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Trace elements in the estuarine systems of the Gulf of Trieste (northern Adriatic Sea): A chemometric approach to depict partitioning and behaviour of particulate, colloidal and truly dissolved fractions

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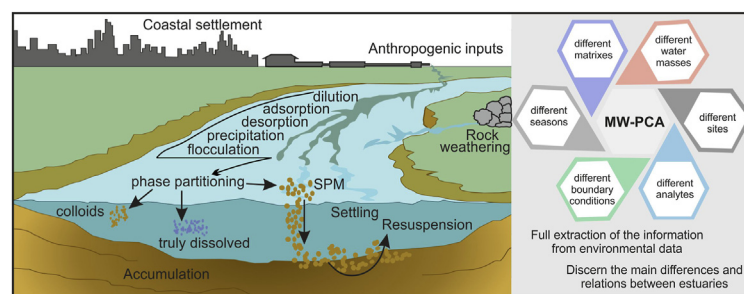
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HIGHLIGHTS

- Trace element partitioning behaviour among different fractions was investigated.
- Trace elements appeared to be mainly partitioned in the suspended particles.
- The truly dissolved fraction was found to be the dominant matrix for As and Cs.
- MW-PCA is very effective in depicting disparities among different estuarine systems.

GRAPHICAL ABSTRACT



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ABSTRACT

Estuaries are transitional water systems where the hydrodynamic processes governing water circulation actively influence suspended particle transport and deposition. In the estuarine mixing zone, the strong physico-chemical gradients resulting from the interaction between river freshwater and seawater may affect the distribution, mobility and fate of several potentially toxic compounds, among which trace elements are of major concern. Knowledge regarding the partitioning behaviour of trace elements would provide essential scientific support for the environmental management of estuaries. In this study, trace element occurrence and phase partitioning among suspended particulate matter, colloidal material and the truly dissolved fraction were investigated in the main Italian and Slovenian estuarine environments of the Gulf of Trieste (northern Adriatic Sea). Further information about the water quality at the river mouths was provided and, in addition to the traditional evaluation of single chemical parameters, a multi-way principal component analysis was employed in order to depict disparities among sampling sites, water layers and seasonal conditions with the final aim of evaluating trace element phase partitioning.

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1. Introduction

Among natural aquatic systems, estuaries are often affected by significant anthropogenic pressure which heavily contributes to render them particularly fragile (Caplat et al., 2005; Casado-Martínez et al., 2006; Vale et al., 2008; Guo et al., 2010; Deycard et al., 2014). Estuaries can also be considered a sedimentary trap since the decrease in flow velocity occurring at the estuarine mixing zone leads to fine particle aggregation and settling (Wright, 1977; Menon et al., 1998). These natural processes can easily involve a variety of potentially toxic compounds adsorbed on the surface of the suspended particles such as trace elements, organometallic compounds and persistent organic pollutants (e.g. Neto et al., 2006; Botwe et al., 2017), which tend to accumulate in the sediments. Moreover, resuspension events, changes in the boundary conditions at the sediment-water interface (SWI) and mixing processes between different water masses may affect the partitioning of trace elements between solid and dissolved phases and their fate in the estuarine system (Fu et al., 2013; Domingos et al., 2015; de Souza Machado et al., 2016; Wang and Wang, 2016; Fiket et al., 2018).

Three fundamental fractions are generally involved in the phase partitioning of organic and inorganic matter in natural aquatic systems: suspended particulate matter (SPM), colloids and the truly dissolved fraction.

The SPM is known as the main carrier for trace elements entering the estuarine environment (e.g. Turner and Millward, 2000; Cenci and Martin, 2004; Fu et al., 2013; Fernandes et al., 2019) though the upper dimensional limit of the particles is not well established and the lower limit has been conventionally defined as being between 0.4 and 0.5 μm . According to Guo and Santschi (1997), the traditionally defined total filterable fraction ($<0.45 \mu\text{m}$) incorporates the truly dissolved fraction (D), which consists of molecules and ions, and colloidal material (C). Colloids consist of submicron particles having a molecular weight lower than 10 kDa (high molecular weight colloids) (e.g. Sañudo-Wilhelmy et al., 1996; Kraepiel et al., 1997; Sigg et al., 2000) or 1 kDa (low molecular weight colloids) (e.g. Wen et al., 1996; Wells et al., 2000; Guéguen and Dominik, 2003). In addition, the strong physico-chemical gradients occurring in estuaries may favour the aggregation of colloids as a result of coagulation and flocculation processes (Guo and Santschi, 2007; Savenko et al., 2014) which can influence the biogeochemical cycles of trace elements (Benoit et al., 1994; Guentzel et al., 1996). These macroaggregates exhibit a reactive surface area for adsorption processes (Filella, 2007) with the subsequent removal of trace elements from the dissolved phase.

The shallow marine area of the northern Adriatic Sea is subject to intense freshwater discharge during autumn and spring (Cozzi et al., 2012) mainly from the Po River, which is the source of the majority of the SPM (Frignani et al., 2005), followed by the Adige and Brenta Rivers (Cozzi and Giani, 2011).

Regarding the easternmost sector of the northern Adriatic Sea,

the main freshwater input is represented by the Isonzo/Soča River followed by the Timavo/Reka River (Cozzi et al., 2012) whereas lower contributions come from the Rižana and Dragonja Rivers, located along the Slovenian coast. The role of SPM as the primary carrier of trace elements was investigated at the Po, Adige and Isonzo Rivers (Juračić et al., 1986, 1987; Juračić and Pravdić, 1991; Covelli et al., 2007; Pavoni et al., submitted), whereas few studies have examined the potential release of trace elements in the aqueous phase (Tankéré and Statham, 1996; Tankéré et al., 2000a; Zago et al., 2002; Pavoni et al., submitted) or their association with colloids (Koron et al., 2013; Klun et al., 2019). This research aims to assess trace element occurrence and phase partitioning among SPM, colloids and the truly dissolved fraction in the main Italian and Slovenian estuarine environments of the Gulf of Trieste, since these issues have not been thoroughly addressed. The general intent of the present study is to provide further information about the water quality at the river mouths, in particular, looking for potential critical conditions and common environmental mechanisms controlling trace element behaviour, mobility and fate. Better information regarding the previously mentioned issues is fundamental to implement scientific support for the environmental management and risk assessment often needed in estuaries. In this context, a multi-way principal component analysis (MW-PCA) was employed to fully exploit the extraction of the information embodied within data and to discern the main differences and relations between estuaries.

