

Environmental implications of metal mobility in marine sediments receiving input from a torrent affected by mine discharge

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Abstract

Acid Mine Drainage (AMD) is one of the most important sources of pollution in fluvial systems and can enrich rivers in dissolved and suspended metals of environmental concern. Colloidal particles may favour the transport of metals to the sea, where metals can be accumulated in bottom sediments.

The aim of this paper was to evaluate the mobility of metals in the “Baia delle Favole” bottom sediments (Sestri Levante, Italy), which receive the input of the AMD impacted Gromolo Torrent, using chemical speciation (BCR sequential extraction).

Basing on the Risk Assessment Code (RAC), our results showed a systematic and widespread high risk classification for Mn, whereas a medium risk is associated to Co, Cu, and Zn in the sediments collected near the mouth of the Gromolo Torrent. Moreover, in these sediments the occurrence of Fe oxyhydroxides has been observed, reflecting an increase of metals in the reducible fraction obtained with BCR.

Introduction

Rivers and torrents bring to the sea their load of sediments, organic matter, and even pollutants if they are impacted by anthropic activities. Mining areas represent important sources of pollution for the riverine system, and water and sediments can be usually enriched in elements of environmental concern (Frau et al., 2015). This fact is particularly true for sulphide mineralisations, as the dissolutive oxidation of sulphide minerals, in particular Fe sulphides, leads to the formation of acidic and metal-rich solutions, known as Acid Mine Drainage (AMD; Blowes et al., 2014; Moodley et al., 2017). The detrimental effects of AMD on both the environment in which rivers discharged their metal load (Albert et al., 2017; Nieto et al., 2013; Parker et al., 2007; Torres et al., 2013) and the biota (Cantonati et al., 2014; Casiot et al., 2009; Lavoie et al., 2012; Rimondi et al., 2012; Sarmiento et al., 2017; Wang et al., 2018) have been the subject of numerous investigations.

When the river drains its load of AMD-derived metals to sea, metals can be deposited in the bottom sediments and/or diffused by the currents and also on the marine environment in which these streams spill their waters (Hierro et al., 2012; Morillo et al., 2004). When AMD mixes with alkaline waters, the formation of Fe and Al colloidal precipitates takes place. This process can happen both in estuarine environment (Asta et al., 2014), if AMD directly flows to the sea, or in fluvial waters (Schemel et al., 2000; Serrano et al., 2015). Whether formed in seawater or transported by rivers, Fe and Al colloidal particles control the dispersion of elements to the bottom sediments, particularly in highly dynamic environment and sandy sediments. Bottom sediments receives the input from contaminated rivers and are enriched in metals deriving from mine drainages (Nieto et al., 2007) both during mining activities and after mine closure. In fact, metal discharge still continues to be present even after the closing of mining operations (Mil-Homens et al., 2016). The effects of this contaminant supply can also be observed in animals living inside or in contact with sediments (Gusso-Choueri et al., 2016; Levings et al., 2005; Netto et al., 2013). For all these reasons, the understanding of the metal speciation inside sediments, in particular of their mobility and availability to biota, is a key issue in evaluating the quality of the marine environment. Moreover, in the case of sediment dredging and/or disposal, metals can be mobilised from sediments due to variations of environmental conditions (pH, temperature, etc.; Carroll et al., 2002; Torres et al., 2009) and data of speciation analysis can provide important information for sediment management.

A widely applied technique to the study of the metal behaviour in soils and sediments that can provide important information on metal mobility and insight into biogeochemical pathways is represented by sequential extraction. Many different schemes have been developed, and some of these procedures have also been specifically designed for sediments impacted by mine drainage (Dold, 2003; Tessier et al., 1979; Torres and Auleda, 2013). The most used sequential extraction scheme applied to the sediment study is the BCR procedure, proposed by the European Community Bureau of References (Ure et al., 1993) and subsequently modified and improved (Quevauviller et al., 1997; Rauret et al., 1999, 2001; Sahuquillo et al., 1999). This scheme has been also applied to marine environments impacted by mining activities (e.g. Morillo et al., 2004, 2005, 2007, 2008; Shumilin et al., 2011).

In the present work, we applied the modified sequential extraction procedure proposed by the Community Bureau of Reference (hereafter BCR-SE; Quevauviller et al., 1997; Rauret et al., 1999, 2001; Sahuquillo et al., 1999; Ure et al., 1993) to the bottom sediments of the “Baia delle Favole” (Sestri Levante, NW Italy). The aim was to evaluate the mobility of metals in these sediments, which are enriched in metals due to the input of the Gromolo Torrent, which receives AMD from the abandoned Cu mine of Libiola.

Study area

The studied area (Fig. 1), the bay known as “Baia delle Favole”, has been chosen as it receives sediments from the heavily contaminated Gromolo Torrent. The derelict Cu mine of Libiola, the most important mining area of the Ligurian ophiolites mine district, is located in the Gromolo Torrent basin. Previous studies on the mining area and torrent sediments highlighted high concentrations of metals, such as Cd, Cu, Ni, and Zn (Carbone et al., 2013; Consani et al., 2016, 2017; Dinelli et al., 2001). In particular, the Gromolo Torrent downstream the mining area is severely impacted

by metals. The concentration of Cu and Zn in the sediments abruptly rises, and the mineralogy becomes dominated by amorphous Fe phases (Consani et al., 2017). The diatom community stress testifies the detrimental effect of metals on biota in the torrent (Tolotti et al., 2019). Capello et al. (2016) observed enrichments in metals in the marine sediments of the studied area, related to the sedimentary input of the Gromolo Torrent.

Geologically, rocks forming the “Val di Vara Supergroup” outcrop in the studied area (ISPRA, 2011). Such rocks represent an ophiolitic sequence with the oceanic crust (peridotites, serpentinites, basalts, gabbros, and breccias) and its sedimentary cover (jaspers, limestones, and shales). The mineralisation of the Libiola mine, mainly hosted inside basalts, consists of bodies of pyrite and chalcopyrite, with subordinate pyrrhotite and sphalerite (Garuti and Zaccarini, 2005; Zaccarini and Garuti, 2008).

The flow of the AMD adits and the Gromolo Torrent are irregular on seasonal and also inter-annual time scales, depending on the Mediterranean climate characterised by a rainfall maximum in autumn (over 180 mm) and a dry season in summer (Provincia di Genova, 2013). The torrent annual mean flow is $0.86 \text{ m}^3 \text{ s}^{-1}$ with the maximum of $1.42 \text{ m}^3 \text{ s}^{-1}$ in December and the minimum of $0.10 \text{ m}^3 \text{ s}^{-1}$ in August.

