

Remobilization of geogenic metals and metalloids associated with fine-grained dam sediments

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Introduction: Dam construction results in changes in the water column properties affecting its hydrology, therefore favoring sediments accumulation [1]. When facing dam management operations (draining, flush valve opening ...) or hydrological events (floods), sediments of the reservoirs are remobilized. Various physicochemical parameters are consequently altered, such as the pH, the redox potential and the solid/liquid ratio. Thus, it allows the solubilization of metallic elements that may naturally be trapped in sediments through time, which can generate toxicity towards aquatic biota [2,3].

The aim of this work is to study the mobility of the geogenic trace elements associated with sediments of a highly exploited reservoir (daily hydropeaking operations, large water-level range, and flush valve opening during favorable periods) of the west border of the French Massif Central (Cantal).

Methods: The surficial sediments sampling was performed using Ekman grab. Samples were sieved to remove plant debris and select the most reactive fraction (<63µm). Total metal concentrations were analyzed after microwave-assisted digestion using atomic absorption spectrometry. Metal mobility was studied using laboratory experiments with physicochemical monitoring, and subsequent solubilized metals were determined using inductively coupled plasma - mass spectrometry. An accelerated BCR sequential extraction protocol [4] was employed to provide information regarding different metal phase association in the sediments. A focus has been set on sulphides and organic matter, both representing a non-negligible fraction of the sediments. The metal-bearing phases were identified and analyzed using an energy dispersive spectrometer coupled to scanning electron microscopy, electron probe micro-analyses and transmission electron microscopy.

Results: The total concentrations of metallic elements associated with sediments are, in µg/g: As (9.1 ± 1.7), Cr (153.6 ± 19.1), Cu (27.5 ± 2.0), Ni (59.3 ± 3.6) and Zn (153.8 ± 16.1). Cr (1.5 at.%) is trapped in Fe, Al and Ti (hydr)-oxides measuring 30-60µm, while Cu, Ni and Zn (respectively up to 65, 0.4 and 4 at.%) are found in 1-3 µm sulphides.

Simulation of differences in the water level using 10 successive dry/wet cycles (12h/12h) with a solid/liquid ratio of 50g/L permitted to release respectively 21, 1.7 and 1.5% of total Ni, As and Cu. Changes in pH conditions in a 6 to 8 range lead to the release of trace metals. Respectively up to 6.6, 3.8, 3.6 and 0.9% of total As, Cd, Cu and Ni are consequently released.

Low solid/liquid ratio (<1g/L), as seen during flush operations and floods, permits to release up to 30% of total Cu and As.

Discussion: The metals issue from parental rock erosion, mainly amphibolites and migmatites, naturally containing these elements. Cr and Ni concentrations exceed tolerated levels of the 08/09/2006 prefectural French decree.

Electron microscopic investigations correlated with sequential extraction showed that the highest amount of metals occurred in the oxidizable (organic matter and sulphides) and residual fractions. The first cited fraction is sensitive to environmental changes, notably pH, which can lead to a massive release of the associated metals.

Cations are solubilized in acidic conditions probably because of their competition with protons and bearing phases dissolution, whereas anions are released in alkaline conditions due to their competition with hydroxide ions and organic matter dissolution. Concerning the impact of sediment remobilization on metallic elements spills, we demonstrated that the lower the sediment concentration, the better the metals are solubilized thanks to a greater contact between solid and liquid phases as well as changes in equilibria sorption.

Conclusion: Using lab experiments correlated with field studies, we proved that variations in water level and physicochemical conditions, as seen during flush valve openings or floods, can disrupt the solid/water interface and therefore generate favorable conditions for metallic elements spills.

References: [1] Friedl et al. (2002) *Aquatic Sciences* **64**:55-65; [2] Calmano et al. (1993) *Wat. Sci. Tech.* **28**:223-235; [3] Chapman et al. (1998) *Can. J. Fish. Aquat. Sci.* **55**:2221-2243; [4] Pérez et al. (2003) *Analytica Chimica Acta* **360**: 35-41.