# Impact of hydroelectric plants exploitation on the evolution of water quality: mobility of metals and metalloids

Influence de la gestion des ouvrages hydroélectriques sur la qualité aval des eaux : mobilité des éléments métalliques et métalloïdes

Franck Frémion<sup>1,\*</sup>; A. Courtin-Nomade<sup>1</sup>; F. Bordas<sup>1</sup> and B. Mourier<sup>1</sup>

1 Groupement de Recherche Eau Sol Environnement (GRESE), University of Limoges, 123 Avenue Albert Thomas, 87060 LIMOGES CEDEX, France (\*corresponding author: franck.fremion@unilim.fr)

# RÉSUMÉ

Les barrages modifient l'écoulement naturel des eaux, des nutriments et des espèces aquatiques. Ils aboutissent à la formation de retenues au sein desquelles la vitesse des courants est faible. Ceci favorise le dépôt des sédiments et matières en suspension, qui piègent naturellement les polluants, tels les éléments métalliques. Cette phase particulaire fait donc l'objet d'une attention particulière puisqu'elle est à la fois un facteur limitant l'exploitation des barrages (envasement) et une source de pollution potentielle du milieu. En effet, l'exploitation courante et exceptionnelle des infrastructures hydroélectriques peut conduire à des modifications importantes des paramètres du milieu. Cela peut altérer la qualité d'un écosystème aquatique via la mobilisation des contaminants présents dans les sédiments accumulés dans la retenue. La présente étude traite donc du lien entre le fonctionnement d'un barrage et l'évolution de la charge métallique contenue dans le compartiment sédimentaire. Le barrage de notre étude fait partie d'un complexe hydroélectrique important. Son fonctionnement par éclusées et sa gestion particulière par chasse annuelle, voire bisannuelle, modifient périodiquement les paramètres physico-chimiques de la retenue et ceux du cours d'eau à l'aval du barrage. Ces modifications drastiques peuvent provoquer des perturbations importantes à l'interface solide-liquide ainsi qu'un relargage des éléments métalliques accumulés naturellement dans les sédiments. Ces processus peuvent générer une dégradation de la qualité de l'eau et une toxicité envers le biote.

# ABSTRACT

Dam presence modifies natural water, nutrients and aquatic organisms' flows. They lead to the formation of reservoirs in which the current velocity is low. This favors sediments and suspended material deposition, which naturally trap pollutants such as metallic elements. Thus, particular attention is drawn to particulate matter as it constitutes a parameter limiting dam exploitation and a potential source of pollution. Indeed, daily and exceptional operations of hydroelectric plants can lead to huge changes in parameters of the medium. This can alter the quality of the aquatic ecosystem through the mobilization of contaminants contained in the sediments of the reservoirs. The present study is dealing with the link between dam exploitation and the evolution of metallic elements of sediment compartment. The studied dam is part of a large hydropower system. It is subjected to a very specific management, completed annually (or every two years), which consisted in flush valve opening during favorable periods. When performed, this type of management modifies periodically the physicochemical parameters of the reservoir and those of the river downstream. It can induce drastic changes at the solid/water interface as well as a spill of metallic elements naturally accumulated by the sediments. These processes can degrade the water quality and generate a potential threat towards aquatic organisms.

### **KEYWORDS**

Dam, Sediments, Metallic Trace Elements, Water Quality.

### 1 CONTEXT: THE IMPORTANCE OF SEDIMENTS IN AQUATIC ECOSYSTEMS

Even if the introduction of the Water Framework Directive resulted in a massive improvement of global ecological quality of the aquatic media during the last decades, many sites remain contaminated. One of the factors explaining the persistency of the degradation of these sites is the key role played by sediments, which accumulate contaminants such as metals and metalloids through time.

Dam reservoirs are typical sites where sediments can become a source of metallic contamination. Dams are physical barriers limiting the natural transfer of water and sediments in rivers. Their presence leads to the formation of reservoirs whose functioning and characteristics are close to lakes, permitting sediment deposition and accumulation (Friedl et al., 2002). Depending on their use and type of exploitation (draining, flush valve opening ...) and hydrological cycles (floods), the water level of the reservoirs can be stable or fluctuate. These natural and anthropogenic processes alter diverse parameters of the media such as the pH, redox potential and solid/liquid ratio, allowing the solubilization of some metals and speciation changes, which can generate toxicity towards aquatic biota (Calmano et al., 1993; Chapman et al., 1998).

The aims of this work are to study the distribution of sediments of a highly exploited reservoir (daily hydropeaking operations, large water-level range, and flush valve opening during favorable periods) and determine the mobility of the associated metallic elements.

### 2 MATERIALS AND METHODS

#### 2.1 Reservoir characterization

The research focused on the sediments from a reservoir of the west border of the French Massif Central (Cantal). Because very few information were available on the intensity of sediment accumulation in this reservoir, mono and multi-beam bathymetry analyses were performed to localize the potential sedimentation zones. The main water physicochemical parameters, such as pH, Eh, conductivity and dissolved  $O_2$  were also measured.