The sea currents in the studied area are characterised, as reported by Doglioli et al. (2004a, 2004b), by the presence of a permanent northwestward current flowing roughly along the isobath and following the narrow shelf, with only short inversion periods (Fig. 1). A south-eastward gyre is generated by the presence of the headland (Doglioli et al., 2004a) and, moreover, an eastward counter-current is present along the north coast with a resulting drift of the coastal materials from the Entella Torrent to the “Baia delle Favole” area (CNR and MURST, 1997; Fig. 1).

The presence of this gyre guided us for the choice of the sampling points (Fig. 1) to be tested with modified BCR-SE. Three different groups, each composed by four samples, have been selected in order to test the whole studied area, whereas a control sample (named “Bianco”) has been collected on the other side of the headland of Sestri Levante (in front of the eastern bay). Group A is composed by samples (2, 3, 6, and 35, in black in Fig. 1) collected immediately in front of the mouth of the Gromolo Torrent. Group B (samples 5, 9, 12, and 14, in red in Fig. 1) is located along the coastal drift. Group C (samples 11, 18, 22, and 24, in blue in Fig. 1) aims at investigating the sediments offshore the “Baia delle Favole”.

Materials and methods

Superficial bottom sediments were sampled using a 5-L Van Veen grab. About 500 mL of sediment was collected at each station and stored in wide-necked plastic jars.

The total elemental content of the investigated elements, except Cd, was obtained by X-ray Fluorescence spectrometry on pressed powder pellets on aliquots of sediments previously dried and grounded in an agate mortar. An Axios 4000 spectrometer was used for the analysis. Cd was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis on 0.5 g of dry and ground sample after modified Aqua Regia (AR) digestion (ISO15587) at the Bureau Veritas Mineral Laboratories (Canada; ISO9001 Quality Management Systems).

The BCR-SE, proposed by the European Community Bureau of Reference (Quevauviller et al., 1997; Rauret et al., 1999, 2001; Sahuquillo et al., 1999; Ure et al., 1993), was applied to the sediment samples. This procedure has been standardised and certified material with known release values in each step is supplied. These facts make the modified BCR-SE procedure a good tool to evaluate metal partitioning in sediment, information useful to delineate sources, identify processes, evaluate mobility and develop management scenario for studied sediment. This procedure operationally identifies the amount of metal bound to different sediment fraction:

- the first fraction comprises exchangeable and acid-extractable metals, such as adsorbed metals and elements contained in carbonates and labile organic compounds;
- the second fraction includes the metals bound to the reducible fraction, such as Mn^{4+} and Fe^{3+} oxides and hydroxides;

- the third one is the fraction which can be mobilised by oxidation, such as metals bound to organic matter and sulphides;
- a fourth fraction, the residual one, including silicates, highly insoluble sulphides, and refractory organic compounds, was not directly solubilised but obtained from the difference between the total content and the three fractions derived from the application of the sequential scheme.

Briefly, acid-labile fraction was extracted with 0.11 M acetic acid; reducible fraction with 0.5 M hydroxylamine hydrochloride adjusted to pH 1.5 with nitric acid (65%) and oxidisable fraction with 8.8 M hydrogen peroxide, followed by 1 M ammonium acetate, adjusted to pH 2 with nitric acid (65%).

Blank analysis of each step of sequential extraction was also carried out, showing negligible contamination.

Each sample was digested in duplicate, and each analytical batch for each step included a blank and the reference material BCR-701. In addition to the certified elements (Cd, Cr, Cu, Ni, Pb, and Zn), also the concentration of other metals of environmental concern, such as Co, Mn, and V have been measured in the leachates.

The BCR-SE leachates were filtered at 0.45 μm and analysed by ICPOES at the Dipartimento di Scienze Biologiche, Geologiche e Ambientali of the University of Bologna. A Thermo Scientific iCAP 6000 series ICP Emission Spectrometer was used for the determination of dissolved elements. Detection limits in solution for the analysed elements were the following: 0.5 $\mu\text{g L}^{-1}$ for Cd, 1 $\mu\text{g L}^{-1}$ for Co, 2 $\mu\text{g L}^{-1}$ for Cr, 2 $\mu\text{g L}^{-1}$ for Cu, 5 $\mu\text{g L}^{-1}$ for Fe, 2 $\mu\text{g L}^{-1}$ for Mn, 2 $\mu\text{g L}^{-1}$ for Ni, 2 $\mu\text{g L}^{-1}$ for Pb, 2 $\mu\text{g L}^{-1}$ for V, 2 $\mu\text{g L}^{-1}$ for Zn. The certified reference material, labelled BCR-701, is a lake sediments from the Orta Lake (Italy), well-known for having serious metal contamination (Pueyo et al., 2001). The comparison of the results obtained in our lab and the certified ones, already reported in a recent study part of the same research project of the present manuscript (Consani et al., 2019), are presented in Table 1, which report the average and the standard deviation on 10 independent extraction runs. In general, the repeatability of the measurements is good, always within a 10% relative error. Higher dispersion was observed for Cd, Ni, and Zn in step 3. The results were in good agreement, as the differences between the observed and the reported values were in the range of the uncertainties of the measurements, expressed with standard deviations for measured values as confidence interval for the certified ones. Cu, Ni, and to a minor extent Zn recovery in step 3 was not satisfying. In particular, the recovery of Cu and Zn was higher than the certified values, whereas Ni had a lower recovery. For this reason, data

