

Evaluation of sequential extraction procedures for metal speciation in model sediments

PP Coetzee*, K Gouws, S Plüddemann, M Yacoby, S Howell and L den Drijver

Department of Chemistry and Biochemistry, RAU, PO Box 524, Auckland Park 2006, South Africa

Abstract

The three-step sequential extraction protocol designed by the BCR (Community Bureau of Reference) was evaluated with regard to total recovery, reproducibility, selectivity of extractants and extent of phase exchanges or redistribution of metals during the extraction. Model sediments of known composition were developed consisting of humic acid and natural minerals like kaolin, quartzite and ochre. Synthetic compounds like calcium carbonate (calcite) and iron oxide (goethite) which could be used to simulate typical components of sediments, were used for comparison. Our results indicate that the procedure gives excellent recoveries for all 6 metals (Cu, Cr, Cd, Zn, Ni and Pb) studied. Reproducibility of 3% was achieved. Redistribution of Pb and Cu in the presence of humic acid was demonstrated. The selectivity of the reagents was insufficient to warrant interpretation of results in terms of a specific origin of a metal in a particular phase. It was shown that the chemistry of a metal can be a more important parameter than the actual phase location of the metal in the sediment in determining its response to the extractants. This was demonstrated in the case of Cr which reported to Step 3 irrespective of its location.

Introduction

Sequential extraction procedures, despite much adverse critique and controversy in the scientific literature (Kheboian and Bauer, 1987; Nirel and Morel, 1990; Martin et al., 1987; Rapin et al., 1986) over the last decade still remain popular for measuring the particulate speciation of trace metals in sediments. There seems to be an important need in especially the environmental sciences to be able to characterise the speciation of trace metals in sediments. Aquatic sediments act as sinks for trace metals in the environment and particulate speciation procedures provide useful information with regard to bio-availability and geochemical fate of trace elements. It is, however, a cause for concern that sequential extraction procedures of which more than ten different schemes (Campbell and Tessier, 1987; Salomons and Forstner, 1980; Towner, 1985; Meguelli et al., 1983) have been developed, are often used in a nondiscriminatory fashion in the belief that the procedures are selective, that phase exchanges or trace element redistribution do not occur, and that matrix effects can be ignored. This despite the fact that various attempts (Kim and Fergusson, 1991; Hakansson et al., 1989; Kersten and Forstner, 1986) to validate these procedures have provided evidence that these assumptions could not generally be made. The method most often used for sequential extractions, is that by Tessier et al. (1979). Various modifications (Lum and Edgar, 1983; Rauret et al., 1989) have been suggested to improve the original technique, none of which really solved the inherent problems associated with the interpretation of results from sequential extractions.

In the application of a sequential extraction procedure to a natural sediment the different geochemical phases which constitute a typical sediment are assumed to be present. These may include clay minerals, calcite, iron and manganese oxides, sulphides and organic matter. A fundamental problem arises because not all sediments include chemically and physically distinct phases. In such cases results from sequential extractions are essentially

meaningless if interpreted in terms of metal content in defined geochemical phases. The non-selectivity of extractants and trace element redistribution among phases during extraction further complicate this type of interpretation of results in terms of phase association of metals. Selectivity studies have been made on single phases with single reagents (Slavek et al., 1982) and redistribution studies have been performed in the presence of mixed substrates (Guy et al., 1987; Rendell and Batley, 1980; Belzile et al., 1989) using the Tessier procedure. The reported results all show that readsorption of metals released during the extraction procedure may occur to varying degrees.

In a bold step to bring some order in this field, various laboratories (Ure et al., 1993) within the EEC are collaborating to develop reference sediments which would be of crucial importance in the ultimate validation of a standard sequential extraction procedure. The ability to distinguish between the reactive load, which could be indicative of the bio-available component, and the inert part of a sediment is in our view the most important requirement of a universally acceptable or standard sequential extraction procedure. In order to achieve this, provision has to be made to accommodate three basic interaction types which could play a role in the remobilisation of metals from sediments, namely:

- acid-base equilibria
- reduction reactions
- oxidation reactions.

By applying these reactions to a sediment using extractants of the appropriate strength, the potential of the sediment to release pollutants into the environment can be estimated. A useful procedure (López-Sánchez et al., 1993) for this purpose has recently been suggested by the Community Bureau of Reference (BCR Protocol). It is basically a simplified Tessier procedure using acetic acid to provide for acid-base, hydroxylamine hydrochloride for reduction, and hydrogen peroxide (H_2O_2) for oxidation interactions.

In this work we attempted a validation of the BCR Protocol with well-defined samples. We studied this procedure for the six elements Zn, Cu, Cd, Cr, Ni and Pb with respect to total recovery, possible phase exchanges during extraction, element specificity

* To whom all correspondence should be addressed.

Received 5 April 1994; accepted in revised form 27 October 1994.