2. Materials and methods

2.1. Environmental setting

The semi-enclosed coastal environment of the Gulf of Trieste is located on the north-eastern sector of the Adriatic Sea (Italy), it covers an area of approximately 500 km^2 , reaching its maximum depth (25 m) in the central sector. The circulation of water masses in the Gulf is primarily dominated by the anticlockwise circulation of the Adriatic Sea, and further influenced by tides, winds and seasonal variations in the freshwater inflow (Malačič and Petelin, 2009).

Along the Italian coast, the Isonzo/Soča River represents the main source of freshwater entering the Gulf of Trieste, followed by the Timavo/Reka River, whereas minor freshwater inputs are conveyed by the Rižana and Dragonja Rivers along the Slovenian sector, discharging into the Bay of Koper and the Bay of Piran, respectively (Fig. 1). The Isonzo River generally shows significant seasonal variations in the river discharge with an average flow of $82 \text{ m}^3 \text{ s}^{-1}$ (Cozzi et al., 2012) and two main flood events usually occur during late spring and autumn. The Isonzo River represents an active source of Hg which appears to be primarily bound to the suspended particles (Covelli et al., 2004, 2006, 2007). Moreover, the impact of long-term cinnabar (HgS) extraction activity from the Idrija mine (Slovenia) (Hines et al., 2000) is well known with regards to the occurrence of dissolved Hg in groundwater (Cerovac

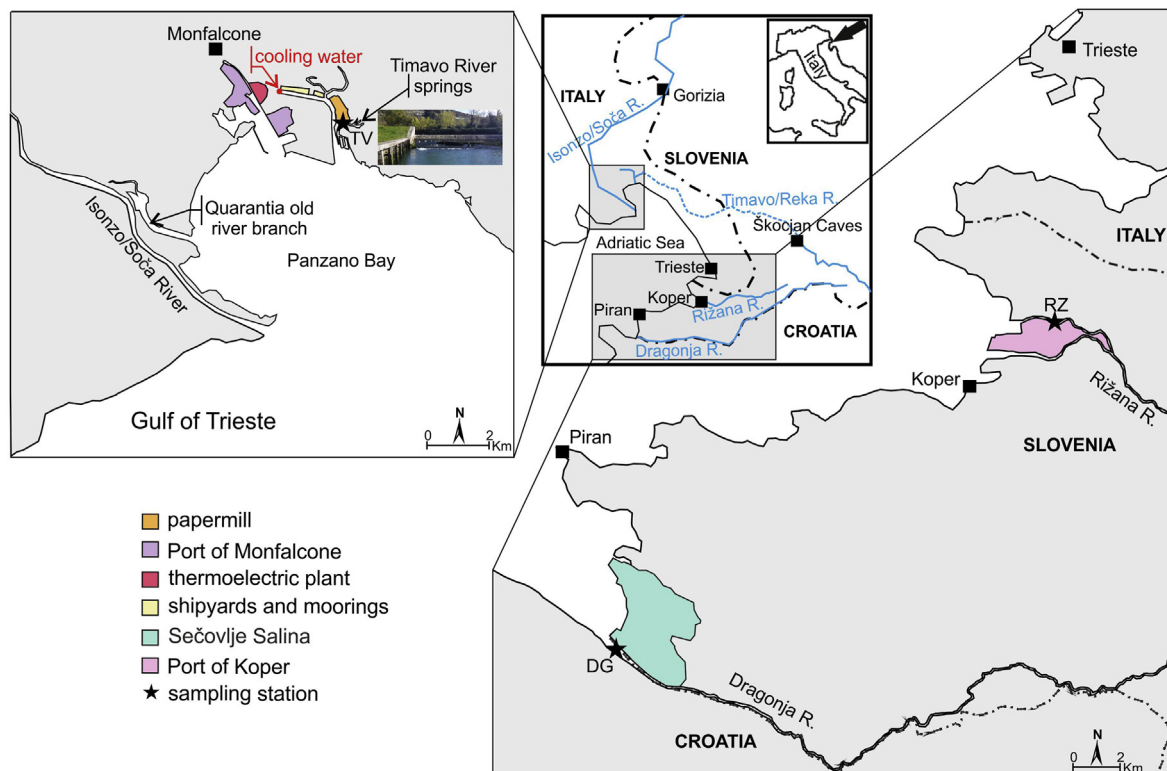


Fig. 1. Map of the study area and location of the sampling stations at the estuarine systems of the Timavo (TV) River along the Italian coast and the Dragonja (DG) and Rižana (RZ) Rivers in the Slovenian sector.

et al., 2018), Hg contamination of surface sediments (Covelli et al., 2001) and Hg cycling at the SWI (Emili et al., 2011).

The Timavo River (TV) originates in Croatia (Snežnik, Slovenia-Croatia border area), it flows on a flysch formation outcropping in the Slovenian sector before sinking into the Karst Plateau at the Škocjan Caves (Slovenia) (Gabrovšek et al., 2018). Its underground river path is approximately 38 km before it re-emerges from several springs with an average discharge of $30.2 \text{ m}^3\text{s}^{-1}$ (Gabrovšek and Peric, 2006) in the innermost sector of the Panzano Bay, home to several anthropogenic activities (Fig. 1).

The Rižana River (RZ) is one of the shortest rivers in Slovenia (14 km); it originates under the Kraško-Slavniška plateau draining directly into the Bay of Koper, which is subject to a variety of industrial settlements (Mandac and Žagar, 2018) (Fig. 1). The anthropogenic pressure present in this area is mainly due to the intense activity at the Port of Koper, which is one of the biggest harbours in the northern Adriatic Sea and where potentially toxic compounds, including trace elements, were found to be present in bottom sediments (Šmuc et al., 2018).

The Dragonja River (DG) begins in Croatia, it flows on flysch terrains for approximately 30 km and its course follows the border between Slovenia and Croatia until discharging into the Bay of Piran (Fig. 1). Its river path is markedly branched and meandered; the river discharge is generally low and often dries up during summer (Brečko Grubar and Kovačič, 2010). The average discharge of the RZ and DG Rivers ranges between 1 and $4 \text{ m}^3\text{s}^{-1}$ (Cozzi et al., 2012).

2.2. Sampling strategy and estuarine water sample size fractionation

Estuarine water samples were collected at the TV, RZ and DG River mouths under different seasonal conditions (winter, summer

and autumn). A CTD multiprobe (Hydrolab H₂O with a 0.10 dbar pressure step) was used to depict the water column stratification in terms of salinity (PSU, Practical Salinity Unit), temperature (°C) and turbidity (NTU, Nephelometric Turbidity Unit). According to the salinity gradient, either a Niskin or Van Dorn bottle were alternatively employed to collect large volume (approximately 15 L) of freshwater-brackish (0–27 PSU) and marine water (27–37 PSU) (Table S1). Furthermore, additional physico-chemical parameters such as pH and redox potential (Eh) were measured *in situ* by portable probes (pH-meter PH25 and Conductivity-meter CM 35+ by Crison Instruments) (Table S1).

