantly decreased following the same trend: 53 ng L^{-1} at the surface and 171 ng L^{-1} at the bottom. A developing overturn situation was observed in the last sampling (h 16.30) at the beginning of the following flood semi-cycle when surface waters showed higher contents of PHg (151 ng L^{-1}) compared to the bottom (110 ng L^{-1}).

When reported in terms of dry weight, differences among PHg concentrations are not significant since they fall in the range 4.1–6.7 $\mu\text{g g}^{-1}$ (avg. 5.2 ± 1.1) at the surface and 5.3–6.2 $\mu\text{g g}^{-1}$ (avg. 5.7 ± 0.4) at the bottom. PMeHg as a percentage of PHg accounts only for a very small fraction: 0.03% (surface) and 0.01% (bottom) in the first sampling, whereas it was 0.02% at the surface in the second sampling (ebb-tide). This evidence suggests that in spite of the high amounts of Hg bound to suspended particles flowing into the lagoon, these significantly low contents of PMeHg entering the tidal inlet cannot justify the MeHg concentrations found in the bottom sediments of the Grado lagoon, which range between 1.1 and 22.0

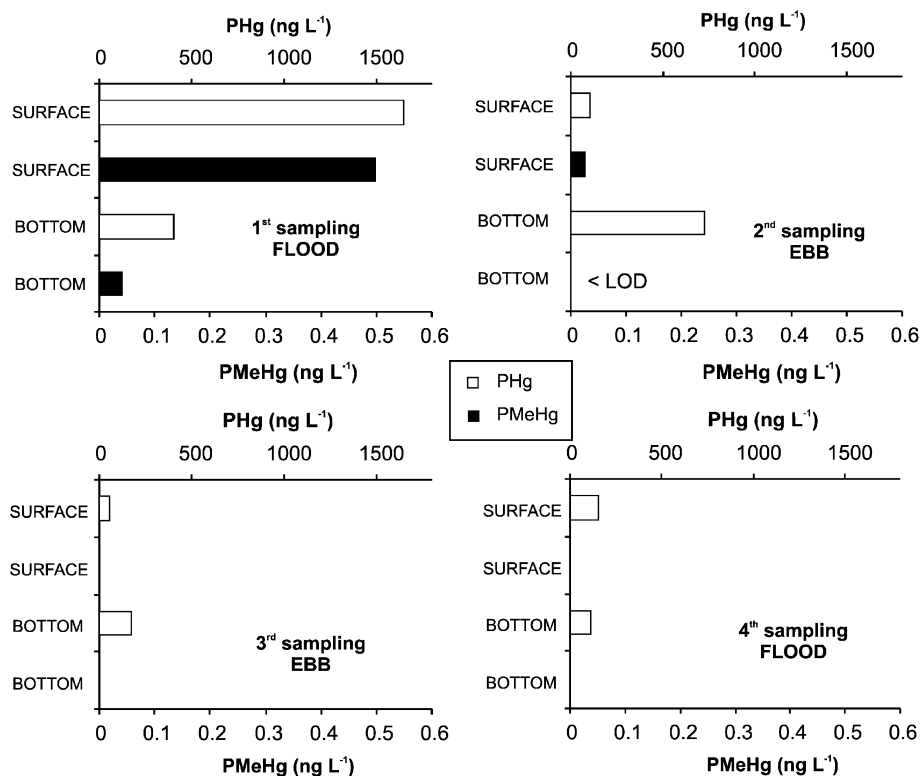


Fig. 11. Particulate mercury (PHg) and methyl-Hg (PMeHg) associated to tidal fluxes at the Primero lagoon inlet during the four sampling stages performed on the 6th, November, 2003. PMeHg was not measured in the 3rd and 4th sampling stages.

ng g^{-1} (Viso, 2004). A possible explanation described by Covelli et al. (2006c) is that most of MeHg in the sediments of the mudflats and the subtidal zone of the lagoon is produced by bacterial activity in this environment as partially revealed by *in situ* benthic fluxes. This study is able to confirm that sedimentary MeHg concentrations in the lagoon are not affected by fluvial SPM associated with river plume formation in the Gulf. In addition, MeHg is very easily oxidized or demethylated in oxygen-rich environments such as canalized water currents (Hines et al., 2004), thus explaining the very low PMeHg concentrations exported by tidal flows from the lagoon during ebb conditions.