#### 2.2 Sediment characterization

The surficial sediments sampling was performed using Ekman grab. Samples were dried at 40°C. Then, sediments were sieved at 2mm and 63µm to remove plant debris and select the most reactive (and contaminated) fraction. The finest fraction (<63µm) was used for subsequent mineralogical and chemical analyses. The mineralogy of the sediment samples was determined by X-Ray diffraction (XRD). The metal-bearing phases were analyzed using an Energy Dispersive Spectrometer coupled to Scanning Electron Microscopy (EDS-SEM) and an Electron Probe Micro-Analyses (EPMA). Total metal concentrations in the sediment samples were analyzed using microwave assisted digestion with HNO<sub>3</sub>, HCI and HF mixture (5:2:1 mL), with successive HF complexation using a saturated H<sub>3</sub>BO<sub>3</sub> solution (6 mL). An accelerated BCR sequential extraction, using focused ultrasounds according to Pérez and Cid (2003) protocol, was employed to provide information regarding different metal phase association in the sediments. Metals and metalloids analyses were performed using ICP - Mass Spectrometry (ICP-MS), Atomic Absorption Spectrometry (AAS) or Microwave Plasma - Atomic Emission Spectrometry (MP-AES).

# 3 RESULTS AND DISCUSSION

The bathymetry results have revealed a low level of sedimentation in the reservoir. This is in accordance with the relatively high number of management operations performed on the dam to prevent its siltation (6 management operations in 10 years). This reservoir is mainly composed of finegrained sediments, at least 70% of it being silts and clays. This can be in relation with the presence of a former regulating dam, which could prevent coarser sediment to enter the reservoir. The organic fraction represents almost 20% of total mass of our sediment.

### 3.1 Elements concentration in sediments

The total concentrations of metallic elements associated with sediments are, in  $\mu$ g/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). Even if these concentrations are low compared to other studies, due to the low anthropogenic activities held in the site, Cr and Ni concentrations exceed tolerated levels of the 08/09/2006 prefectoral decree. This can be related to the watershed lithology containing amphibolites and migmatites, naturally accumulating these elements.

Zn, perhaps coming from agricultural activities, is also an element of concern. A high spatial homogeneity of metals in the reservoir has been found. Low enrichment factors were calculated compared to metallic concentrations in parental rock: Cr (1.5  $\pm$  0.2), Cu (3.0  $\pm$  0.4), Ni (1.5  $\pm$  0.2) and Zn (2.0  $\pm$  0.2).

### 3.2 Metal bearing phases

Two metal bearing phases were found. Cr-bearing Fe, Al and Ti (hydr-)oxides large particles (30-60  $\mu$ m) with c.a. 1.45 at.% Cr, while sulphides (1-3  $\mu$ m) contain Cu, Ni, Sn and Zn (respectively 65, 0.4, 1.2 and 3.5 at.%). These results agreed with the sequential extraction results showing that the highest amount of metals occurred in the oxidizable (organic matter and sulphides) and residual fractions. The oxidizable fraction is sensitive to environmental changes, notably pH and Eh, which could lead to a massive release of the associated metals.

### 3.3 Metal mobility

Using lab experiments correlated with field studies, we characterized how variations in water level and physicochemical conditions during flush valve opening or floods (represented by the blue rectangle on the figure below) can disrupt the solid/water interface in order to know whether they generate favorable conditions for metallic elements spills.

Differences in the water level were simulated using dry/wet cycles (12/12hours), under stirring conditions (70 rpm). For a solid/liquid ratio of 50g/L, after 10 cycles, respectively 21, 1.7 and 1.5% of total Ni, As and Cu were solubilized. Cations are solubilized (up to 10%) in acidic conditions due to their competition with protons and bearing phases dissolution, whereas anions are released (up to 50% for As) in alkaline conditions, due to their competition with hydroxide ions and organic matter dissolution (Fig1-A). The lower the sediment concentration, the better the metals are solubilized thanks to a greater contact between solid and liquid phases. Low solid/liquid ratio (<1g/L), as seen during flush operations and floods, permits to release up to 30% of total Cu and As (Fig1-B).



Fig1. Influence of the pH (A) and sediments/water ratio (B) on metal mobility (contact time: 12 days = pseudoequilibrium, data not shown)

# 4 CONCLUSION AND PERSPECTIVES

The lithology of the site plays a significant role on the intensity of metallic concentrations found in sediments of this non-anthropized reservoir. The distribution of the metallic elements into the sediments depends on the physicochemical properties and the affinities of such elements with the geochemical composition and characteristics of both dissolved and solid phases. The exploitation of reservoirs and the associated physicochemical modifications offer favourable conditions for metal solubilization. Such solubilization decreases the water quality and can generate a threat towards aquatic organisms, which remains to be studied. The identification of alteration degree of metal-bearing phases at the particle scale, using TEM,  $\mu$ XRD or  $\mu$ XAFS techniques is also in progress.

# LIST OF REFERENCES

Calmano, W., Hong, J. & Förstner, U. (1993). Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. *Wat. Sci. Tech.*, 28, 223-235.

Chapman, P.M., Wang, F., Janssen, C., Persoone, G. & Allen, H.E. (1998). Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk assessment, and remediation. *Can. J. Fish. Aquat. Sci.*, 55, 2221-2243.

Friedl, G. & Wüest, A. (2002). Disrupting biogeochemical cycles - Consequences of damming. *Aquatic Sciences*, 64, 55-65.