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Partitioning and mixing behaviour of trace elements at the Isonzo/Soča River mouth (Gulf of Trieste, northern Adriatic Sea)

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ABSTRACT

Estuaries are unique water systems and represent a vital link between land and sea. River transported contaminants, among which trace elements are of major concern, are subjected to a variety of physical, chemical and biogeochemical processes in the estuarine mixing zone.

The Isonzo/Soča River is the main source of freshwater into the Gulf of Trieste (northern Adriatic Sea) and is known as the primary source of Hg due to long-term *cinnabar* (HgS) extraction from the Idrija mining district (Slovenia). Mercury distribution, cycling and speciation have been intensively studied at the Isonzo/Soča River mouth. Still, little information is currently available regarding other trace elements (As, Co, Cu, Cs, Cr, Fe, Ni, Mn, Pb and Zn). Indeed, this research aims to evaluate trace element occurrence and partitioning behaviour among suspended particulate matter ($> 0.45 \mu\text{m}$), colloidal material ($0.45 \mu\text{m} - 10 \text{kDa}$) and the truly dissolved fraction ($< 10 \text{kDa}$) at the mouth of the Isonzo/Soča River.

Generally, trace elements are mainly associated with suspended particulate matter, which represents their main effective vehicle to coastal environments. In addition, dilution effects between riverine and marine particles are responsible for the decrease in particulate trace element concentrations along the water column. Mercury was notably present in winter in the freshwater, as expected under conditions of high river discharge. As opposed to other trace elements, particulate Mn was found to be high in the marine water, particularly in summer when high water temperatures could promote oxidation and precipitation processes. The Isonzo/Soča River mouth is characterised by a strong salinity gradient and geochemical processes appear to affect trace element partitioning behaviour. In this context, Fe, Mn and Cu were found to be mainly associated with the suspended particles and displayed the highest concentration in the colloidal material. Conversely, the truly dissolved fraction prevailed for As and Cs, which are often present in ionic dissolved forms in natural water systems.

1. Introduction

Estuaries and river mouths are crucial environments for the transfer of chemicals from land to open sea (Fu et al., 2013; de Souza Machado et al., 2016; Wang and Wang, 2016; Fiket et al., 2018). In this context, mixing between river freshwater and marine saltwater represents a key process for the regulation of the fate and distribution of contaminants, among which trace elements are of major concern (Yigiterhan and Murray, 2008; Deycard et al., 2014; Domingos et al., 2015). Indeed, estuaries generally show strong physico-chemical gradients (salinity, density, flow velocity) which may affect trace element speciation and

their partitioning between solid and dissolved phases (Savenko et al., 2014). In addition, organic matter production and oxidation (de Souza Machado et al., 2016), the oxygenation state and potential release of trace elements from the sediment-water interface (SWI) (Petranich et al., 2018 and references therein) are also influential factors.

Organic and inorganic matter in natural aquatic systems can be associated with three main fractions: suspended particulate matter (SPM), colloids and the truly dissolved fraction. By convention, particulate matter in suspension is defined as the material retained on a filter with a nominal porosity of between 0.4 and $0.5 \mu\text{m}$. The upper dimensional limit of the particles is not well-defined, although Visser

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(1969) proposed a value of 100 μm , which is the limit between the particles that move by saltation under a laminar flow regime and those transported in suspension. Colloids are generally defined as submicron particles enclosed within the traditionally defined dissolved fraction ($< 0.45 \mu\text{m}$) (Guo and Santschi, 1997).

The role of SPM as the main carrier for trace elements in estuarine and river mouth environments has been investigated in several studies (e.g. Turner and Millward, 2000; Cenci and Martin, 2004; Fu et al., 2013). As a consequence of SPM settling, bottom sediments represent an important sink for contaminants associated with fine particles. However, bottom sediments may act as a secondary source when processes such as bioturbation and resuspension are responsible for the release of trace elements back to the water column (Sigg et al., 2000).

Trace elements bound to the colloidal material may have a different fate. Indeed, very small particles can settle extremely slowly or be trapped in the commonly defined maximum turbidity zone or may eventually form larger aggregates (Guo and Santschi, 2007). Colloidal material can also influence the transport, bioavailability and fate of trace elements and other contaminants in aquatic systems (Benoit et al., 1994; Guentzel et al., 1996). In addition, colloids represent essential intermediaries in several removal processes such as coagulation and flocculation (Savenko et al., 2014) that often take place in estuarine environments where strong physico-chemical gradients occur, especially in terms of salinity.

The Isonzo River represents the primary freshwater input entering the Gulf of Trieste (northern Adriatic Sea) and it is known to be the main source of Hg (Covelli et al., 2001; Covelli et al., 2007) due to long-term *cinnabar* (HgS) extraction from the Idrija mine, located in the Slovenian sector of the river drainage basin. During mining operations, mineralised tailings generated by HgS roasting processes were dumped along the banks of the Idrijca River, swept away by floodwaters towards the Isonzo River and finally transported into the Gulf of Trieste. According to Baptista-Salazar et al. (2017), the amount of Hg in the soil ranged between 0.08 and 46.3 $\mu\text{g g}^{-1}$ and the maximum concentrations were found in the vicinity of the mining district, most likely due to the presence of ore tailings. Furthermore, the same authors also stated that

the amount of Hg associated with the SPM in the Idrijca River freshwater is significantly affected by hydrological conditions. Indeed, particulate Hg ranged between 4.13 and 37.2 $\mu\text{g g}^{-1}$ during rain events whereas significant variations of dissolved Hg were not detected during low and high flow conditions (Baptista-Salazar et al., 2017).

In addition, along the Isonzo River drainage basin, the decommissioned Pb–Zn mining district of Raibl (Cave del Predil village, northern Italy) represents a source of Zn, Pb and other trace elements since the major drainage of the mine discharges directly into the Isonzo River in Slovenia (Petrini et al., 2016). Waste water discharge from a cement factory (near Kanal, Slovenia) as well as rainwater runoff from cropping areas of the Isonzo River alluvial plain (Comici and Bussani, 2007; Cozzi et al., 2012) may further contribute to increase the amount of dissolved and particulate trace elements in the river freshwater.

The behaviour of Hg in the Gulf of Trieste has been intensively studied with regard to Hg contamination in coastal sediments (Covelli et al., 2001), transport and dispersion of particulate Hg (Covelli et al., 2007) and Hg cycling at the SWI (Emili et al., 2011). With the only exception being Hg, the occurrence and distribution of other trace elements and their partitioning between solid and dissolved phases have not yet been thoroughly addressed in the eastern sector of the northern Adriatic Sea, as well as the Gulf of Trieste. The aim of the present work is to assess trace element occurrence and partitioning behaviour among SPM, colloidal and truly dissolved fractions in estuarine water at the mouth of the Isonzo/Soča River, where a strong salinity gradient occurs. The behaviour of trace elements was investigated in the very high salinity range under different seasonal conditions at the river mouth and further insight regarding partitioning was provided by the inclusion of the colloidal fraction.

2. Materials and methods

2.1. Environmental setting

The Gulf of Trieste is a semi-enclosed marine basin located in the north-eastern Adriatic Sea (Italy). The water depth is generally shallow,

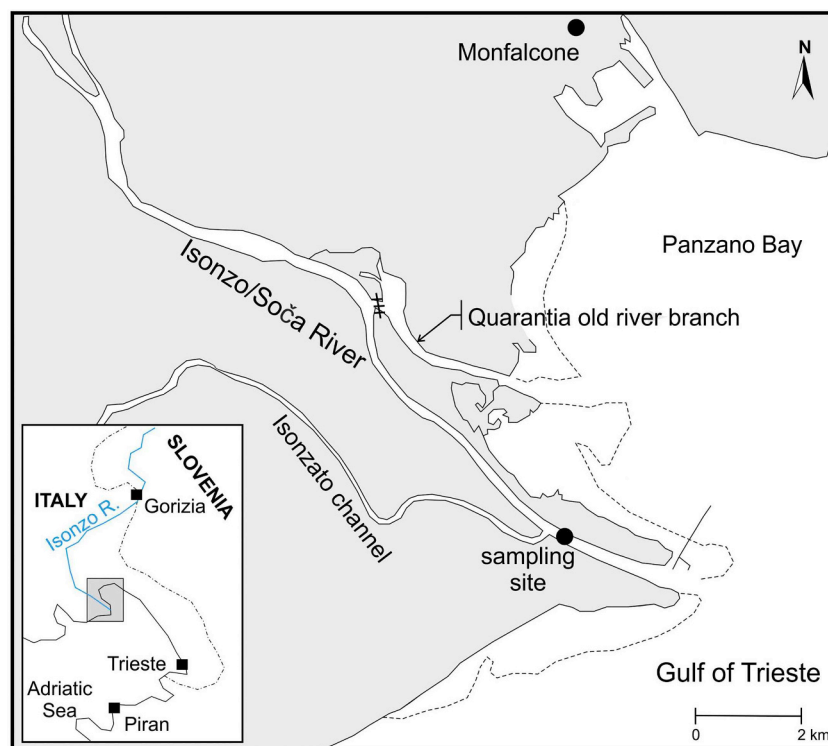


Fig. 1. Map of the study area and location of the sampling station at the Isonzo/Soča River mouth.

reaching a maximum depth of 25 m in the central area of the Gulf where the Isonzo/Soča River represents the main freshwater input (Fig. 1). The average annual flow rate at the river mouth is assessed to be about $82 \text{ m}^3 \text{ s}^{-1}$ in the period from 1998 to 2008 (Cozzi et al., 2012). The Isonzo River mouth can be defined as a microtidal, low-energy and fine-grained deltaic system (Covelli et al., 2004). It is affected by significant seasonal variations in the river discharge with two main flood periods during the year related to snowmelt and rainfall. Furthermore, brief peaks of intense discharge associated with a high level of SPM are followed by extended periods of low-medium riverine flow.