Hg concentrations and grain-size of the suspended particles revealed a similar relationship to that observed for the river plume in the Gulf, although PHg concentrations were two-three folds higher. In fact, PHg (dry weight) was positively correlated with fine silt ($r = 0.835$; $n = 8$; $P < 0.01$), without distinction between surface and bottom samples, although the 8–16 μm particles showed concentrations, on average, that were higher (28–41%) than river plume samples in the Gulf. Apart from the different scale in terms of water discharge and suspended load between the two flood events, a progressive enrichment in the finest component during transport from the river mouth to the tidal inlet may have occurred.

In spite of the higher POC levels at the tidal inlet (3186.8–330.5 $\mu\text{g L}^{-1}$ at surface and 2093.2–226.2 $\mu\text{g L}^{-1}$ at the bottom, respectively), the organic component of

SPM when expressed as dry weight was slightly higher than in the Gulf: from 1.47% to 2.25% at surface and from 1.00% to 2.20% at the bottom. The good correlations between POC and PHg, expressed as volume, and between POC and the fine silt fraction, seem to support the importance of organic matter as a metal carrier. However, this behaviour was not apparent when data were compared as dry weight, as reported for the river plume in the Gulf.

3.5. Preliminary budget for PHg accumulation in the lagoon during a tidal semi-cycle

Results obtained from the tidal inlet can be used to make an indicative assessment of the amount of Hg bound to suspended particles which are trapped and accumulate in the lagoon following the action of tidal flow during a tidal semi-cycle.

The four samplings were considered as instantaneous events: T_1 and T_4 in flood while T_2 and T_3 in ebb. Water flowing (Q) through the tidal inlet section ($A = 696 \text{ m}^2$ from Cirilli, 1999) for each sampling was calculated as $Q = A \times v$, where v is the average current speed measured for each water layer *in situ* (Fig. 8b). As previously described, the water column appeared stratified in two layers. The area belonging to each layer, which was considered rectangular, was estimated taking into account the thickness of the layer, which was variable according to the salinity profile for each time T_n (Fig. 9). The amount of PHg

(kg s^{-1}) flowing through the tidal inlet section in the surface layer and in the bottom layer, was calculated at time T_n as follows:

$$\text{PHg}_{\text{water layer}} (\text{kg s}^{-1}) = \text{PHg} (\text{ng L}^{-1}) \times Q (\text{m}^3 \text{s}^{-1}) \times 10^{-9}$$

The total amount of PHg (kg s^{-1}) transported at time T_n through the tidal inlet section was the sum of the $\text{PHg}_{\text{water layer}}$ obtained from each layer. Both samplings during ebb conditions (T_2 and T_3) were consecutively performed along the same decreasing tide. However, for flood tides the first sampling (T_1) was carried out at the end of the first flood-tide, where the second (T_4) was performed at the beginning of the following flood-tide (Fig. 8b). In the following calculation, T_4 was considered as a hypothetical sampling conducted in flood-tide before T_1 . It is most probable that PHg concentration could be much higher before T_1 than what was obtained at T_4 , therefore making our following calculation an underestimate. However, taking into consideration all the approximations, at least a semi-quantitative assessment of the amount of PHg (kg) ultimately entrapped in the lagoon, after six hours of flood and six hours of ebb tide, can be obtained as follows:

$$\begin{aligned} \text{PHg}(\text{kg}) = & (\text{PHg}_{\text{tidal inlet}}(T_1) + \text{PHg}_{\text{tidal inlet}}(T_4))/2 \\ & - (\text{PHg}_{\text{tidal inlet}}(T_2) + \text{PHg}_{\text{tidal inlet}}(T_3))/2 \end{aligned}$$

It must be noted that all these components (i.e. SPM, PHg, current velocity, etc.) were considered as approximated mean values since they are strictly variable and dependent on time. Yet, this simple estimation provides a positive sedimentary budget for the lagoon. The amount of PHg entrapped in the lagoon basin following a tidal semi-cycle accounts for 1.4 kg/12 h, which corresponds to about 49% of the total mercury carried by the tidal flow. Since this mechanism is incessantly repeated every 12 h, as a sort of “transport belt”, it is presumable that the amount of PHg delivered into the lagoon following a similar plume event can be even higher. The lagoon, not only the Gulf itself, seems to be a final sink for Hg bound to suspended sediments during high Isonzo River flood stages. The occurrence of cinnabar in the bottom sediments of the central sector of the Marano and Grado lagoons further west (Piani et al., 2005) can then be explained through longshore current dispersion of the Hg-rich Isonzo River suspended load followed by transport and settling due to tidal fluxes.

