Assessment of a sequential extraction protocol by examining solution chemistry and mineralogical evolution

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Knowledge of the behavior of heavy metals, such as copper and zinc in sediments, is a key factor to improve the management of rivers. The mobility of these metals, which may be harmful to the environment, depends directly on their concentration and speciation , which in turn depend on physico-chemical parameters such as mineralogy of the sediment fraction, pH, redox potential, salinity etc ... (Anderson et al., 2000; Sterckeman et al., 2004; Van Oort et al., 2008).

Several methods based on chemical extractions are currently applied to assess the behavior of heavy metals in soils and sediments. Among them, sequential extraction procedure is widely used in soil and sediment science and provides details about the origin, biological and physicochemical availability, mobilization and transports of trace metals elements. It is based on the use of a series of extracting reagents to extract selectively heavy metals according to their association within the solid phase (Cornu and Clozel, 2000) including the following different fraction : exchangeable, bound to carbonates, associated to oxides (reducible fraction), linked to organic matter and sulfides (oxidizable fraction) as well as silicate minerals so called residual fraction (Hickey and Kittrick, 1984; Tessier et al., 1979). Consequently sequential extraction method is expected to simulate a lot of potential natural and anthropogenic modifications of environmental conditions (Arey et al., 1999; Brannon and Patrick, 1987; Hickey and Kittrick, 1984; La Force et al., 1999; Tessier et al., 1979).

For three decades, a large number of protocols has been proposed, characterized by specific reagents and experimental conditions (concentrations, number of steps, extraction orders and solid/solution ratio) (Das et al., 1995; Gomez Ariza et al., 2000; Quevauviller et al., 1994; Rauret, 1998; Tack and Verloo, 1995), but it appeared that several of them suffer from a lack of selectivity of applied reagents: besides target ones, some of them are able to leach several solid phases.

In this context, the aim of the present study is to investigate the effectiveness and the selectivity of different reagents for metal extraction from target geochemical fraction. It is based on solid analyses with the use of X-ray diffraction and a scanning electron microscopy (SEM) coupled to a microRaman spectrometer in conjunction with chemical analyses of extracting solutions at each step. This methodology provides the opportunity to assess more accurately the effect of each reagent. The study focuses on extraction of Cu and Zn from sediment samples collected at two sites from river banks and characterized by presence of Quartz, Feldspar K, Micas, Kaolinite but with differences regarding accessory phases (pyrite, organic matter, iron oxyhydroxide, calcite). The interaction of the samples with eight different reagents was assessed and compared ($Ca(NO_3)2$ and $CaCl2$ for the exchangeable fraction; buffered solutions of sodium acetate/acetic acid at pH = 5.5 and pH = 5 for the acido-soluble fraction; hydroxylamine hydrochloride and a solution of ammonium oxalate/oxalic acid for reducible fraction; hydrogen peroxide and sodium hypochlorite for the oxidizable fraction. In-depth characterization of solid residue at each step allowed proposing the best protocol for both metals.

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