As previously mentioned, the Isonzo River is the main source of Hg entering the Gulf of Trieste and Covelli et al. (2001) reported that high Hg concentrations are restricted mainly to sandy-silty sediments near the Isonzo River mouth, where the element is present in detrital form (HgS, *cinnabar*). However, suspended fine sediments strongly affect the distribution of Hg associated with the SPM as a result of resuspension events involving the silty bottom sediments (Covelli et al., 2006). In addition, the same authors stated that most of the Hg transported by the river freshwater was associated with SPM, especially after periods of river plume when particulate Hg influx into the Gulf ranges between 37.0 and 112 ng L^{-1} (Covelli et al., 2007).

2.2. Sampling activity and water sample size fractionation

Estuarine water samples were collected at the Isonzo River mouth under different seasonal conditions (winter, summer and autumn). Before sampling, vertical profiles of salinity, temperature ($^{\circ}\text{C}$) and turbidity (NTU, Nephelometric Turbidity Unit) were recorded by means of a CTD multiprobe (Hydrolab H₂O with a 0.10 dbar pressure step) in order to identify the water masses. Freshwater-brackish (0–27) and marine (27–37) water samples (approximately 15 L) were alternatively collected using a Niskin or a Van Dorn bottle depending on the thickness of the water layer to sample. In addition, the main physico-chemical parameters (pH, redox potential (Eh) and dissolved oxygen) were promptly measured on ship using portable probes (pH-meter PH25, Conductivity-meter CM 35+ and Oxygen-meter OXI 45P by Crison Instruments).

Fractionation of water samples allowed for the isolation of three size fractions: 1) suspended particulate matter (SPM) fraction is defined as particles having a diameter larger than $0.45 \mu\text{m}$; 2) colloidal retentate solution which consists of submicron particles and macromolecules having a diameter $< 0.45 \mu\text{m}$ and a molecular weight $> 10 \text{ kDa}$; 3) dissolved permeate solution. The last fraction is also known as *ultrafiltrate solution* or *truly dissolved* (Guo and Santschi, 1997; Wells et al., 2000; Town and Filella, 2002), which consists of molecules and ions able to pass through an ultrafiltration membrane having a theoretical MWCO (Molecular Weight Cut-Off) of 10 kDa .

Size fractionation was performed by vacuum filtration (pre-conditioned and pre-weighed membrane filters, Millipore HA, ϕ 47 mm, $0.45 \mu\text{m}$ pore size) and cross-flow ultrafiltration (ultrafiltration membranes, Sartorius Vivaflow 200, MWCO 10 kDa) in order to isolate the SPM and the colloidal retentate solution, respectively. Specifically, the ultrafiltration system was pre-conditioned with pre-filtered water sample, the ultrafiltration was performed under recirculation mode and using a concentration factor of approximately 60. The ultrafiltration system was rinsed with NaOH (0.5 M) and 10 L of MilliQ water after each sample.

According to other studies (Sigg et al., 2000; Ingri et al., 2004), recovery (R%) and colloid concentrations were estimated as follows (Eqs. (1), (2)):

$$(1) \quad R\% = \{((\text{permeate}) + (\text{colloid})) / (\text{total dissolved})\} * 100 \quad (1)$$

(2)

$$\text{Colloid} = \{(\text{retentate}) - (\text{permeate}) / \text{cf}\} \quad (2)$$

where cf is the concentration factor of the single ultrafiltration run (Eq. 3).

(3)

$$\text{cf} = \text{Volume}_{\text{tot}} / \text{Volume}_{\text{retentate}} \quad (3)$$

The recovery (%) (Table S1) was not calculated when the concentration was below the limit of detection (LOD, Table S2) for one or more fractions. Reasonable mass balances were obtained although losses/contamination did occur. Unfortunately, it was not possible to provide mass balance for Hg since its concentration in the total dissolved fraction was often found to be below the LOD. We suspect this could be due to the effects of bubbling during filtration and ultrafiltration which become significant at very low concentrations (ng L^{-1}) and considering that Hg may be present as dissolved gaseous form in coastal waters (Floareani et al., 2019).

Sample aliquots for trace element determinations in total dissolved, colloidal retentate and truly dissolved fractions were collected into pre-conditioned (hot suprapure HNO₃ (VWR), $\geq 69\%$, $10\% \text{ v/v}$, heated at 50°C for 12 h and rinsed with Milli-Q water and estuarine water sample before sample collection) PTFE containers and acidified with nitric acid (suprapure HNO₃, $\geq 69\%$, $1\% \text{ v/v}$) to preserve sample composition. For Hg detection, samples were collected into pre-conditioned (hot suprapure HCl (VWR), $\geq 37\%$, $10\% \text{ v/v}$, heated at 50°C for 12 h and rinsed with Milli-Q water and estuarine water sample before sample collection) borosilicate glass containers and immediately oxidised with bromine chloride (BrCl Brooks Rand, $500 \mu\text{L}/100 \text{ mL}$ until the samples turned yellow) following EPA Method 1631e (2002).

Moreover, blank samples were collected at each step to validate both filtration and ultrafiltration systems. Blank values were mainly below LOD. The only exception was represented by Zn, which in some cases was observed to be higher than $0.50 \mu\text{g L}^{-1}$, as already reported by Sigg et al. (2000).

Regarding SPM samples, filters were acid-digested in PTFE vessels through a total dissolution using inverse *aqua regia* (HNO₃ and HCl, 3:1) in a closed microwave system (Multiwave PRO, Anton Paar) according to EPA Method 3052 (2007) for trace element detection.

2.3. Analytical measurements

Major elements (Al, Fe, Ca and Mg) in the SPM were detected by means of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using an Optima 8000 ICP-OES Spectrometer (PerkinElmer, USA) equipped with an S10 Autosampler (PerkinElmer, USA). Instrument calibration was performed using standard solutions (ranging between 1 and 100 mg L^{-1}) prepared by dilution of a multistandard solution (100 mg L^{-1}) for ICP analysis (Instrument Calibration Standard 2, PerkinElmer, USA).

Trace element (As, Co, Cu, Cs, Cr, Fe, Ni, Mn, Pb and Zn) concentrations in the sample solutions (total dissolved, colloidal retentate and truly dissolved) as well as in the SPM were detected by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a NexION 350 $\times$ Spectrometer (PerkinElmer, USA) equipped with an ESI SC Autosampler. Water samples were diluted 1:10 with Milli-Q to avoid the problems caused by high salt concentrations. The instrument was calibrated using standard solutions (ranging between 0.5 and $10 \mu\text{g L}^{-1}$) obtained by dilution of a multistandard solution (10 mg L^{-1}) for ICP analysis (Periodic Table MIX 1, Sigma Aldrich).

Analysis was performed in KED mode (Kinetic Energy Discrimination) to control and reduce cell-formed polyatomic ion interference. Quality control was performed by the analysis of laboratory-fortified samples prepared by spiking $1 \mu\text{g L}^{-1}$ of trace elements into actual estuarine water and particulate samples. For this purpose, we diluted a multi-standard solution (10 mg L^{-1}) different from the solution used for instrument calibration. Allowable recoveries on 6 spiked samples of both estuarine water and particulate samples were obtained (ranging between 77 and 104% and between 90 and 116% for water and particulate samples, respectively) (Table S2). The performance of the analysis over time was evaluated by means of laboratory-fortified blanks which were analysed every 10 samples. Those laboratory-fortified blanks consisted of standard solutions of $1 \mu\text{g L}^{-1}$ (depending on trace element concentrations in the current batch) prepared by the dilution of a multistandard solution (10 mg L^{-1}) different from the solution used for instrument calibration.

Mercury determination in the water samples was conducted by means of Cold Vapor Atomic Fluorescence Spectrometry coupled with a gold trap pre-concentration system (CV-AFS Mercur, Analytic Jena). Specifically, Hg determination was performed through a pre-reduction using $\text{NH}_2\text{OH}\cdot\text{HCl}$ ($250 \mu\text{L}/100 \text{ mL}$ sample) until the yellow colour disappeared, followed by a reduction with SnCl_2 (2% in HCl 2% v/v) according to EPA Method 1631e (2002). Instrument calibration was performed using standard solutions (ranging between 1 and 50 ng L^{-1}) prepared by dilution of a Hg standard solution (mercury standard solution, Merck Millipore, 1000 mg L^{-1}) and acidified with BrCr (0.5% v/v) in order to avoid matrix effects. Certified reference solution (ORMS-5, Canada) was analysed in the same batch as the water samples for quality control and allowable recovery was obtained (105%).

