Baseline

Comparison of partial extraction reagents for assessing potential bioavailability of heavy metals in sediments

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ABSTRACT

Assessment of heavy metal bioavailability in sediments is complex because of the number of partial extraction methods available for the assessment and the general lack of certified reference materials. This study evaluates five different extraction methodologies to ascertain the relative strengths and weaknesses of each method. The results are then compared to previously published work to ascertain the most effective partial extraction technique, which was established to dilute (0.75–1 M) nitric acid solutions. These results imply that single reagent; weak acid extractions provide a better assessment of potentially bioavailable metals than the chelating agents used in sequential extraction methods.

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Assessing heavy metal contamination in sediments is a complex exercise as there are numerous methods for assessing metal concentrations, and total metal concentration is generally not considered to be a good indicator metal bioavailability (Ahdy and Youssef, 2011; Lee et al., 2012; Shikazono et al., 2012; Shilla and Dativa, 2011). This is particularly true with more recent research results, which demonstrates that the mode of occurrence of a metal (Sundaray et al., 2011) and the form in which that metal is present (Zhong et al., 2011) are essential for understanding the potential ecological impacts of contamination on sediment and its associated water body. For this reason, a holistic approach to sediment contamination should seek to assess metal mobility (Beltrán et al., 2010) in order to assess potential effects on aquatic systems.

There have been a number of suggestions and much debate over the best method for assessing the mobility and bioavailability of metals in sediments. Recommended techniques range from using 1 M acid solutions (Hu et al., 2011), to the use of chelating agents such as EDTA (Sahuquillo et al., 2003) and the use of more complicated sequential extraction methods such as the Tessier method (Tessier et al., 1979) or the Bureau Communautaire de Référence (BCR) method recognised by the European Community Bureau of Reference (Rauret, 1998).

This range of suggested methods demonstrate that there is no unanimity in the adoption of a preferred single method for assessing sediment contamination by heavy metals (Chapman and Wang, 2001; Ruiz, 2001) and that no method currently exists, which can give a reliable estimate of bioavailability (Luoma, 1989). However, the work of Martin et al. (1987) demonstrated that methods, which assess potential bioavailability have been widely applied in environmental studies as they can distinguish between "background" and "abnormal" concentrations of heavy metals and can be used to identify anthropogenic contamination. Yet, Luoma (1989) highlighted that these methods are probably insufficient as they fail to consider the complex environments. In contrast, Hart (1982) found that cautious interpretation of the results of sequential studies can provide information on how heavy metals are distributed across different geochemical phases.

The two most common sequential extraction methods in use are the Tessier method (Tessier et al., 1979) and the BCR method (Cuong and Obbard, 2006; Rauret, 1998). Both of these methods adopt a similar approach to assessing the three major mobile fractions (exchangeable/carbonate, reducible and oxidisable fractions) (Table 1) and both tend to under-report metal concentrations when dealing with low levels of contamination (Sahuquillo et al., 2003) but the Tessier method is most widely used in the research literature (Cuong and Obbard, 2006). However, issues in relation to the extraction process employed in this method have been noted, with re-adsorption processes having the largest effect on the method (Whalley and Grant, 1994). This led to the development of the BCR extraction procedure (Cuong and Obbard, 2006; Rauret, 1998). Nevertheless, the multi-step extractions nurtured in both methods have a number of limitations, including operationally defining the extraction methods (in terms of aims and methodology), redistribution of heavy metals through the different fractions (Gleyzes et al., 2002) and difficulties in

Table 1
Comparison of various heavy metal extraction techniques.

Fraction	Weak acid	BCR digestion (Cuong and Obbard, 2006)	Tessier digestion (Tessier et al., 1979)
Exchangeable	1 M HCl	0.11 M acetic acid	1 M $MgCl_2$ at pH 7
Carbonate			1 M CH_3COONa buffered to pH 5 with CH_3COOH
Reducible		0.5 M $NH_2OH.HCl$ buffered to pH 1.5 with HNO_3	0.04 M $NH_2OH.HCl$ in 25% CH_3COOH heated to 95 °C
Oxidisable		10 mL H_2O_2; 1 M CH_3COONH_4 buffered to pH 2 with HNO_3	30% H_2O_2 adjusted to pH 2 with 0.02 M HNO_3 heated to 85 °C. Treatment with 3.2 M CH_3COONH_4 in 20% HNO_3
Residual			Dissolution in HF and $HClO_4$ at 95 °C

Table 2
Preparation of extraction reagents.

Reagent	N	Preparation
0.04 M EDTA	7	7.04 g into 450, buffered with NaOH to pH 8, diluted to 500 mL
1 M CH_3COONa	7	41 g CH_3COONa into 450 mL, pH adjusted to 5, using CH_3COOH, diluted to 500 mL
0.11 M CH_3COOH	7	30 mL H_2O, 6.4 mL glacial acetic acid added, diluted to 50 mL
0.25 M HNO_3	7	0.8 mL HNO_3 into 50 mL
0.5 M HNO_3	7	1.6 mL HNO_3 into 50 mL
0.75 M HNO_3	7	2.4 mL HNO_3 into 50 mL
1 M HNO_3	7	3.2 mL HNO_3 into 50 mL
0.5 M HCl	7	2.5 mL HCl into 50 mL
1 M HCl	7	5 mL HCl into 50 mL

undertaking a viable comparison between methods (Hart, 1982; Martin et al., 1987; Rauret, 1998). Table 1 provides a comparison of the Tessier and BCR Digestion methods.

