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A study of metal contaminant availability in sediments

Roberta Guerra roberta.guerra@unibo.it – Centro Interdipartimentale di Ricerca per le Scienze Ambientali (C.I.R.S.A.), University of Bologna, Ravenna, (I) – Department of Physics, University of Bologna, (I)

Simona Bonaiuti – Centro Interdipartimentale di Ricerca per le Scienze Ambientali (C.I.R.S.A.), University of Bologna, Ravenna, (I)

Giuliana Bonvicini, Adelia Albertazzi – Italian Ceramic Centre, Bologna, (I)

Summary

Of the many different chemical extraction or digestion procedures that have been proposed to quantify metal contamination, partial acid extractions are probably the best overall compromise between selectivity, sensitivity, precision and cost. The extent to which measured metal concentrations relate to the anthropogenic fraction that is bioavailable is controversial, but is one of the desired outcomes of an assessment or prediction of biological impact. As part of a survey on metal contamination in a coastal lagoon, we wanted to identify an extraction protocol that would allow a reasonable definition of the anthropogenic bioavailable fraction in sediment samples. From a kinetic study of the 1M HCl- extraction of two test sediments, we concluded that a 24 h extraction time allows the equilibrium dissolution of relatively labile metal contaminants.

Riassunto

Tra le diverse procedure di estrazione o digestione proposte per quantificare la contaminazione da metalli, le estrazioni parziali probabilmente rappresentano il miglior compromesso in termini di selettività, sensibilità, precisione e costo. La misura in cui le concentrazioni di metalli rappresentano la frazione di origine antropica, e quindi biodisponibile, è controversa ma è uno dei risultati auspicabili di una valutazione o previsione di impatto biologico. Nell'ambito di una ricerca sulla contaminazione da metalli in una laguna, si è voluto applicare un protocollo di estrazione che permettesse di determinare la frazione antropica biodisponibile in campioni di sedimento. Dallo studio della cinetica di estrazione con HCl 1 M di due campioni rappresentativi di sedimento possiamo concludere che un tempo di estrazione di 24 ore porta alla dissoluzione della frazione labile dei metalli legati al sedimento.

1. Introduction

The concentration of bioavailable metals in sediments is of key interest, as this fraction is likely to be toxic and cause an impact to biota. Depending on the type of interacting organism and physico-chemical character of the sediment, the bioavailable fraction could be dominantly in porewater, or adsorbed to sediment particles such as organic matter, Fe-Mn oxides, carbonates, or sulphides. More likely, the fraction that is biologically available to the benthic community as a whole will be a combination of several of these phases. Although many different partial or multiple extraction methods have been proposed to specifically target the anthropogenic bioavailable fraction in marine sediments [1, 2, 3], the only sure way to measure bioavail-

ability involves biological uptake experiments [4], but such approaches are currently not feasible for an extensive local or regional assessment of metal contamination. So far the most commonly adopted analytical method employed for these assessments has involved total or near-total digestions with concentrated strong acids. Although this approach offers very good reproducibility, and has been used to derive most sediment quality guidelines (SQGs), there are two major disadvantages: (a) the local/regional variability in total metals often exceeds anything but the most intense local contamination, which could lead to an error in many sediment assessments (i.e. where a contaminated site is not identified as being significantly different from background); (b) a significant proportion of the total metal load in sediment is not likely to be bioavailable and as total sediment digests correlate poorly with bioavailability. Partial extractions are an attractive alternative because they are simple, relatively safe, they target labile phases and reservoirs containing metals, and provide the most useful chemical technique for identifying anthropogenic anomalies in a regional survey [5, 6], and they are reported to closely correlate with the bioavailable fraction [7]. The main aim of the research presented here is to evaluate the effect of reaction time on the extraction efficiency of trace metals over a 24 h period. We then compared the data sets from two sediments from a coastal lagoon using the 1 M HCl-extraction method at different reaction times from 2 to 24 hours.

2. Relation

2.1 Methods

2.1.1 Sediment

To assess extraction efficiency for a range of metals, two coastal sediments were analysed in detail. The two sediments were collected as part of a local survey using an orthogonal-hierarchical sampling design in Pialassa Baiona lagoon (North Adriatic Sea, Italy). One sample was from an impacted area site of known metal pollution, which is adjacent to a petro-chemical complex but far from the tidal influence. The second lagoon sample was from a non-impacted area site under the tidal influence [8]. Samples were oven dried to constant weight at <60 °C. Samples were first sieved using a sieve with nylon mesh to 2 mm to remove large clasts or shells, and then an aliquot was sieved to 63 mm.

2.1.2 Sample preparation and analysis

Total concentration of metals in sediment was determined by microwave assisted acid digestion based on a modification of EPA Method 3052 [9]. In brief, 0.2 g of sample was digested using Suprapur quality HNO_3 , HF and HCl into a 100-mL Teflon-PFA microwave digestion vessel. Trace element analyses in digests were performed using ICP-OES (Perkin Elmer Optima 3200 XL). Certified reference material MESS-3 (Marine Sediment, National Research Council of Canada) together with blanks and replicate samples were included to study the accuracy and analytical precision. The recoverability of the expected concentration had a mean value of 80%, the variation ranging from 1% to 11% depending on the metal.