A summary of major and trace element concentrations in the different fractions (SPM, colloidal material and truly dissolved) of the water samples collected at the Isonzo River mouth are reported in Tables S3 and S4.

3. Results and discussion

3.1. Physico-chemical characterisation of the water column

River discharge was found to be notably higher in winter ($275 \text{ m}^3 \text{ s}^{-1}$) and autumn ($230 \text{ m}^3 \text{ s}^{-1}$) rather than in summer ($20 \text{ m}^3 \text{ s}^{-1}$). Two distinct layers in terms of salinity were detected in the water column at the river mouth, as a consequence of the interaction between the freshwater input and the salt-wedge intrusion (Fig. 2). Indeed, salinity vertical profiles displayed a sharp halocline, as previously reported by Covelli et al. (2004). The surface water layer showed salinity values typical of riverine waters (< 2) in winter and autumn, whereas marine salinity values were recorded at the bottom (35.8 and 35.0 in summer and autumn, respectively). However, brackish water (28.2) was recorded at the bottom in winter along with freshwater prevalence up to a depth of 4 m due to the heavy rainfall which occurred for several days before sampling.

The water column stratification was also confirmed by the turbidity trend, especially in autumn (ranging between 20.3 and 93.4 NTU) and, to a lesser extent, in winter (ranging between 11.4 and 32.5 NTU). Indeed, turbidity reached higher values in the freshwater-brackish water decreasing with depth in winter as a consequence of the river flood events, whereas turbidity values were found to be lower in summer (ranging between 6.37 and 15.5 NTU) and slightly increased at the bottom most likely due to resuspension induced by tidal currents.

Regarding the temperature, slight variations were observed along the water column and among the different seasons. The lowest temperatures were obviously recorded in winter (7.37 and 10.2°C in the surface and bottom water layers, respectively), whereas warm water prevails in summer both at the surface (25.1°C) and at the bottom (27.2°C). Conversely, the vertical temperature profile acquired in autumn shows intermediate values ranging between 11.4°C and 17.1°C in the surface and bottom water layers, respectively (Fig. 2).

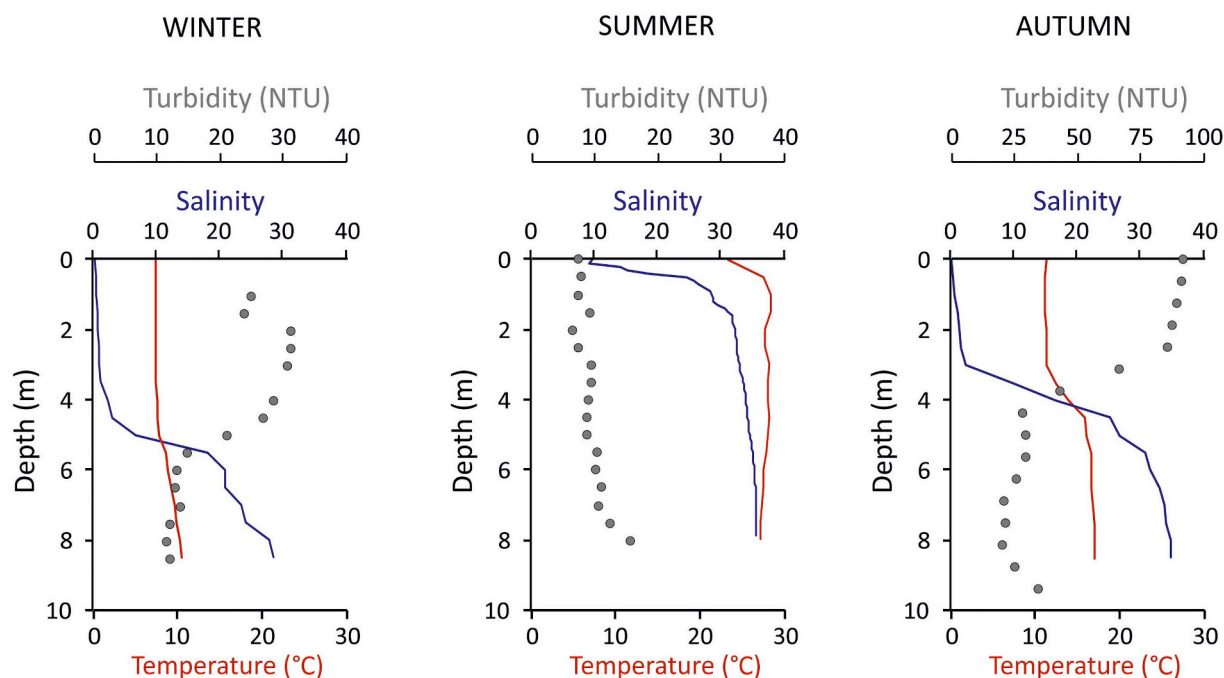


Fig. 2. Vertical profiles of salinity, temperature ($^\circ\text{C}$) and turbidity (NTU, Nephelometric Turbidity Unit) recorded at the Isonzo River mouth under different seasonal conditions.

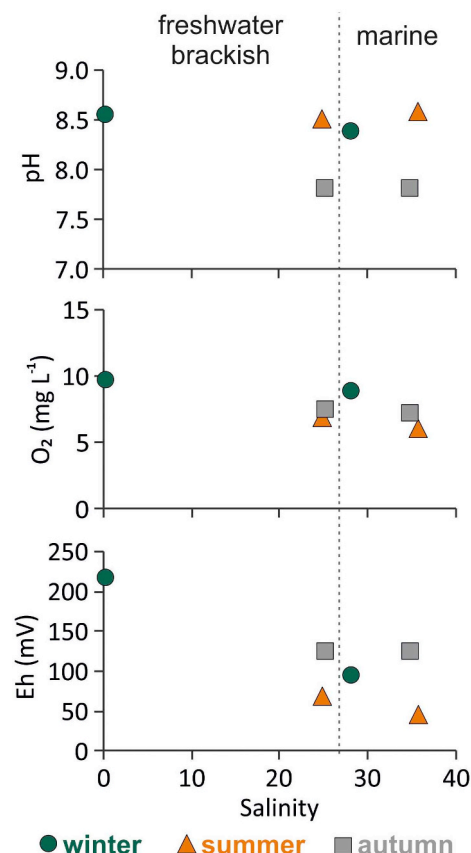


Fig. 3. pH, dissolved oxygen and redox potential in the surface, mixing and bottom layers measured at the Isonzo River mouth under different seasonal conditions.

Values of dissolved oxygen, pH and redox potential (Eh) measured at the Isonzo River mouth under different seasonal conditions are shown in Fig. 3. Significant disparities in terms of pH were not found, although water samples collected in autumn show slightly lower pH. Dissolved oxygen and redox potential are significantly correlated ($r = 0.793$) and decrease with increasing salinity. In particular, lower values of both parameters were recorded in summer, when the strong stratification of the water column does not allow for mixing between the water masses.

3.2. Occurrence of trace elements in the suspended particulate matter

Generally, the freshwater-brackish water samples showed higher amounts of particulate trace elements compared to the marine water at the bottom (Fig. 4, Table 1). The highest concentrations of Al (5.16%), Co (27.4 $\mu\text{g g}^{-1}$), Cr (128 $\mu\text{g g}^{-1}$), Cs (11.4 $\mu\text{g g}^{-1}$), Cu (116 $\mu\text{g g}^{-1}$), Fe (2.94%), Hg (12.1 $\mu\text{g g}^{-1}$) and Ni (105 $\mu\text{g g}^{-1}$) in the SPM were found in winter, most likely due to the river flood period which occurred for several days before sampling. Conversely, As and Mn reached the highest concentrations in summer both in the brackish (54.2 and 3445 $\mu\text{g g}^{-1}$ of As and Mn, respectively) and marine (18.5 and 7060 $\mu\text{g g}^{-1}$ of As and Mn, respectively) water samples.

The commonly observed decline in particulate trace element concentrations along the water column could account for dilution effects between riverine and marine particles (Turner, 1999; Hatje et al., 2001).

