

EFFECTS OF SELECTIVE EXTRACTION SCHEMES ON REDOX-SENSITIVE Sb: IMPLICATIONS FOR ENVIRONMENTAL QUANTITATIVE Sb RADIONUCLIDE DISPERSION SCENARIOS

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Keywords: antimony; sediments; selective extractions; Gironde Estuary

Introduction

Antimony (Sb) is a toxic metal/metalloid and a priority contaminant (EU Directive 2006/11/EC). Recently, research has focused on Sb because Sb radionuclides (e.g. ¹²⁵Sb; $t_{1/2} = 2.76$ y) may enter the aquatic environment during Fukushima-type Nuclear Power Plant accidents (e.g.; Gil-Díaz et al., 2016). Reliable scenarios for radionuclide behavior/dispersal require quantitative understanding of their biogeochemical behavior, including processes controlling their partitioning, speciation, mobility and bioavailability. Solid-state speciation methods for metals often rely on chemical extraction methods derived from sequential extractions, addressing operationally defined carrier phases (e.g., Tessier et al., 1979; BCR). Nevertheless, there is no standard method for Sb and the accuracy of published methods is not validated due to the lack of certified reference materials for single/specific carrier phases. Furthermore, several studies report differences in Sb extractions from the same operationally-defined carrier phase obtained from sequential or parallel/single selective extractions (Filella, 2011), which could be due to both sediment-inherent properties and/or extraction conditions. The present work aims at assessing (i) the solid-state partitioning of Sb in estuarine suspended particulate matter (SPM), (ii) the (non-) selectivity of single extractions for major Sb carrier phases and (iii) the resulting implications for radionuclide dispersal scenarios.

Methods

Water and SPM from the Gironde Estuary Maximum Turbidity Zone were collected into 40 l acid-washed polyethylene (PE) drums with a PP peristaltic pump and tubing at 1 m above the consolidated sediment. Particles were recovered by centrifugation (Westfalia; 12,000 g), freeze-dried, grinded and homogenized (agate mortar). Total digestions and single selective extractions (Table 1) were performed in triplicates on sediment aliquots following the modified method of Tessier et al. (1979) as described in Audry et al. (2006). In addition, extractions for F2 (with and without buffer) and F4 fractions were combined to check consistency of these protocols. Total (Sb_p) and selectively extracted Sb fractions were determined by ICP-MS (X7 Series 2, THERMO).

Results

Results (Table 1) suggest that the main reactive carrier phases of Sb in estuarine sediments are the reducible (ascorbate, pH=8) and the acid-soluble (1M HCl) fractions accounting for <10% of Sb_p, implying a great dominance of the residual (non-reactive) fraction accounting for ~90% of total Sb_p. After single extractions, the reducible fraction (F2. Fe/Mn oxy-hydroxides) was 2-fold greater than the acid-soluble fraction (F4). Moreover, the combined effect of both ascorbate and 1M HCl (F2 + F4) extracted even more Sb than the sum of the respective single fractions (F2, F4; Table 1).

Table 1. Results of single selective extractions.

Fraction	Sb _p (mg kg ⁻¹)	Fraction relevance (%)	Quality check
F2. Fe/Mn oxides (reducible)	0.118 ± 0.001	5%	
F3. Organic matter/sulphides (oxidizable)	0.015 ± 0.003	1%	
F4. Acid soluble	0.052 ± 0.001	2%	≥10-fold the limit of quantification
F2 + F4	0.201 ± 0.002	9%	
F2 without buffer + F4	0.232 ± 0.011	10%	
Total extraction	2.31	-	~100% recovery NIST 8704 + NCS DC 70317

Conclusion

By definition, F4 fraction includes F2+carbonate+amorphous monosulfurs+phyllosilicate phases (Audry et al., 2006), thus F4 should be ≥ F2. Unexpected results for Sb extracted from estuarine sediments suggest maximum Sb solubility under reducing conditions (F2), which cannot be explained by reductive dissolution of reactive Fe and Mn oxy-hydroxides, because this carrier phase would also be extracted by HCl. Furthermore, maximum Sb mobility by combining F2+F4 extractions (i.e., reducing conditions in the presence of chloride) with/without pH buffer suggests combined influences of redox conditions, chloride and pH on Sb solubility in estuarine salinity and redox conditions. These observations and similar results obtained for freshwater sediments (unpublished) suggest that classical sequential and parallel extraction schemes may produce biased information on sediment solid-state partitioning of redox-sensitive elements such as Sb. Given that both contamination assessment and radionuclide dispersal scenarios need reliable information on the reactive Sb fractions in sediments, these results warrant further research on appropriate extraction schemes for Sb and other redox-sensitive elements.

References

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