4. Conclusions

The present study has attempted to verify the role of suspended fine sediments as an important path of Hg dispersion into the Northern Adriatic sea and the adjacent Grado lagoon system during peak river discharges and river plume formation. In addition, there has been no experimental evidence regarding the current role of tidal fluxes in carrying Hg into the lagoon basin and, subsequently, to the fish farms, compared to the amount of

metal “entrapped” in the bottom sediments when the Idrija mine was operational.

Our results have demonstrated that, although extreme flood events are not frequent during the year, their contribution of particulate Hg into the Gulf of Trieste still remains considerable. Washout of contaminated sediments from the mining region, from the Idrija-Isonzo River drainage basin and from the flood plains of the river system, where mining residues have been deposited (Žibret and Gosar, 2006), will provide Hg in particulate form to the river discharge. When the river plume is stretched and diverted SW under the influence of strong E–NE wind, tidal fluxes act as a sort of “transport belt” conveying Hg bound to suspended, mostly inorganic, particulates into the lagoon, where they eventually accumulate on the mudflats as well as in the fish farms. An annual mass-balance of particulate Hg in the Grado lagoon will never be obtained from a limited number of experimental data. However, our preliminary assessment suggests that considerable amounts of Hg might enter the lagoon when peak river discharges and specific wind conditions concurrently occur in the study area.

This result, therefore, should be taken into account in the future if remediation strategies have to be planned for recovering those fish farms whose bottom sediments are shown to be Hg contaminated down to 20–30 cm depth (Brambati, 1997). For instance, dredging operations in the fish farms could guarantee total recovery for a certain number of years but the processes of sedimentation will continue depositing contaminated sediments which will enter the fish farms during tidal fluxes, thus undermining the remediation process. Therefore, the usual water exchange with the lagoon channels through sluice gates should be automatically regulated by stopping the flow of water during flood events and/or intense wave motion in the lagoon basin. This simple procedure will help to avoid a notable inflow of Hg-rich suspended sedimentary load into the fish farms which could slowly re-establish the original contaminated conditions. However, another possibility is the replacement of sluices with revolving gates to guarantee an inward and outward unidirectional flow in order to prevent sedimentation of most of the suspended sediments.

Future research should focus on seasonal measurements of particulate Hg concentrations associated with tidal fluxes at the Primero tidal inlet during the year, and, possibly, at the other inlets of the lagoon, in order to calculate an annual mass-balance of Hg in this coastal ecosystem.