Manganese was found to be relatively high in the marine water, especially in summer (7060 $\mu\text{g g}^{-1}$), as also stated by Sondi et al. (1994) in another estuarine system (Raša River estuary, Croatia). Remobilisation of particulate Fe and Mn in reducing sediments and/or resuspension of bottom sediments (Hatje et al., 2001; Petranich et al., 2018) are known to be two of the most important processes influencing trace element mobility in the aquatic compartment. Moreover, Fe and Mn oxy-hydroxides are important host phases for contaminants due to

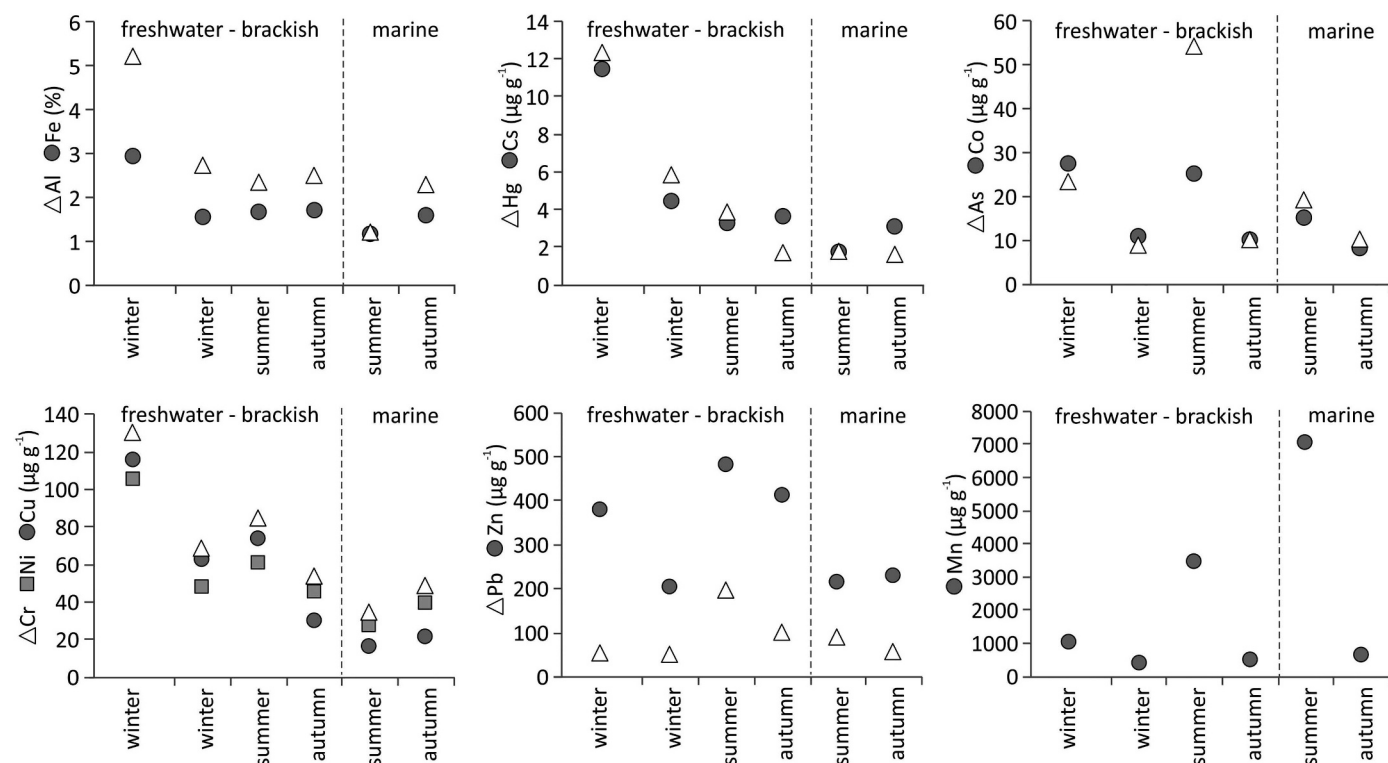


Fig. 4. Concentrations of Hg, Co, As, Cs, Cr, Ni, Cu, Pb, Zn and Mn ($\mu\text{g g}^{-1}$) and of Al and Fe (%) in the water samples collected at the Isonzo River mouth under different seasonal conditions.

Table 1

Concentrations of Al and Fe (%), As, Co, Cr, Cs, Cu, Hg, Mn, Ni, Pb and Zn ($\mu\text{g g}^{-1}$) in the suspended particulate matter collected at the Isonzo River mouth and in analogous estuarine environments as reported in the literature (W = winter; S = summer; A = autumn; F = freshwater; B = brackish water; M = marine water; LOD: limit of detection; nd: not determined; *: average).

Site	Season	Salinity	Al	As	Co	Cr	Cs	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Reference
Isonzo River ¹	W	F	5.16	22.8	27.4	128	11.4	116	2.94	12.1	1017	105	45.0	377	This work
	B	B	2.67	8.08	10.7	67.2	4.44	62.9	1.58	5.71	414	47.9	41.3	201	
	S	B	2.29	54.2	25.2	83.5	3.25	73.5	1.68	3.71	3445	189	61.1	478	
	M	M	1.18	18.5	15.0	33.3	1.71	16.8	1.16	1.59	7055	28.0	80.9	214	
Isonzo River ¹	A	B	2.46	9.50	10.1	52.4	3.59	30.2	1.72	1.57	505	45.6	91.8	410	Covelli et al., 2006
	M	M	2.24	9.73	8.11	47.0	3.11	21.5	1.58	1.45	628	39.4	49.3	228	
	W	F	nd	nd	nd	nd	nd	nd	nd	10.2	nd	nd	nd	nd	
	B	B	nd	nd	nd	nd	nd	nd	nd	10.2	nd	nd	nd	nd	
Isonzo River ¹	M	M	nd	nd	nd	nd	nd	nd	nd	9.94	nd	nd	nd	nd	Covelli et al., 2002
	S	F	nd	nd	nd	nd	nd	nd	nd	11.0	nd	nd	nd	nd	
	B	B	nd	nd	nd	nd	nd	nd	nd	20.7	nd	nd	nd	nd	
	M	M	nd	nd	nd	nd	nd	nd	nd	24.9	nd	nd	nd	nd	
Isonzo River ¹	W	F	17.8	nd	nd	60.3	nd	69.9	nd	7.48	nd	205	315	nd	Covelli et al., 2002
	B	B	9.50	nd	nd	36.7	nd	25.0	nd	4.13	nd	5.19	273	nd	
	M	M	3.59	nd	nd	38.9	nd	15.7	nd	1.34	nd	10.7	25.6	nd	
	bulk	bulk	nd	nd	nd	150	nd	35	nd	nd	507	57	90	225	
Adige River ¹	A	bulk	5.24	nd	nd	207	nd	108	2.79	nd	nd	38	62	329	Boldrin et al., 1989
Adige River ¹	F	F	nd	nd	nd	126–159	nd	47–50	nd	nd	nd	32–42	49–78	213–270	Juračić et al., 1987
Krka River ²	W	F	nd	nd	nd	150	nd	180	nd	nd	nd	150	92	210	Juračić and Pravić, 1991
Po River ¹	S	F	nd	nd	nd	nd	nd	nd	0.26–0.83	nd	824–1373	18.8–43.4	nd	nd	Camusso et al., 1997
Adriatic Sea	W	F	nd	nd	5.30–10.0	nd	nd	nd	0.45–0.58	nd	989–1209	35.8–93.9	nd	nd	Sondi et al., 1994
	S	F	nd	nd	1.18–5.89	nd	nd	nd	0.14–0.45	nd	220–604	12.3–17.0	nd	nd	
Raša River ³	S	F	nd	nd	2.36–10.0	nd	nd	nd	0.13–0.43	nd	714–1428	29.4–35.2	nd	nd	Sondi et al., 1994
	S	F	nd	nd	nd	129	nd	161	nd	nd	518	nd	38	55	
Mejerda River ⁴	A	M	nd	nd	nd	216	nd	274	nd	nd	633	nd	281	165	Helali et al., 2016
	W	M	4.46	nd	nd	129	nd	66	nd	nd	568	nd	129	133	
Guanabara Bay ⁵	S	F	3.01	nd	18.2	106	nd	< LOD	1.70	nd	935	82	67.8	143	de Melo et al., 2015
	W	F	1.00	nd	8.70	61.2	nd	37.3	1.77	nd	78.0	65.5	61.3	264	
Italy; ² Slovenia; ³ Croatia; ⁴ Tunisia; ⁵ Brazil	M	M	2.20	nd	nd	180	nd	nd	0.80	1.90*	3000	nd	79.6*	1040*	
	M	M	nd	nd	nd	270	nd	nd	1.50	nd	1000	nd	nd	nd	

Table 2

Log K_D ($L\ kg^{-1}$) values for As, Co, Cr, Cs, Cu, Fe, Hg, Ni, Mn, Pb and Zn in water samples collected at different depths and under different seasonal conditions at the Isonzo River mouth.

Water layer	Season	As	Co	Cr	Cs	Cu	Fe	Hg	Ni	Mn	Pb	Zn
Freshwater	Winter	4.88	6.00	5.82	6.70	5.36	7.32	6.55	6.18	5.80	6.48	5.32
Brackish	Summer	4.66	5.66	6.22	4.52	4.72	7.03	5.76	6.83	5.80	5.82	4.72
	Autumn	3.72	5.69	4.94	4.42	4.71	6.90	5.60	4.83	4.87	5.64	3.84
	Winter	3.85	5.17	6.17	4.60	5.22	7.29	6.98	5.43	4.75	6.44	5.89
Marine	Summer	3.88	5.21	5.82	3.95	4.04	6.98	6.73	6.49	5.88	5.91	4.52
	Autumn	3.59	4.69	5.14	4.17	4.48	6.60	5.54	4.68	4.55	4.94	3.80

their high adsorptive capacities (Gagnon and Saulnier, 2003). The notably high concentration of particulate Mn observed in summer ($7060\ \mu g\ g^{-1}$) could be related to oxidation processes and the subsequent precipitation of Mn oxy-hydroxides promoted by high water temperatures (Morris et al., 1982; Hatje et al., 2001).

As opposed to what was found for particulate Fe, concentrations of particulate Mn displayed significant disparities among seasons. Indeed, the Fe/Mn ratio would indicate the relative abundance of each sorbent phase throughout the year. This ratio is considerably high in winter both in the freshwater (28.9) and in the brackish (38.1) water samples, thus revealing the concomitant decrease in particulate Mn and increase in particulate Fe. This ratio remained of the same order of magnitude in autumn, whereas it reached values of 4.88 and 1.65 in the brackish and marine water samples respectively in summer, testifying to the increase in particulate Mn.

