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Assessing metal-contaminated Fe-rich colloids in fluvial environment: the case study of the Gromolo Torrent (Liguria, NW Italy)

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Assessing metal-contaminated Fe-rich colloids in fluvial environment: the case study of the Gromolo Torrent (Liguria, NW Italy)

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Abstract

Metal-polluted mine waters represent a major threat to the quality of waters and sediments in the downstream basin. The aim of this work is to characterise the colloids which form at the confluence between mine waters and the unpolluted waters of the Gromolo Torrent (North-West Italy), evaluating the transport and dispersion of metals in the sediments. The mineralogy and the concentrations of different elements of environmental concern (Cu, Zn, Cd, Co, Cr, Mn, Ni, Pb, As, and Sb) were analysed in the precipitates down to the mouth of the Gromolo Torrent in the Ligurian Sea. In order to evaluate the possible remobilisation of ecotoxic elements from the sediments, bulk leaching tests were performed with both deionised and sea water. The amorphous colloids contain elevated concentration of Fe (up to 20.99%), Al (up to 7.57%), Cu (up to 47,170 mg kg^{-1}), and Zn (up to 9,139 mg kg^{-1}). Bulk leaching tests with deionised water mobilised high Pb percentages (more than 50%), but also considerable amounts of Fe, Al, Cu, and Zn (up to 937, 256, 477, 60.8 mg kg^{-1}, respectively) are released in the leachate. The sea water tests showed different results, with the only exception of Pb. Fe, Al, Cu, and Zn (up to 193 and 95.1 mg kg^{-1}, respectively) were less released, while other elements like Mn (up to 42.32%), Cd (up to 30.58%), Co (up to 14.40%), and Ni (up to 5.80%) increased in the released fraction The results show that the interaction of colloids and sea water can remobilise high concentrations of metals, thus affecting the quality of the surrounding environment.

Keyword

Amorphous colloidal precipitates, environmental contamination, metals mobility, bulk leaching test, Acid Mine Drainage (AMD), Libiola mine, Sestri Levante (Italy).

1 Introduction

The weathering of sulphide minerals can generate solutions with low pH values and a high amount of dissolved sulphate and metals of environmental concern (Blowes et al. 2003). The formation of these acid solutions, known as Acid Mine Drainage (AMD), is typical of coal and sulphide ore mining environments. The discharge of AMD in torrents and rivers can lead to severe environmental problems downstream (Nieto et al. 2007; Schemel et al. 2000). When AMD flows into rivers with higher pH values, the solubility of metals is greatly reduced and the precipitation of Fe^{3+} and Al^{3+} phases takes place (Stumm and Morgan 1996). Fe^{3+} minerals form the so called “ochre deposits”, characterised by a quite variable mineralogy. Minerals of ochre deposits have small size, which lies generally in the nanometre range, and poor crystallinity, and, therefore, are difficult to characterise. Moreover, a pure geochemical modelling approach for the prediction of the mineralogy of ochre deposits is not recommended; in fact, the thermodynamics constraints of low crystallinity (sometimes metastable) phases are poorly described, and also a strong control of the kinetic factor on the precipitation of theses minerals has been recognised (Bigham 1994). The main minerals in ochreous deposits are goethite (α-FeOOH), jarosite [$KFe_3(SO_4)_2(OH)_6$], ferrihydrite ($Fe_{10}O_{14}(OH)_2$), schwertmannite [$Fe_{16}(OH,SO_4)_{12\text{-}13}O_{16}\cdot10\text{-}12H_2O$], basaluminite [$Al_4(SO_4)(OH)_{10}\cdot4\text{-}5H_2O$], and amorphous Fe- or Al-(oxy)hydroxides (Bigham and Nordstrom 2000; Frau et al. 2015; Kim 2015; Silva et al. 2013; Sracek et al. 2011). The formation of these colloidal minerals is also possible in a fully natural setting, depending on the ratio between acid generation capacity of the source and acid consumption capacity of the receiving watercourse (Schwertmann et al. 1995). These natural colloidal particles with heterogeneous composition and low crystallinity can have a crucial role in the transport and dispersion of ecotoxic elements inside river basins (Grosbois et al. 2007). In fact, colloidal particles can concentrate ecotoxic elements from the solutions, thanks to their high surface-to-volume ratio and their high surface reactivity due to the high proportions of surface groups which bind metals (Montarges-Pelletier et al. 2014). Though precipitation of colloids produces a positive effect on water quality due to their metal and/or anionic species uptake capacity, colloidal particles can severely affect the quality of the habitat for benthic invertebrates and aquatic plants/algae (Cantonati et al. 2014; Niyogi et al. 1999). Moreover, colloidal particles and related metals can enter the food chain through benthic organisms and produce toxic effects when eaten by fishes (Casiot et al. 2009; Woodward et al. 1995). Fe and Al rich-precipitates and other elements coprecipitated or sorbed to them (such as Cu, Zn, Cd, Pb, and As) can aggregate and deposit in the river bed or can be transported for long distances until they flow into the sea (Kimball et al. 1995). In the marine environment, colloidal particles and related metals transported by rivers sink into coastal sediments or can be dispersed offshore. Variations of physical and chemical parameters, such as pH, Eh, flood events, and biological activities can result in dissolution of Fe and Al colloids or in the desorption of ecotoxic elements, thus releasing a considerable amount of pollutants in the surrounding aquatic system. When metal-rich colloidal particles are transported to the sea, the interaction with sea water, characterised by high salinity and alkaline pH, can result in a release of metals and in the formation of contaminant plumes (Boutier et al. 2000; Elbaz-Poulichet et al. 2001; Morillo et al. 2004; van Geen et al. 1997).

Previous investigations conducted in the studied area, located in the catchment area of the Gromolo Torrent (Liguria, North-West Italy), mainly focused on the geochemistry of mine waters or on AMD precipitates (Carbone et al. 2013; Cortecci et al. 2001, 2008; Dinelli et al. 1998; Dinelli and Tateo 2002; Marescotti et al 2012) and on the geochemical modelling of the Gromolo Torrent (Accornero et al. 2005). The only research dealing with the stream sediments of the Gromolo Torrent is Dinelli et al. (2001), which studied the chemistry of the sediments of a long part of the torrent, but did not take into account their mineralogy. In a study performed on marine sediments offshore the mouth of the Gromolo Torrent, Capello et al. (2016) highlighted the presence of high concentrations of Cu, Zn, Cd, and Ni, correlating this with the output of the torrent.

The aims of this work are: a) the characterisation of colloids generated by mixing of AMD with alkaline torrent waters; b) the determination of colloidal capacity to retain some ecotoxic metals (Fe, Al, Cu, Zn, Mn, Ni, Pb, Co, Cd, and Cr) in the solid fraction by bulk leaching test experiments; and c) the evaluation of the metal mobility into torrent precipitates up to the Ligurian Sea. The tests are performed with both deionised water to simulate the interactions with meteoric water, and sea water to investigate metal fate when they are transported by the torrent into the sea.

2 Study area

The study area (**Fig. 1**) is located inside the catchment area of the Gromolo Torrent, an 18.2 km^2 widespread basin (Liguria, North-West Italy) with a high mean steepness and a short course torrent typical of the catchments of the Ligurian territory. The Gromolo Torrent, after its spring in Mount Roccagrande, flows for 11 km down to the Ligurian Sea. The upper part of the basin is located in an ophiolithic sequence composed by serpentinites, basalts, gabbros, cherts, and limestones outcrops, while in the central part of the basin sandstones and shales are the dominating rocks (Abbate et al. 1980; ISPRA 2011). Finally, the Gromolo Torrent flows across the town of Sestri Levante on the alluvial plain (Fig. 1). Two tributaries of the Gromolo Torrent, Rio Boeno and Rio Cattan, drain the abandoned Cu mine of Libiola, where intense AMD generation processes are still active (Carbone et al. 2005). Moreover, in two different points of its course, the Ida and the Castagna mine adits (Fig. 1) directly discharge AMD in the torrent with a 2.4-2.6 pH and a mean EC value of 6000 μS. As a result of the mixing, a massive formation of colloidal precipitates takes place, covering the entire bed of the torrent. The Libiola mine complex comprises 18 galleries which develop over 30 km of underground excavations and 3 major open pits. Inside the mine area, which is extended for about 4 km^2, there are five main waste-rock dumps and several minor deposits (Carbone et al. 2013). The mineralised ore body consists of massive lenses and stockwork veins of pyrite, chalcopyrite ± sphalerite hosted in a quartz, chlorite ± calcite gangue (Zaccarini and Garuti 2008).

