Effects of sample preparation and extraction protocols on availability of metals in leaching dredged sediments

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Abstract: Sequential extractions provide strictly operationally defined results and are of lesser value in evaluation of metal leaching from dredged sediments. Single extraction with acetic acid is a reliable simplified technique and allows more rapid evaluations of dredged areas of coastal lagoons in the Northern Adriatic.

Key words: metals, extraction, leaching, dredged sediments

Introduction

Potential uses of dredged sediments have raised questions about leaching of contaminants from such material once transported to other locations and exposed to other environments. The available fraction, i.e. potentially leachable to the surrounding environment upon disposal, is referred as *non-detrital* fraction. This value is lower than the total concentration, since the fraction of metals originating from the rock-producing sediment, i.e. *detritus*, is usually not released through simple leaching procedures (Almeida et al., 2001).

In this work we compared the results obtained with a single extraction with acetic acid, proposed by the UNEP, and with the original and the modified protocols of the three-step sequential extraction procedure, proposed by the Standards, Measurements and Testing Programme (SM&T, formerly BCR). The procedures were applied on the certified reference material, CRM 601, and are described in Table 1.

Table 1: The UNEP and SM&T extraction procedures

Fraction/ Method	Extractant used	Extracted sediment components	Environmental condition that would release the metals
Acid soluble (UNEP)	25% vv acetic acid, 16 h	Exchangeable ions, carbonates, easily soluble Fe and Mn oxides, weakly bound to organic matter	Acidic conditions, like acid rain or anaerobic conditions. Short and long-term availability.
Acid soluble, F1 (SM&T)	0.11 M HOAc, 16 h	Exchangeable ions and carbonates	Acidic conditions, like acid rain or anaerobic landfill
Reducible, F2 (SM&T)	Orig.: 0.1 M NH_2OHHCl, pH 2 (HNO_3), 16 h	Iron-manganese oxides	Reductive conditions
	Modif.: 0.5 M NH_2OHHCl, pH 1.5 (HNO_3), 16 h		
Oxidizable, F3 (SM&T)	30% H_2O_2, pH 2 (HNO_3), 2 h at 85°C, extracted with 1 M NH_4OAC, pH 2 (HNO_3), 16 h	Sulphides/organics	Oxidative conditions, like during dredging
Residual, F4 (SM&T)	Mixture of HF and *aqua regia*.	Metals bond in crystalline structures of the minerals	

Short scientific paper

In addition, we performed the sequential extraction on wet and dried sediment samples from dredging of the Škocjan lagoon, a part of the Northern Adriatic, to evaluate the effects of sample preparation on metal availability and consequently on reliability of the procedure in environmental risk assessment. Sample preparation and metal determinations were made under clean room conditions (class 10000). All metal determinations were made either by ETAAS using a Hitchachi Z-8270 polarized Zeeman atomic absorption spectrophotometer, or by FAAS using a Varian Spectra AA 110 atomic absorption spectrophotometer. Quantification was by reference to calibration curves obtained using standards prepared in matrices matching those of the samples. The accuracy of the analytical procedures and the quality of data for total metal determination were checked with a certified reference material.

RESULTS AND DISCUSSION

Significant differences were found when the original and the modified SM&T protocol were applied, Figure 1. In each fraction, different amount of metals were extracted when the concentration and pH of the extractant was changed, suggesting that results provided were operationally defined and should only be related to the protocol used and not expressed as available, mobilizable etc.

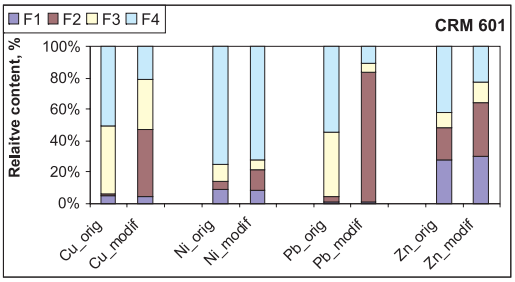

Figure 1: Comparison of the original and modified protocol of the SM&T three step sequential extraction

A shift from less available to more available fractions occurred in air-dried sediments in comparison to field-moist samples, but great spread of the results was observed due to less efficient homogenization of wet samples, Table 2. Repeatability and recovery relative to total values were generally acceptable for air-dried samples, but not for wet samples, as also reported by some other authors (DAVIDSON ET AL., 1999).