Vacuum filtration was performed using pre-conditioned and pre-weighed membrane filters (Millipore HA, ϕ 47 mm, 0.45 μm pore size) to isolate the SPM ($>0.45 \mu\text{m}$), which was then acid digested through a total dissolution (inverse *aqua regia*, suprapure HNO₃ ($\geq 69\%$) and HCl ($\geq 37\%$), 3:1) in a closed microwave system (Multiwave PRO, Anton Paar) following the modified EPA Method 3052 (2007) for the analytical determination of trace elements. Further sample fractionation involved the total filterable fraction, which was ultrafiltered (ultrafiltration membranes, Sartorius Vivaflow 200, Molecular Weight Cut-Off 10 kDa) allowing the isolation of the colloidal retentate solution (10 kDa– $0.45 \mu\text{m}$) from the permeate solution ($<10 \text{ kDa}$), also known as ultrafiltrate solution or truly dissolved (Guo and Santschi, 1997; Wells et al., 2000; Town and Filella, 2002). The ultrafiltration system was pre-conditioned with actual pre-filtered water sample and every ultrafiltration run was carried out under recirculation mode, applying a concentration factor of approximately 60 and NaOH (water solution, 0.5 M) followed by large amounts of MilliQ water were used to rinse the ultrafiltration system.

Mass balances and concentrations of the colloidal material were estimated according to the following Eqs. (1) and (2) (Sigg et al.,

2000; Ingrid et al., 2004) and recoveries between 75 and 113% were considered acceptable.

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

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

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

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

Sample aliquots for trace element determination were promptly acidified with suprapure HNO_3 (1 mL/100 mL sample) and stored in PTFE containers, whereas borosilicate glass containers were preferred for Hg storage and detection. The water samples used for Hg detection were immediately oxidised with bromine chloride (BrCl Hg-free from Brooks Rand Instruments, 500 μL /100 mL until the sample turned yellow) according to the EPA Method 1631 (2002).

Blank samples were collected at each step and were found to be mainly below the limit of detection (LOD) with the only exception being Zn, which was occasionally found to be higher than 0.50 $\mu\text{g L}^{-1}$, as previously reported by Sigg et al. (2000).

2.3. Analytical measurements

Concentrations of As, Co, Cr, Cs, Cu, Fe, Ni, Mn, Pb and Zn in the different sample fractions (SPM, colloidal retentate solution and truly dissolved fraction) were quantified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a NexION 350x Spectrometer (PerkinElmer, USA) equipped with an ESI SC Autosampler. Standard solutions (0.50–100 $\mu\text{g L}^{-1}$) obtained via the dilution of a multistandard solution for ICP analysis (10 mg L^{-1} , Periodic Table MIX 1, Sigma Aldrich) were analysed for instrument calibration and the analysis was performed in KED mode (Kinetic Energy Discrimination) to avoid and minimise cell-formed polyatomic ion interference. The limits of detection (LOD) are reported in Table S2 and the precision of the analysis expressed as RSD% was <3%. Particulate Al and Fe were detected by 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 the dilution of a multistandard solution (100 mg L^{-1}) for ICP analysis (Instrument Calibration Standard 2, PerkinElmer, USA). The precision of the ICP-OES analysis expressed as RSD% was <5%.

Mercury analysis was preceded by a pre-reduction using $\text{HN}_2\text{OH-HCl}$ (250 μL /100 mL sample until the yellow colour disappeared), followed by a reduction via SnCl_2 (2% in HCl 2%) (EPA Method 1631e, 2002) and performed by means of Cold Vapor Atomic Fluorescence Spectrometry coupled with a gold trap pre-concentration system (CV-AFS Mercur, Analytic Jena). The instrument was calibrated using standard solutions (1–50 ng L^{-1}) prepared by the dilution of a Hg standard solution (mercury standard solution, Merck Millipore, 1000 mg L^{-1}) and stabilised with BrCl (500 μL /100 mL). 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%). The LOD was 0.60 ng L^{-1} and the precision of the analysis expressed as RSD% was <3%.

Laboratory-fortified samples prepared by spiking 1 or 5 $\mu\text{g L}^{-1}$ (depending on the trace element concentrations in the samples) of trace elements into actual water and particulate samples were

analysed for quality control. For this purpose, a different multi-standard solution (10 mg L^{-1}) from that used for instrument calibration was diluted into the actual samples. Acceptable recoveries from 6 spiked samples were obtained for both estuarine water (ranging between 77 and 99%) and SPM samples (ranging between 90 and 116%).

2.4. Exploratory multivariate data analysis

Experimental data were analysed using a 5-way principal component analysis (5W-PCA) by the Tucker-3 algorithm (Smilde et al., 2004), as an unsupervised exploratory tool for the visual identification of relationships within the five investigated modes (matrices, water layers, seasons, rivers and variables) (Oliveri et al., 2020). A Log-transform was applied to all the variables to normalise their frequency distribution and column autoscaling (j-scaling) (Smilde et al., 2004) was applied to data matrices to minimise systematic differences between the experimental variables (Oliveri et al., 2019).

3. Results and discussion

3.1. Water column characteristics and physico-chemical boundary conditions

River discharge was notably higher at the TV River mouth (40.0, 18.3 and 17.3 $\text{m}^3 \text{s}^{-1}$ during winter, summer and autumn sampling campaigns, respectively) rather than at the RZ (0.43, 0.23 and 6.55 $\text{m}^3 \text{s}^{-1}$) and DG (2.65, 0.33 and 0.64 $\text{m}^3 \text{s}^{-1}$) estuarine systems.

The water column stratification varied among different sampling sites and seasons, although the salt-wedge intrusion could clearly be identified (Fig. 2) and the water depth is generally shallow (approximately 5, 4 and 3 m depth at the TV, RZ and DG River mouths). Salinity vertical profiles displayed a sharp halocline at the TV River mouth, attesting to the evident and permanent salt-wedge intrusion among the different seasons (Fig. 2). Results were similar for the mouth of the DG River, where a strong stratification occurred during the year, although the surface freshwater layer demonstrated variable thicknesses among different seasons (Fig. 2). The strongest salt-wedge intrusion was found at the RZ River mouth where the brackish water was found in the surface layer of the water column during both winter (23.8 PSU) and summer (27.2 PSU).

Turbidity did not display notable differences with depth in winter and autumn, whereas a slight increase in turbidity values was evident in summer at both TV and RZ River mouths (Fig. 2). The highest turbidity values were measured at the DG River mouth, especially in summer when turbidity gradually increased with depth (from 30.5 to 79.6 NTU along the water column). Indeed, since the DG estuarine system is very shallow, it is often exposed to resuspension events followed by re-deposition of fine resuspended particles to the estuarine sediments.