The climate of the area is Mediterranean humid and is characterised by a mean air temperature of 14 °C and average rainfall of 1550 mm year^{-1} (Provincia di Genova, 2013). The rainfall distribution is unimodal, with a maximum in November (over 180 mm) and a dry season in summer (Provincia di Genova, 2013).

3 Materials and methods

3.1 Sampling and *in situ* measurements

The colloidal precipitates were sampled at 10 stations (from upstream to downstream GR0-1, and GR3-10) (**Fig. 2**) in the Gromolo Torrent during 4 sampling days carried out between the 26th March and the 17th April, 2015. The sampling period was characterised by stable weather conditions with low precipitations. Moreover, an upstream unpolluted sample of fine sediment (GRB) was taken before the confluence with the first AMD affected tributaries (Rio Boeno) and the nearby AMD discharge from the Ida mine adit (Fig. 2).

Fine sediment samples of GRB were sieved in the field to 2 mm and air dried. Precipitates generated by the mixing with AMD were collected at the confluence with AMD affected tributaries and the mine adits in the torrent with a plastic syringe, for a total volume of 30 L each station, stored in polypropylene bottles and filtered through 16 μm filters and air-dried.

The pH and Electrical Conductivity (EC) of waters were measured in the field using a portable “WTW PH330i” pH-meter, equipped with both the “SenTix41” and “SenTix ORP” electrodes and a “Eutech XS COND6+” conductimetre.

3.2 Methods

The mineralogical characterisation of the samples was determined by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) analyses. XRD diagrams were collected with a Philips PW1140 diffractometre equipped with CoKα radiation (current 20 mA, voltage 40 kV). Samples were first ground with an agate mortar and pestle, and then mounted on zero-background silicon plates. Each sample was scanned between 5 and 80° 2θ at a scan rate of 5° min^{-1}. The minerals found in each sample were identified using the Powder Diffraction File™ (PDF) database of the International Centre for Diffraction Data (ICDD).

Precipitate samples were studied by SEM using a Tescan Vega 3 LMU scanning electron microscope equipped with an Energy Dispersive Spectroscopy (EDS) EDAX Apollo X SDD, at 20 kV accelerating voltage, 1.2 nA beam current, and 5-10 μm beam diameter. In order to prevent damage to the coated surface of the samples, counting times were set at 60 s.

The major element composition was investigated with an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-ES) on 1 g of samples digested in hot Aqua Regia, while minor and trace elements were determined by an Inductively coupled plasma mass spectrometry (ICP-MS) analysis on 0.5 g of sample after modified Aqua Regia digestion (ISO 15587) at Bureau Veritas Mineral Laboratories (Canada; ISO9001QualityManagement Systems). Standard quality assurance procedures include: analysis of blanks within each batch; a routine testing of certified reference material standards; duplicate samples included in each batch to ensure that reproducible results are being achieved.

Bulk leaching tests were performed in order to quantify the release of metals and metalloids (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, S, and Zn) in the surrounding environment. Three different precipitates were selected on the basis of the mineralogical observations, and the experiments were carried out on 1 g of solid material suspended in 100 ml of both deionised and sea water in a pyrex beaker at room temperature. Sea water was sampled in an area located at 5 km from the mouth of Gromolo Torrent and filtered through 0.45 μm filters. The solution was continuously stirred with a magnetic stirrer in the first 24 hours, and then occasionally stirred at least once a day for the whole duration of the experiment (one week). During the first hour of the experiments, pH and EC were measured every 15 minutes, then checked every hour for the first 8 hours and finally daily. To exclude the possibility of phase transition or dissolution of the samples, the solution was centrifuged to separate the solid to the liquid fraction at the end of each experiment. Leaching test was repeated 4 times for every sample with different increasing times (4, 8, 24, and 96 hours) in order to obtain a release trend for the tested elements. The leachate was analysed for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) at the "Dipartimento di Scienze Biologiche, Geologiche e Ambientali" of the University of Bologna (Italy). The results obtained for bulk leaching tests performed with sea water were corrected subtracting the concentration of metals measured in sea water blank samples.

The choice of deionised water in the leaching experiment was made on the indication of the DM 5/2/1998, a regulatory note of the Italian Government for the characterisation of waste deposits, which was also applied in other studies aimed at the characterisation of mine waste material (Carbone et al. 2013; Hageman and Briggs 2000; Hageman et al. 2015).

4 Results and discussion

4.1 Mineralogical characterisation

Water chemical parameters, such as pH and EC, show different trends (**Tab. 1**) in the Gromolo Torrent. The pH value drops in two points, GR0 and GR3 (Fig. 2), in correspondence of the AMD input in the torrent, and, subsequently, rises again fluctuating around the values of 8-8.2, with two maxima in GR7 and GR9 (8.44 and 8.53, respectively). On the contrary, EC value rises after the both confluences of AMD, although slightly, indicating that dissolved metals carried by AMD are effectively removed from solution by the formation of mixing precipitates. EC reaches its maximum value near the mouth of the torrent (GR9 and GR10), probably for the influence of sea water and marine aerosol.

Across the Gromolo Torrent, the mineralogy of the samples differs significantly (**Table 2** and **Fig 3**). The XRD pattern of the sediments before the confluence of AMD (GRB) shows the presence of minerals deriving from the surrounding lithologies such as quartz, serpentine, sodic plagioclase, chlorite, talc, illite, calcite, and amphibole with mineral accessory diopside, hematite and magnetite. At the confluence with acid drainages (GR3), a massive precipitation of an X-ray amorphous phase with accessory cuprite (Cu_2O) occurs, and this precipitate becomes the major constituent of the sediments in the central sector of the torrent, with detrital minerals still present but in lower concentrations.

From the XRD and chemical data, the presence of ferrihydrite and basaluminite seems unlikely as well as the presence of separated Al-Cu colloids seems to be excluded, predicted by the thermo-dynamical model developed by Accornero et al. (2005) and by the chemical recalculations reported in Dinelli et al. (2001), respectively. In fact, the characteristic reflection of ferrihydrite is not detected in the XRD pattern, and the bulk chemistry of the mixing colloids is quite different from the ferrihydrite one, as it is highly enriched in Al, Cu, and Zn and depleted in Fe.

SEM observations (**Fig. 4**) indicate that the presence of different colloids seems to be excluded. The amorphous material occurs in globular to massive homogeneous aggregates (**Fig. 4a**), and EDS semi-quantitative analyses showed the presence of high amounts of Fe, Cu, Al, Zn, Mg, and Ca. The presence of Si and C is to be linked with diatoms, which are micro-algae with frustules composed of amorphous silica. Distinct phases such as cuprite (when present) already observed by the XRD measurements, are easily recognised also in the SEM observations (**Fig. 4b**). No Al-bearing phase has been observed. The colloidal phase seems to be completely amorphous rather then nanocrystalline, and the chemical data of this precipitate are comparable to the data obtained for the Fe-rich amorphous colloids generated in Cu mine sites affected by AMD as indicated by Koski et al. (2008). After 4.5 km from its formation, the Fe-rich amorphous precipitate is progressively diluted by detrital minerals which become the dominant phases in torrent sediments. However, the Fe-rich amorphous precipitate is still XRD detectable all along the torrent down to its mouth in the Ligurian Sea (GR10).

4.2 Bulk chemistry distribution of elements in the colloids

The bulk chemistry distribution of some representative elements in the Gromolo Torrent is shown in **Fig. 5** and summarised in **Table 3**. Three areas of contaminant introduction can be identified in the torrent course starting from the sampling GRB station. The first zone (zone I) corresponds to the first discharge of metal-contaminated water by the Rio Boeno and the Ida mine adits (Fig. 2). The second mine water discharge zone

(zone II), located approximately 1.6 km downstream, is included between the Castagna mine adit and Rio Cattan (Fig. 2). Finally, the zone III is located at the beginning of the town of Sestri Levante and ends at the mouth of the torrent (Fig. 2).

The main elements supplied by the sulphide ore body (**Fig. 5a**) show a similar trend: their concentration abruptly increases in the zone I, remains approximately constant across zone II, and then decreases in zone III. This pattern is related to the concentration of the Fe-rich amorphous phase in the sediments, with the exception of the conservative S, whose concentration does not show a marked decrease in zone III.

Mg, Mn, Ni, and Cr (**Fig. 5b**), due to the degradation of the outcropping rocks, show instead a decrement at the beginning of zone I followed by an increase in their concentration at the end of zone II. The concentration of Ca is controlled by the amount of calcite in the sediments. Pb, As, and Sb (**Fig. 5c**) keep fairly constant until zone III, where a sharp increase is observed. The amount of V in the sediments does not show any change across the entire course of the Gromolo Torrent (Fig. 5c). The concentration of the elements in the sediments and colloids normalised to the background sample (GRB) is shown in **Fig. 5d**.