Considering that *non-detrital* (available) fraction was the highest possibly potentially mobilizable amount of metals, the preparation of samples should ensure good reproducibility of the results. It was demonstrated that air-

Table 2: Effects of sample preparation on fractionation of metals and on the reproducibility of the results

	Cu		Ni		Zn		Pb	
	wet	dried	wet	dried	wet	dried	wet	dried
F 1	2.1±0.7	2.8±0.4	7.5±1.9	9.5±1.8	6.1±1.9	7.4±2.8	LOD	LOD
F 2	0.7±0.5	1.0±0.1	10.7±1.7	12.7±1.9	23.5±7.6	29.1±7.0	0.8±0.2	1.3±0.8
F 3	18.7±8.0	25.2±6.7	20.3±4.3	30.0±2.7	20.5±7.9	31.8±6.3	9.0±3.6	20.9±3.2
F 4	20.6±7.1	24.2±6.4	54±17	52±11	44±5	45±4	28.4±7.1	16.7±2.4
Sum	42±11	53±9	93±18	105±12	94±12	113±11	38±8	39±4
Bulk	47±3		101±6		107±10		27±1	

dried samples were far more homogeneous, thus they yielded more consistent results. In addition, the oxidized sediments are of particular importance in a biological context (Luoma and Davis, 1983). While comparing the ratio of leachable to total metal content for air-dried and wet samples, it was demonstrated, that drying/oxidizing of the sediment influenced mainly the redistribution of metals within *non-detrital* fraction, and did not influenced significantly the total available amount, i.e. sedimentary phases *of* all *non-detrital* fraction, potentially leachable or available to biota.

In addition, significant differences between the three procedures were observed while comparing the UNEP procedure with the cumulative amounts of the steps 1,2 and 3 of the original and especially, modified SM&T protocol, Figure 2.

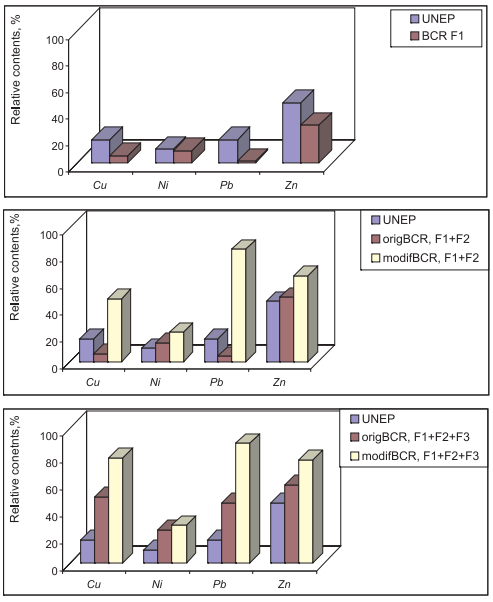

Figure 2: Comparison of the UNEP procedure with the original and modified protocols of the SM&T, applied on CRM 601

The UNEP procedure yielded higher amounts of extractable metals than F1 of the SM&T procedure (upper figure) and higher or relatively similar amounts to the cumulative amount of the step 1 and 2, (F1+F2) of the original protocol of the SM&T procedure (middle figure), but significantly lower than the cumulative amount of the step 1 and 2, (F1+F2) of the modified protocol (bottom figure). Due to vigorous reagents of the three-step sequential extraction procedure, the (bio)availability of metals and thus the risk of leaching dredged sediments were considerably overestimated. Alternatively, the fractions of metals extractable with 25% acetic acid satisfactory estimate the potential bioavailability of metals in leaching dredged sediments.

Conclusions

Sequential extraction procedures were found strictly dependent on the protocol used and induced a strong decline in reproducibility of the analysis of wet samples. At present, the UNEP procedure was considered to be a reliable for the rapid evaluation of dredged areas in coastal lagoons in the Northern Adriatic, especially with regard to its simplicity, speed and repeatability. Potential mobility of Pb, Zn, Ni and Cu in the sediment samples investigated with acetic acid extraction increased in the order Cu<Ni<Zn<Pb.

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