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References

- Alliot, E., Younes, W.A.N., Romano, J.C., Rebouillon, P., Masse, H., 2003. Biogeochemical impact of a dilution plume (Rhône River) on coastal sediments: comparison between a surface water survey (1996–2000) and sediment composition. *Estuarine Coastal and Shelf Science* 57, 357–367.
- Biester, H., Gosar, M., Müller, G., 1999. Mercury speciation in tailings of the Idrija mercury mine. *Journal of Geochemical Exploration* 65, 195–204.
- Biester, H., Gosar, M., Covelli, S., 2000. Mercury speciation in sediments affected by dumped mining residues in the drainage area of the Idrija mercury mine, Slovenia. *Environmental Science and Technology* 34, 3330–3336.
- Boldrin, A., Langone, L., Miserocchi, S., Turchetto, M., Acri, F., 2005. Po river plume in the Adriatic continental shelf: dispersion and sedimentation of dissolved and suspended matter during different river discharge rates. *Marine Geology*, 135–158.
- Brambati, A., 1997. Metalli pesanti nelle lagune di Marano e Grado. Piano di studi finalizzato all'accertamento di sostanze persistenti nelle Lagune di Marano e Grado ed al loro risanamento. (RFVG) Direzione Regionale dell'Ambiente, Servizio dell'Idraulica, Trieste, 174 pp.
- Brambati, A., 2001. Coastal sediments and biota as indicators of Hg contamination in the Marano and Grado Lagoons. *RMZ – Material Geoenvironment* 48, 165–171.
- Brezina, J., 1979. Macrogranometer parts; Granometry. D-6903 Neckargebund-3, W. Germany (unpublished technical documentation), 18 pp.
- Cirilli, S., 1999. Morfodinamica sedimentaria della bocca di Primero (Grado). Università degli Studi di Trieste, Facoltà di Scienze Matematiche, Fisiche e Naturali, Dipartimento di Scienze Geologiche Ambientali e Marine, unpublished Thesis, 139 pp.
- Covelli, S., Fontolan, G., Faganeli, J., Ogrinc, N., 2006a. Anthropogenic markers in the Holocene stratigraphic sequence of the Gulf of Trieste (northern Adriatic Sea). *Marine Geology* 230, 29–51.
- Covelli, S., Piani, R., Kotnik, J., Horvat, M., Faganeli, J., Brambati, A., 2006b. Behaviour of Hg species in a microtidal deltaic system: The Isonzo River mouth (northern Adriatic Sea). *Science of the Total Environment* 368, 210–223.
- Covelli, S., Faganeli, J., De Vittor, C., Predonzani, S., Acquavita, A., Horvat, M., Ogrinc, N., 2006c. Benthic fluxes of mercury in a lagoony environment: diel cycling. In: 8th Int. Conf. of “Mercury as a Global Pollutant”, Madison, Wisconsin, USA, 6–11 August 2006, Book of Abstract, DEStech Publications Inc.:Lancaster, Pennsylvania, USA, pp. 474–475.
- Covelli, S., Piani, R., Faganeli, J., Brambati, A., 2004. Circulation and suspended matter distribution in a microtidal deltaic system: the Isonzo river mouth (northern Adriatic Sea). *Journal of Coastal Research*, S.I. 41, 130–140.
- Covelli, S., Faganeli, J., Horvat, M., Brambati, A., 2001. Mercury contamination of coastal sediments as the result of a long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic Sea). *Applied Geochemistry* 16, 541–558.
- Eisma, D., 1993. Particle size. In: Eisma, D. (Ed.), *Suspended matter in the aquatic environment*. Springer-Verlag, 315pp.
- EPA Method 1631, Revision C, 2001. Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. United States Environmental Protection Agency, EPA-821-R-01-024.
- EPA Method 3052, 1996. Microwave assisted acid digestion of siliceous and organically bound matrices. United States Environmental Protection Agency, EPA.
- Faganeli, J., Horvat, M., Covelli, S., Fajon, V., Logar, M., Lipej, L., Cermelj, B., 2003. Mercury and methylmercury in the Gulf of Trieste (northern Adriatic Sea). *Science of the Total Environment* 304, 315–326.
- Faganeli, J., Planinc, R., Pezdic, J., Smodis, B., Stegnar, P., Ogorelec, B., 1991. Marine geology of the Gulf of Trieste (northern Adriatic): geochemical aspects. *Marine Geology* 99, 93–108.
- Ferrara, R., Seritti, A., Barghigiani, C., Petrosino, A., 1986. Mercury levels in the dissolved and particulate fractions of the Thyrrenian sea. *Marine Chemistry* 18, 227–232.
- Garvine, R.W., 1984. Radial spreading of buoyant, surface plumes in coastal waters. *Journal of Geophysical Research* 89, 1989–1996.
- Gaston, T.F., Schlacher, T.A., Connolly, R.M., 2006. Flood discharges of a small river into open coastal waters: Plume traits and material fate. *Estuarine Coastal and Shelf Science* 69 (1–2), 4–9.
- Gosar, M., Pirc, S., Bidovec, M., 1997. Mercury in the Idrija River sediments as a reflection of mining and smelting activities of the Idrija mercury mine. *Journal of Geochemical Exploration* 58, 125–131.
- Hedges, J.I., Stern, J.H., 1984. Carbon and nitrogen determinations in carbonate-containing solids. *Limnology & Oceanography* 29, 657–663.
- Hines, M.E., Faganeli, J., Horvat, M., 2004. Methylation and demethylation of mercury throughout the Idrija River System. *RMZ – Materials & Geoenvironment* 51, 1060–1063.
- Hines, M.E., Faganeli, J., Adatto, I., Horvat, M., 2006. Microbial mercury transformations in marine, estuarine and freshwater sediment downstream of the Idrija Mercury Mine, Slovenia. *Applied Geochemistry* 21 (2), 1924–1939.
- Horvat, M., Bloom, N.S., Liang, S., 1993. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part 1. Sediments. *Analytica Chimica Acta* 281, 135–152.
- Horvat, M., Covelli, S., Faganeli, J., Logar, M., Mandic, V., Rajar, R., Širca, A., Žagar, D., 1999. Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. *Science of the Total Environment* 237/238, 43–56.
- Horvat, M., Jereb, V., Fajon, V., Logar, M., Kotnik, J., Faganeli, J., Hines, M.E., Bonzongo, J.C., 2002. Mercury distribution in water, sediment and soil in the Idrija and Soča river systems. *Geochemistry, Exploration Environmental Analysis* 2, 287–296.
- INTERREG II, 2001. Progetto di monitoraggio dell'Alto-Adriatico – Relazione Conclusiva, Luglio 1998 – Giugno 2001. Direzione Regionale dell'Ambiente 2001, Laboratorio di Biologia Marina, Trieste, Italia, 112pp.
- Kocman, D., Horvat, M., Kotnik, J., 2004. Mercury fractionation in contaminated soils from the Idrija mercury mine region. *Journal of Environmental Monitoring* 6, 696–703.
- Miklavčič, V., 1999. Mercury in the town of Idrija (Slovenia) after 500 years of mining and smelting activity. In: Ebinghaus, R., Turner, R.R., Lacerda, L.D., Vasiljev, O., Salomons, W. (Eds.), *Mercury contaminated sites*. Springer-Verlag, Berlin, pp. 259–270.
- Mybeck, M., 1982. Carbon, nitrogen and phosphorus transport by world rivers. *American Journal of Science* 282, 401–450.
- Mosetti, F., 1983. Sintesi sull'idrologia del Friuli-Venezia Giulia. *Quaderni dell'Ente Tutela Pesca* 6, 295.