On the basis of XRD results, the samples can be divided in two groups. The first, collected in zones I/II, is dominated by the Fe-rich amorphous colloids (samples GR0-GR7) and is heavily enriched in elements such as Cu (up to 336 times compared to GRB), Zn, and Cd, and depleted in Mg, Mn, Ni, Cr, and Pb. Besides, these samples are enriched also in Fe (up to 4 times), Al, Co, and S, while As and Sb fluctuate around the value of 1, thus have a concentration comparable to the background value. The second group, composed by samples GR8-GR10, is dominated by detrital minerals and represents zone III. These samples are still enriched in Cu, Zn, and Cd while other elements, such as Fe, Al, Co, and Mn show values comparable to the background. On the contrary, in these samples, Pb, As, and Sb are quite enriched, almost by a factor of 10 respect to background values. Mg, Ni, and Cr depletion could be explained by the fact that background values refer to the sediments collected in the upper part of the basin, where ophiolitic rocks outcrop. Soils and sediments generated by ophiolitic rocks have very high concentration of these elements (Albanese et al. 2015), and the dilution operated by sandstones and shales cropping out in the lower part of the Gromolo basin results in a lowering of the concentration of these elements in the sediments.

The correlation coefficients between ecotoxic elements (Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, and V) allowed to group together the elements and are reported in **Table 4**. The first group includes Fe, which is strongly correlated to Al and Cu (0.98 and 0.97, respectively) and also with Zn and Cd (0.76 and 0.70, respectively), suggesting that the concentration of these elements is controlled by Fe and by the precipitation of amorphous phases. Al, Cu, Cd, and Zn show also a strong linear correlation between each other. Moreover, Zn and Cd are the only elements with a strong linear correlation with Co (0.79 and 0.87, respectively), thus suggesting that Co is bound to the amorphous phases, too. The second group includes Mg, which has generally a negative trend with all the elements related to Fe amorphous phase (from -0.59 to -0.69) and a positive trend with Ni and Cr (0.75 and 0.72, respectively). This fact suggests that Mg, which tends to behave conservatively in these settings, and the related elements are correlated to detrital minerals, such as serpentine and chlorite for Ni and chromite or magnetite for Cr. Mn is poorly correlated with Mg (0.61) and Ni (0.60), while it shows a negative trend with Fe, Al, and Cu. This correlation suggests that Mn does not substitute Fe inside the amorphous precipitates as instead happens in goethite, but it is rather related to detrital minerals. The conservative S and V do not show any clear correlation with any elements, but S has a marked negative trend with Ni. Finally, As, Pb, and Sb are strongly correlated, and display generally negative correlation with the other elements. These three elements are present in small amounts in the rocks outcropping in this area as well as in the mineralisation, and their concentrations slightly rise as the torrent flows across the town of Sestri Levante. This trend seems to suggest for these ecotoxic elements a common anthropogenic origin, such as traffic emissions, leaching of urban surfaces and soils, urban wastes, industrial activities, rather than indicate a common carrier. The interaction between Fe precipitates and As and Pb is well documented (Cornell and Schwertmann 2003), and the lack of a correlation between Fe and these elements could be explained with the contemporary dilution of Fe amorphous precipitates in the samples and the immission of As, Pb, and Sb in the torrent.

4. 3 Bulk leaching tests

The bulk leaching tests were performed on two different type of samples characterised with the results of the chemical and mineralogical analyses: GR0 and GR4 are representative of iron rich amorphous precipitates, while GR1 is representative of the amorphous precipitates containing cuprite. All the tested aliquots were checked with XRD after the experiments, and the results (not reported in this paper) permitted to exclude any change in the mineralogical composition during bulk leaching tests.

The results of the bulk leaching tests are reported in **Fig. 6** and **Fig. 7**. The starting condition of the experiments carried out with the deionised water shows a value of 5.50 measured after a few seconds (the black dot in Fig. 6); after, pH shows a sudden rise up to 6.7-6.8 in the first 10 hours of the experiment for all the samples tested; after this moment, the pH becomes approximately constant. The EC shows a similar trend, with a marked increase in the first 10 hours of the experiment, followed by a less marked increase trend for all the samples, with final values in the range of 750-1000 μS. The experiments conducted with seawater displayed a very different behaviour: in the first 2 hours of the experiment, a decrease for pH and EC compared to the starting condition of sea water (pH = 7.8, EC = 37.7 mS cm^{-1}, black dots in Fig. 6) was observed. The pH values have a slight increase throughout the experiment with a flat trend, reaching a final value in the range of 7.7-7.8. Instead, after an initial decrease in the first 2 hours, EC shows a linear increase, with a final value 4000-5000 μS higher than the starting one. This result represents a higher release of metals in the sea water leachate respect to deionised water experiments.

The leachates deriving from the tests were analysed and the results for the investigated elements with deionised water are reported in **Table 5a**, while the results obtained for sea water are reported in **Table 5b**, either as measured concentrations and extracted percentages. In general, according with the EC results described before, the leachate generated by the interaction with deionised water shows a lower metals release than with the sea water. Again, the results obtained for the three tested aliquots (GR0, GR1, and GR4) are similar, with the only exception of GR4 which shows for deionised water aliquot a partial riequilibration of the released metals that are adsorbed on the surface of the samples.

In the experiments, the most extracted element is Pb, which always reaches release percentages higher than 50%, showing that Pb is not strongly bound to the Fe amorphous phase and is easily released even using a low ionic strength reactant as deionised water. Furthermore, the tests performed with sea water show a very different elements behaviour respect to deionised water and these differences will be discussed briefly in the following lines.

For deionised water experiments, the only elements with a high relative extraction is Pb, while the other elements show a release in the leachate generally lower than 2%, with Mn, Co, Cr, and Ni usually in the 0.X mg kg^{-1} range. It is important to note, however, that some metals like Al, Fe, Cu, and Zn reach high concentration in solutions during the experiments: 937 mg kg^{-1} for Fe, 256 mg kg^{-1} for Al, and 477 mg kg^{-1} for Cu in GR4 after 4 h, and 60.8 mg kg^{-1} for Zn in GR1 after 24 h.

For experiments performed with sea water, the concentrations in the leachate of Fe, Al, and Cu are significantly lower, with only Cu still showing high concentration in solutions, especially in the GR1 sample (up to 193 mg kg^{-1}). On the contrary, Cd, Co, Mn, and Ni concentration in the leachate raises sensibly, with release percentages variable from 3-4% for Ni to 25-30% for Mn. The increase of these metals in the sea water leachate could be attributed to both the formation of soluble chloro complexes, as reported for example for Cd (Elbaz-Poulichet et al. 1987), and an exchange between sea water cations and the most loosely bound cationic fraction of the precipitates. The tested aliquots have a very high cationic exchange capability (CEC), in the range of 34.7-42 meq · (100 gr)$^{-1}$, so a wide exchange between sea water and the samples is plausible. Besides, also organic ligands contained in sea water could interact with colloidal particles releasing metals (Waeles et al. 2008). Finally, Cr, Pb, and Zn do not show an appreciable variation of their behaviour respect to the test conducted with deionised water.

4.4 Comparison between Gromolo Torrent and AMD precipitates

As already mentioned in the Introduction, in the past in the studied area, more attention has been paid on the precipitates generated by acidic mine waters rather than on the stream sediments of the Gromolo Torrent. However, a comparison between torrent and AMD related precipitates could be helpful to better understand the environmental relevance of these sediments and colloids.

The precipitates of the Gromolo Torrent form at the confluence of mine water, were the mixing of weakly alkaline (pH ≈8; Dinelli et al. 2001) and bicarbonate-dominated water of the torrent and acidic (pH ≈3) and sulphate dominated water takes place. The abrupt rise of pH to value close to neutrality favours the precipitation of metals, with the consequent formation of amorphous precipitates. For these reasons, these precipitates are able to scavenge higher amounts of metals like Al, Cd, Co, Cu, and Zn from solution, than the ochreous precipitates occurring in this area (Carbone et al. 2005, 2013; Dinelli and Tateo 2002). Greenish-blue precipitates, present in the area although not extensively in the Libiola mining area near the Margherita adit (Carbone et al. 2013), show higher concentration of Al and Cu and comparable amounts of Cd, Co, and Zn.