The highest differences in temperature were found at the TV River estuarine system, where warm water was recorded in the mixing and bottom layers due to the discharge of cooling water from a thermal plant. The increase in temperature was notably evident among different seasons, reaching a maximum value of 27.0 $^{\circ}\text{C}$ at approximately 2 m depth in autumn. On the contrary, slight variations were observed at the DG and RZ estuarine systems, where the temperature was rather homogeneous with increasing depth in winter and autumn, whereas higher values were measured in summer, as expected. This is especially evident at the RZ River mouth where the shallow water depth and scarce water circulation led to a temperature equal to approximately 28 $^{\circ}\text{C}$.

Significant disparities in terms of pH were not found among the

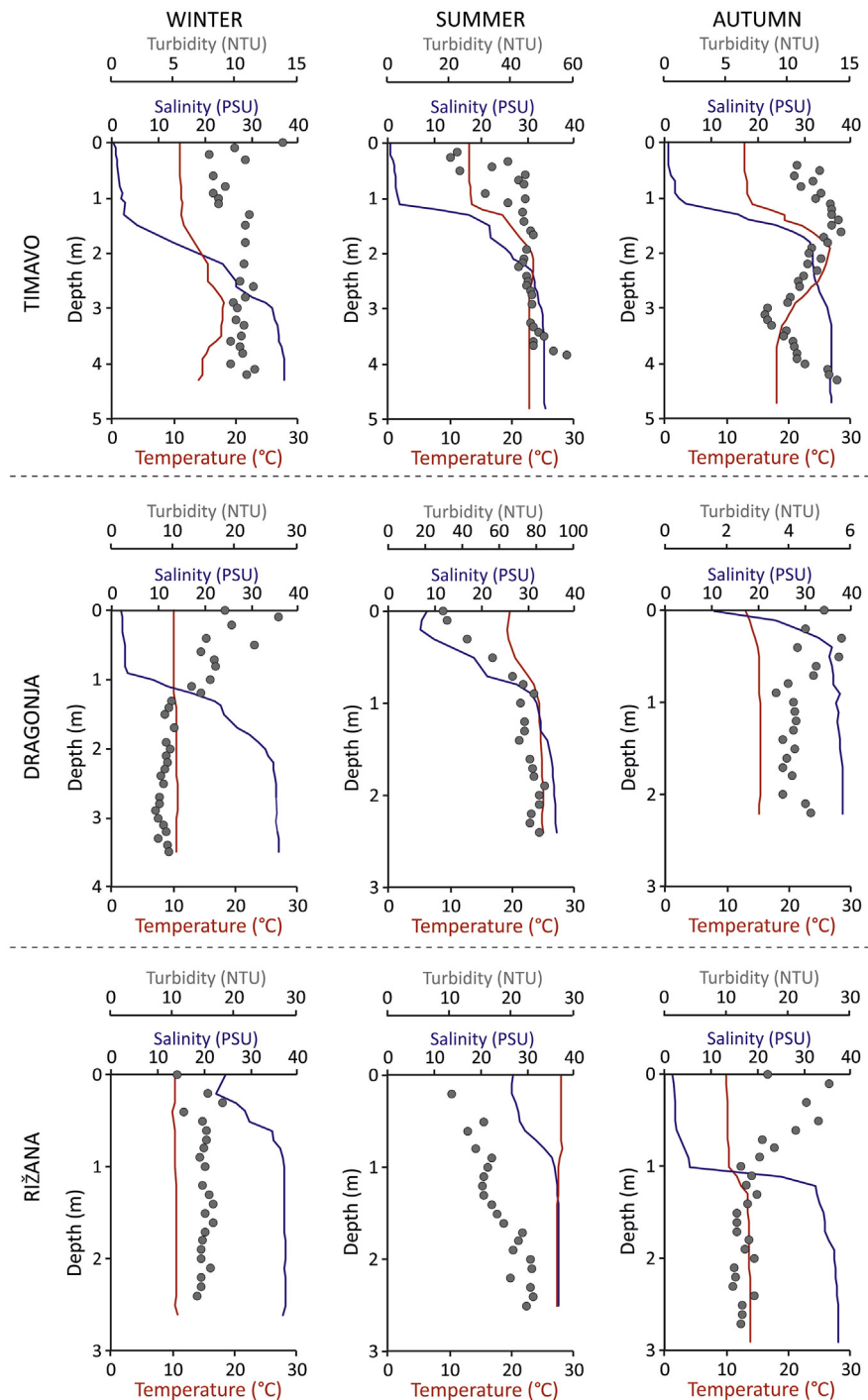


Fig. 2. Vertical profiles of salinity (PSU, Practical Salinity Unit), temperature (°C) and turbidity (NTU, Nephelometric Turbidity Unit) recorded at the Timavo (TV), Dragonja (DG) and Rižana (RZ) River mouths under different seasonal conditions.

sampling sites and among different seasons, although the marine water generally showed slightly higher pH values (Table S1). The redox potential testified to oxidative conditions in the freshwater-brackish water layer and slightly lower values were generally found at the bottom. The only exception was the RZ estuarine system which showed reductive conditions in the whole water column in winter and autumn, whereas slightly higher Eh values were found in summer (Table S1).

3.2. Occurrence of trace elements in the suspended particulate matter

At the three investigated estuarine systems, the concentrations of particulate trace elements were generally higher in the freshwater-brackish water than in the marine water (Table S3) likely due to dilution effects and mixing processes between different water masses (Turner, 1999; Hatje et al., 2001). This trend of general dilution was evident for most of the investigated trace elements at the TV, RZ and DG River mouths in winter and autumn,

whereas minor differences along the water column were found in summer. In addition, the quite low river discharge could not entirely avoid mixing and dilution processes with the only exception being the TV River in winter ($40 \text{ m}^3 \text{ s}^{-1}$). The highest concentrations of particulate trace elements were found at the RZ River mouth, especially in the freshwater-brackish water in autumn. Since there is intense activity at the Port of Koper, as well as the presence of industrial settlements in the vicinity of the river mouth, it cannot be excluded that the high concentrations of trace elements such as Cu, Pb and Zn in the SPM may be related to the transit of massive cargo and nearby anthropogenic activities. However, previous research on the surface sediments in the port area highlighted marginal enrichments for those elements, also pointing to a scarce mobility, most likely due to their strongly association with the residual fraction of sediments (Šmuc et al., 2018).