For the partial HCl-extractions, solutions were prepared from an AR-grade concentrated HCl (32% w/w) and deionized water. All plastic labware was soaked for >24 h with 3 M AR HNO_3 (69% w/w) and then triple-rinsed in deionized water. Partial extractions (1 M HCl) were conducted on an orbital platform shaker and the supernatants were filtered immediately through 0.45 mm cellulose nitrate membranes and stored at 4°C until analysis. All extractions used 1 g of sediment to 20 ml 1 M HCl solution (1:20 w/v) and were analysed by ICP-OES for Cr, Cu, Pb, Ni and Zn. The variable time experiment was undertaken on two samples. These were extracted in four replicates over five time periods: 2, 4, 8, 16 and 24 h. Sediments were extracted in sametime batches consisting of eight samples and one procedural blank. Extractions

were prepared at staggered intervals and were promptly filtered, and the extracts stored at 4°C until analysis.

2.2 Results and discussion

The total concentrations and HCl-extractable concentrations of five selected metal elements (Cr, Cu, Ni, Pb and Zn) in test sediments are listed in Table 1. In general, concentrations of metals were higher at the impacted location than the non impacted location. In particular, consistently higher concentrations of total Cr, Cu, Pb and Zn were found in sample from the impacted area. The order of metals ranked by decreasing concentration was Zn > Cr > Cu > Ni > Pb in sample at the impact location, and Zn > Cr > Ni > Cu > Pb in sample at the non-impacted location. These metals were selected because they have known toxic effects on marine organisms and they represent the full range of metal concentrations in association with sediment in the area of study. Hence, it is important to determine whether the concentrations of trace metals found in sediments are likely to pose a threat to aquatic life. Sediment quality guidelines such as TEL (threshold effects level) are interpreted as concentrations below which adverse biological effects rarely occur, and thus is considered to provide a high level of protection for aquatic organisms. Similarly, PEL (probable effects level) are the concentrations above which adverse biological effects frequently occur [10, 11]. At the impacted area, Ni and Zn exceeded the PEL in sediment at the impacted area location, and Cr, Cu, Pb were between the TEL and the PEL. At the non-impacted area, sediment reported concentrations of Cr and Ni between the TEL and PEL with Cu, Pb and Zn at or below the TEL. The above results lead to the conclusion that toxic metals like Cr, Cu, Ni, Pb and Zn are of concern in the impacted area and that may occasionally or frequently be associated with adverse biological effects. Conversely, Cu, Pb and Zn at the non-impacted area are not of environmental concern.

	Total		HCl-extractable				TEL	PEL
	Impacted area	Non impacted area	Impacted area		Non impacted area			
			4 h	24 h	4 h	24 h		
Cr	128	61	41	49	2.7	5.9	52	160
Cu	76	19	62	66	11	13	18	108
Ni	57	41	9.4	22	8.7	15	16	43
Pb	32	13	25	25	6.8	7.2	30	112
Zn	392	64	225	246	20	27	124	271

Tab. 1 – The total concentrations and HCl-extractable metal concentrations in test sediments (mg kg⁻¹ dry wt).

Table 1 and Figure 1 show HCl-extractable metal concentrations for the five metal elements. Extracted metal concentrations were highly variable from 2 to 24 hours, ranging from 2.1 to 246 mg kg⁻¹, and the extraction efficiency varied from 3 to 86 %.

At impacted location, Zn was highest, followed by Cu > Cr > Pb > Ni. At non-impacted location, the order of metals was Zn > Cu > Ni > Pb > Cr. Except for Zn, which was the highest in both test samples, the order of the extractable metal concentration rankings was not the same as the order of the total metal concentration rankings.

The extraction of Cr, Zn and particularly Ni, increased rapidly in the first hours of the experiment and then began to plateau as the reactions slowed down and approached equilibrium after 16 h; in contrast to this, extracted Cu and Pb increased very slowly during the experiment (Figure 1). The first-order kinetic equation provided a good fit to the metal concentration data only for Ni (Figure 1).

In general, fast extraction kinetics are produced by highly labile and weakly sorbed metals, especially anthropogenic metals. Moderately extraction kinetics are produced by less labile, moderately sorbed and some strongly sorbed or bound metals, which includes both anthropogenic and some natural fractions. Slow extraction kinetics reflect extraction of relatively inert phases typical of naturally occurring metals in the sediment matrix. Examination of the reaction kinetics extracted by 1 M HCl at different times, from different sediments, were not uniform and the time taken to reach equilibrium varied from 4 to 24 h, depending on the element and the sediment confirming that a typical sediment matrix is a complex physico-chemical system.