- Pethick, J., 1984. Tidal landforms: mudflats and salt marshes. In: *An Introduction to Coastal Geomorphology*, John Wiley & Sons Eds, pp. 145–166.
- Pettine, M., Patrolecco, L., Camusso, M., Crescenzo, S., 1998. Transport of carbon and nitrogen to the northern Adriatic Sea by the Po river. *Estuarine, Coastal and Shelf Science* 46, 127–142.
- Piani, R., Covelli, S., Biester, H., 2005. Mercury contamination in Marano Lagoon (Northern Adriatic sea, Italy): Source identification by analyses of Hg phases. *Applied Geochemistry* 20, 1546–1559.
- RAFVG (Regione Autonoma Friuli-Venezia Giulia), 1986. Piano di risanamento del bacino idrografico del fiume Isonzo. Rapporto conclusivo. Cappella & C. s.a.s., Trieste, pp. 6–13.
- Rajar, R., Žagar, D., Širca, A., Horvat, M., 2000. Three-dimensional modelling of mercury cycling in the Gulf of Trieste. *Science of the Total Environment* 260, 109–123.
- Salomons, W., Förstner, U., 1984. *Metals in the hydrocycle*. Springer-Verlag/Heidelberg, Berlin/New York, Tokyo, 349pp.
- Širca, A., Rajar, R., Harris, R., Horvat, M., 1999a. Mercury transport and fate in the Gulf of Trieste (Northern Adriatic) – a two-dimensional modelling approach. *Environmental Modelling Software* 14, 645–655.
- Širca, A., Horvat, M., Rajar, R., Covelli, S., Žagar, D., Faganeli, J., 1999b. Estimation of mercury mass balance in the Gulf of Trieste. *Acta Adriatica* 40, 75–85.
- Strickland, J.D.H., Parsons, T.R., 1972. *A practical handbook for seawater analysis*, 2nd ed. Bulletin Fishery Research Board of Canada, 1972, 167pp.
- Turner, A., Millward, G.E., 2000. Particle dynamics and trace metals reactivity in estuarine plumes. *Estuarine Coastal and Shelf Science* 50, 761–774.
- van Maren, D.S., Hoekstra, P., 2005. Dispersal of suspended sediments in the turbid and highly stratified Red River plume. *Continental Shelf Research* 25, 503–519.
- Viso, Y., 2004. Meccanismi di trasporto e dispersione del mercurio di provenienza isontina nel Golfo di Trieste. Università degli Studi di Trieste, Facoltà di Scienze Matematiche, Fisiche e Naturali, Dipartimento di Scienze Geologiche Ambientali e Marine, unpublished Thesis, 139 pp.
- Žibret, G., Gosar, M., 2006. Calculation of the mercury accumulation in the Idrijca River alluvial plain sediments. *Science of the Total Environment* 368, 291–297.