Similarly high particulate trace element concentrations were found at the TV estuarine system where the maximum values of Cu ($399 \mu\text{g g}^{-1}$ in the freshwater-brackish layer in autumn) and Pb ($6237 \mu\text{g g}^{-1}$ in the freshwater-brackish layer in summer) were detected. The notable presence of particulate Pb at the TV River mouth may be related to the additional water supply provided by two additional channels (the Lôcavaz and the East-West channels). Between them, the Lôcavaz channel originates in the northern sector of the estuarine system where a highway is located. It could be hypothesised that, as a consequence, water run-off from soils enriched in Pb may be responsible for its notably high particulate concentrations which reached the maximum value in summer when a weaker dilution effect occurred. Conversely, the estuarine system of the DG River showed lower particulate trace element concentrations, especially in the marine water in the summer season (Table S3).

Particulate Mn was found to be high in summer at the three investigated estuarine systems (1182 , 1839 and $1074 \mu\text{g g}^{-1}$ at the TV, RZ and DG River mouths, respectively) compared to the concentrations measured in winter and autumn (Table S3). As reported in other studies (Morris et al., 1982; Sondi et al., 1994; Hatje et al., 2001; Pavoni et al., submitted), considerably high amounts of particulate Mn in summer could be due to oxidation and precipitation processes promoted by high water temperatures. Furthermore, this is in agreement with other estuarine systems of the northern Adriatic Sea, where concentrations of particulate Mn were generally found to be of the same order of magnitude (e.g. Sondi et al., 1994; Camusso et al., 1997; Pavoni et al., submitted).

Moreover, the redox behaviour of Mn and Fe are strongly linked in natural aquatic systems where Fe and Mn oxy-hydroxides are important host phases for adsorption processes due to their high adsorptive capacities (Tankéré et al., 2000b; Gagnon and Saulnier, 2003). For these reasons, the Fe/Mn ratio represents a useful index to understand their relative prevalence under different seasonal conditions. In this study, this ratio was high in winter and autumn for the three investigated estuarine systems, varying collectively between 38.7 and 160. Conversely, lower values were found in summer (ranging overall between 11.1 and 23.3), thus revealing the concomitant decrease in particulate Fe and increase in particulate Mn. This could be due to the different rate of oxidation of the redox couples Mn(II)/Mn(IV) and Fe(II)/Fe(III). It can be assumed that dissolved Fe and Mn could diffuse from the SWI into the water column where re-precipitation of Fe and Mn oxy-hydroxides may occur. Indeed, under oxic conditions, Fe(II) is rapidly oxidised to Fe(III), which is the most abundant form of Fe in oxic water, whereas Mn(II) shows a slower rate of oxidation which could be responsible for the persistence of dissolved Mn along the water column. This is especially evident in summer, both in the freshwater-brackish water (12.8 , 30.4 and $19.8 \mu\text{g L}^{-1}$ at the TV, RZ

and DG River mouths, respectively) and at the bottom (14.2 , 8.21 and $20.4 \mu\text{g L}^{-1}$ at the TV, RZ and DG River mouths, respectively). In addition, the strong stratification that usually occurs in summer could promote the aggregation and subsequent accumulation of mucilage at the pycnocline (Fajon et al., 1999; Granéli et al., 1999). These organic materials represent important reactive surface for adsorption of trace elements as also indicated by the relatively high Cu, Cr, Fe, Mn and Ni concentrations in the colloidal material. However, bacteria can rapidly colonise and degrade these organic aggregates (Fogg, 1995; Serratore et al., 1995) leading to a local decrease in the dissolved oxygen (Tankéré et al., 2000b) which, in turn, may induce the reduction of Mn oxides and increase in dissolved Mn.

Particulate Hg was mainly below LOD, except for the TV River mouth, where Hg was high in the freshwater-brackish water (1.33 – $9.79 \mu\text{g g}^{-1}$) and low at the bottom (0.90 – $1.17 \mu\text{g g}^{-1}$). The occurrence of Hg at the TV River mouth could be explained by the role of the Isonzo River as the main vehicle for particulate Hg entering the Gulf of Trieste (Covelli et al., 2007). Indeed, stream losses from the Isonzo River may act as a groundwater source for the unconfined aquifer of the Isonzo River alluvial plain (Cerovac et al., 2018) and mixing processes between the two types of waters could occur, especially under conditions of low discharge from the Isonzo River (Calligaris et al., 2018). On the other hand, the tidal currents and the anticlockwise water circulation in the Gulf of Trieste may also contribute to transporting particulate Hg, conveyed by the Isonzo River or resuspended in the Bay of Panzano ($5.54 \mu\text{g g}^{-1}$ in surface sediments, Acquavita et al., 2010), into the TV River estuarine system. Chromium has previously been reported at high levels in the bottom sediments of the Gulf of Trieste with an average concentration of $77 \pm 30 \mu\text{g g}^{-1}$ (Covelli and Fontolan, 1997; Faganeli et al., 1991) and Dolenec et al. (1998) stated that trace element distribution in the northern Adriatic Sea generally decreased towards the open sea. In addition, Acquavita et al. (2010) reported slightly higher concentrations ($112 \pm 41 \mu\text{g g}^{-1}$ on average) also stating that the surface sediments from the Gulf of Trieste did not appear to be affected by evident anthropogenic inputs of Cr despite its high levels. This suggests that river inputs may act as the source of Cr as indicated by its high concentrations in the SPM found at the TV (45.4 – $137 \mu\text{g g}^{-1}$), RZ (66.4 – $288 \mu\text{g g}^{-1}$) and DG (30.5 – $153 \mu\text{g g}^{-1}$) River mouths. The same was true for Ni, which was also found at high levels in the bottom sediments of the Gulf of Trieste ranging between 12 and $230 \mu\text{g g}^{-1}$ (Faganeli et al., 1991; Covelli and Fontolan, 1997). This range of concentration is also consistent with the results reported by Acquavita et al. (2010) (20 – $231 \mu\text{g g}^{-1}$ of Ni). In this research, particulate Ni ranged between 27.9 and $132 \mu\text{g g}^{-1}$, between 45.2 and $161 \mu\text{g g}^{-1}$ and between 22.5 and $121 \mu\text{g g}^{-1}$ at the TV, RZ and DG estuarine systems. Indeed, Cr and Ni are lithogenic and their origin is due to runoff and erosion of the flysch formation outcropping in the continental area (Lenaz and Princivalle, 1996; Zupančič and Skobe, 2014). Moreover, particulate Cr and Ni were generally higher in the freshwater-brackish water (Table S3) and comparable to other estuarine environments of the northern Adriatic Sea (Juračić and Pravdić, 1991; Pavoni et al., submitted). The common lithogenic origin of Cr and Ni was also confirmed by the strong correlation ($r = 0.883$, $N = 18$, $p < 0.001$) between these two elements in the estuarine water collected at the three investigated sites (Fig. S1). Equally significant correlations were also found between Ni, Cr and Co ($r = 0.905$, $N = 18$, $p < 0.001$ and 0.861 , $N = 18$, $p < 0.001$ for Cr and Ni, respectively) since Co could also derive from alteration processes of flysch terrains (Francisković-Bilinski et al., 2014) (Fig. S1). Normality of experimental data distributions shown in Fig. S1 was positively verified by means of the Lilliefors' test, at a 5%