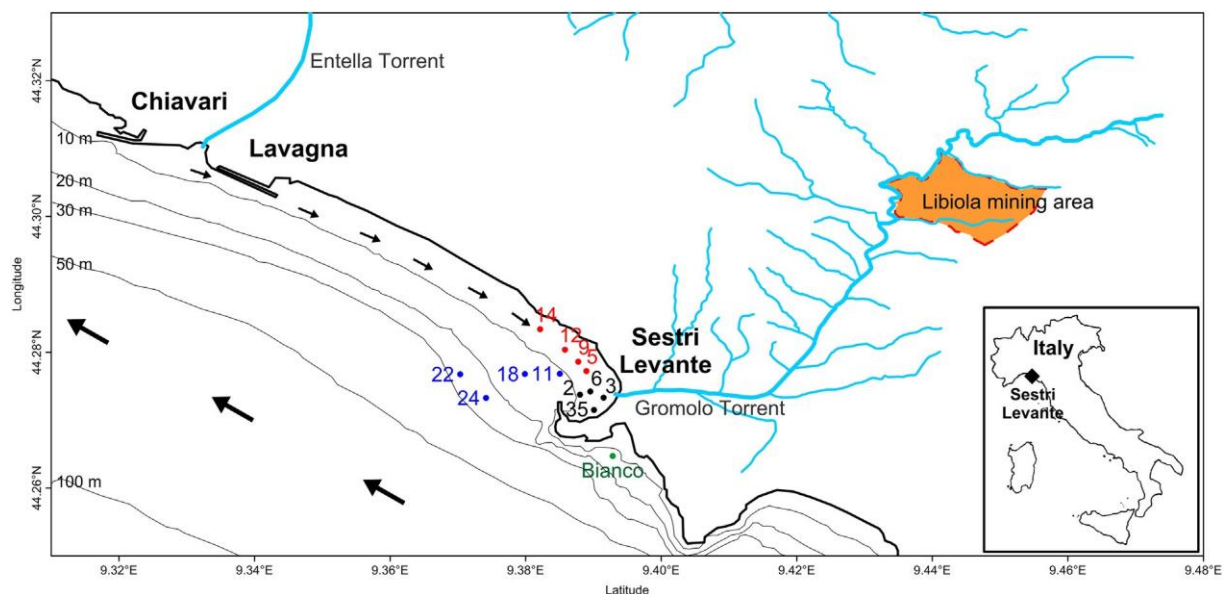


Fig. 1. Simplified sketch of the studied area and position of the sampling sites. In the map on the bottom left, the dynamics of the area (black arrows) is shown.

regarding these metals in oxidisable fraction will be discussed keeping in mind the not complete reliability of absolute values, as suggested also by the higher standard deviations observed in the reference material.

The results regarding Cd on the certified material were satisfactory, but the overall sum of the fraction extracted for the sediment samples resulted greater than the result of the AR digestion. Heterogeneity of the sample or not complete mineralisation of Cd-bearing phases could be possible explanation. Despite the problems encountered in the analyses, we kept Cd results for the three fractions in our discussion basing on the fact that those problems did not originate from errors in the extraction procedure.

XRD diagrams were collected before and after each step of the modified BCR-SE with a Philips PW1140 diffractometre in order to observe selective dissolution of minerals. Samples were first ground in an agate mortar, and then mounted on zero-background silicon plates. The diffractometre was equipped with a radiogenic tube with a Co anode (producing X-rays with a wavelength of 1.78901 Å), the current was set at 20 mA, and the voltage at 40 kV. Each sample was scanned between 5° and 70° 2θ with a step size of 0.02° 2θ with an acquisition time of 1 s per step.

Scanning electron microscope (SEM) observations were performed on selected samples using a Tescan Vega 3 LMU scanning electron microscope equipped with an energy-dispersive spectrometer (EDS) EDAX Apollo X SDD, at 20 kV accelerating voltage, 1.2 nA beam current, and 5–10 µm beam diameter.

Results and discussion

Sediment characterisation

The bulk chemistry of the analysed sediments is reported in Table 2, along with the absolute concentration of the elements in the leachates of the BCR-SE. In general, the “Bianco” sample had a lower concentration of metals compared to the samples collected inside the “Baia delle Favole”. Among the investigated elements, excluding Fe, Cr and Mn showed the highest total concentration (up to 1813 and 1168 mg kg⁻¹, respectively). Some elements, such as Co, Pb, and V showed a uniform distribution in the “Baia delle Favole” sediments, whereas Cu (maximum of 380 mg kg⁻¹), Zn (maximum of 210 mg kg⁻¹), and Ni (maximum of 465 mg kg⁻¹) tended to have higher concentrations in samples of Group A. Finally, it is worth noting that for all the tested elements, the concentration in the oxidisable fraction invariably decreased westward along the coastal transect formed by samples of Group B (from sample 5 to sample 14). The distribution of the investigated elements will be reported and discussed in the following paragraphs, grouping elements with common partitioning.

Table 1

Concentration of metals extracted following the modified BCR-SE procedures on the CRM BCR-701 standard sample compared with the certified values. For the measured concentrations, the standard deviations are reported in parentheses; for certified values, uncertainty (in mg kg⁻¹) is reported in parentheses.

	Obtained values (mg kg ⁻¹)						Certified values					
	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn
Step 1	7.15 (0.15)	2.30 (0.17)	52.51 (1.26)	15.1 0 (0.42)	2.98 (0.14)	197.4 4 (7.23)	7.34 (0.40)	2.26 (0.16)	49.30 (1.70)	15.4 0 (0.90)	3.18 (0.21)	205.0 0 (6.00)
Step 2	3.69 (0.37)	44.85 (1.25)	121.6 3 (3.54)	26.7 3 (1.17)	112.9 3 (1.32)	110.7 8 (3.47)	3.77 (0.28)	45.7 0 (2.00)	124.0 0 (3.00)	26.6 0 (1.30)	126.0 0 (3.00)	114.0 0 (5.00)

Step	0.27	153.2	70.55	10.1	7.93	33.25	0.27	143	55.20	15.3	9.28	45.70
3	(0.18	5	(4.15)	2	(1.45)	(11.36	(0.06	(7.00)	(4.00)	0	(2.00)	(4.00)
)	(13.81		(2.87))			(0.90		
)))		

Table 2

Localisation of samples, concentrations (in mg kg⁻¹) of the tested elements in the sediments, and concentration (in mg kg⁻¹) in the leachates of the various steps.

-1 = step 1; -2 =step 2; -3 =step 3; -res =residual fraction; AR = Aqua Regia; total =total concentration. n.c. = not computed.