Bulk leaching tests with deionised water were performed also on two ochreous precipitates, composed by goethite + jarosite and schwertmannite, and on greenish-blue precipitates, composed by allophane + woodwardite, collected in the area (Consani et al. 2016). In general, the amorphous precipitates of the Gromolo Torrent show a higher release in solution of Al, Fe, Cu, and Zn and a comparable release of Mn, Co, Cr, and Ni respect to ochreous precipitates. Only Cd shows a higher release in schwertmannite rich precipitates. On the contrary, greenish-blue precipitates show generally higher amounts of metals, like Mn, Co, Ni, Cu, and Zn in the leachates, with only Al and Fe being more released by amorphous precipitates. This fact could be due to the very high CEC of amorphous mixing and greenish-blue precipitates, the latter supposable as these precipitates are allophane-rich (Wada 1989), respect to ochreous precipitates, which causes the presence of a higher amounts of loosely bound and easily exchangeable metal fraction, although a partial dissolution of these precipitates, occurring at both neutral and weakly alkaline solutions, is to be considered.

5 Conclusions

The Gromolo Torrent receives directly AMD from the abandoned Cu mine of Libiola. The sediments of the Gromolo Torrent were collected and analysed in order to characterise the precipitates generated by the mixing of AMD and the water of the torrent and to understand the mobility of hazardous elements down to the Ligurian Sea. The precipitates of the Gromolo Torrent are completely amorphous and are transported along the entire course up to its mouth in the Ligurian Sea, controlling the dispersion of metals inside the Gromolo basin and to the sea. AMD from the Libiola mining area introduces in the sediments of the Gromolo Torrent metals like Al, Cd, Co, Cu, Fe, and Zn, which precipitate as amorphous colloids, while other elements, as As, Sb, and Pb seem to be correlated with anthropogenic activities, such as traffic emissions, leaching of urban surfaces and soils, urban wastes, industrial activities. The concentration of Ca, Cr, Mg, Mn, and Ni in the sediments is instead controlled by the detrital minerals deriving from the surrounding rocks.

The precipitates of the Gromolo Torrent are richer of metals than ochreous precipitates occurring in AMD settings, and bulk leaching tests show that they have higher release of Al, Cu, Fe, Mn, and Zn in deionised water than in sea water, representing a major threat to the environment. In particular, the released fraction of Al, Cu, Fe, and Zn is of several dozens, or hundreds, of mg kg^{-1}. Only greenish-blue precipitates show a release of metals higher, or at least comparable, to the amorphous precipitates of the Gromolo Torrent. The amorphous precipitates tested with sea water show a higher release of Mn, Cd, Co, Ni, and Zn, due to interactions with sea water, showing that these colloids are able to release significant amounts of metals in sea water.

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Figure Captions

Fig. 1 Simplified geological sketch of the studied area (modified from ISPRA 2011). The dashed lines delimit the Libiola mining area, while the two red dots are the Ida and Castagna mine adits

Fig. 2 Schematic sketch of the sampling points. In grey the Sestri Levante town area, in yellow the Libiola mining area, while the red spots are the Ida and Castagna adits. In the insets the pictures of the GR0, GR3, GR5, and GR8 sampling points

Fig. 3 XRD diagrams of three different samples before the confluence of AMD (GRB), immediately after (GR3), and near the mouth of the Gromolo Torrent (GR10). Am = amphibole; Cal = calcite; Chl = chlorite; Cup = cuprite; Di = diopside; Hem = hematite; Ill = illite; Mag = magnetite; Pl = plagioclase; Qtz = quartz; Srp = serpentine; Tlc = talc

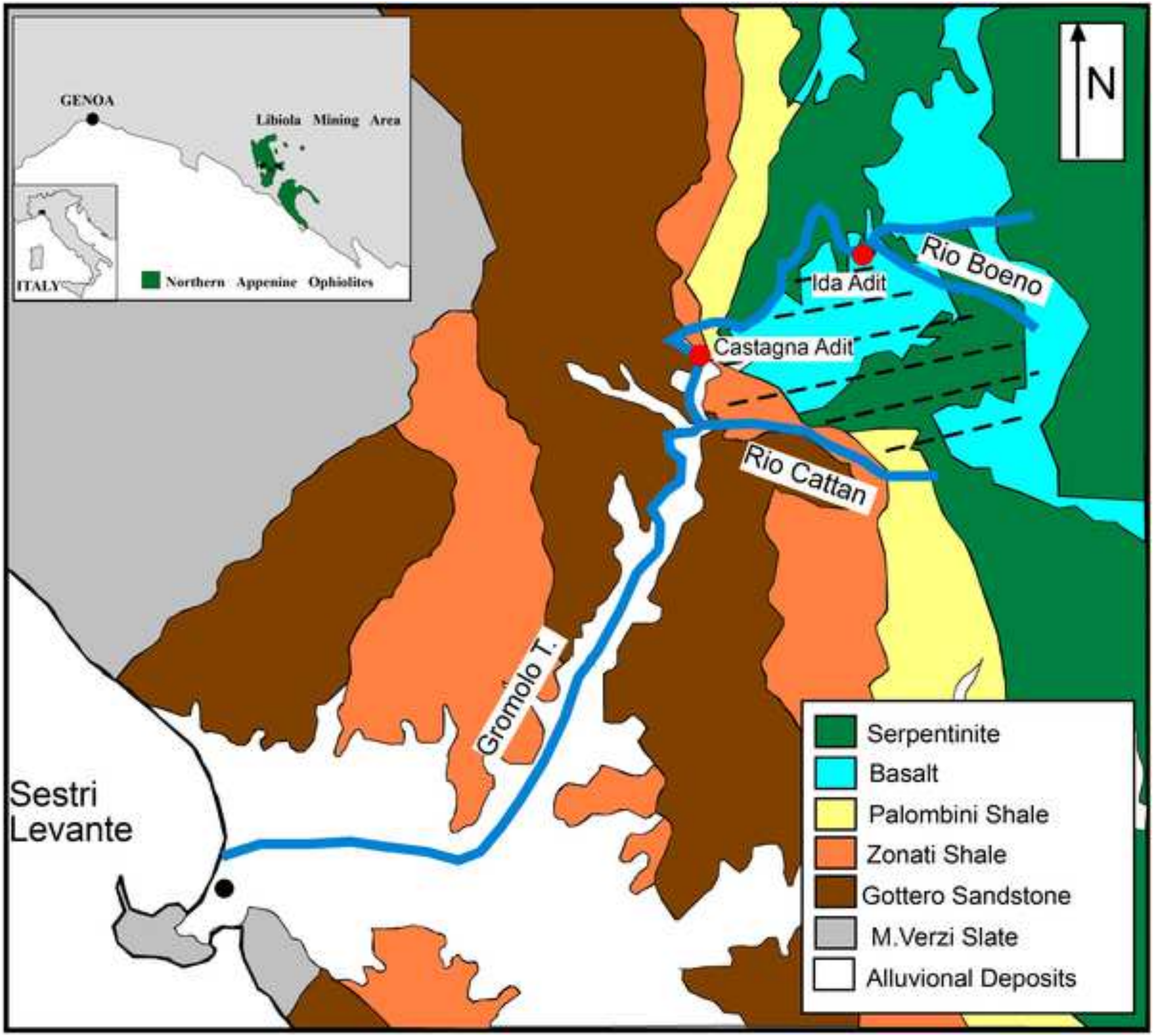
Fig. 4 Scanning Electron Microscope (SEM) images of the amorphous colloids and relative diagrams derived from the EDS semi-quantitative analyses. a) globular to massive aggregates of amorphous colloids and diatoms; b) particular of a rounded crystal of cuprite inside the colloidal precipitates

Fig. 5 Distribution of chemical elements in the samples of the Gromolo Torrent taking into account: a) elements from sulphide mineralisation; b) elements from outcropping rocks; c) other potential ecotoxic elements; d) reports the sample composition normalised to the background value (GRB)

Fig. 6 Plots of pH (above) and EC (µS; below) variations (*y* axis) over log time (*x* axis) of the tested samples with deionised water (on the left) and sea water (on the right). pH and EC starting values measured for deionised water and sea water are reported by black dots on the *y* axis. To better highlight the results of the tests, the scale of each plot is different from the others

Fig. 7 Metal release trends of the tested samples over time with deionised water (on the left) and sea water (on the right)

Figure 1


GENOA
Libiola Mining Area
ITALY
Northern Appenine Ophiolites
N
Rio Boeno
Ida Adit
Castagna Adit
Rio Cattan
Gromolo T.
Sestri Levante
Serpentinite
Basalt
Palombini Shale
Zonati Shale
Gottero Sandstone
M.Verzi Slate
Alluvional Deposits


N
GR0
GR5
GR8
GR3
Gromolo T.
GRB
GR0
Ida adit
Rio Boeno
GR1
Castagna adit
GR3
GR4
Libiola mine
GR5
Rio Cattan
GR6
GR7
Sestri Levante
Ligurian Sea
GR 10
GR 9
GR8

