Correction to: Colloidal Organic Matter and Metal(loid)s in Coastal Waters (Gulf of Trieste, Northern Adriatic Sea)

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Abstract Large volumes of seawater were sampled in the Gulf of Trieste (northern Adriatic Sea) in order to study the interactions between colloidal organic matter (COM) and metal(loid)s (Me) in coastal waters. COM (> 5 kDa) was isolated by ultrafiltration and characterized using ¹H NMR spectroscopy and elemental C_{org} and N_{tot} analyses. COM in the gulf represents about one quarter of the dissolved organic carbon (DOC), and according to ¹H NMR analysis, it is composed of polysaccharides (30–45%), lipids (30–55%), proteins and carboxyl-rich alicyclic molecules (CRAM) (15–20%), and humics (< 1%). An accumulation of COM was observed in the late spring–early summer. The polysaccharide and lipid fractions increased up to twofold and the protein fraction decreased, reflected in a higher C_{org}/N_{tot} (28, molar) ratio. Higher concentrations of humics were observed due to local freshwater discharges in spring. COM from the Isonzo/Soča River differed from the marine COM exhibiting higher protein/CRAM and higher humic contents. COM from the Isonzo/Soča mouth at salinities 16–33 was compositionally similar to marine COM. Analysis of Me, performed by ICP-MS and CVAFS (Hg), showed that Hg (nearly 100%), Cu (20%), Cr (10%), and Se (10%) have the highest Me affinity to colloids. Similar to COM, Hg and Cu rapidly increased till summer due to their sequestration in accumulated COM (transfer to particulate phase). The observed Me/C_{org} ratios (Co, Cd, Hg < U, Cr, Ni,

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Mn < As, Zn, Cu, V < Se, Al, Fe) differ somewhat from those of the Irving–Williams series and can be explained by the composition of COM and variable background concentrations of studied Me in the northern Adriatic. Data from the salinity gradient in the metal-contaminated (especially Hg, Pb, Zn) Isonzo/Soča mouth showed flocculation of Al and Ba and desorption of V, Co, As, Se, Cs, U, and Hg, from the riverine particles with increasing ionic strength, while Fe, Mn, Cu, Cr, Ni, Zn, Cd, and Pb did not correlate with salinity.

Keywords Colloidal organic matter · Dissolved organic carbon · NMR · Metals · Metalloids · Northern Adriatic Sea

Introduction

Only a small fraction of dissolved metals in seawater is present as free hydrated cations and in inorganic complexes (Donat and Bruland 1995). A great quantity of metals and metalloids (metal(loid)s–Me) in seawater is associated with organic matter (Stordal et al. 1996; Morel and Price 2003; Ravichandran 2004; Lamborg et al. 2004) influencing their biogeochemical behavior (Wells 2002; Fitzgerald et al. 2007). The size ranges that define the dissolved (DOM), colloidal (COM), and particulate organically (POM) bonded metals are nominal (Verdugo et al. 2004) and based on the pore size or the molecular weight cut-off of the filtration procedure employed (Aiken 2006). In addition to analytical difficulties, due to low concentration levels of metals and DOM in seawater, the compositional and structural complexity of DOM, consisting of various molecules of different sizes, shapes, conformations, and molecular weights and their separation, is a research challenge to determine factors governing these processes. Earlier investigations did not consider the distribution (continuum) of particles in natural waters discriminating only between particulate and dissolved phases. The development of separation procedures and analytical methods in metal-DOM investigations (Guentzel et al. 1996; Stolpe et al. 2010) and the complexometric determination of stability constants (Lamborg et al. 2004; Han et al. 2006) showed that an important fraction of dissolved metals in natural waters is bonded onto colloids (macromolecules) containing various binding sites (Wells 2002; Doucet et al. 2007). They are important in natural waters since they exhibit larger surface area and higher abundance compared to particles as well as being more reactive compared to particles and aggregating to macrogels/macroaggregates (Filella 2007).

The interactions between metals and organic matter are largely dependent on the chemical composition and structure of organic matter. The organic components contain various potential bonding sites with a range of binding constants (van Leeuwen and Buffle 2009). These seem dependent on the central heteroatom (O, N, S), structure of neighboring groups (aliphatic, aromatic, electron acceptor and donor), and stereochemistry (Aiken 2006). The bonding of metals, especially Hg, in natural waters is particularly dependent on quantitatively small DOM fractions containing thiol groups, but only a smaller part of reduced S groups, often in excess, strongly binds metals (Skylberg 2012). The variability of the nature and the content of DOM in various aquatic environments with special reference to polarity and aromaticity of molecules are therefore important factors governing the metal and DOM reactivity. The mechanisms of these processes and transformation pathways are not completely known at present (Wells 2002; Doucet et al. 2007).