Samples	2	3	6	35	5	9	12	14	11	18	22	24	Bianco
Latitude (° N)	44.2738	44.2733	44.2742	44.2715	44.2772	44.2786	44.2804	44.2834	44.2769	44.2768	44.2768	44.2733	44.2647
Longitude (° E)	9.3880	9.3915	9.3896	9.3901	9.3890	9.3878	9.3858	9.3822	9.3851	9.3799	9.3703	9.3742	9.3928
Depth (m)	0	2.8	6	3	7.1	7	7	7	10	13.9	26	23.1	15
Sample group	A	A	A	A	B	B	B	B	C	C	C	C	
Cd-1	0.08	0.03	0.07	0.03	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Cd-2	0.27	0.02	0.26	0.27	0.04	0.02	0.04	0.04	0.07	0.25	0.24	0.02	0.10
Cd-3	0.02	0.17	0.02	0.02	0.15	0.12	0.02	0.02	0.02	0.02	0.02	0.06	0.02
Cd-res	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Cd AR	0.25	0.11	0.20	0.09	0.08	0.09	0.07	0.10	0.09	0.07	0.08	0.09	0.12
Co-1	6.01	4.90	5.78	4.58	3.02	2.30	3.13	2.24	3.24	2.88	2.56	3.76	0.49
Co-2	7.87	7.51	7.93	7.82	4.60	5.07	4.57	3.93	4.76	5.25	5.42	5.15	1.05
Co-3	2.81	2.04	2.76	2.52	1.38	1.72	1.05	0.83	1.25	1.86	1.89	1.49	0.35
Co-res	21.3	23.6	22.5	29.1	20.0	19.9	18.3	24.1	19.8	29.9	27.1	32.6	5.1
Co total	38	38	39	44	29	29	27	31	29	40	37	43	7
Cr-1	2.38	2.08	2.56	2.14	1.81	2.12	1.72	1.65	2.01	1.45	1.00	1.71	0.79
Cr-2	17.2	15.3	17.5	19.9	12.9	12.9	14.3	12.7	14.0	13.6	10.4	11.7	4.0
Cr-3	32.6	30.6	32.5	27.1	26.5	21.1	15.1	12.9	19.9	22.9	20.8	20.0	3.2
Cr-res	553.8	393.0	656.4	700.9	642.8	590.9	446.9	1785.8	499.1	374.0	303.8	276.6	181.0
Cr total	606	441	709	750	684	627	478	1813	535	412	336	310	189
Cu-1	65.8	37.9	73.6	35.3	4.76	2.93	2.92	1.74	5.70	4.94	6.16	6.75	0.76
Cu-2	130	84.3	141	109	15.2	10.9	11.2	7.2	15.9	15.7	20.1	16.3	3.90
Cu-3	63.2	50.2	59.2	45.2	5.43	3.03	2.83	0.89	4.54	4.59	7.94	4.21	1.08
Cu-res	101	108	106	111	21	31	19	14	23	54	61	43	6
Cu total	360	280	380	300	46	48	36	24	50	80	95	70	12
Fe-1	249	285	213	340	206	135	179	290	261	226	306	395	131
Fe-2	2651	2249	2696	2711	1559	1547	1539	1425	1675	1580	1796	1765	934
Fe-3	473	509	303	875	636	300	170	109	614	555	562	408	122
Fe-res	41,56	39,62	42,53	38,52	39,87	41,31	37,65	51,29	40,24	41,14	30,34	40,16	18,19
	5	0	3	7	3	0	3	8	8	2	7	5	1

Fe total	44,93 8	42,66 3	45,74 5	42,45 3	42,27 4	43,29 2	39,54 1	53,12 3	42,79 8	43,50 3	33,01 1	42,73 3	19,37 8
Mn-1	273	323	250	340	407	387	403	435	430	412	375	384	169
Mn-2	70	67	72	72	56	60	57	56	57	62	63	56	13
Mn-3	26	30	24	25	28	21	14	13	19	32	28	22	4
Mn-res	420	432	453	260	421	464	426	664	441	501	231	545	170
Mn total	789	852	799	697	912	932	900	1168	947	1007	697	1007	356
Ni-1	18	14	17	13	12	10	12	10	12	9	6	10	1
Ni-2	67	61	69	73	49	48	51	45	48	48	38	42	7
Ni-3	46	44	46	35	31	24	17	13	21	27	25	21	3
Ni-res	321	313	333	334	246	262	253	219	239	151	151	202	49
Ni total	452	432	465	455	338	344	333	287	320	235	220	275	60
Pb-1	0.9	0.9	1.0	0.9	0.8	0.7	0.9	1.2	0.9	1.0	1.5	1.4	1.3
Pb-2	10.9	9.5	10.5	11.6	6.9	6.6	7.1	8.3	7.3	7.8	9.4	8.3	4.2
Pb-3	1.4	1.2	1.2	0.9	1.0	0.8	0.7	0.6	1.0	1.0	1.1	0.6	0.5
Pb-res	7.8	5.4	5.3	4.6	7.3	6.9	6.3	11.9	6.8	6.2	5.00	8.7	9.0
Pb total	21	17	18	18	16	15	15	22	16	16	17	19	15
V-1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
V-2	4.5	5.0	4.4	7.0	5.0	4.6	5.6	5.9	5.1	5.7	5.4	4.7	2.7
V-3	4.1	5.3	3.8	4.0	5.4	3.9	3.3	4.5	4.1	4.5	4.8	4.9	1.4
V-res	73.4	59.7	74.8	59.0	71.6	78.5	67.1	139.6	70.8	76.8	63.8	72.4	42.9
V total	82	70	83	70	82	87	76	150	80	87	74	82	47
Zn-1	30	19	33	20	6	6	6	5	7	7	8	10	4
Zn-2	61	46	66	51	15	14	14	12	16	18	23	18	9
Zn-3	23	20	22	13	6	5	8	2	8	9	10	5	3
Zn-res	62	66	89	51	56	60	50	78	52	89	64	69	34
Zn total	176	151	210	135	83	85	78	97	83	123	105	102	50

The mineralogy, obtained by XRD, was quite homogeneous among the tested samples. In brief, the minerals detected in the sediments were quartz, plagioclase, illite, chlorite, serpentine, talc, calcite \pm amphibole and pyroxenes. These results are consistent with what observed in previous works by Capello et al. (2016, 2017).

Distribution of Cr, Fe, and V

The distribution of Cr, Fe, and V in the different steps was similar in all the tested samples, and it was quite homogeneous among the samples of the “Baia delle Favole” (Fig. 2). Their concentration in the exchangeable fraction was very low, and therefore should not be considered a threat for the quality of the environment. These elements tended invariably to concentrate mostly in the residual fraction (Fig. 2), followed by the reducible fraction. Cr can be considered a marker of basic and ultrabasic rocks in sediments, and is known to have a limited mobility unless extreme conditions are reached. Among the minerals present in the bay sediments (Capello et al., 2016), Cr could be present in amphiboles (Hawthorne et al., 2012), pyroxenes (Cameron and Papike, 1982), talc (Evans and Guggenheim, 1988), and chlorites (Bailey, 1988), but also in small amounts of spinel from ultrabasic rocks. The similar behaviour of Fe and V could be explained with the fact that V often substitutes Fe^{3+} in minerals, particularly in magnetites (Craig et al., 1996), but also in amphiboles (Hawthorne et al., 2012), and chlorites (Bailey, 1988). These considerations might explain the similar behaviour observed for such elements. It is worth noting that for Fe the reducible fraction in samples of Group A slightly

increases, indicating that the concentration of Fe oxides is higher. From the BCR-SE results it is possible to conclude that these elements are contained in silicates or in other highly insoluble minerals.