Figure 3

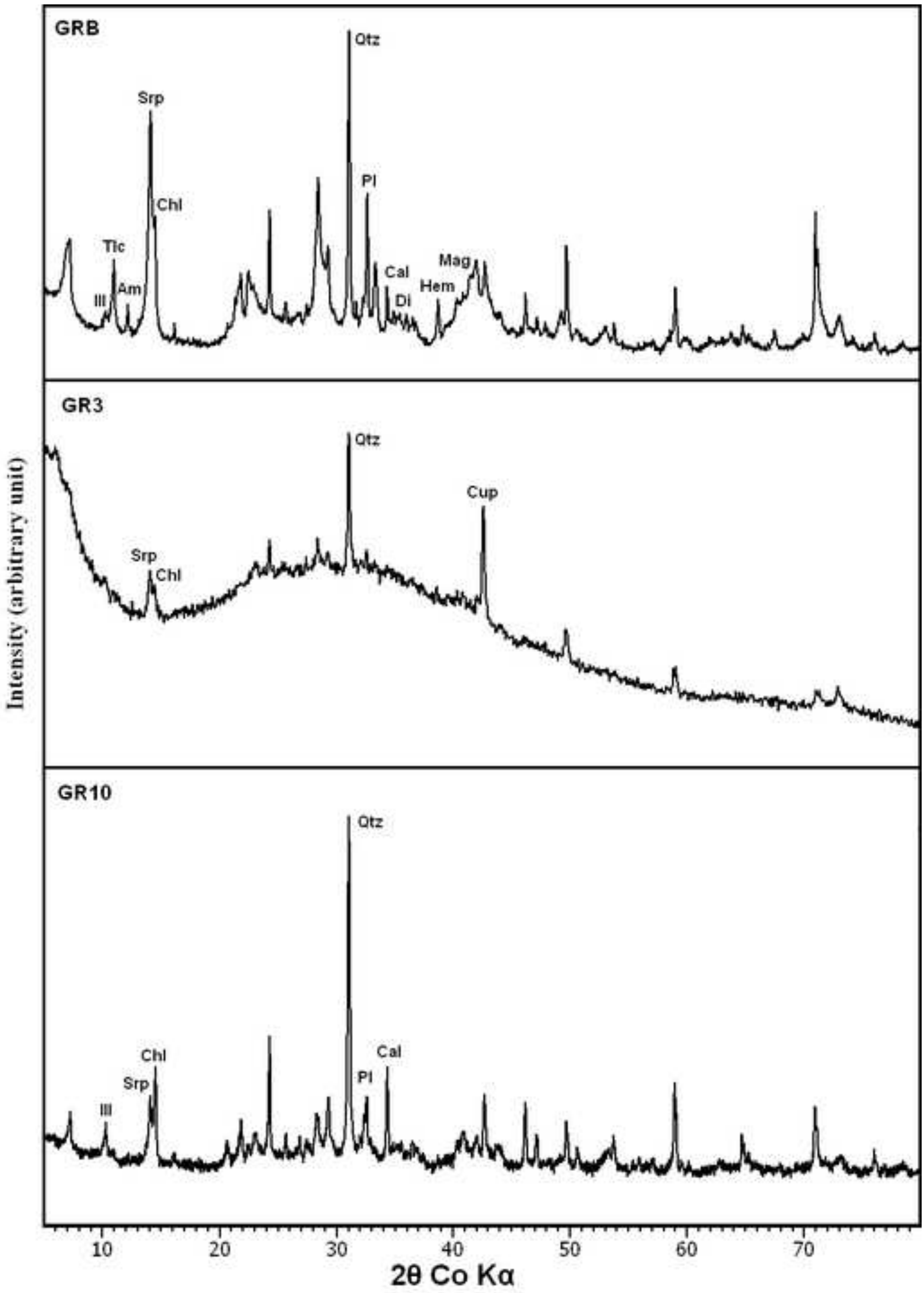

GRB
Qtz
Srp
Pl
Chl
Tlc
Am
Ill
Cal
Di
Hem
Mag
GR3
Qtz
Cup
Srp
Chl
GR10
Qtz
Chl
Srp
Ill
Pl
Cal
Intensity (arbitrary unit)
10
20
30
40
50
60
70
2θ Co Kα