If compared with the results obtained from other studies focused on the Isonzo River and other estuarine environments (Table 1), particulate Hg concentrations (ranging overall between 1.45 and $12.1\ \mu g\ g^{-1}$) confirmed the results obtained by Covelli et al. (2006) although the authors reported higher particulate Hg concentrations in the marine water in summer. The river is still an active source of Hg in particulate form, which was found to be high in the freshwater and brackish water samples (12.1 , 5.71 and $3.71\ \mu g\ g^{-1}$, in winter, summer and autumn, respectively) decreasing in the marine water (1.59 , 1.57 and $1.45\ \mu g\ g^{-1}$, in winter, summer and autumn, respectively). In this study, Hg content is comparable to that measured at Guanabara Bay (de Melo et al., 2015), a shallow water basin along the Brazilian coast subjected to high anthropogenic impact. Regarding the other elements, we measured comparable particulate concentrations with respect to preliminary measurements performed by Covelli et al. (2002). The only exception is represented by the freshwater sample collected in winter found to be enriched in several trace elements such as Cr, Cu, Hg and Pb, likely due to the higher river flow conditions during sampling (Table 1). However, the suspended particles collected at the Isonzo River mouth were not particularly enriched in Cr (the only exception being the freshwater sample collected in winter that showed a value of $128\ \mu g\ g^{-1}$) when compared to other Adriatic estuarine environments (Juračić and Pravdić, 1991; Sondi et al., 1994) (Table 1). On the other hand, SPM samples generally showed higher concentrations of Fe, Al and Mn with respect to those reported for the estuarine system of the Po River, whereas comparable content was found for Co, Cu and Zn (Zago et al., 2002).

3.3. Trace element phase partitioning between suspended particles and the total dissolved fraction

The distribution coefficient (K_D) has often been used in order to evaluate the tendency of a chemical constituent to be preferentially partitioned in the solid or in the aqueous phase, as a result of sorption and precipitation (EPA, 1999; Gagnon and Saulnier, 2003; Guéguen and Dominik, 2003; Wang and Wang, 2016). Although K_D values does not provide any specific information on the kind of metal associations, K_D could be considered an important index to better understand circulation of contaminants among different environmental compartments

(Gagnon and Saulnier, 2003; La Colla et al., 2015).

According to Turner (1996), K_D ($L\ kg^{-1}$) was calculated as the ratio of particulate concentration to total dissolved concentration and expressed on a logarithmic scale (Table 2) using the following Eq. (4)

$$\text{Log } K_D = \text{Log} ([TE_{SPM}]/[TE_{DISS}]) \quad (4)$$

where TE_{SPM} and TE_{DISS} are the trace element concentrations in the SPM and in the total dissolved fraction, respectively. In addition, the relative percentages of As, Co, Cr, Cs, Cu, Fe, Hg, Ni, Mn, Pb and Zn in the SPM and in the total dissolved fraction from the water samples collected at the Isonzo River mouth under different seasonal conditions are plotted in Fig. 5 in order to better highlight disparities between seasons and water masses. The highest Log K_D values were observed for Fe, Hg and Pb, followed by Cr and Mn, reflecting their high reactivity of these elements to the SPM. Generally, trace elements appear to be mainly associated with the suspended particles, especially in the water samples collected during winter river discharge. This is particularly evident for Hg and Pb, which are almost completely partitioned in the solid phase both in the freshwater (96.8% and 96.3%, for Hg and Pb respectively) and in the brackish water (99.5% and 96.5%, for Hg and Pb respectively). This is also confirmed by Log K_D values which were found to be quite elevated both for Hg ($6.55\ L\ kg^{-1}$) and Pb ($6.48\ L\ kg^{-1}$) in the freshwater collected in winter. Regarding Hg, this behaviour confirms the results found by Covelli et al. (2007) who stated that the contribution of particulate Hg into the Gulf of Trieste still remains considerable, although extreme flood events are not frequent during the year. In addition, the evidence that Hg conveyed by the Isonzo River is mainly associated with the solid phase is also confirmed by the element particulate percentages recovered in autumn and summer. Indeed, Hg remains considerably present in the suspended particles, showing on average a Log K_D equal to $6.19\ L\ kg^{-1}$ to the detriment of the total dissolved fraction, which reaches the maximum percentage of only 36.4% in the brackish water sample collected in summer.

If compared with the results obtained from other studies focused on the Isonzo River and other estuarine environments, dissolved Hg concentrations were found to be lower than those reported by Covelli et al. (2006), likely due to disparities in the river flow conditions during sampling (Table 3). However, the estuarine water samples showed dissolved Hg concentrations which were notably higher than those reported by Kwokal and Lovrić (2006) (Krka River estuary, Croatia) for an estuarine system not affected by Hg anthropic sources near the river mouth or along the river drainage basin.

Similar behaviour is also evident for Pb, Cr and Ni, which are strongly associated with the suspended particles in winter and summer, showing quite elevated values of Log K_D (5.87 , 5.68 and $5.74\ L\ kg^{-1}$ on average for Pb, Cr and Ni). Consequently, those elements displayed quite low concentrations in the aqueous phase. To a lesser extent, this behaviour is also evident for Co, which shows a Log K_D of $6.00\ L\ kg^{-1}$ in the freshwater collected in winter. However, dissolved Co percentages increased in summer (41.8% and 49.2% in the brackish and marine water samples, respectively) and autumn, especially in the marine water (55.1% and Log K_D of $4.69\ L\ kg^{-1}$). Similar concentrations of dissolved Co were also found in different estuarine

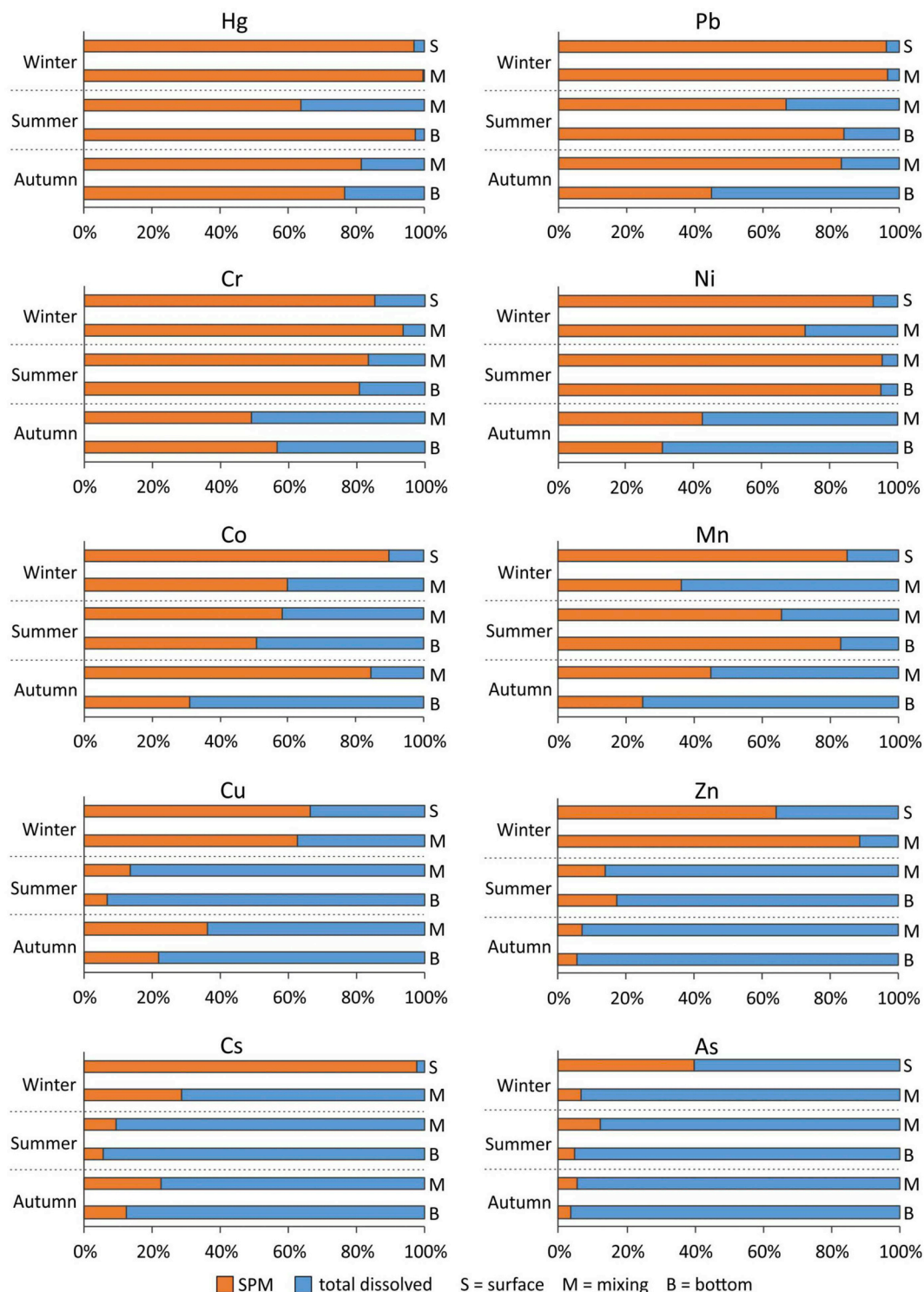


Fig. 5. Percentages of trace elements (Hg, Pb, Cr, Ni, Co, Mn, Cu, Zn, Cs, As) associated with suspended particulate matter and with the total dissolved fraction in estuarine water samples collected at the Isonzo River mouth under different seasonal conditions.

environments (Zago et al., 2002) (Table 3).