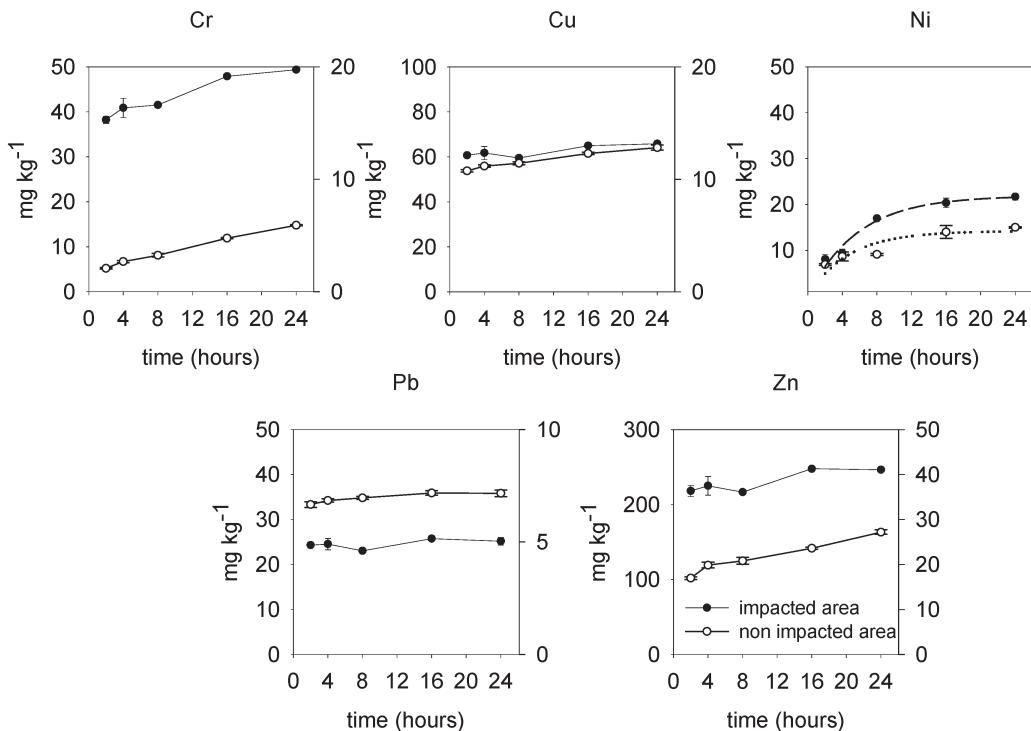


Fig. 1 – Extraction efficiency of 1 M HCl in sediments from the impacted and non-impacted areas. Best-fit curves for Ni are first-order kinetic relations.

Copper and Pb had the greatest extraction efficiency and Cr and Ni the least (Figure 2). Since metal bioavailability is related to metal solubility, extractable metal concentrations may correspond to the bioavailable metal concentrations. Results from the extraction experiments indicated that Cu should be the most bioavailable metal compared to the other metals studied. In addition, overall extraction efficiencies for the sediment from the impact area, were higher than the sediment from the non impacted area, as shown in Figure 2.

Even though sediment characteristics can influence extraction efficiency in either positive or negative ways, the dominant factor that determined the time taken to approach an equilibrium condition, appears to be whether the metals were ultimately of natural origin or anthropogenic.

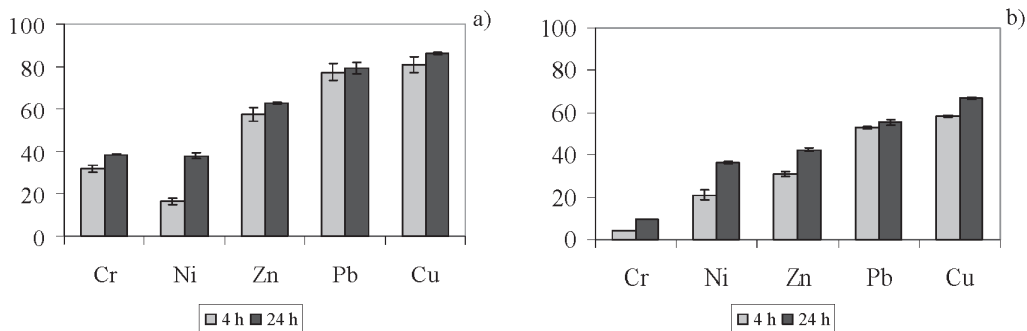


Fig. 2 – Comparison of 4 and 24 h 1M HCl concentrations for sediments from the impacted (a) and non-impacted area location (b). Mean and standard deviation are shown based on four replicates. All concentrations are in mg kg⁻¹.

Conclusions

For Cr, Zn and Ni, increasing extraction time predictably increased extraction efficiency, although Pb and Cu had no consistent trend with only small changes with time. Factors such as solubility, speciation/mineralogy, grain size, organic content and redox condition could greatly affect the extractability of metals by HCl. Even though these characteristics can influence extraction efficiency, the dominant factor appears to be whether the metals were ultimately of natural origin or anthropogenic – with the generally weaker bound anthropogenic metals not surprisingly having faster extraction kinetics than those from natural sources. From the very limited number of samples studied here, chemical data are unlikely to accurately reflect the true bioavailability of metals in the sediments, but it will provide a reasonable approximation. This information can then be used to target a large number of samples for more detailed study linking observations about biota to other more carefully defined but time consuming chemical parameters.

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