Figure 4

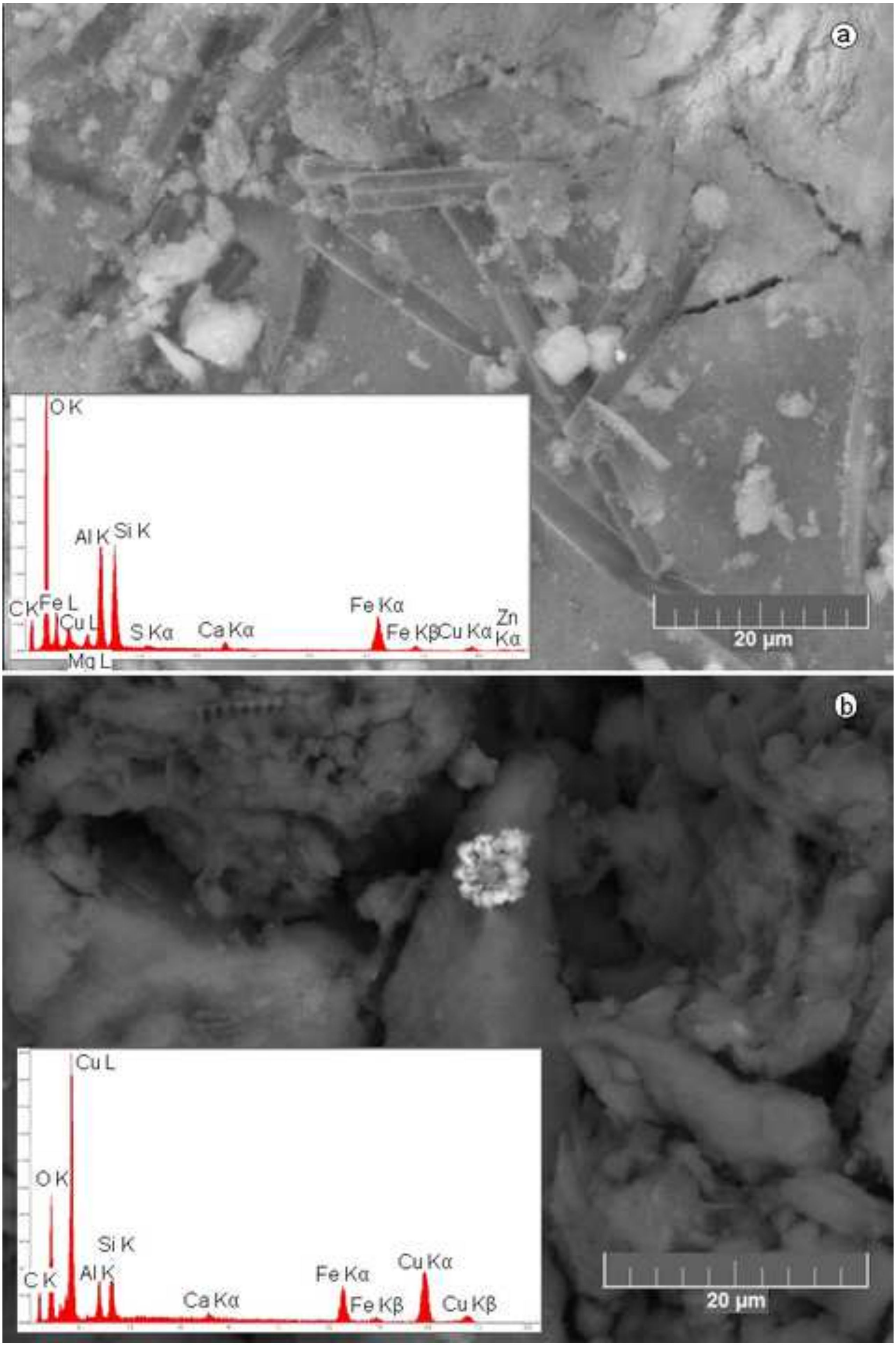
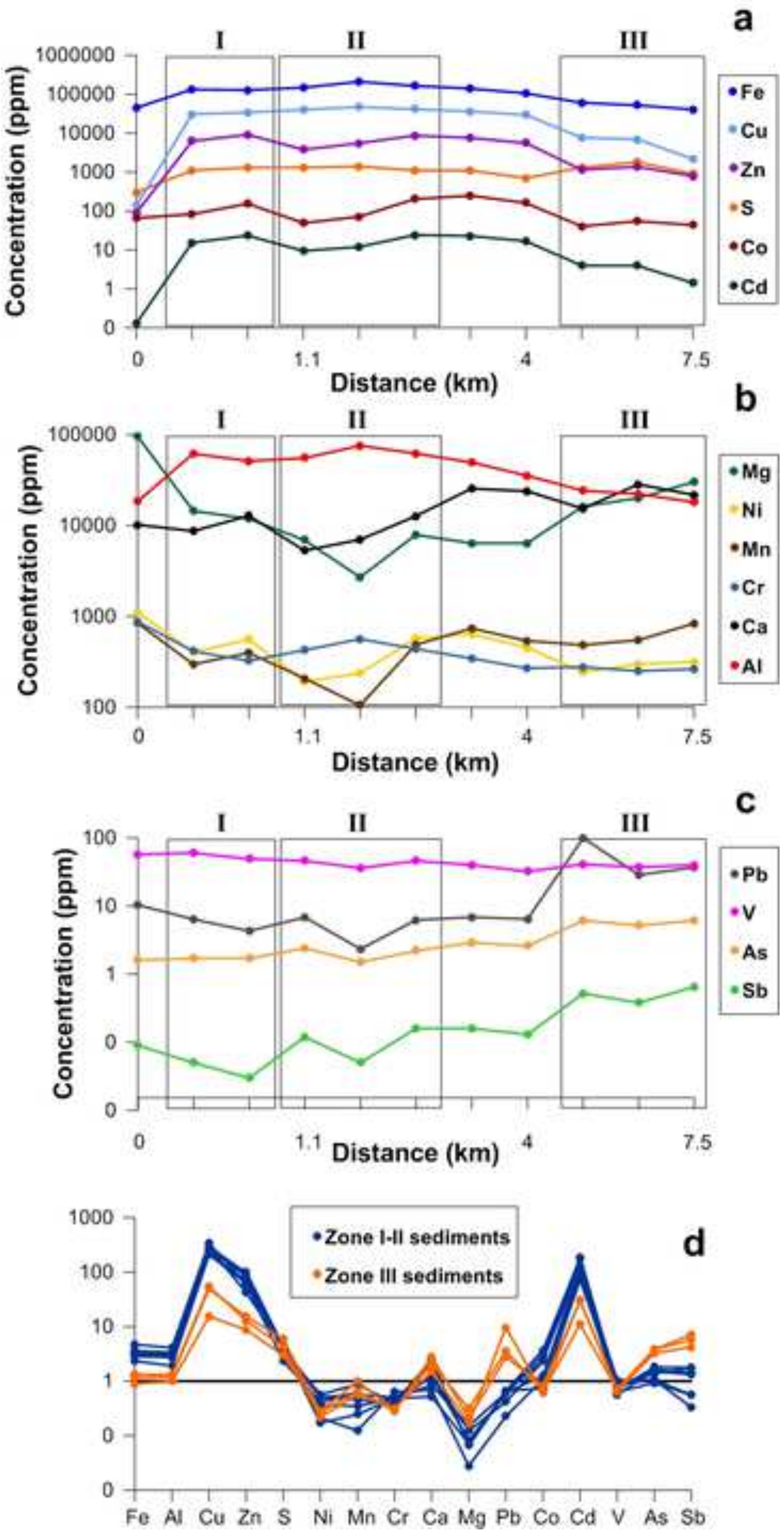
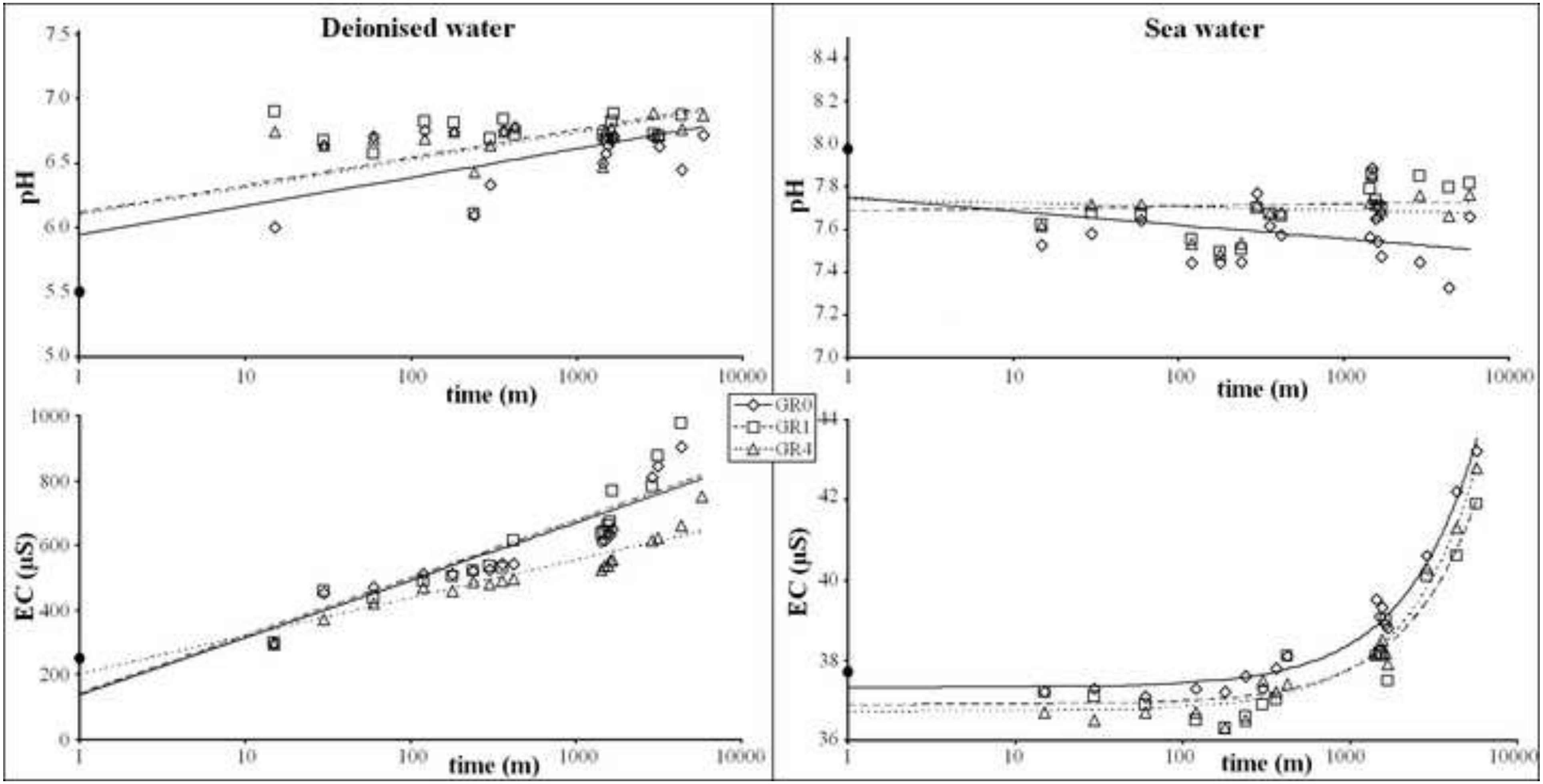

a
O K
Al K
Si K
C K
Fe L
Cu L
S Kα
Ca Kα
Fe Kα
Fe Kβ
Cu Kα
Zn Kα
Mg L
20 µm
b
Cu L
O K
Si K
C K
Al K
Ca Kα
Fe Kα
Fe Kβ
Cu Kα
Cu Kβ
20 µm

Figure 5


a
I
II
III
1000000
100000
10000
1000
100
10
1
0
Concentration (ppm)
0
1.1
4
7.5
Distance (km)
Fe
Cu
Zn
S
Co
Cd
b
I
II
III
100000
10000
1000
100
Concentration (ppm)
0
1.1
4
7.5
Distance (km)
Mg
Ni
Mn
Cr
Ca
Al
c
I
II
III
100
10
1
0
0
Concentration (ppm)
0
1.1
4
7.5
Distance (km)
Pb
V
As
Sb
d
1000
100
10
1
0
0
Zone I-II sediments
Zone III sediments
Fe
Al
Cu
Zn
S
Ni
Mn
Cr
Ca
Mg
Pb
Co
Cd
V
As
Sb


Deionised water
Sea water
pH
EC (µS)
time (m)
7.5
7.0
6.5
6.0
5.5
5.0
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
1000
800
600
400
200
0
44
42
40
38
36
1
10
100
1000
10000
GR0
GR1
GR4