Although particulate percentages are quite high in the freshwater collected in winter, Cu, Zn, and especially Cs and As, appear to be mainly present in dissolved form. Among those elements, the lowest values of Log K_D (4.10 L kg^{-1} on the average) and particulate percentages (12.1% on the average) are reached by As, confirming its affinity to the aqueous phase.

Redox conditions are found to be one of the most important factors

in regulating the behaviour of As and other trace elements in natural water systems (Smedley and Kinniburgh, 2002). In addition, Andreae et al. (1983) stated that processes such as diffusion from sediment porewaters, co-precipitation with Fe oxides or anthropogenic input could be responsible for the occurrence of As in estuarine systems. Moreover, Smedley and Kinniburgh (2002) suggested that the simultaneous effects of dissolution and desorption processes can lead to an increase of dissolved As. Since the adsorption and desorption

Table 3

Dissolved concentrations of As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn ($\mu\text{g L}^{-1}$) and Hg (ng L^{-1}) at the Isonzo River mouth and in analogous estuarine environments as reported in the literature (W = winter; S = summer; A = autumn; F = freshwater; B = brackish water; M = marine water; LOD: limit of detection; nd: not determined; *: average).

Site	Season	Salinity	As	Co	Cr	Cs	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Reference
Isonzo River ¹	W	F	0.19	0.03	< LOD	< LOD	0.28	< LOD	6.25	1.07	< LOD	< LOD	< LOD	This work
	B	B	1.29	0.10	< LOD	0.13	0.25	< LOD	4.09	7.97	0.24	< LOD	< LOD	
	S	B	1.13	0.07	0.06	0.09	1.77	6.64	8.60	2.97	< LOD	0.30	9.99	
	A	M	2.10	0.12	< LOD	0.19	1.74	< LOD	< LOD	6.09	< LOD	0.08	6.93	
Isonzo River ¹	F	B	1.69	< LOD	0.29	0.13	0.15	1.78	1.85	6.75	0.81	< LOD	57.9	
	M	M	2.31	0.13	0.31	0.17	0.41	3.51	4.16	16.9	0.70	< LOD	31.2	
	W	F	nd	nd	nd	nd	nd	nd	15.4	nd	nd	nd	nd	Covelli et al., 2006
	B	B	nd	nd	nd	nd	nd	nd	10.4	nd	nd	nd	nd	
Isonzo River ¹ *	M	M	nd	nd	nd	nd	nd	nd	5.59	nd	nd	nd	nd	
	F	F	nd	nd	nd	nd	nd	nd	17.0	nd	nd	nd	nd	
	B	B	nd	nd	nd	nd	nd	nd	28.5	nd	nd	nd	nd	
	M	M	nd	nd	nd	nd	nd	nd	33.4	nd	nd	nd	nd	
Gulf of Trieste ² *	Bulk	Bulk	0.07	0.03	0.21	0.01	0.51	41.9	0.001	0.93	0.35	nd	5.03	Klun et al., 2019
	M	M	1.50	0.06	0.62	0.27	2.61	12.5	0.001	1.54	0.88	nd	4.64	
	F	F	nd	nd	nd	nd	0.27–0.56	0.18–0.63	nd	0.44–1.53	0.65–1.13	0.004–0.03	nd	Martin et al., 1995
	B	B	nd	nd	nd	nd	0.29	0.15	nd	0.45	0.39	0.013	nd	
Venice Lagoon ¹	M	M	nd	nd	nd	nd	0.24–0.29	0.08–0.14	nd	0.27–0.36	0.38–0.48	0.007–0.010	nd	Tankéré and Statham, 1996
	S	M	nd	nd	nd	nd	1.59	nd	nd	nd	1.76	nd	0.39	
Po River ¹	S	F	nd	0.04	nd	nd	0.44	< LOD	nd	0.91	nd	nd	0.86	Zago et al., 2002
Po River ¹	S	M	nd	0.03	nd	nd	0.30	< LOD	nd	1.03	nd	nd	1.71	
Po River ¹	W	F	nd	0.05	nd	nd	0.66	0.20	nd	2.69	nd	nd	0.42	
	M	M	nd	0.03	nd	nd	0.34	0.08	nd	0.48	nd	nd	0.39	
	W	F	nd	nd	nd	nd	3.65	2.34	nd	2.75	3.06	0.32	6.15	Tankéré et al., 2000a
	S	F	nd	nd	nd	nd	2.63	2.10	nd	1.41	2.8	0.24	3.06	Camusso et al., 1997
Po River ¹	W	F	nd	0.01–0.05	nd	nd	nd	1.01–4.86	nd	2.27–8.36	0.59–0.94	nd	nd	
Adriatic Sea	S	F	nd	0.01–0.02	nd	nd	nd	0.67–1.12	nd	0.54–1.46	1.41–2.88	nd	nd	
	W	F	nd	0.02–0.06	nd	nd	nd	0.28–1.84	nd	2.10–5.66	0.29–1.17	nd	nd	
Krka River ³	S	B	nd	0.01–0.04	nd	nd	nd	0.34–0.95	nd	1.40–3.67	0.29–0.76	nd	nd	
	W	F	nd	nd	nd	nd	nd	nd	0.50–0.60	nd	nd	nd	nd	Kwokai and Lovrić, 2006
Zrmanja River ³	M	M	nd	nd	nd	nd	nd	nd	0.90–1.10	nd	nd	nd	nd	
	F	F	0.25	0.01	0.22	0.01	< 0.05	6.14	nd	0.13	0.04	54.3	nd	Fiket et al., 2018
	M	M	1.74	0.26	1.10	0.20	1.04	10.1	nd	3.22	6.36	127	nd	

¹ Italy; ² Slovenia; ³ Croatia

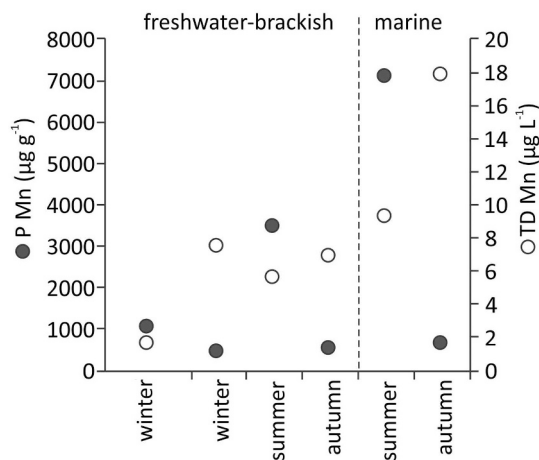


Fig. 6. Concentration of Mn in the suspended particulate matter (PMn, $\mu\text{g g}^{-1}$) and in the total dissolved fraction (TDMn, $\mu\text{g L}^{-1}$) in the water samples collected at different depths and under different seasonal conditions at the Isonzo River mouth.

characteristics of As in estuaries are strongly salinity dependent (Benoit et al., 1994; Balzer et al., 2013), a high concentration of salt in water can weaken adsorption of As on the surface of the suspended particles due to the formation of weak As dissolved complexes (Hong et al., 2018).

As previously mentioned, Mn is the element which shows the highest disparities between different water masses and seasons both in the SPM and in the total dissolved fraction (Fig. 6). Manganese is a redox sensitive element, and the fact that particulate Mn increases when total dissolved Mn decreases and vice versa is likely due to the relative prevalence of oxidation and reduction or dissolution processes. This is in agreement with other Adriatic estuarine environments where dissolved Mn was found to be relatively high, ranging from 0.55 and $3.22 \mu\text{g L}^{-1}$, with a general increase towards the SWI (Tankéré et al., 2000b; Fiket et al., 2018). This element is mainly partitioned in the solid phase in the freshwater collected in winter (84.6% of PMn and 15.4% of TDMn with a $\text{Log } K_D$ value of 5.80 L kg^{-1}), whereas it is mainly present in dissolved form in the brackish water sample (36.0% of PMn and 64.0% of TDMn with a $\text{Log } K_D$ value of 4.75 L kg^{-1}). According to de Melo et al. (2015), hydrodynamic conditions with a strong stratification of the water column and low water temperature could be responsible for the relatively low concentrations of particulate Mn in the marine water. Furthermore, the oxidation of dissolved Mn is influenced by the low water temperature, which slows this process down (Turner et al., 1991; Hatje et al., 2001).