3.3. Trace element partitioning: relationships between suspended particulate matter, colloids and truly dissolved

The partitioning between solid and dissolved phases is essential for the evaluation of trace element fluxes carried by rivers to estuaries (e.g. Morris et al., 1982; La Colla et al., 2015; Wang and Wang, 2016). A 5W-PCA was employed, as an additional chemometric tool to the traditional evaluation of single parameters, to depict trace element partitioning between the solid phase, represented by the SPM and colloidal material, and the truly dissolved fraction (Tables S4 and S5), highlighting relations and differences between sampling sites, water masses and seasons (Fig. 3). Although more detailed information about trace element phase partitioning and mixing behaviour for the Isonzo River has previously been reported elsewhere (Pavoni et al., submitted), it was decided to include those results in the multi-way model. In this way, a complete overview of the main differences and relationship between the main estuarine environments of the Gulf of Trieste, among which the Isonzo River represents the primary freshwater input, was provided. In addition, distribution coefficients (Turner, 1996; EPA, 1999; Gagnon and Saulnier, 2003; Guéguen and Dominik, 2003; Wang and Wang, 2016) and the relative percentages of As, Co, Cr, Cs, Cu, Fe, Mn, Ni, Pb and Zn in the SPM with respect to their total concentration in the estuarine water samples are reported in Table S6. In detail, according to Guéguen and Dominik (2003), distribution coefficients (K_p L kg⁻¹) were calculated as the ratio between particulate and truly dissolved concentration and expressed as a logarithmic scale.

The 5W-PCA clearly denotes the difference between the three sample fractions (SPM, colloids and truly dissolved) and between the different water masses. Moreover, the distribution of trace elements in the plot (Fig. 3) appears to be governed by their partitioning behaviour. In fact, trace elements found to be mainly associated with the solid phase (Fe, Hg, Cr, Pb, Ni and Cu) were clearly distinguished from those prevailing in dissolved forms (As

and Cs).

The SPM is known to play a crucial role as the main vehicle for several trace elements from continental areas to coastal environments (Turner and Millward, 2000; Vignati and Dominik, 2003; Beck et al., 2013; Helali et al., 2016). This is notably evident for Fe, Pb and Cr which are almost completely partitioned in the solid phase, as seen by their elevated percentages in the SPM (>90% for Fe, between 71.3 and 99.4% for Pb and from 54.1 to 98.5% for Cr). This was also confirmed by the Log K_p values which were found to be high for Fe and Pb, followed by Cr, Cu and Ni, reflecting their high affinity to the suspended particles. According to Benoit et al. (1994), Pb is highly particle reactive and rapid adsorption onto the suspended particles, as well, removal processes such as co-precipitation with Fe oxy-hydroxides may easily occur in the estuarine mixing zone (Fu et al., 2013; Fiket et al., 2018).

The 5W-PCA output clearly demonstrated that the SPM was the dominant matrix for Fe, Cr and Pb, especially in the freshwater-brackish water in winter as also indicated by their elevated percentages in the SPM at the TV (99.7, 94.0 and 77.6% of Fe, Cr and Pb), RZ (96.3, 91.5 and 99.3% of Fe, Cr and Pb) and DG (99.8, 95.8 and 99.4% of Fe, Cr and Pb) River mouths. Indeed, the highest concentrations of particulate Fe were found at the Isonzo (254 µg L⁻¹) (Pavoni et al., submitted) and DG River (281 µg L⁻¹) mouths, whereas dissolved Fe was found to be below LOD in winter as evidenced by the fact that the truly dissolved fraction is plotted on the opposite side in the 5W-PCA output. This is also confirmed by the quite low percentages of Fe in the truly dissolved fraction, ranging between 0.17 and 5.42% overall. This is similar to Cr and Pb, which were found to be mainly below LOD in the truly dissolved fraction.

With the only exception being at the mouth of the Isonzo River (Pavoni et al., submitted), dissolved Hg was mainly below LOD and primarily associated with the solid phase confirming the role of the Isonzo River as the main source of particulate Hg in the Gulf of Trieste (Covelli et al., 2007). The relationship between particulate Hg and the Isonzo River is clearly evident in the 5W-PCA output, from their closeness in the plot of Fig. 3, since the maximum concentrations of particulate Hg were reached at the Isonzo River mouth in winter, both in the river freshwater (105 ng L⁻¹) and at the bottom (57.3 ng L⁻¹) (Pavoni et al., submitted).

To a lesser extent, the solid phase was found to be the dominant fraction in the case of Cu and Ni, which appeared to be strongly associated with the suspended particles in winter, especially in the freshwater-brackish water of the DG River (98.9 and 98.8% for Cu and Ni, respectively). Conversely, the dissolved Cu was below the LOD in winter and generally prevailed at the bottom in summer (71.0, 51.1 and 72.2% of Cu at the TV, RZ and DG River mouths) (Fig. 3).

On the contrary, As and Cs appeared to be almost completely partitioned in the truly dissolved phase showing lower Log K_p values (ranging between 3.16 and 4.33 L kg⁻¹ and between 3.94 and 4.96 L kg⁻¹ for As and Cs, respectively) (Table S6). This is also confirmed by the relatively high percentages in the truly dissolved fraction for both As (>90% at the TV and RZ River mouths and >85% at the DG River mouth) and Cs (ranging between 77.5 and 88.4%, 74.8 and 91.2%, 53.3 and 90.3% at the TV, RZ and DG River mouths, respectively) with respect to their percentages in the SPM which were found to be especially low for As (ranging between 5.03 and 7.40%, 4.68 and 9.10%, 1.79 and 16.6% at the TV, RZ and DG River mouths, respectively). Both elements were found to reach high truly dissolved concentrations in the marine water, especially in summer and autumn, as indicated by the 5W-PCA output (Fig. 3), since these elements are generally present under dissolved ionic forms in uncontaminated aquatic systems (Smedley and Kinniburgh, 2002). Moreover, dissolution and desorption