The aim of this study was to investigate the interaction of COM with metals and metalloids (metal(loid)s) as a function of the COM composition and metal concentrations

present in coastal waters, using the Gulf of Trieste (northern Adriatic Sea) as an example. It is affected by various metal(loid)s, especially Hg introduced by the Isonzo/Soča river inflow as a consequence of nearly 500 years of cinnabar mining and smelting activity in Idrija (NW Slovenia), the second largest Hg mine in the world (Hines et al. 2000; Horvat et al. 2002; Faganeli et al. 2003; Covelli et al. 2006), and Pb and Zn in Raibel (NE Italy). Metal–organic matter interactions are thought to be important since they are a significant metal immobilization pathway leading to lower metal bioavailability and thus lower activity in biogeochemical processes and transport in food webs (Lamborg et al. 2004; Miller et al. 2007) as well as increasing their removal rate from the seawater column (Wen et al. 1997). Conversely, marine DOM as a bacterial substrate may also enhance Hg methylation and reduction activities (Graham et al. 2012; Schartup et al. 2015; Bratkič et al. 2018). Degradation of the colloids with bound metals would, on the other hand, release them again into the water phase.

Materials and Methods

3.1 Study Site and Sampling

The Gulf of Trieste is a shallow marine basin in the northernmost part of the Adriatic Sea (Fig. 1) approximately 500 km² in area with a maximum depth of 25 m and is partially isolated from the rest of the northern Adriatic Sea by a shoal extending SE–NW, from the Istrian peninsula to the Grado–Marano Lagoon. Vertical temperature and salinity gradients in late summer result in bottom water oxygen depletion and occasionally hypoxia and even anoxia. The main circulation is cyclonic and the outflow of seawater mostly occurs along the shallow northern coast after mixing with river waters (Solidoro et al. 2009). The mean seawater exchange rate in the gulf is about 4 weeks. The main freshwater inflow is from the Isonzo/Soča River in the north with an average flow of 82 m³ s^{−1} exhibiting late spring and autumn floods governed by snowmelt and rain, respectively. The second tributary is Timavo River, entering the gulf in the northeastern side with an average flow of approximately 30 m³ s^{−1}. Smaller coastal rivers entering the gulf on its eastern side are the Rosandra and the Ospo (discharging into the Bay of Muggia), the Rižana (discharging into the Bay of Koper), and the Dragonja (discharging into the Bay of Piran) with average flows ranging between 1 and 4 m³ s^{−1} (Cozzi et al. 2012).

Large (90–100 L) seawater samples were collected monthly from January to December 2012 from a depth of 19 m, 3 m above the bottom, at the Marine Biological Station oceanographic buoy Vida (sampling site F0) located in the southern part of the Gulf of Trieste (45°32′55.68″N, 13° 33′1.89″E) approximately 1.2 nautical miles off Piran (Fig. 1). The average winter and summer seawater temperatures at the sampling depth were 11 °C and 17 °C, respectively, and the salinity during the whole sampling period varied only slightly between 37.7 and 37.8. Water samples in the Isonzo/Soča River (Fig. 1) were collected at salinity of 0.2 and those in the Isonzo/Soča River mouth (Fig. 1) at depths of 0, 0.5 and 1 m at salinities of 16, 26 and 33, respectively, in July 2013 during low flow (50 m³ s^{−1}). All samples were collected using Niskin-X samplers.

Water samples were first gently vacuum-filtered through 0.45-μm pore-size Millipore HA membrane filters to isolate suspended particulate matter (SPM). To isolate colloids, the filtrates were additionally gently vacuum-filtered through 0.22-μm Nucleopore filters and successively ultrafiltered through a membrane with a nominal molecular weight cutoff

Fig. 1 Map of the Gulf of Trieste (northern Adriatic Sea) with sampling sites: Oceanographic buoy Vida (F0), Isonzo/Soča River and mouth

(MWCO) of 5 kDa using six Vivascience Vivaflow 200 units (Sartorius) with three Masterflex S/L membrane pumps (Cole-Palmer) at a flow rate of 300 ml min^{-1} at 2.5 bar at 20°C . The average concentration factor (CF) was 65. Retentates for COM characterization were freeze-dried and desalted by dialysis (Engel and Handel 2011) in Milli-Q water for 18 h at 4°C using MWCO 1 kDa RC membranes (Spectrapor 7, Spectrum Lab). The surrounding Milli-Q water was exchanged twice after 2 and 4 h to reduce salinity from 37 to 0.2. A schematic diagram showing the processing procedure and operational terms used in this study is depicted in Fig. 2.