This was confirmed in the present study when the low temperature (10.3°C) measured in the brackish water in winter may not have promoted the oxidation of dissolved Mn resulting in a lower concentration of the element in the SPM ($4.15 \mu\text{g L}^{-1}$). At the same time, Mn shows a quite high concentration in the aqueous phase ($7.38 \mu\text{g L}^{-1}$) which could be due to dissolution processes from oxy-hydroxides. Indeed, the brackish water sample is characterised by quite a low value of redox potential ($E_h = 93 \text{ mV}$) if compared to the river freshwater (216 mV), although dissolved oxygen shows a value of 8.87 mg L^{-1} most likely due to the fact that E_h measurements take into account different redox couples which may not rapidly equilibrate with dissolved oxygen.

Water samples taken in summer showed the opposite situation, although $\text{Log } K_D$ remained quite high (5.80 and 5.88 L kg^{-1} in the brackish and marine water samples, respectively), thus testifying to the prevalence of particulate Mn ($45.2 \mu\text{g L}^{-1}$ at the bottom) likely due to oxidation and the subsequent precipitation favoured by high water temperature (27.2°C), or remobilisation from surface sediments by resuspension processes (Hatje et al., 2001). The relatively low value of the redox potential (only 46.0 mV) could be responsible for dissolution

or desorption processes which led to the increase in the dissolved Mn concentration ($9.24 \mu\text{g L}^{-1}$), although there was no evidence of reductive conditions and the amount of dissolved oxygen was equal to 6.10 mg L^{-1} . A similar situation was also found in the estuarine environment of the Po River, where quite elevated concentrations of dissolved Mn were detected at the bottom despite oxidative conditions (90–150%) (Tankéré et al., 2000b). Moreover, the aggregation and accumulation of mucilage and marine snow (which consists of mucus and large flakes of polymeric exudates and dead phytoplankton cells) at the pycnocline is favoured by a stratified water column and low turbulence (Fajon et al., 1999; Granéli et al., 1999). These organic aggregates are rapidly colonised and degraded by bacteria (Fogg, 1995; Serratore et al., 1995) through biological processes that lead to the consumption of the dissolved oxygen causing suboxic conditions (Tankéré et al., 2000b).

The highest percentages of dissolved Mn were found during autumn, both in the brackish (55.1%) and in the marine (75.1%) water samples, likely due to a slight stratification and an increase in mixing favouring exchanges between the water masses. The occurrence of dissolved Mn in autumn is also confirmed by lower $\text{Log } K_D$, which reaches values of 4.87 and 4.55 L kg^{-1} in the brackish and marine water, respectively.

Iron was almost completely partitioned in the suspended particles, reporting particulate percentages higher than 90%. Indeed, the high Fe reactivity to SPM was also confirmed by the $\text{Log } K_D$ values (7.02 L kg^{-1} on average) if compared to those reported for the other elements.

3.4. The role of salinity in trace element phase partitioning

Estuarine and river mouth environments are characterised by strong physico-chemical gradients in salinity, density and flow velocity, and varied composition of the suspended particles (Elliott and McLusky, 2002). The interaction of these environmental gradients, especially in terms of salinity, and geochemical processes that often occur at the river mouth are often responsible for the non-conservative behaviour of several trace elements (Benoit et al., 1994; de Souza Machado et al., 2016).

In order to evaluate the behaviour of trace elements at the Isonzo River mouth, mixing diagrams for Mn, Fe, Cu, Ni, As, Co and Cs are reported in Figs. 7 and 8, although few estuarine water samples were collected. In fact, the mixing diagrams do not extend over a continued salinity gradient and results provide only a snapshot of trace element behaviour between water layers of very different salinity at different seasons at the mouth of the Isonzo River. In addition, different fractions (the SPM, truly dissolved and colloidal material) were shown to better evaluate removal and/or addition processes among different phases.

Generally, a conservative or quasi-conservative behaviour was found for As, Co and Cs at the Isonzo River mouth (Fig. 7). Arsenic concentration in the suspended particles were quite low and the element appears to behave conservatively showing a linear decrease with increasing salinity (0.20 and $0.12 \mu\text{g L}^{-1}$ for the two salinity end-members) as also seen in other estuarine environments (Zrmanja River Croatia) (Fiket et al., 2018). In this study, As appears to be preferentially partitioned in the truly dissolved phase, showing concentrations below $4 \mu\text{g L}^{-1}$, typical for estuarine waters under natural conditions according to Smedley and Kinniburgh (2002). In addition, the prevalence of dissolved As could be confirmed by the slight removal of this element depicted from the mixing diagram for colloidal material, although very low colloidal concentrations were found.

The mixing behaviour of Co and Cs at the Isonzo River mouth is similar to that reported for As, with the only exception being the brackish water taken in autumn. Although the colloidal material generally shows very low concentrations, which are notably lower compared to the other fractions, an increase in the colloidal concentration of these elements is evident in this season. This is particularly marked for Co, where the increase in the colloidal material corresponds to a decrease in the truly dissolved fraction. On the contrary, Mn, Fe and Cu

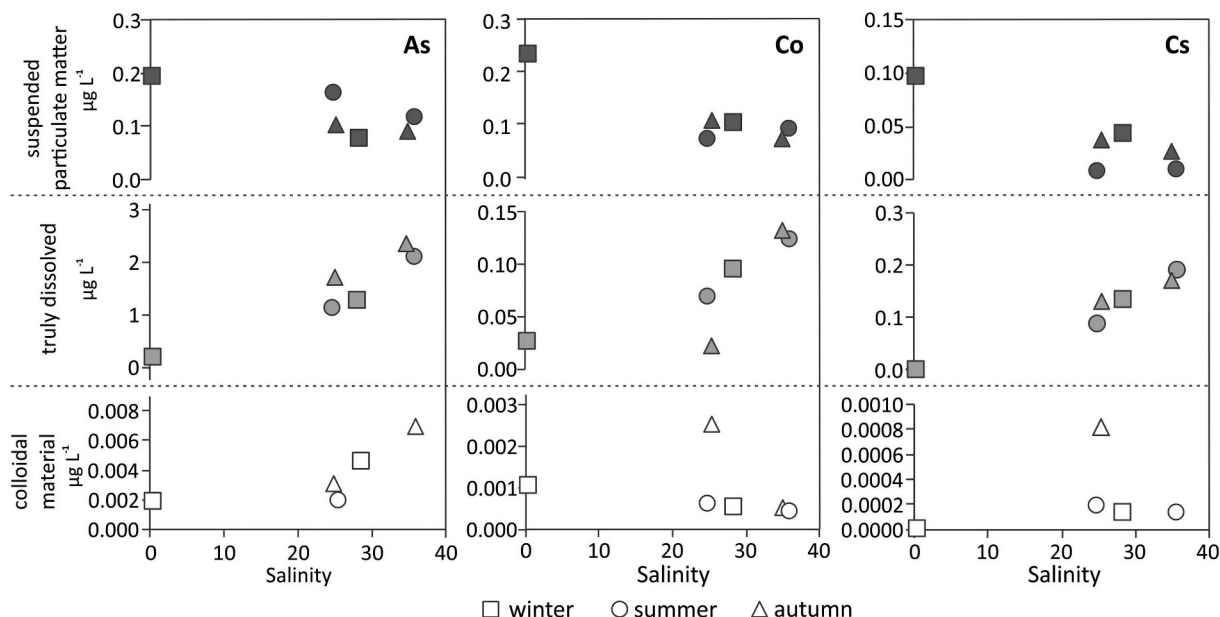


Fig. 7. Arsenic, Co and Cs in the suspended particulate matter, truly dissolved and colloidal material plotted as a function of salinity at the Isonzo River mouth under different seasonal conditions.

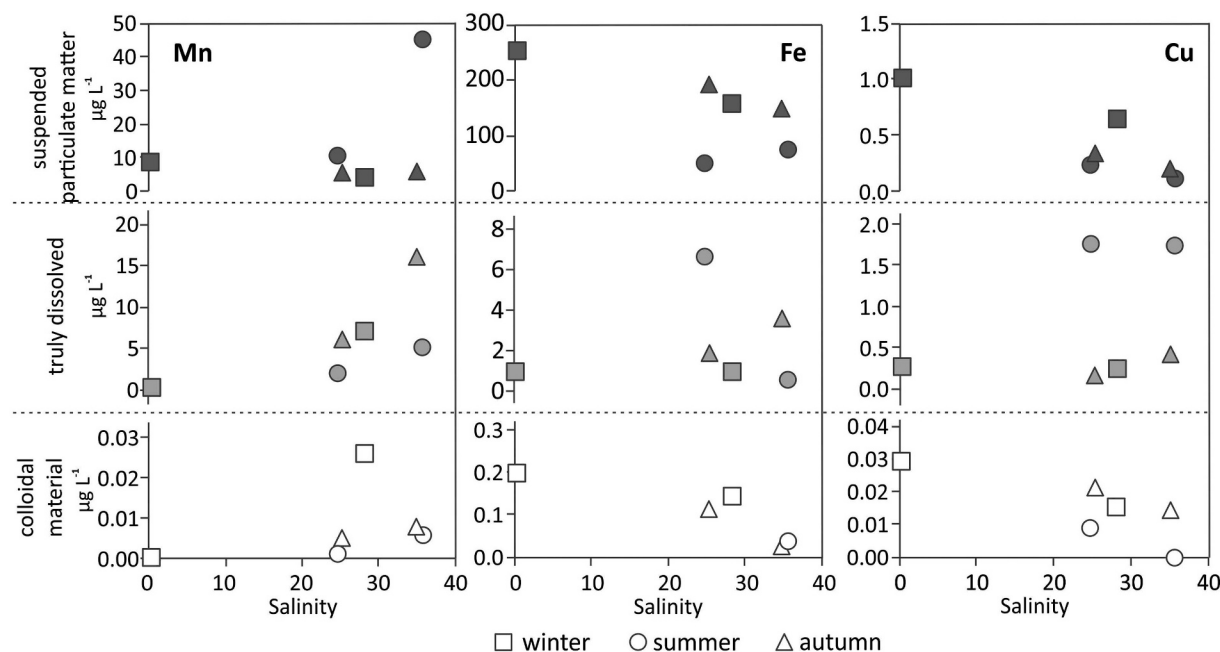


Fig. 8. Manganese, Fe, and Cu in the suspended particulate matter, truly dissolved and colloidal material plotted as a function of salinity at the Isonzo River mouth under different seasonal conditions.

appear to behave non-conservatively during mixing at the Isonzo River mouth and simultaneously show a higher content of colloidal material if compared to that reported for trace elements that behave conservatively (Fig. 8).