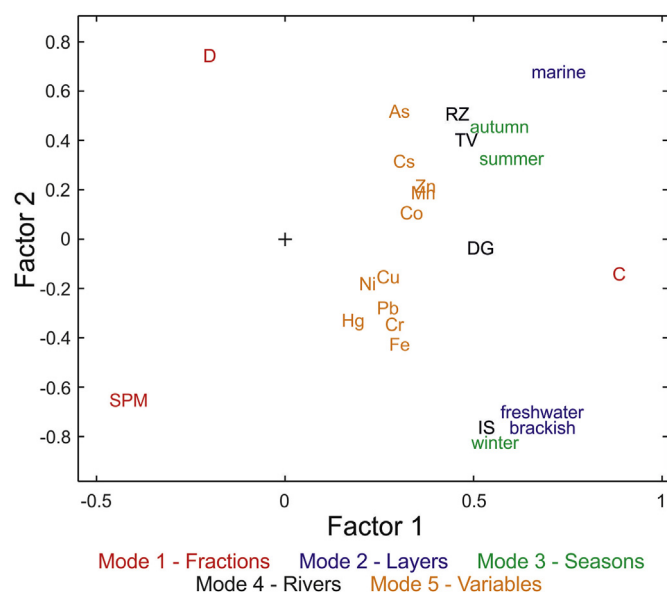


Fig. 3. Plot resuming the results of 5W-PCA performed on the trace element phase partitioning among suspended particulate matter (SPM), colloidal material (C) and the truly dissolved fraction (D) in the estuarine water samples collected at the Isonzo (IS), Timavo (TV), Rižana (RZ) and Dragonja (DG) River mouths under different seasonal conditions.

processes can favour the increase of dissolved As (Smedley and Kinniburgh, 2002), especially in estuarine and marine environments where high concentration of salts in the water can weaken adsorption on the surface of the suspended particles (Hong et al., 2018). In addition, As and Cs are plotted on the opposite side with respect to the SPM (Fig. 3) suggesting that a weak relationship occurred between these elements and the solid phase. The partitioning behaviour described for As and Cs and their occurrence in the dissolved phase is in agreement with other estuarine environments of the northern Adriatic Sea (Fiket et al., 2018; Klun et al., 2019; Pavoni et al., submitted).

Major differences in the partitioning between solid and dissolved phases were found for Co, Zn and Mn, as confirmed by Log K_p values ranging between 4.75 and 5.57 $L\ kg^{-1}$ for Co, between 4.12 and 6.79 $L\ kg^{-1}$ for Zn and between 4.34 and 5.28 $L\ kg^{-1}$ for Mn (Table S6). According to the 5W-PCA output, a strong relationship is evident between Mn and Zn in summer (Fig. 3). Indeed, dissolved Mn and Zn were generally found to be higher both in the freshwater-brackish water (12.8, 30.4 and 19.8 $\mu g\ L^{-1}$ for the TV, RZ and DG Rivers, respectively) and at the bottom (14.2, 11.8 and 20.4 $\mu g\ L^{-1}$ for the TV, RZ and DG Rivers, respectively) in summer.

3.4. Occurrence of trace elements in the colloidal material

The concentrations of trace elements in the colloidal material were notably lower than those measured in the SPM and in the truly dissolved fraction (Tables S4 and S5) and in agreement with the results obtained at the Isonzo River mouth (Pavoni et al., submitted). Moreover, trace element contents in the colloidal material was found to be generally low if compared to other studies focused on riverine and estuarine systems (e.g. Sañudo-Wilhelmy et al., 1996; Jäiry et al., 1999; Guéguen and Dominik, 2003; Ingri et al., 2004). In order to evaluate the influence of the colloidal material in the total filterable fraction, the colloidal percentages were calculated with respect to the total filterable fraction (Table S7). The highest percentages bound to colloids were reached by those elements (Cr, Cu, Fe, Ni and Pb) that showed relatively low concentrations in the truly dissolved fraction (Table S7). Coagulation and/or flocculation processes (Fu et al., 2013; Kraepiel et al., 1997) could be responsible for increasing colloidal Fe in the freshwater-brackish layer. This is particularly evident at the DG River mouth where 887 and 421 $ng\ L^{-1}$ of colloidal Fe were detected in summer and autumn, respectively (Fig. 4). The same is verified for the TV River mouth, where colloidal Fe prevailed both in the freshwater-brackish water (219 $ng\ L^{-1}$) and at the bottom (527 $ng\ L^{-1}$) in summer. Furthermore, colloidal Fe was found to be

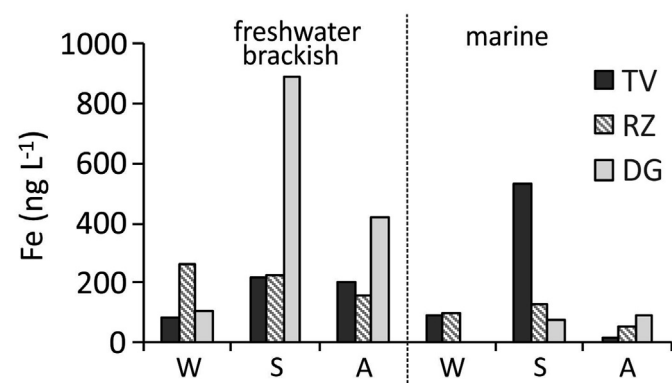


Fig. 4. Concentration of colloidal Fe ($ng\ L^{-1}$) in the estuarine water samples collected at the Timavo (TV), Rižana (RZ) and Dragonja (DG) River mouths under different seasonal conditions (W = winter, S = summer, A = autumn).

of the same order of magnitude as the results for the Bay of Piran (424 $ng\ L^{-1}$, Klun et al., 2019) and for the Isonzo River mouth (196 $ng\ L^{-1}$, Pavoni et al., submitted), and lower if compared to water samples from the Lagoon of Venice, where colloidal Fe, Mn, Ni and Pb were found to be notably present, especially in the surface freshwater (Martin et al., 1995). Indeed, the higher amounts of organic matter that generally occur in lagoon aquatic systems could favour colloid aggregation with subsequent high amounts of trace elements in the colloidal material. In addition, changes in trace element phase partitioning among colloidal material and the truly dissolved fraction may have occurred upstream and may be partly responsible for the low colloidal concentrations found at the investigated river mouths.