3.2 Analyses

The ETHOS 1 (MILESTONE) microwave digestion system was used for the digestion and extraction of metal(loid)s. An amount of sample was weighed in acid pre-cleaned Teflon tubes and 1 ml of conc. HNO_3 (s.p., Merck) and 1 ml of H_2O_2 (30%, Merck) were added.

Fig. 2 A schematic diagram showing the processing procedure and operational terms used in this study

Microwave digestion conditions were as follows: 35 min ramp to 220 °C and hold at that temperature for 20 min. The maximum power of the microwave system was 1200 W and was automatically temperature controlled. After digestion, the samples were left to cool, and the content of Teflon tubes was quantitatively transferred to 10-ml tubes where Milli-Q water was added. For quality control and yield calculation, we used certified reference material (TORT-2), lobster hepatopancreas, from the National Research Council Canada (Table 1). Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine trace metal and metalloid contents. Prior to measurement, the standard calibration solutions were prepared from ICP Multi Element Standard solution XXI (Certipur, Merck). Measurements were done using an Agilent 7500ce instrument with an octopole reaction cell and a Babington spray chamber, which allows for the direct analyses of seawater. To reduce interferences accompanying analyses, a He mode was used while analyzing Cd, Ni, Pb, As, Co, Cr, Cu, Mo, and Zn contents and H₂ mode in Se analyses. Quality control was ensured using a certified reference material available CASS-5, Nearshore Seawater for Trace Elements, from National Research Council Canada (Ottawa, Ontario, Canada) (Table 1). For determination of Hg_{tot} levels, a double amalgamation system and detection with cold vapor atomic fluorescence (CV AFS) were used. Briefly, after the decomposition of the samples in the presence of strong acids, Hg²⁺ is reduced to volatile elemental mercury (Hg⁰) with an excess of SnCl₂ (Horvat et al. 1991). Elemental mercury is concentrated

Table 1 Certified and measured values for elements in certified TORT-2 and CASS-5 reference materials from National Research Council of Canada

Element	Certified	Measured	Certified	Measured
<i>TORT-2</i> ($\mu\text{g g}^{-1}$)			<i>CASS-5</i> ($\mu\text{g L}^{-1}$)	
V	1.64 ± 0.19	1.91	$1.32 \pm 0.14^*$	$1.31 \pm 0.20^*$
Cr	0.77 ± 0.15	0.72	0.606 ± 0.013	0.777 ± 0.101
Mn	13.6 ± 1.2	13.3	2.62 ± 0.20	2.75 ± 0.15
Fe	105 ± 13	112	1.44 ± 0.11	1.49 ± 0.13
Co	0.51 ± 0.09	0.55	0.095	0.098 ± 0.009
Ni	2.50 ± 0.19	2.16	0.330 ± 0.023	0.335 ± 0.030
Cu	106 ± 10	102	$0.880 \pm 0.053^*$	$1.14 \pm 0.17^*$
Zn	180 ± 6	188	0.719 ± 0.068	0.702 ± 0.105
As	21.6 ± 1.8	26.8	1.24 ± 0.09	1.45 ± 0.14
Se	5.63 ± 0.67	8.03	$0.50 \pm 0.05^*$	$0.62 \pm 0.09^*$
Cd	26.7 ± 0.6	29.2	$0.522 \pm 0.044^*$	$0.566 \pm 0.057^*$
Pb	0.35 ± 0.13	0.41	0.511 ± 0.045	0.567 ± 0.051
<i>BCR-61</i> ($\mu\text{g g}^{-1}$)			<i>BCR-579</i> (ng L^{-1})	
Hg	0.23 ± 0.02	0.233 ± 0.017	1.9 ± 0.5	1.96 ± 0.03
<i>IAEA140/TM</i> ($\mu\text{g g}^{-1}$)				
Hg	0.038 ± 0.006	0.039 ± 0.002		

For Hg determinations three reference materials were used, BCR-61 (IRMM), BCR-579 (IRMM) and IAEA-140/TM (IAEA). Results are presented as arithmetical means of two determinations for TORT-2, three determinations $\pm$ standard deviation for BCR-579 and six determinations $\pm$ SD for CASS-5, BCR-61, and IAEA 140/TM, respectively

*Since in the certified reference material the concentrations were too low, the material was spiked with $0.5 \mu\text{g L}^{-1}$

on a gold trap and detected after desorption at 600°C by CV AFS (Tekran mod. 2500). For method validation and further quality and accuracy control, three commercially available reference materials were used, aquatic moss (BCR-6, IRMM), coastal seawater (BCR-579, IRMM), and seaweed (IAEA-140/TM, IAEA) (Table 1). As an external standard, gas-phase Hg (Hg^0) (Tekran, model 2505 mercury vapor calibration unit) kept at 10°C was used. Detection limits for microwave digested and undigested samples are reported in Koron et al. (2013).