Studies suggesting the use of single, non-selective extraction techniques that target the metals in mobile (or labile) fractions are available in the literature (Agemian and Chau, 1976; Hamdoun et al., 2015; Hu et al., 2011; Malo, 1977; Rauret, 1998; Sutherland, 2002). The use of dilute acids, known as the Weak acid Extractable Metals (WE-M) has been reported considerably in the literature and comparisons with similar fractions (the exchangeable and carbonate fractions in particular) from sequential extractions have been undertaken by a number of researchers, including Malo (1977), who examined the applicability of HCl as a WE-M reagent; Sutherland (2002), who found that a 1 M HCl leach was more efficient than the BCR three step extraction procedure; and others who used WE-M extraction protocols to extract heavy metals from marine sediments (Agemian and Chau, 1977; Brady et al., 2014; Brady et al., 2015).

Generally, these methods were found to be similar to or more efficient than sequential extractions (Agemian and Chau, 1976, 1977; Hamdoun et al., 2015; Hu et al., 2011; Malo, 1977; Rauret, 1998; Sutherland, 2002) and have been used in conjunction with other methods, such as Simultaneously Extractable Metals, Acid Volatile Sulphides (SEM-AVS) (Allen et al., 1993; Casas and Crecelius, 1994; van den Hoop et al., 1997) with 1 M HCl extraction plus AVS recommended in the Australian Interim Sediment Quality Guidelines (Simpson et al., 2005).

Given the wide applicability of these methods, the use and chemistry (such as chemical reactivity, solubility, adsorption–desorption processes and equilibria) of the dilute mineral acid used to conduct extractions of the weakly bound heavy metals needs to be known. Currently, most WE-M methods use HCl rather than HNO_3, despite the known insolubility of some metal chlorides compared to metal nitrates in this acid.

It has been acknowledged that the use of dilute mineral acid extractions provides information on which elements are likely to become bioavailable if suitable environmental conditions exist (Malo,

Table 3
Comparison of extraction reagents (n = 7) against Townsend et al. (2007) (recoveries expressed in mg·kg-1).

Element	Certified value	(Townsend et al., 2007)	EDTA	Acetic acid	Sodium acetate	1 M HCl	1 M HNO_3
Al	85,900 ± 2300	1870 ± 270	600 ± 100	570 ± 130	190 ± 50	2700 ± 300	4400 ± 900
Ti	4400 ± 600	a	9.8 ± 1.7	1.2 ± 0.4	2.3 ± 0.8	52 ± 4	70 ± 20
V	243 ± 10	27 ± 3	24 ± 4	15 ± 4	11 ± 3	27 ± 2	38 ± 7
Cr	105 ± 4	3.3 ± 0.07	21 ± 5	15 ± 1	b	7.3 ± 0.5	10 ± 2
Mn	324 ± 12	179 ± 11	191 ± 37	190 ± 50	140 ± 30	143 ± 15	230 ± 50
Fe	43,400 ± 1100	9040 ± 920	4400 ± 700	3300 ± 700	2800 ± 700	12,800 ± 900	17,000 ± 3000
Co	14.4 ± 2.0	4.4 ± 0.4	2.1 ± 0.4	2.8 ± 0.7	2.0 ± 0.5	4.8 ± 0.4	7 ± 1
Ni	46.9 ± 2.2	8 ± 1	47 ± 8	23 ± 1	30 ± 10	41 ± 5	34 ± 5
Cu	33.9 ± 1.6	a	20 ± 3	14 ± 3	11 ± 3	15 ± 1	22 ± 3
Zn	159 ± 8	53 ± 4	53 ± 9	50 ± 10	40 ± 10	65 ± 6	90 ± 30
As	21.2 ± 1.1	a	17 ± 4	7 ± 2	11 ± 3	18 ± 2	13 ± 3
Cd	0.24 ± 0.01	0.16 ± 0.2	0.28 ± 0.04	0.25 ± 0.05	0.27 ± 0.7	0.25 ± 0.02	0.29 ± 0.04
Hg	0.091 ± 0.009	a	b	0.04 ± 0.01	0.05 ± 0.02	0.06 ± 0.02	b
Tl	0.9 ± 0.06	a	0.05 ± 0.01	0.02 ± 0.002	0.04 ± 0.01	0.15 ± 0.01	0.18 ± 0.03
Pb	21.1 ± 0.7	13 ± 2	21 ± 3	7 ± 2	14 ± 4	21 ± 1	20 ± 3
U	4 ± 1	0.68 ± 0.07	0.23 ± 0.03	0.6 ± 0.1	0.5 ± 0.1	1.07 ± 0.09	1.1 ± 0.2

a = Recovery not reported by Townsend et al. (2007).
b = Recovery suggests contamination of the reagent.