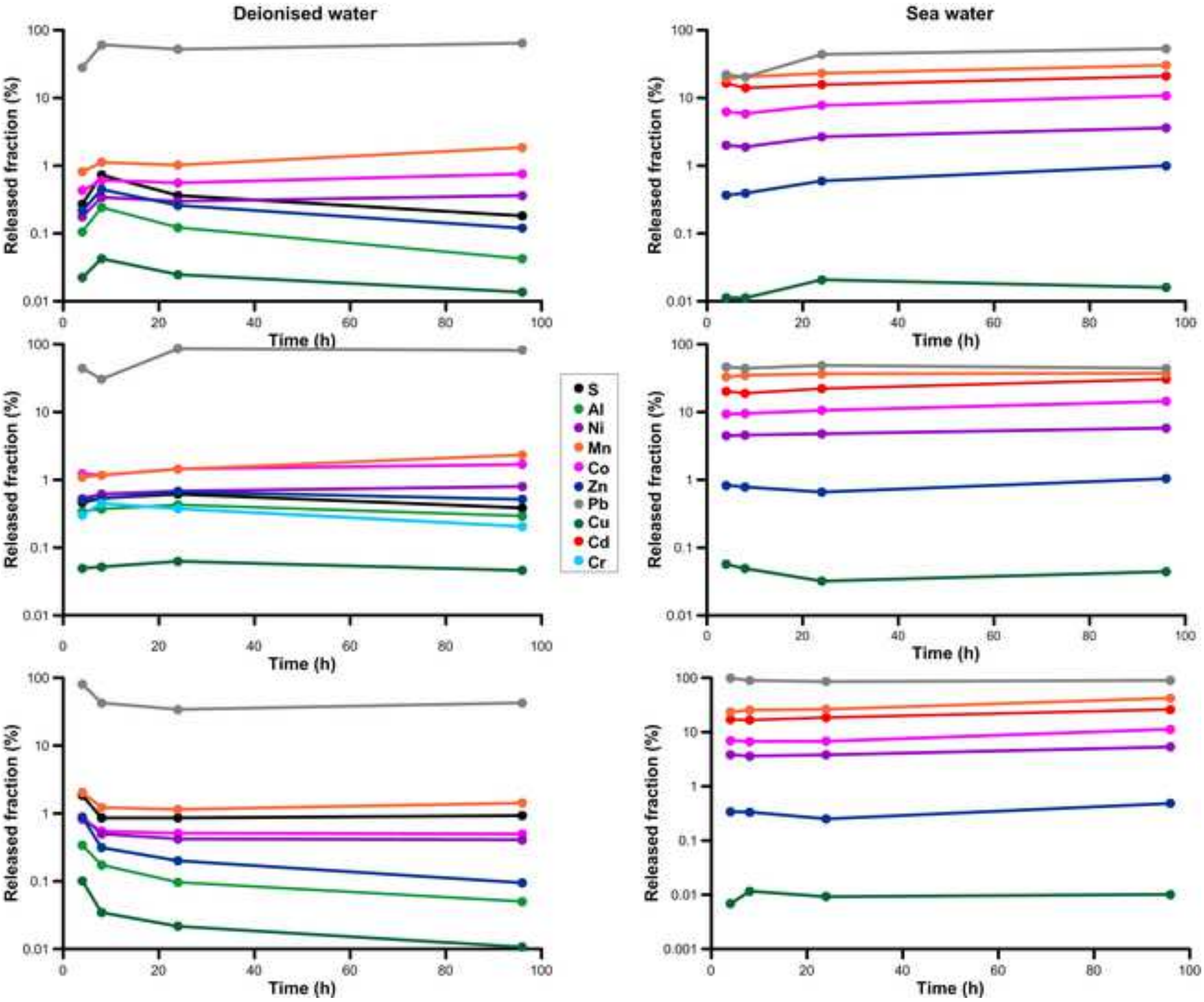

Deionised water
Sea water
Released fraction (%)
Time (h)
100
10
1
0.1
0.01
0.001
0
20
40
60
80
100
S
Al
Ni
Mn
Co
Zn
Pb
Cu
Cd
Cr

Table 1. Sampling point localisation and pH and Electrical Conductivity (EC) values of related torrent waters. n.a. = not analysed.

Station	Lat (°N)	Long (°E)	Water thickness (cm)	pH	EC (μS)
GRB	44.3093	9.4422	10	8.33	340
GR0	44.3092	9.4418	25	7.39	n.a.
GR1	44.3056	9.4381	20	7.48	n.a.
GR3	44.3028	9.4351	35	6.97	472
GR4	44.3008	9.4338	20	7.62	n.a.
GR5	44.2994	9.4346	15	7.96	441
GR6	44.2938	9.4304	15	8.17	417
GR7	44.2860	9.4255	10	8.44	432
GR8	44.2771	9.4190	15	7.97	463
GR9	44.2735	9.4112	40	8.53	525
GR10	44.2738	9.3941	40	7.92	690

Table 2

Table 2. Semi-quantitative mineralogical composition of the torrent sediments. XXX = abundant, XX = medium, X = present

Samples	GRB	GR0	GR1	GR3	GR4	GR5	GR6	GR7	GR8	GR9	GR10
Amorphous		XXX	XXX	XXX	XXX	XXX	XX	XX	X	X	X
Cuprite			XXX	X		XX	XXX	X			
Quartz	X	X	X	X	X	XX	X	XX	X	XXX	XX
Serpentine	XXX	X	X	X	X	X	X		X	X	X
Chlorite	XXX	X	X	X		X	X	X	X	XX	X
Plagioclase	X	X				X	XXX		X	X	X
Talc	XX	X				X			X	X	X
Illite	XX							X	X	X	X
Calcite	X		X				XX	XX	X	X	X
Amphibole	X										
Diopside	X										
Magnetite	X										
Hematite	X										
Clay				X	X						

Table 3

Table 3 Bulk chemical composition in weight percent (wt%) or mg kg^{-1} of the sediments and colloids of the Gromolo Torrent.

	GRB	GR0	GR1	GR3	GR4	GR5	GR6	GR7	GR8	GR9	GR10
Fe (wt %)	4.49	13.22	12.78	14.73	20.99	16.31	13.98	10.49	6.03	5.20	4.03
Al (wt %)	1.84	6.19	5.12	5.53	7.57	6.20	4.96	3.54	2.42	2.22	1.81
S (wt %)	0.03	0.11	0.13	0.13	0.14	0.11	0.11	0.07	0.13	0.18	0.09
Ca (wt %)	1.02	0.87	1.28	0.53	0.70	1.27	2.55	2.39	1.54	2.84	2.17
Mg (wt %)	9.65	1.45	1.19	0.69	0.27	0.79	0.64	0.64	1.62	2.01	3.02
P (wt %)	0.02	0.02	0.02	0.03	0.01	0.03	0.04	0.04	0.10	0.06	0.05
Ti (wt %)	0.06	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.02	0.02
Na (wt %)	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01
K (wt %)	0.03	0.02	0.03	0.02	0.01	0.02	0.04	0.03	0.08	0.07	0.08
Cu (mg kg^{-1})	140	30650	33983	40060	47170	41080	36200	29340	7607	6946	2170
Zn (mg kg^{-1})	90	6232	9139	3767	5507	8646	7570	5540	1143	1367	780

Ni (mg kg^{-1})	1118	404	556	192	237	571	637	454	244	300	315
Mn (mg kg^{-1})	848	298	396	208	105	487	739	539	484	548	837
Cr (mg kg^{-1})	876	414	324	425	564	438	346	268	278	250	264
Mo (mg kg^{-1})	0.13	0.27	0.26	0.45	0.27	0.36	0.31	0.23	0.47	0.54	0.76
Pb (mg kg^{-1})	10.3	6.4	4.3	6.8	2.3	6.2	6.9	6.4	99	28.5	37.0
Co (mg kg^{-1})	66	83	154	49	71	203	248	161	40	55	44
Cd (mg kg^{-1})	0.13	15.38	23.26	9.47	11.96	24.19	22.95	16.73	3.96	3.94	1.42
V (mg kg^{-1})	57	60	49	46	36	46	40	32	41	37	4
As (mg kg^{-1})	1.6	1.7	1.7	2.4	1.5	2.2	2.9	2.6	6.1	5.2	6.1
Sb (mg kg^{-1})	0.09	0.05	0.03	0.12	0.05	0.16	0.16	0.13	0.52	0.38	0.65
Zr (mg kg^{-1})	1.6	0.8	0.6	0.7	0.3	0.4	0.2	0.3	0.6	0.8	0.8
U (mg kg^{-1})	0.2	0.9	0.8	1.8	2.3	1.7	1.3	0.9	0.4	0.4	0.3
Th	0.6	0.3	0.2	0.4	0.2	0.3	0.3	0.3	1.2	1.5	1.6