^1H NMR spectra of dialyzed COM samples were obtained on an Agilent Technologies VNMRs 800 MHz NMR spectrometer in D_2O at a temperature of 298 K using cold probe. Standard 1D ^1H NMR spectra were acquired using DPGFSE solvent suppression. The experimental conditions were: number of scans 256, pulse width 7.7 ms, spectral width 16,000 Hz, acquisition time 1 s and pulse delay 1.5 s. C_{org} and N_{tot} in COM were analyzed using an Elementar vario MICRO CUBE CHNS analyzer at a combustion temperature of 1020°C after vapor phase acidification with 1 M HCl, calibrated using sulfanilamide and quality control ensured with Algae (Spirulina) OAS (IVA Analysentechnik e.K.). DOC was analyzed by a high-temperature catalytic method using Shimadzu TOC 5000A analyzer after acidifying samples with 6 M HCl (Sugimura and Suzuki 1988), calibrated using K-phthalate and quality control ensured with CRM (University of Miami, FL). Precision of both methods was 3%.

Results and Discussion

4.1 Colloidal Organic Matter

COC levels increased by nearly twofold from the winter to summer months due to the microbial degradation resistance and a lag in increased bacterial production in late summer (Fonda Umani et al. 2007; Tinta et al. 2014). High DOC concentrations are generally found in late spring–early summer, but high concentrations of COC continued throughout the whole summer. In summer, when the gulf is characterized by high DOC (Faganeli and Herndl 1991; De Vittor et al. 2008) and to a lesser extent higher POC (Posedel and Faganeli 1991; Lipizer et al. 2012) concentrations, the COM can be further aggregated. DOC and POC in the gulf mostly originate from phytoplankton (Faganeli et al. 2009) mainly composed of diatoms and nanoflagellates (Mozetič et al. 2012). The phytoplankton biomass exhibits early spring and autumn maxima, while a higher primary productivity period normally appears throughout the entire spring till summer (Fonda Umani et al. 2007). COM was found to be according to $\delta^{13}\text{C}_{\text{org}}$ values, ranging between -21 and -26‰ , prevalently of phytoplankton origin ($\delta^{13}\text{C}_{\text{org}} - 21\text{‰}$) only in winter (Klun et al. 2015). In other periods, an increased terrigenous influence and the prevalence of lipids in COM, generally known with lower $\delta^{13}\text{C}_{\text{org}}$ values (Hoefs 2009), were encountered. In the Isonzo/Soča River (Table 2), the concentration of DOC ($114 \mu\text{mol L}^{-1}$), also previously reported by Bonzongo et al. (2002), was nearly at the same level as in seawater in the gulf ($58\text{--}119 \mu\text{mol L}^{-1}$) and in the Isonzo/Soča River mouth ($66\text{--}101 \mu\text{mol L}^{-1}$). Conversely, the % of COC in DOC in the river and mouth were lower ($9\text{--}16\%$) compared to seawater (25%). These contributions are on average lower than those reported by Repeta et al. (2002) for freshwaters (approx. 50%) and similar to values reported by Mopper et al. (2007) for seawater.

According to ^1H NMR spectroscopy (Fig. 3), the lipid fraction of COM ($\delta = 0\text{--}1.8$ ppm) proportionally increased by 44% toward late spring–early

Table 2 Colloidal C_{org} (COC) and N_{tot} concentrations, $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$ ratio and COC/DOC in the Isonzo/Soča River and mouth, and in the southern part of the Gulf of Trieste (sampling site F0, Klun et al. 2015)

Locality salinity	Fraction	C_{org} ($\mu\text{mol L}^{-1}$)	N_{tot} ($\mu\text{mol L}^{-1}$)	C/N (molar)	COC/DOC (%)
Isonzo/Soča River	0.2 μm filtrate	113.6	26.2	4.3	9.2
	5 kDa retentate	10.5	0.9	11.3	
	5 kDa permeate	130.3	27.3	4.8	
Isonzo/Soča mouth 16	0.2 μm filtrate	66.3	/	/	13.6
	5 kDa retentate	9.0	/	/	
	5 kDa permeate	106.9	/	/	
Isonzo/Soča mouth 26	0.2 μm filtrate	90.6	/	/	16.1
	5 kDa retentate	14.6	/	/	
	5 kDa permeate	83.9	/	/	
Isonzo/Soča mouth 33	0.2 μm filtrate	100.7	/	/	12.8
	5 kDa retentate	12.9	/	/	
	5 kDa permeate	91.4	/	/	
F0 38	5 kDa retentate	13.6–27.1	1.1–5.2	3.5–28.5	16.3–32.4