Colloidal Cu, Ni and Cr prevailed at the TV River mouth followed by the RZ River mouth, whereas lower contents were found at the estuarine system of the DG River (Fig. 5). Although colloidal Cu reached low concentrations compared to those of colloidal Fe, it was demonstrated that Cu plays an important role in the chemistry of Fe especially regarding oxidation and precipitation processes (González et al., 2016). In this context, colloidal Cu appeared to

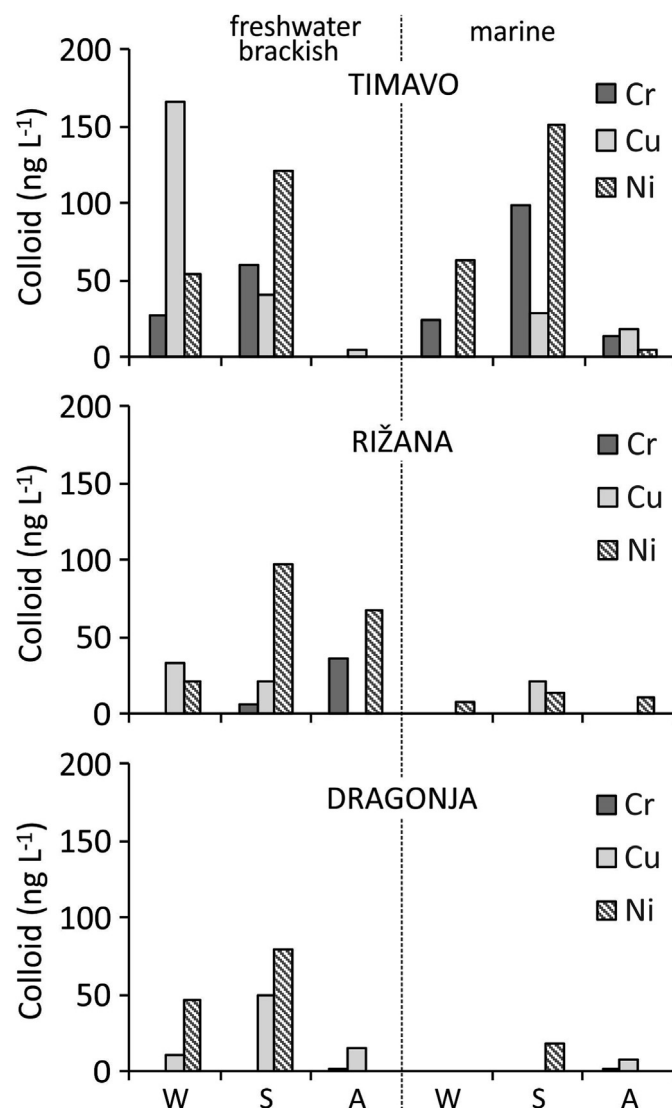


Fig. 5. Concentration of colloidal Cr, Cu and Ni ($ng\ L^{-1}$) in the estuarine water samples collected at the Timavo (TV), Rižana (RZ) and Dragonja (DG) River mouths under different seasonal conditions (W = winter, S = summer, A = autumn).

follow the behaviour of colloidal Fe at the DG estuarine system where both elements increased in the freshwater-brackish water in summer (50.2 and 887 ng L⁻¹ of Cu and Fe, respectively) becoming undetectable or minimally present in the marine water. The same is also true for the RZ River mouth whereas, although colloidal Cu clearly prevailed in the freshwater-brackish water, the maximum concentration (166 ng L⁻¹) was found at the mouth of the TV River in winter.

Despite colloidal Cr occasionally not being detectable in the marine water of the DG and RZ Rivers, extremely similar behaviour was found for Cr and Ni, which clearly prevailed both in the freshwater-brackish water and at the bottom in summer, especially at the TV River mouth (60.2 and 99.0 ng L⁻¹ of Cr and 122 and 151 ng L⁻¹ of Ni).

As previously mentioned, the common lithogenic origin of Cr and Ni (Lenaz and Princivalle, 1996; Zupancić and Skobe, 2014) could explain the strong correlation in the suspended particles, whereas the concentrations in the truly dissolved fraction were generally low and often below LOD. Moreover, their preferential partitioning in the solid phase was also evident in the colloidal material, especially at the TV River mouth ($r = 0.944$, $N = 5$, $0.01 < p < 0.05$) (Fig. S2). In addition, strong correlations were also found between colloidal Ni, Cr and Fe ($r = 0.905$, $N = 5$, $0.01 < P < 0.05$ and 0.986 , $N = 5$, $p < 0.001$ for Ni and Cr, respectively) and Mn ($r = 0.902$, $N = 5$, $0.01 < P < 0.05$ and 0.794 , $N = 5$, $p < 0.05$ for Ni and Cr, respectively) (Fig. S2). Normality of experimental data distributions shown in Fig. S2 was positively verified by means of the Lilliefors' test, at a 5% significance level (Lilliefors, 1967; Iman, 1982).

4. Conclusions

The evaluation of the partitioning behaviour of trace elements, as well as disparities among different estuarine systems, is supported by a MW-PCA, which was found to be an effective chemometric tool to fully extract information regarding environmental datasets. Results highlight that the major role in trace element transport and distribution is played by the SPM and that dilution processes between different water masses occurring at the river mouths are responsible for the decrease in the particulate trace element concentrations. The highest concentrations of particulate trace elements, especially in case of Pb and Cu, were found at the Timavo and Rižana River mouths, and may partially be related to the high anthropogenic pressure in these areas. On the contrary, a common lithogenic origin was ascertained for particulate Cr and Ni, which derive from alteration processes and runoff from flysch terrains outcropping in the continental area.

Regarding the partitioning behaviour among the investigated trace elements, Cu, Cr, Fe, Hg, Ni and Pb appeared to be mainly associated with the suspended particles, showed a high affinity for the colloidal material and the elevated K_p values indicated enhanced adsorption processes. Conversely, the truly dissolved fraction was identified as the dominant phase for As and Cs, especially in the marine water, whereas major differences in the partitioning behaviour were observed for Co, Mn and Zn.

Generally, colloidal Cr, Cu and Ni prevailed at the Timavo River mouth, where elevated average percentages of Cr (42.7%), Cu (17.6%) and Ni (21.8%) were found. However, compared to the SPM and the truly dissolved fraction, colloids were scarcely present at the investigated river mouths, where the hydrodynamic conditions presumably inhibit aggregation processes involving very fine particles. Results suggested that the colloidal material played a minor role in regulating trace element phase partitioning at the river mouths of the Gulf of Trieste. Future research should address to investigate the interaction of dissolved and colloidal organic matter

with trace elements in estuarine environments and in the nearby coastal lagoons, which are highly productive and organic-rich water systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Elena Pavoni: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization, Writing - review & editing. **Matteo Crosera:** Methodology, Resources, Supervision. **Elisa Petranich:** Methodology, Investigation, Resources. **Paolo Oliveri:** Formal analysis, Writing - review & editing. **Katja Klun:** Methodology, Investigation, Resources. **Jadran Faganeli:** Supervision, Project administration. **Stefano Covelli:** Investigation, Supervision, Project administration. **Gianpiero Adami:** Supervision, Project administration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.126517>.

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