



Trace element-bearing phases during the solid transport: in-situ characterization and temporal variability in the Loire bed-sediments (France)

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As a result of increased of agriculture, land use, urban areas, industry, traffic and population density, trace element inputs have altered considerably fluvial system (sediment, water quality and biota). The Loire River Basin (117,800 km², total population of 8.4 Mp in 2010), even if it is considered one of the least human-impacted hydrosystem among the 5 large French basins, has been exposed to multiple sources of metals during the last 150 years, originating from major mining districts (coal and non-ferrous metals) and their associated industrial activities (Grosbois et al, 2012; Dhivert et al, 2013). Two major contamination periods were recorded in several core sediments throughout the basin: <1900-1950, an early contamination period, mainly associated to intensive coal use and metal mining and 1950-1980, a severe contamination period related to industrial and ore-processing activities superimposed to urban development of the basin. The limited dilution by detrital material (Loire sediment load between 1.5 and 3.5 Mt/y) was an additional cause of such severe contamination. After 1950, river eutrophication was well-marked by the general increase of endogenic calcite in the mid and downstream part of the basin, slightly diluting all major and trace element bulk concentrations by 20% (Grosbois et al, 2012). Since 1980, a generalized and gradual decontamination of bed sediments started while mines were gradually closing, urban waste waters collected and treated in addition to new environmental regulations. They aim to limit metallic pollutant dispersion like industrial recycling of metal wastes and to reduce atmospheric emissions and consequently atmospheric fall out wet and dry deposition

In-situ chemical and mineralogical techniques (EPMA, SEM-EDS/ACC system and synchrotron based μ XRD) were used (i) to highlight anthropogenic activities by a specific mineralogical signature and (ii) to determine potential effects of post-depositional remobilization and access trace element mobility during the solid transport. Trace element-bearing phases were identified at a micron scale during both <1900-1950 and 1950-1980 contamination periods with respect to maximum contamination peaks.

The most frequent trace element-bearing phases were aggregates of various fine clay particles and they were characterized at both contamination periods. According to in-situ chemical composition and μ -XRD patterns, mineralogy of these aggregates match with chlorite-phlogopite-illite-kaolinite assemblages. Iron and Mn oxyhydroxides were another type of trace element-bearing phases but appeared less frequent than clay aggregates. They were present as discrete particles or associated to clay minerals in aggregates. The majority of clay aggregates and (Fe, Mn) oxyhydroxides reflect mechanical erosion and solid transport. However, some others also reflect post-depositional mechanisms like authigenic pyrites and Fe hydroxides into clay layers.