Fig. 3 Comparison of ^1H NMR spectra of COM from the Isonzo/Soča River (1) and mouth at salinity 26 (2)

summer, while the polysaccharide ($\delta = 3\text{--}4.6$ ppm) and protein ($\delta = 1.8\text{--}3$ ppm) fractions decreased, approximately by 18 and 40%, respectively (Table 3), indicating the refractory property of the summer COM also supported by its high $\text{C}_{\text{org.}}/\text{N}_{\text{tot.}}$ ratios (17–60, molar). The COM composition appears in general similar to the northern Adriatic macroaggregates (Kovac et al. 2002) and oceanic COM (Benner et al. 1992; Aluwihare et al. 1997). The refractory component at $\delta = 1.8\text{--}3$ ppm can be composed of carboxylic-rich alicyclic organic molecules—CRAM thought to be the major

Table 3 Distribution of the main groups of proton resonance in ^1H NMR spectra (δ /ppm) in COM from the Isonzo/Soča River and mouth and from the Gulf of Trieste (sampling site F0, Klun et al. 2015)

Range	Lipids $\text{HCH}_2\text{--CH}_2\text{--}$	Proteins/CRAM HC--HCOR	Polysaccharides HC--OH HC--O--C	Humics $\text{H}_{\text{Arom.}}$
δ /ppm	0–1.8	1.8–3.0	3.0–5.5	6.0–8.5
Isonzo/Soča River	37.9	25.6	32.4	4.1
Isonzo/Soča mouth 16	39.3	13.2	46.9	0.5
Isonzo/Soča mouth 26	42.6	13.2	43.8	0.4
Isonzo/Soča mouth 33	41.3	13.8	44.3	0.6
F0/Period				
Jan' 12	33.2	20.4	46.1	0.3
Apr' 12	38.4	14.8	45.9	0.9
May' 12	36.9	14.0	48.6	0.5
Jun' 12	43.1	12.6	43.8	0.5
Jul' 12	47.9	13.1	38.8	0.3
Aug' 12	44.8	15.1	39.3	0.8
Sep' 12	47.9	15.8	35.5	0.8
Oct' 12	42.9	14.5	41.7	0.8
Nov' 12	59.9	13.4	26.3	0.4
Dec' 12	46.4	15.9	27.2	0.4

component of the lacustrine (Lam et al. 2007) and marine DOM (Hertkorn et al. 2007). In contrast to Repeta et al. (2002), we found some compositional differences between marine and riverine COM. It was especially notable in > 10-fold higher humic content ($\delta = 6\text{--}8.5$ ppm) in the Isonzo/Soča river mouth samples and in the higher proportion of structural component at $\delta = 1.8\text{--}3$ ppm (Table 3), likely composed of CRAM derived from cyclic and linear terpenoids (Lam et al. 2007). The lower resolution of the riverine COM ^1H NMR spectrum compared to marine spectra (Fig. 3) could indicate the greater macromolecular/aggregated nature of riverine COC (Lam et al. 2007). The composition of COM at salinity 16 and higher salinities was similar to marine COM, suggesting flocculation of riverine colloids at a higher ionic strength.

4.2 Metals and Metalloids in Dissolved and Colloidal Phases

The concentrations of dissolved Al, Cr, Mn, Fe, Cu, Zn, Se, and Hg in the gulf (Table 4) varied during the year, while those of V, Co, Ni, As, Cd, Cs, Ba, and U were nearly constant. Among them, the concentrations of Cr, Mn, Cu, and Hg increased in summer. The majority of dissolved metal(loid)s, except Se, Cu, Zn, and Ni, were at the same concentration level as previously reported by Koron et al. (2013) for the Gulf of Trieste and similar to those reported in other, including Mediterranean, estuarine, and coastal waters (Ourisel et al. 2013; Stolpe et al. 2010; Wen et al. 1999) but substantially higher than those reported for the ocean surface (Donat and Bruland 1995). Hg (nearly 100%), Cu (20%), Cr (11%), and Se (11%) showed the highest percentages of colloiddally bonded metal(loid)s. These levels are also comparable to those of Koron et al. (2013). In the Isonzo/Soča River (Table 5), dissolved metal concentrations were comparable to the world average river

Table 4 Average metal and metalloid concentrations in dissolved, colloidal, and particulate (SPM) fractions ($N=11$) from the southern part of the Gulf of Trieste (sampling site F0)