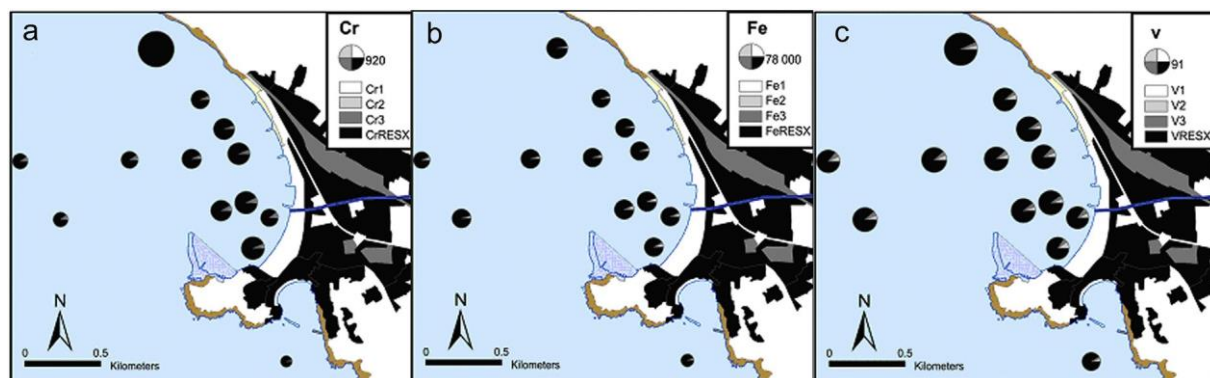


Fig. 2. Distribution and results of BCR-SE for Cr, Fe, and V in the bottom sediments.

Distribution of Co and Ni

Also for Co and Ni, the residual fraction was the dominant one, but they show an increase in the easily extractable fraction of step 1 (Table 2 and Fig. 3), and therefore the mobility of these elements is to be considered higher. Co and Ni, the latter being present in remarkable concentrations (between 220 and 465 mg kg⁻¹; Table 1), when associated to high concentrations of Cr such as in the studied area, can be considered markers of the presence of sediments related to basic and ultrabasic rocks, which are enriched in these elements (Mielke, 1979). Among the minerals reported by Capello et al. (2016), Co and Ni can be found as common trace elements in serpentine (Wicks and O'Hanley, 1988), talc (Evans and Guggenheim, 1988), chlorites (Bailey, 1988), amphiboles (Hawthorne et al., 2012), and pyroxenes (Cameron and Papike, 1982). The presence of these minerals could account for the amount of Co and Ni in the residual fraction.

Compared to the “Bianco” sample, all the stations inside the “Baia delle Favole” had however a lower relative weight of the residual fraction. In particular, the concentrations of Co and Ni in the exchangeable (step 1) and reducible fraction (step 2) increased significantly in the samples inside the bay, particularly for Co. For this element the labile fraction, calculated as the sum of exchangeable, reducible and oxidisable fraction, gave an average of 32% inside the bay against 27% in the control area, with the exchangeable fraction (step 1) being more than double inside the “Baia delle Favole” samples compared to the “Bianco” sample. These differences could be probably explained with the effect of the Gromolo Torrent input. In fact, the sediments of this torrent are enriched in metals due to the presence of an amorphous Fe phase generated by the mixing of AMD from the Libiola mine with the Gromolo Torrent water (Consani et al., 2017; Dinelli et al., 2001). Such amorphous phase, interacting with sea-water, releases elements such as Co and Zn (Consani et al., 2017), which can be sorbed by clay minerals and measured in leachates of exchangeable fraction, and is dissolved during step 2 of the BCR-SE.

Distribution of Mn

Mn is the element that showed the highest concentration in the labile fraction along with Cu, which will be treated separately in a following paragraph.

Mn tended to concentrate in the exchangeable fraction, followed by the residual fraction (Fig. 4). This fact suggests that Mn is hosted in great part inside carbonates (calcite or eventually rhodocrosite), which are known to dissolve in this step (Quevauviller, 2002). Such indication is supported by XRD analyses of the samples after step 1 treatment,

which highlighted the disappearance of calcite reflections due to its dissolution (Fig. 5). In the samples of Group A, the concentration of Mn in the reducible fraction was slightly higher, probably due to the Fe and Mn oxyhydroxides (*sensu lato*) transported by the Gromolo Torrent.

1.1. Distribution of Pb

Pb showed in all samples a marked preference to concentrate in leachates of the reducible fraction (average of 50%; Fig. 6), thus showing a great affinity towards oxides. This affinity has been already observed in marine sediments under oxic conditions (Chakraborty et al., 2016, 2018). It is worth noting that the concentration of Pb in this fraction in the control sample was lower (28%) than the average of the samples from the bay, even if the total concentration of Pb in the sediments did not vary very much. The reducible fraction of Group A samples (58%) was higher than the reducible fraction of samples of Group B and Group C (43% and 48%, respectively), suggesting that the Gromolo Torrent input could be responsible for this variation. Pb was the elements extracted with the highest percentages within the bay, with an origin that is probably not directly linked to AMD according to data of Consani et al. (2017).

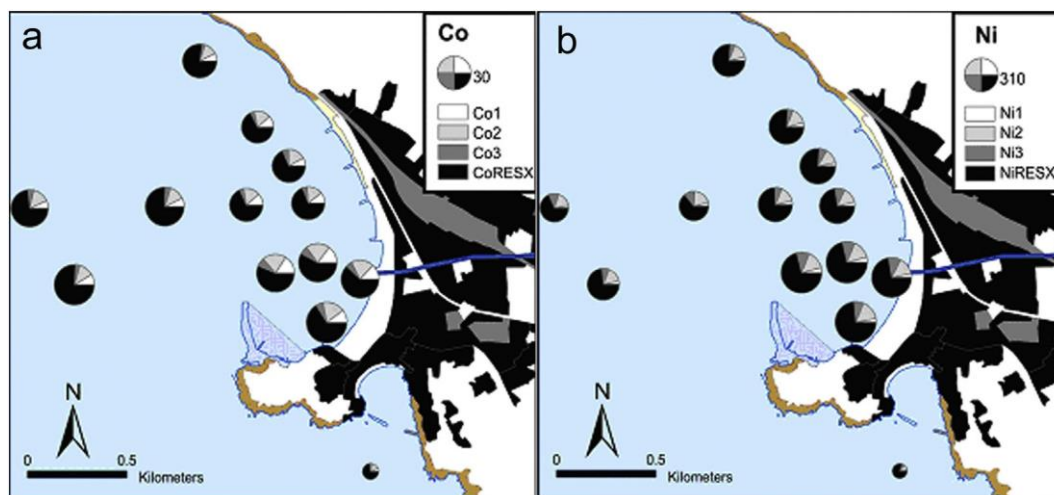


Fig. 3. Distribution and results of BCR-SE for Co and Ni in the bottom sediments.