In addition, despite no data currently being available for the amount of trace elements associated with the colloidal material in the estuarine environments of the northern Adriatic Sea, a comparison between the Isonzo River mouth and the Venice Lagoon is provided in Table 4, as well as other estuarine and riverine systems worldwide. As expected, lagoon water samples (Martin et al., 1995) displayed concentrations of colloidal Cu, Fe, Mn, Ni and Pb, which are notably higher, especially in the surface freshwater and at the seawater-freshwater interface, than those reported for the mouth of the Isonzo River. This could be related

to lower turbulence conditions, which could lead to a local source for colloidal Fe, Mn, Cd and Pb due to biological activity and physico-chemical boundary conditions.

As previously mentioned, particulate Mn is highly present in the marine water in summer ($45.2 \mu\text{g L}^{-1}$) due to oxidation and precipitation, which are processes enhanced by high water temperatures. This markedly high concentration in the marine end-member seems to highlight a non-conservative behaviour of the other samples, thus suggesting that the release of dissolved Mn may have occurred. Indeed, remobilisation of dissolved Mn from the SPM and/or resuspension of surface sediments could be responsible for the increase in the concentration of dissolved Mn (Tankéré et al., 2000b). In addition, reduction processes at the SWI or bacterial degradation of particulate

Table 4

Colloidal concentrations of As, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn (ng L^{-1}) at the Isonzo River mouth compared to other estuarine and riverine environments as reported in the literature (W = winter; S = summer; A = autumn; F = freshwater; B = brackish water; M = marine water; LOD: limit of detection; nd: not determined; *: average).

Site	Season	Salinity	As	Co	Cr	Cs	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Reference
Isonzo River ¹	W	F	1.94	1.06	27.5	0.01	29.1	196	0.16	0.50	19.2	nd	nd	This work
	B	B	4.72	0.58	14.1	0.14	15.0	142	0.08	26.3	34.8	nd	nd	
	S	B	3.11	0.69	7.28	0.20	9.41	nd	0.22	1.83	21.1	1.64	nd	
	A	M	7.03	0.49	5.01	0.15	0.16	39.3	0.03	6.66	14.9	1.71	6.11	
Isonzo River ¹ *	B	B	2.21	2.54	32.7	0.82	20.8	114	0.16	5.40	51.6	5.01	nd	
	M	M	0.56	0.56	7.60	nd	14.3	25.6	0.08	7.97	10.9	0.52	nd	
	Bulk		4.50	1.47	26.5	3.99	165	1016	0.80	33.0	45.8	nd	172	Klun et al., 2019
	M	M	52.4	2.95	41.6	3.99	254	949	0.80	33.0	29.3	nd	111	
Gulf of Trieste ² *	S	M	89.9	nd	31.2	nd	445	nd	1003	22	47.0	19.5–203	196	Koron et al., 2013
Gulf of Trieste ²	S	F	nd	nd	nd	nd	274–530	2843–62642	nd	422–1451	101–281	19.5–203	nd	Martin et al., 1995
Venice Lagoon ¹	S	F	nd	nd	nd	nd	75	391	nd	257	4.7	0.41	nd	
Penzé Estuary ³	M	M	nd	nd	nd	nd	120–416	291–1142	nd	247–860	12.9–221	2.28–14.5	nd	Waeles et al., 2008
Marne River ³	B	B	nd	nd	nd	nd	136–182	nd	nd	nd	nd	6.21–55.9	nd	Jairy et al., 1999
Vistula River ⁴	S	F	nd	nd	nd	nd	230–1300	700–24600	nd	nd	nd	nd	nd	Guéguen and Dominik, 2003
	A	F	nd	7.00–24.0	55.0–338	nd	nd	18–347	0.1–8.5	230–2820	nd	18.0–68.0	210–3450	Ingrt et al., 2004
Ekshagen Bay ⁵	W	F	nd	7.66	nd	nd	477	nd	nd	49.4	299	nd	nd	Sañudo-Wilhelmy et al., 1996
	S	F	nd	10	nd	nd	235	nd	nd	< LOD	211	nd	nd	
San Francisco Bay ⁶	W	F	nd	nd	nd	nd	50.8	815	nd	1099	13.5	nd	19.6	
	B	B	nd	nd	nd	nd	19.1	278	nd	nd	nd	nd	6.54	
	M	M	nd	nd	nd	nd	3.18	145	nd	54.9	nd	nd	3.27	

¹ Italy; ² Slovenia; ³ France; ⁴ Poland; ⁵ Sweden; ⁶ United States

organic matter could have led to an increase in the dissolved Mn in the marine water (Fiket et al., 2018). An increase in dissolved Mn is clearly evident only in the marine water collected in autumn. On the contrary, the removal of particulate Mn in the brackish water collected in winter appears to correspond to an increase in the colloidal concentration, thus suggesting that the element could be partially present in colloidal form. Moreover, colloidal Mn concentrations are significantly lower than those reported for other estuarine environments (Sañudo-Wilhelmy et al., 1996; Guéguen and Dominik, 2003) likely because the element tends to be more linked to the suspended particles at the Isonzo River mouth. Our results are comparable to those found in southern sector of the Gulf of Trieste during summer (Koron et al., 2013). Iron associated with the suspended particles reaches the maximum value of $254 \mu\text{g L}^{-1}$ in the freshwater and it significantly decreases with depth upon increasing salinity. Moreover, Fe concentrations in the truly dissolved fraction ($< \text{LOD}$) and in the colloidal material (196 ng L^{-1}) suggest that colloidal Fe precipitates could have formed in the freshwater as a result of coagulation and/or flocculation processes (Förstner and Wittmann, 1979; Kraepiel et al., 1997). However, the brackish water shows a slight enrichment in particulate Fe with the only exception of the sample collected in summer, showing a lower concentration of particulate Fe. In addition, the relatively low Fe concentrations in the truly dissolved fraction and the quite high content in the colloidal material would confirm the fact that the element is preferentially partitioned in the solid phase. The only exception is the brackish water collected in summer, which displays a truly dissolved concentration of $6.64 \mu\text{g L}^{-1}$ likely due to the dissolution of Fe oxy-hydroxides. In addition, processes such as reduction mediated by biological activity and diffusion from the SWI could be responsible for the increase in dissolved Fe in oxic seawater (Hopwood et al., 2015).

The behaviour of Cu is similar to that described for Fe, although its concentration in the SPM appears to decrease linearly with increasing salinity at the Isonzo River mouth. Copper plays an important role in the chemistry of Fe and it was demonstrated that the Fe oxidation process is favoured by the presence of Cu (González et al., 2016). In addition, the non-conservative behaviour of Cu was also found in other transitional systems, especially regarding the truly dissolved phase (Martin et al., 1995). However, a depletion in truly dissolved Cu was clearly evident in autumn and winter in the brackish and marine water at the river mouth. Moreover, the enrichment in terms of colloidal material confirms that this element is preferentially partitioned in the solid phase with the only exception of the brackish water sample collected in summer, which displayed a truly dissolved Cu concentration of $1.77 \mu\text{g L}^{-1}$.

4. Conclusions

At the Isonzo/Soča River mouth, trace elements appear to be mainly associated with the suspended particulate matter, thus confirming its crucial role in the transfer of contaminants from land to coastal and marine environments. Dilution processes between riverine and marine particles occurring at the river mouth are responsible for the decrease in the particulate trace element concentrations along the water column. However, significant levels of particulate Mn were detected in the marine water in summer, when the warm water conditions could promote oxidation and consequent precipitation of Mn oxy-hydroxides.

Regarding Hg, the results discussed herein are in agreement with previous studies attesting that the Isonzo/Soča River still represents an active source of particulate Hg. Furthermore, the element appears to be mainly partitioned in this solid phase, especially after river flood events.

At the Isonzo/Soča River mouth, the strong physico-chemical gradients, especially in terms of salinity, lead to a non-conservative behaviour for Fe, Mn and Cu, which are also partially partitioned in the colloidal material. Conversely, As and Cs behaves conservatively at the

river mouth and were found to be primarily present under ionic dissolved forms showing a linear increase at increasing salinity.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marchem.2020.103800>.

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