	Dissolved metal(loid)s (nmol L ⁻¹)	Colloids (nmol L ⁻¹)	Colloidally bonded (%)	SPM (nmol L ⁻¹)
Al	334 ± 248	2.9 ± 2.9	1.5	1595
V	38	1.1 ± 0.1	3	1.5
Cr	12	0.8 ± 0.3	11	2.5
Mn	28	0.6 ± 0.4	7.5	16
Fe	223	17.0	7.6	342
Co	1	0.05 ± 0.01	5	0.2
Ni	15	0.5 ± 0.1	4	0.8
Cu	41	4 ± 0.3	20	1.5
Zn	71	1.7 ± 0.7	1.3	3.5
As	20	0.70 ± 0.07	3	0.2
Se	15	2.9 ± 0.5	11	0.05
Cd	1	0.010 ± 0.003	1	0.35
Cs	2 ± 0.3	0.030 ± 0.004	1.5	/
Ba	46 ± 38	0.50 ± 0.09	1.5	0.75
U	13 ± 1	0.20 ± 0.02	1.7	0.4
Hg	0.003	0.004 ± 0.003	100	0.03

Table 5 Metal and metalloid concentrations in dissolved, colloidal, and particulate (SPM) fractions from the Isonzo/Soča River

	Dissolved metal(loid)s (nmol L ⁻¹)	Colloids (nmol L ⁻¹)	Colloidally bonded (%)	SPM (nmol L ⁻¹)
Al	2023	28.9	1.4	1595
V	4	0.13	3	1.5
Cr	4	0.51	13	2.5
Mn	17	0.6	3.5	16
Fe	751	18.2	2.4	342
Co	0.5	0.025	5	0.2
Ni	6	0.78	17	0.8
Cu	8	2.6	33	1.5
Zn	77	2.63	3.4	3.5
As	1	0.06	6	0.2
Se	0.9	BDL	BDL	0.05
Cd	0.04	0.001	2.5	0.35
Cs	0.08	0.03	38	/
Ba	166	6.27	3.8	0.75
U	0.26	0.001	0.4	0.4
Hg	0.003	0.004	100	0.03

BDL below detection limit

values (Gaillardet et al. 2003) including small Mediterranean rivers (Oursel et al. 2013). Hg (100%), Cs (38%), and Cu (33%) showed the highest affinity to colloids followed by Ni (17%) and Cr (13%).

For, V, Co, Ni, Cd, Cs, Ba and U in the gulf's waters, the concentrations of colloiddally bonded were approximately constant (Fig. 4), suggesting that the COM and DOM do not influence the fate of colloidal bonded meta(lloid)s since the concentration and composition of COM and DOM were temporarily changing (De Vittor et al. 2008; Klun et al. 2015). Conversely, the concentrations of Al, Cr, Mn, Fe, Cu, Zn, Se, and Hg were temporarily changed probably originating from terrestrially sources (Fig. 4). Hg and Cu showed the highest affinity to colloidal organic matter, since they were positively correlated with COC ($R^2_{\text{Hg}}=0.56$; $R^2_{\text{Cu}}=0.68$) reported in Klun et al. (2015). Hg is considered a soft metal with light polarizable outer electron orbitals, and it is bonded to soft ligands, i.e., sulfur-containing functional groups (Fitzgerald et al. 2007). Cu is a hard metal with heavy polarizable outer electron orbitals also bonded with high stability constants onto oxygen-containing functional groups (Midorikawa and Tanoue 1998a, b). CRAM rich in carboxylic groups are possible structural candidate. Previous FTIR analyses of COM from the Gulf of Trieste indicated the presence of OH (carbohydrates and lipids)-, COOH (proteins and

Fig. 4 Seasonal variations of total dissolved Hg (Hg_{tot}) and colloidal Hg (Hg_{coll}), Mn, Cu, Zn, Cr, Co, and Ni at Oceanographic buoy Vida (F0)

lipids)-, and NH (proteins)-containing functional groups (Klun et al. 2015). Colloidal Hg and Cu contents were increased in parallel with COM contents until early summer but afterward rapidly decreased. It appears that Hg and Cu in late summer can be less bonded to COM (>5 kDa), but more to LMW DOC. In the Isonzo/Soča River mouth, the colloidal metal(loid)s V, Co, As, Se, Cs, U, and Hg, with a positive correlation with salinity (Table 6), may originate from riverine particle desorption. Among them, Hg is significantly bonded onto the particulate phase in seawater and river water (Tables 4, 5) in oxides and sulfides (Stolpe et al. 2010). Oursel et al. (2013) showed desorption of Cu, Cd, Co, Pb, and Zn from suspended particles into dissolved phase in the salinity gradient of small Mediterranean river mouths. Metals Al and Ba with a negative correlation with salinity may be transferred (flocculated) into particulate phase at higher ionic strengths (Sanudo-Wilhelmy et al. 1996). Colloidal Fe, Mn, Cu, Cr, Ni, Zn, Cd, and Pb showed non-conservative mixing behavior with salinity. Similar was reported by Tang et al. (2002) for dissolved Ni, Zn, Pb, Cd, and Cu in Galveston Bay and explained by their binding to reduced sulfur compounds.