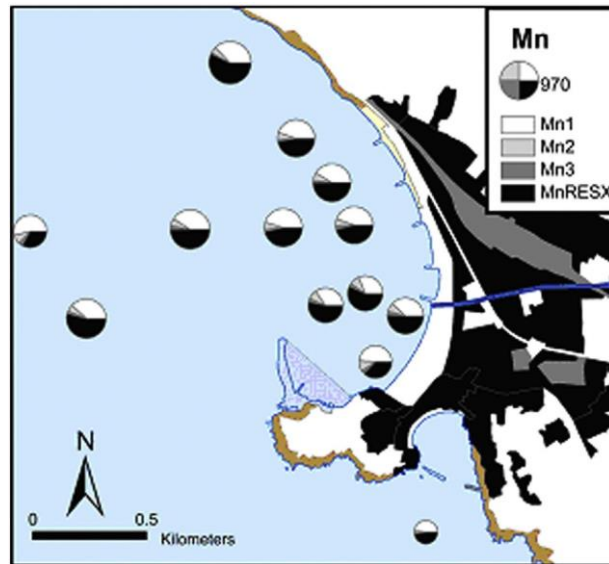


Fig. 4. Distribution and results of BCR-SE for Mn in the bottom sediments.

Distribution of Cu, Zn, and Cd

Cu, Zn and Cd displayed a similar partitioning, all having the highest extracted concentration in the reducible fraction (step 2).

Cu and Zn display a complex spatial distribution (Fig. 7a), and some differences in their partitioning can be however pointed out. The relatively high concentrations of these elements in the “Baia delle Favole” sediments could be linked with the input of sediments of the Gromolo Torrent, which displayed anomalous values (up to 4.7 wt% for Cu and 0.9 wt% for Zn; Consani et al., 2017) of these metals, due to the presence of the Libiola mine. The most enriched samples were those belonging to Group A (Table 2), confirming that the input of the Gromolo Torrent plays an important role in the occurrence of these metals in the bay sediments. In the “Bianco” sample, the 50% of Cu was in the residual fraction, whereas the extracted fraction (sum of step 1-2-3) was divided as follows: reducible fraction 33%, oxidisable fraction 8.3%, and exchangeable fraction 8.3%.

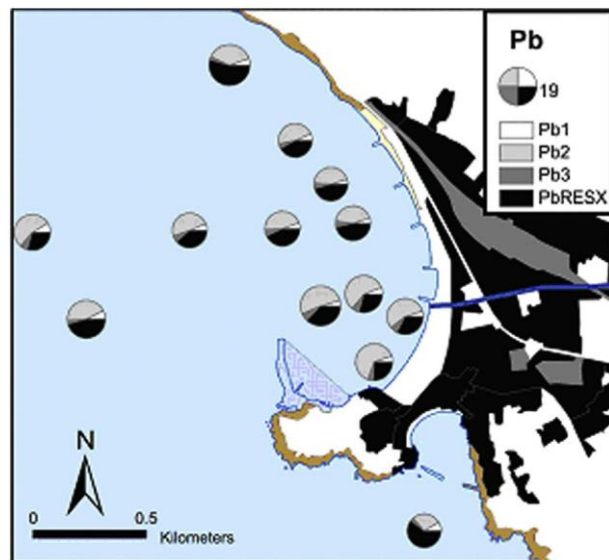


Fig. 6. Distribution and results of BCR-SE for Pb in the bottom sediments.

In samples of Group A, the weight of the residual fraction was lower (33%); the extracted fraction was dominated by the reducible fraction (35%), which became comparable to the residual one, whereas the exchangeable fraction (16%) and the oxidisable fraction (16%) increase. Samples of Group B and Group C had average values for the various fractions comparable with the control zone. It must be noted, however, that sample 5, the nearest to Group A samples, had Cu relative abundances similar to such samples, and that the weight of the residual fraction increased moving away from the Gromolo Torrent mouth along the coast in a NW direction.

Zn reached a relative abundance of 68% in the residual fraction of the “Bianco” sample, whereas the extracted fraction (sum of steps 1-23) reached 32%, divided as follows: reducible fraction 18%, oxidisable fraction 6%, and exchangeable fraction 8% (Fig. 7b). The results of the sediment samples of the “Baia delle Favole” were similar, but there were some differences among them. The residual fraction of samples of Group A was lower than the control zone (40%), due to the increase of the exchangeable and reducible fractions (average of 15% and 34%, respectively). Samples of Group B and Group C showed a distribution in the different fractions comparable to the control zone, with the exchangeable and reducible fractions showing an average of 6.8% and 16%, respectively.

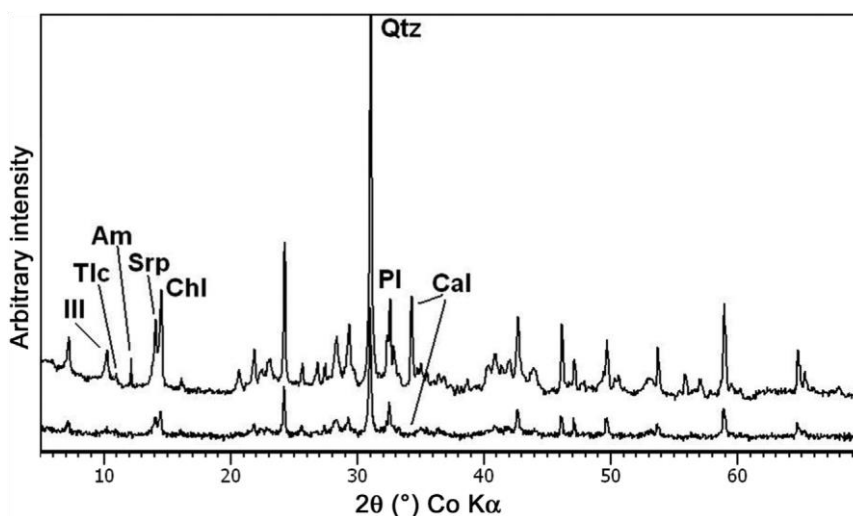


Fig. 5. XRD diagrams of one sample of marine sediments (sample 9) before and after step 1 of BCR-SE. Am = amphibole; Cal = calcite; Chl = chlorite Ill = illite; Pl = plagioclase; Qtz = quartz; Srp = serpentine; Tlc = talc.