(mg kg^{-1})											
Ba (mg kg^{-1})	18	33	49	25	19	50	89	71	87	56	38
Sr (mg kg^{-1})	19.5	48.2	73.5	37.4	40.8	96.5	158.6	134.7	57.6	73.8	64.6

Table 4

Table 4. Correlation coefficients calculated for the elements in the sampled sediments. In bold the high positive correlation, in italic the high negative correlation

	Fe	Al	Cu	Zn	S	Ni	Mn	Cr	Mg	Pb	Co	Cd	V	As	Sb
Fe	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Al	**0.98**	1	-	-	-	-	-	-	-	-	-	-	-	-	-
Cu	**0.97**	**0.94**	1	-	-	-	-	-	-	-	-	-	-	-	-
Zn	**0.76**	**0.77**	**0.84**	1	-	-	-	-	-	-	-	-	-	-	-
S	0.27	0.29	0.27	0.16	1	-	-	-	-	-	-	-	-	-	-
Ni	-0.23	-0.24	-0.24	0.02	*-0.72*	1	-	-	-	-	-	-	-	-	-
Mn	*-0.73*	*-0.77*	*-0.70*	-0.40	-0.56	0.60	1	-	-	-	-	-	-	-	-
Cr	0.10	0.10	-0.03	-0.17	-0.54	0.67	0.07	1	-	-	-	-	-	-	-
Mg	-0.61	-0.59	-0.69	-0.60	-0.65	**0.75**	0.61	**0.72**	1	-	-	-	-	-	-
Pb	-0.56	-0.55	-0.59	-0.56	0.18	-0.32	0.19	-0.34	0.04	1	-	-	-	-	-
Co	0.42	0.36	0.52	**0.79**	-0.14	0.36	0.16	-0.13	-0.32	-0.45	1	-	-	-	-
Cd	**0.70**	0.69	**0.79**	**0.98**	0.12	0.07	-0.29	-0.22	-0.59	-0.52	**0.87**	1	-	-	-
V	-0.05	0.11	-0.09	0.05	-0.33	0.49	0.01	0.54	0.49	-0.19	-0.11	0.00	1	-	-
As	-0.67	-0.68	-0.66	-0.67	0.28	-0.43	0.40	-0.59	-0.04	**0.81**	-0.39	-0.54	-0.43	1	-
Sb	-0.67	-0.68	-0.68	-0.63	0.14	-0.36	0.47	-0.48	0.05	**0.77**	-0.41	-0.58	-0.37	**0.97**	1

Table 5a

Table 5a Released fraction (wt %) after bulk leaching tests with deionised water for the tested elements. In parenthesis the total amount (mg kg^{-1}) measured in solution. b.d.l.= below detection limit

Tests with deionised water	**Al**	**Fe**	**Mn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
GR0 4h	0.11% (66)	0.15% (199)	0.82% (2.4)	b.d.l.	0.43% (0.36)	b.d.l.	0.02% (68.2)	0.18% (0.72)	28.24% (1.8)	0.22% (13.5)
GR0 8h	0.24% (150)	0.34% (452)	1.12% (3.3)	b.d.l.	0.61% (0.51)	0.07% (0.3)	0.04% (130)	0.34% (1.38)	60.86% (3.9)	0.45% (27.9)
GR0 24h	0.12% (76)	0.18% (232)	1.02% (3.1)	b.d.l.	0.56% (0.46)	b.d.l.	0.02% (71.8)	0.30% (1.21)	52.26% (3.3)	0.26% (16.2)
GR0 96h	0.04% (26)	0.07% (87)	1.86% (5.5)	b.d.l.	0.76% (0.63)	b.d.l.	0.1% (41.8)	0.36% (1.47)	64.25% (4.1)	0.12% (7.5)
GR1 4h	0.34% (176)	0.39% (496)	1.09% (4.3)	b.d.l.	1.23% (1.02)	0.30% (0.98)	0.05% (168)	0.53% (2.94)	44.19% (1.9)	0.51% (46.2)
GR1 8h	0.37% (190)	0.42% (537)	1.18% (4.7)	b.d.l.	1.17% (0.97)	0.45% (1.45)	0.05% (177)	0.62% (3.44)	30.55% (1.3)	0.53% (48.2)
GR1 24h	0.43% (219)	0.51% (648)	1.44% (5.7)	b.d.l.	1.45% (1.2)	0.38% (1.22)	0.06% (214)	0.68% (3.8)	86.22% (3.7)	0.66% (60.8)

GR1 96h	0.29% (151)	0.37% (479)	2.34% (9.3)	b.d.l.	1.68% (1.39)	0.20% (0.66)	0.05% (157)	0.80% (4.43)	81.77% (3.5)	0.52% (47.1)
GR4 4h	0.34% (256)	0.45% (937)	2.05% (2.2)	b.d.l.	0.82% (0.68)	0.67% (3.8)	0.10% (477)	0.89% (2.1)	81.20% (1.9)	0.88% (48.4)
GR4 8h	0.17% (132)	0.24% (494)	1.22% (1.3)	b.d.l.	0.55% (0.45)	0.22% (1.24)	0.03% (163)	0.50% (1.18)	42.74% (1)	0.31% (17.2)
GR4 24h	0.10% (73)	0.13% (282)	1.15% (1.2)	b.d.l.	0.51% (0.42)	0.06% (0.31)	0.02% (102)	0.42% (1)	34.19% (0.8)	0.20% (11)
GR4 96h	0.05% (38)	0.07% (142)	1.43% (1.5)	b.d.l.	0.50% (0.41)	0.01% 0.06)	0.01% (50.4)	0.41% (0.97)	42.74% (1)	0.09% (5.2)

Table 5b

Table 5b Released fraction (wt %) after bulk leaching tests with sea water for the tested elements. In parenthesis the total amount (mg kg^{-1}) measured in solution.

b.d.l.= below detection limit

Tests with sea water	**Al**	**Fe**	**Mn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
GR0 4h	0.00% (1.8)	b.d.l.	19.37% (58)	16.42% (2.53)	6.24% (5.17)	b.d.l.	0.01% (34.5)	2.01% (8.1)	22.04% (1.4)	0.37% (22.9)
GR0 8h	0.01% (3.7)	b.d.l.	20.49% (61)	14.01% (2.15)	5.88% (4.88)	b.d.l.	0.01% (34.3)	1.89% (7.65)	20.38% (1.3)	0.39% (24.5)
GR0 24h	0.00% (1.7)	b.d.l.	23.06% (69)	15.66% (2.41)	7.76% (6.43)	b.d.l.	0.02% (43.7)	2.67% (10.8)	43.89% (2.8)	0.60% (37.2)
GR0 96h	0.00% (1.8)	b.d.l.	30.27% (90)	20.97% (3.23)	10.80% (8.95)	b.d.l.	0.02% (48.8)	3.61% (14.57)	53.29% (3.4)	1.00% (62.3)
GR1 4h	b.d.l	b.d.l.	32.93% (130)	20.33% (4.73)	9.34% (14.36)	0.07% (0.23)	0.06% (193)	4.48% (24.9)	46.51% (2)	0.83% (75.8)
GR1 8h	b.d.l	b.d.l.	34.95% (138)	18.96% (4.41)	9.53% (14.65)	b.d.l.	0.05% (167)	4.58% (25.46)	44.19% (1.9)	0.79% (71.8)
GR1 24h	b.d.l	b.d.l.	36.62% (145)	22.19% (5.16)	10.59% (16.28)	0.07% (0.23)	0.03% (109)	4.79% (26.64)	48.84% (2.1)	0.66% (60.3)

GR1 96h	b.d.l	b.d.l.	37.30% (148)	30.58% (7.11)	14.40% (22.14)	0.04% (0.14)	0.04% (150)	5.80% (32.29)	44.19% (1.9)	1.04% (95.1)
GR4 4h	0.00% (3.5)	b.d.l.	23.55% (25)	16.94% (2.03)	6.99% (4.99)	0.05% (0.29)	0.01% (32.2)	3.82% (9.06)	98.29% (2.3)	0.34% (18.6)
GR4 8h	0.01% (6.1)	0.00% (3.6)	25.53% (27)	16.71% (2)	6.73% (4.8)	0.04% (0.23)	0.01% (55)	3.62% (8.57)	89.74% (2.1)	0.34% (18.5)
GR4 24h	0.01% (4.3)	b.d.l.	26.31% (28)	18.53% (2.22)	6.76% (4.83)	0.08% (0.45)	0.01% (43.4)	3.80% (9.02)	85.47% (2)	0.25% (13.8)
GR4 96h	0.00% (1.8)	b.d.l.	42.32% (44)	26.15% (3.13)	11.31% (8.08)	0.07% (0.38)	0.01% (47.9)	5..32% (12.61)	89.74% (2.1)	0.48% (26.6)