4.3 Metal(loid)/Organic Carbon ($\text{Me}/\text{C}_{\text{org}}$) Ratios in Colloids

Since C_{org} is a major organic constituent in marine colloids and carrier of accompanying metals (Guo and Santschi 1997; Ravichandran 2004), the metal concentrations can be normalized to C_{org} (Table 7). This permits the comparison of our results with those in marine colloids reported elsewhere (Guo et al. 2000; Guo and Santschi 2007). The C_{org} normalization reveals that the majority of $\text{Me}/\text{C}_{\text{org}}$ ratios in the gulf ranged between 1×10^{-5} and 8×10^{-5} . The exceptions are Fe (67), Al (21) and Se (14) at the upper side and Co (0.3), Cd (0.04), Cs (0.2) and Hg (0.02) at the lower side. For metals with constant concentration levels, $\text{Me}/\text{C}_{\text{org}}$ ratios decreased in summer due to the increase in C_{org} content. $\text{Hg}/\text{C}_{\text{org}}$ ratio increased, up to fivefold, from winter to early summer as a consequence of higher COM content and higher available complexing

Table 6 Concentrations of colloidal metals and metalloids (nmol L^{-1}) in the Isonzo/Soča River and mouth and correlations between colloidal metal(loid)s and salinity including sampling point F0 (salinity 37) in the gulf ($N=5$)

Locality	Salinity	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Isonzo Mouth 33	33	18.63	1.02	0.63	1.55	12.79	0.07	0.75	0.82	6.91
Isonzo Mouth 26	26	7.70	0.86	0.46	1.93	13.08	0.05	0.48	1.74	2.35
Isonzo Mouth 16	16	23.97	0.43	0.33	1.99	5.83	0.03	0.33	0.95	BDL
Isonzo/Soča River	0.2	28.97	0.13	0.51	0.57	18.17	0.03	0.78	2.56	2.63
Correlation versus Salinity R^2		-0.68	0.97	0.38	0.03	0	0.75	0.05	-0.02	0.05
	Salinity	Se	As	Cd	Cs	Ba	Pb	U	Hg	
Isonzo Mouth 33	33	1.87	0.64	0.05	0.06	1.61	0.04	0.21	0.003	
Isonzo Mouth 26	26	1.00	0.55	0.03	0.04	2.08	0.02	0.21	0.004	
Isonzo Mouth 16	16	0.37	0.28	0.01	0.01	3.35	0.01	0.11	0.002	
Isonzo/Soča River	0.2	BDL	0.12	BDL	BDL	6.27	0.02	0.01	0.001	
Correlation versus Salinity R^2		0.92	0.97	0.31	0.75	-0.98	0.29	0.91	0.71	

BDL below detection limit

Table 7 Comparison of average metal and metalloid affinity to COM ($\text{Me}/\text{C}_{\text{org.}} \times 10^{-5}$; molar ratio, $N=11$) with previous studies in the Gulf of Trieste (Koron et al. 2013) and in the Gulf of Mexico and Mid-Atlantic Bight (Guo et al. 2000)

	Gulf of Trieste	Gulf of Trieste (Koron et al. 2013)	Gulf of Mexico (Guo et al. 2000)	Central Atlantic (Guo et al. 2000)
Al	21.1 ± 20.9	62.3	2.8 ± 2.5	3.3 ± 2.6
V	6.8 ± 0.4	6.1	0.26 ± 0.31	0.34 ± 0.39
Cr	5.4 ± 8.8	1.8	2.6 ± 1.1	20 ± 24
Mn	3.2 ± 1.8	1	0.23 ± 0.18	1.1 ± 1.2
Fe	66.9 ± 31.9	/	/	/
Co	0.28 ± 0.04	/	0.083 ± 0.053	0.12 ± 0.01
Ni	2.5 ± 2.3	2.5	1.6 ± 1.0	5.5 ± 4.3
Cu	7.4 ± 2.8	19.2	1.93 ± 0.0	2.5 ± 1.9
Zn	8.3 ± 4.2	8.9	8.8 ± 6.7	2.8 ± 2.6
As	3.6 ± 0.8	3.5	/	/
Se	14.1 ± 3.1	1.4	/	/
Cd	0.04 ± 0.01	/	0.013 ± 0.08	0.059 ± 0.052
Cs	0.15 ± 0.04	/	/	/
Ba	2.7 ± 0.5	3.8	0.031 ± 0.014	0.084 ± 0.050
U	1.1 ± 0.2	1.2	/	/
Hg	0.02 ± 0.02	0.03	/	/