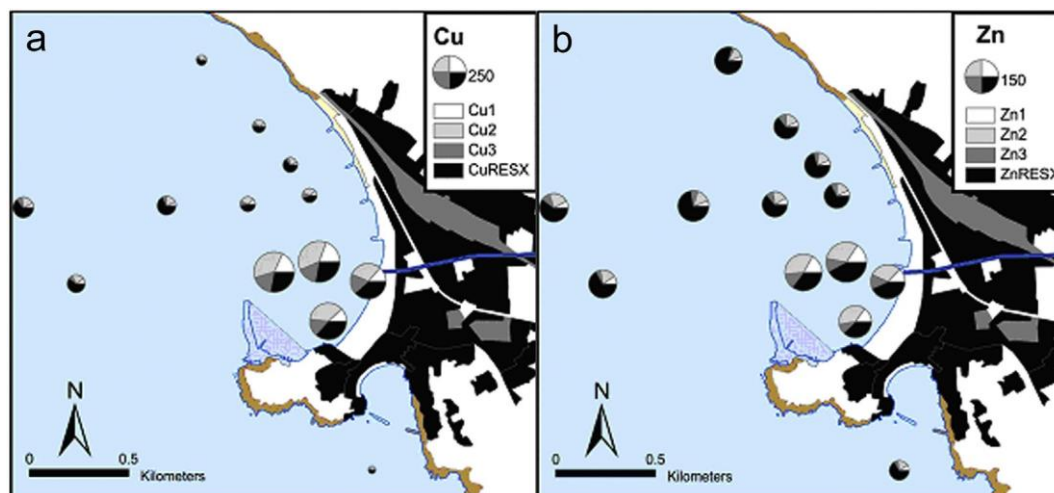


Fig. 7. Distribution and results of BCR-SE for Cu and Zn in the bottom sediments.

The discussion on Cd is problematic, as we were not able to compute the residual fraction. In any case, using the concentrations in the leachates (Table 2), it is possible to state that Cd tended to be released in the reducible fraction (step 2) in most samples, whereas in sample 3, 5, and 9 Cd seemed to be preferably associated to the oxidisable fraction (step 3). The samples with the highest total release of Cd were 2, 6, 18, 22, and 35. Three of them (2, 6, and 35) are part of Group A, and were characterised by the highest concentrations of Cu and Zn. These facts suggest that Cd origin and fate could be similar to the other two elements.

In samples of Group A, the ones closer to the mouth of the Gromolo Torrent, the presence of coatings of Fe oxyhydroxides (*sensu lato*) has been frequently observed (Fig. 8). It is possible to directly correlate the higher concentrations of Cu and Zn in the reducible fraction in samples of Group A to the higher presence of these Fe compounds, which were found to control the concentration of elements in the Gromolo Torrent sediments (Consani et al., 2017; Dinelli et al., 2001). The Fe compounds could also be responsible for the higher concentration of elements inside the exchangeable and oxidisable fraction. Consani et al. (2017) found that important concentrations of some metals, including Cu and Zn, are easily released in sea-water from Gromolo Torrent sediments. Moreover, during early diagenesis after their deposition Fe oxyhydroxides could be involved in organic matter degradation through Fe reduction (Carignan and Tessier, 1988), with the consequent release of Fe^{2+} and other metals in solution. Such metals can form either complex with organic matter, be sorbed by clay minerals, or form monosulphides if also S is reduced by organic matter (Scholz and Neumann, 2007). This process of dissolution of Fe oxyhydroxides might explain the higher relative abundance of Cu and Zn in the exchangeable and oxidisable fraction. The torrent influence could also be invoked for the slightly higher concentration of organically-bound Cu and Zn, due to organic matter transported by the torrent, but also the presence of the sewer of Sestri Levante could have played a role. In general, the partitioning of Cu in the oxidisable fraction is higher than any other metal, especially in the sediments near the mouth of the torrent. This fact reflects the high affinity of Cu towards organic ligands (Chakraborty et al., 2012), but this metal has also a rapid release kinetic from organic compounds, which can be enhanced by the competition of other cations (such as Ca) naturally present in high concentration in seawater (Chakraborty and Chakrabarti, 2006).

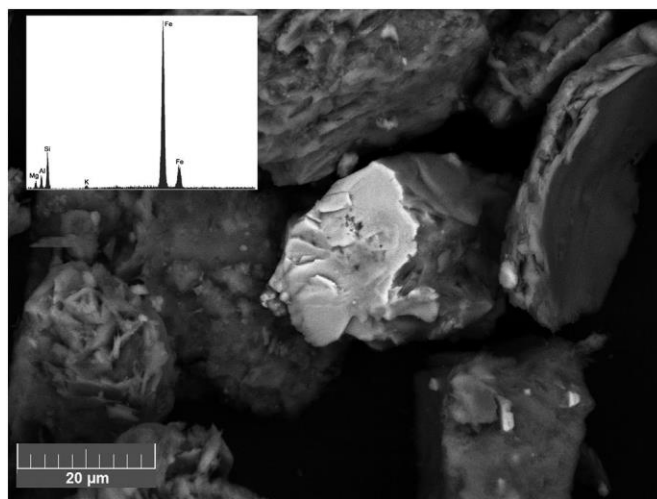


Fig. 8. Bright coating of Fe oxyhydroxides on a silicate grain of the sample 2. The EDS analysis is shown in the inset.

The distribution of Cu and Zn in the other samples might probably reflect the currents role, as in this case mineralogy of the samples does not change. Currents tend to concentrate the input of the Gromolo Torrent sediments in front of the torrent mouth, whereas the spread of those sediments along the coast (Group B) is not favoured by the coastal drift from

the Entella Torrent zone (Fig. 1). Probably the input from the Gromolo Torrent is partly transported offshore, as Group C samples have a content of labile Cu and Zn generally higher compared to Group B samples.

Environmental implications

From the study conducted on the sequential extractions, important information on the possible environmental implications can be obtained, in particular concerning mobility and potential toxicity (Maiz et al., 2000).

In our experiment, the step 1, which extracts metal fractions related to carbonates or in exchangeable position, is a critical one, because metals in these conditions are weakly bound and can become bioavailable. Fractions mostly influenced by human activity include the exchangeable and carbonate-bound fractions, in which metals are weakly retained and can become more bioavailable due to reequilibration reactions in the sedimentary environment (Rath et al., 2009). The potential risk related to the incidence of this metal fraction in sediments has been evaluated in literature applying the criteria of the Risk Assessment Code (RAC), for the first time proposed by Perin et al. (1985) and widely applied in literature (Canuto et al., 2013; de Andrade Passos et al., 2010; Ghrefat and Yusuf, 2006; Jain, 2004; Karak et al., 2011; Sarkar et al., 2014). The RAC is based on the metal fraction that is exchangeable (usually associated with carbonates), as metals of this fraction are weakly retained and able to equilibrate with the aqueous phase, becoming more rapidly bioavailable. This approach classifies the sediment in different categories as presenting no risk (exchangeable fraction < 1%), low risk (1–10%), medium risk (11–30%), high risk (31–50%), and very high risk (> 50%) to the ecosystem (Jain, 2004; Perin et al., 1985).

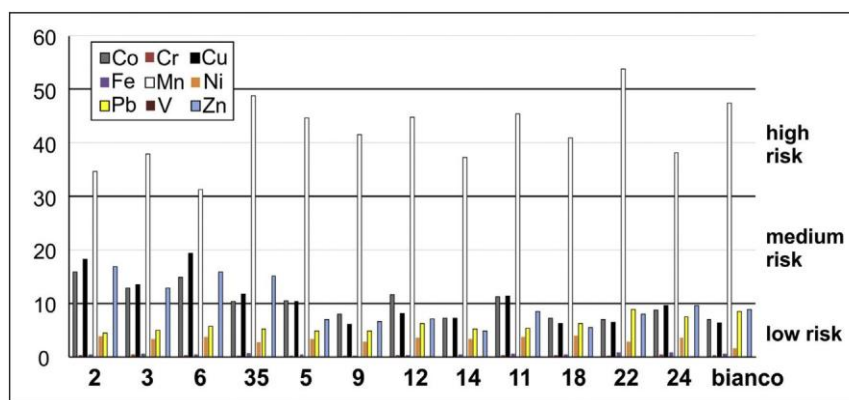


Fig. 9. Risk Assessment Codes (RAC) for Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in the bottom sediments of “Baia delle Favole”.

Our results (Fig. 9) indicate systematic and widespread high risk classification for Mn, and medium risk for Zn, Cu, and Co in all the stations of Group A; occasional medium risk in two samples of Group B for Co (stations 5 and 12) and Cu (station 5); unique medium risk for Co and Cu in station 11 of Group C. Stations 5 and 11 are proximal to those of Group A, in particular to the NW along the coast and to the SW towards deeper waters. They are indicative of sediment dispersion patterns and could invite to some attention since small variation in environmental conditions could lead to remobilisation. However, all three elements are considered as essential trace elements for aquatic organisms (Mason, 2013) and thus negative effects could be limited.

Following the indications of Long et al. (1995), the Effects RangeLow (ERL) and Effects Range-Median (ERM) guideline values were calculated for Cu and Zn. The concentration of these elements in the control station lied below the ERL, i.e. effects on biota would be rarely observed. For Cu, most of the stations lied in the range between ERL and ERM, a possible-effects range within which effects would occasionally occur, with only station 14 below ERL. On the contrary, the four stations in front of the Gromolo Torrent (2, 3, 6, and 35) had Cu concentration above ERM, a probable-effects range within which effects would frequently occur. A minor concern should be adopted for Zn, which lies below

ERL in all station but 2, 3, and 6, where it is in the range between ERL and ERM. These data are in good agreement with the RAC results, and highlighted the possibility of metal-related negative effects on biota in the studied area.

Mn association to acid-soluble fraction in marine sediments has been observed also in other conditions (Kiratli and Ergin, 1996; Marin and Giresse, 2001; Morillo et al., 2004, 2007) and should be not surprising. It is a partitioning shared by all stations, even the control one, so it could be considered to be a regional pattern and not one related to pollution. Besides also Mn is an essential trace element, and given the absolute concentrations measured should not represent a critical environmental issue. Anyway, it is not possible to exclude problems for biota related to high Mn concentration. In fact, Mn (as well as Co) might have acute and chronic toxicity on fishes or other benthic organisms (Dave and Nilsson, 2005).

Conclusions

The results of this study allowed obtaining a further insight on metal distribution and possible mobility in the “Baia delle Favole” bottom sediments.

Cr, Fe, and V were predominantly associated to the residual fraction, suggesting an association to silicates or other insoluble minerals, testifying for limited mobility in the sedimentary environment. It must be stressed that Fe had clearly higher concentrations in the reducible fraction of samples of Group A that can be explained by the contribution of Fe³⁺-rich colloidal sediments transported by the Gromolo Torrent. Ni and Co showed a similar preference for the residual fraction, although both displayed a relative increase in the extracted fraction relative weight, with a prevalent association to the reducible fraction, probably due to Fe oxyhydroxides (*sensu lato*) transported by the Gromolo Torrent. Mn was the only element that was strongly partitioned in the first extraction step, the one principally referable to carbonates, independently from the spatial position. Cu and Zn extracted relative abundance in samples from Group A was higher than the labile samples of these elements in the rest of the bay. In sediments from Group A, the presence of Fe oxyhydroxides coatings could account directly for Cu increase in step 2 leachates, and indirectly for Zn increase in step 1, after exchanges with sea-water or dissolution due to early diagenesis.

Based on the percentage of extracted metal (all the three fractions) compared to the total one, it was possible to identify some differences between the areas, in particular between “Bianco” station and all the others:

A: Pb > Cu > Zn > Mn > Co > Ni > V > Cr > Fe B: Pb > Mn > Cu > Zn > Co > Ni > V > Cr > Fe C: Pb > Mn > Cu > Zn > Ni > Co > V > Cr > Fe

“Bianco”: Mn > Cu > Pb > Zn > Co > Ni > V > Fe > Cr.

Pb was the elements extracted with the highest percentages within the bay. Cu and Zn in Group A clearly reflected the Gromolo Torrent contribution and in that area record higher extraction percentages compare to Mn, otherwise more easily extractable in the other areas, and the dominant in the control station (52% cumulatively extracted). The comparison with benchmark values (ERL-ERM) showed effects on biota, mainly due to Cu concentration, should be expected to be frequent in the sediments near the mouth of the Gromolo Torrent. Possible effects could occur in the whole studied area and are always related to Cu, with Mn and Zn which could have adverse effects on biota, too.

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