functional groups, for example N-containing macromolecules (aminopolysaccharides) (Hunter and Beveridge 2008) carboxyl (Quigley et al. 2002) and especially S-containing functional groups (Xia et al. 1999; Alvarado Quiroz et al. 2006; Skyllberg 2012). Comparison with colloids in macroaggregates from the gulf (Koron et al. 2013) revealed higher values, especially for Cr, Mn, and Ni, in macroaggregate interstitial water colloids due to a higher COM content in macroaggregates. The majority of $\text{Me}/\text{C}_{\text{org.}}$ ratios in the Isonzo/Soča River mouth were in the same order as those in the waters of the gulf with the exception of lower ratio of Se (3–15) and with higher ratios of Al (48–176), Fe (43–100) and Ba (13–25) originating from Isonzo/Soča River (Table 7). High $\text{Me}/\text{C}_{\text{org.}}$ ratios of Al, Fe, and Ba may partially originate from inorganic colloids.

Some differences were observed between the Irving–Williams order of binding strength of metals with organic ligands, i.e., $\text{Cd}, \text{Mn} < \text{Co} < \text{Zn}, \text{Ni} < \text{Cu} < \text{Hg}$, and our $\text{Me}/\text{C}_{\text{org.}}$ ratios in the gulf's waters, i.e., $\text{Cd}, \text{Co}, \text{Cs}, \text{Hg} < \text{Ni}, \text{U}, \text{Cr}, \text{Mn}, \text{Ba} < \text{Zn}, \text{Cu}, \text{As}, \text{V} < \text{Se}, \text{Al}, \text{Fe}$. Our order was more similar to plankton (Millero 2006) due to affinity of metals to the COM of the gulf, composed mainly of heteropolysaccharides and lipids of plankton origin (Klun et al. 2015), and specific concentration ranges of metal(loid)s in the waters of the gulf. The colloidal $\text{Me}/\text{C}_{\text{org.}}$ ratios order in the Isonzo/Soča River were different $\text{Hg}, \text{Cs}, \text{Cd} < \text{U} < \text{Co} < \text{V} < \text{Cr}, \text{Mn} < \text{Ni} < \text{Cu} < \text{Zn} < \text{Ba} < \text{Fe} < \text{Al}$, more similar to reported metal–humic association in river waters (Hiraide et al. 1994) in accordance with higher humic and CRAM contents. Al may be bonded in inorganic colloids. Comparison with other marine areas (Table 7) shows that the affinity of metals Al, V, Mn, Co, Cu, Cd, and Ba onto colloids is higher in the Gulf of Trieste compared to the Gulf of Mexico and central Atlantic (Guo et al. 2000). This can be due to higher concentration levels of dissolved metal(loid)s and COM in the coastal waters of the Gulf of Trieste.

Conclusions

COM in the Gulf of Trieste, isolated by ultrafiltration, represents about one quarter of dissolved organic carbon (DOC) and, according to ^1H NMR analysis, it is composed of polysaccharides (30–45%), lipids (30–55%), proteins and carboxyl-rich alicyclic molecules (CRAM) (15–20%) and humics (<1%). Higher concentrations of humics were observed due to local freshwater discharges in spring. COM from the Isonzo/Soča River, the principal tributary to the gulf, differed from the marine COM exhibiting higher protein/CRAM and higher humic contents. COM from the Isonzo/Soča River mouth at salinities of 16–33 was compositionally similar to marine COM. In the gulf, analysis of metal(loid)s, performed by ICP-MS and CVAFS (Hg), showed that Hg (nearly 100%), Cu (20%), Cr (10%) and Se (10%) have the highest affinity to colloids. Similarly to COM, the levels of colloidal Hg and Cu increased till summer, due to their sequestration in accumulated COM (transfer to particulate phase), but later decreased. The observed $\text{Me}/\text{C}_{\text{org}}$ ratios (Co, Cd, Hg < U, Cr, Ni, Mn < As, Zn, Cu, V < Se, Al, Fe) differ somewhat from those of the Irving–Williams series and can be explained by the composition of COM and variable background concentrations of studied metal(loid)s in the northern Adriatic. Data from the salinity gradient in the Isonzo/Soča River mouth suggested flocculation of Al and Ba and desorption of V, Co, As, Se, Cs, U, and Hg from the riverine particles with increasing ionic strength while Fe, Mn, Cu, Cr, Ni, Zn, Cd, and Pb did not correlate with salinity. These results can contribute to a better understanding of the temporal dynamics of COM, as an important metal carrier, in coastal waters affected by the metal-contaminated river inflows. Since the colloiddally bonded metal(loid)s can be less bioavailable to plankton these data can help to establish their levels at the base of the coastal/estuarine food web at the onset of marine bioaccumulation.

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