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Short-term variability of dissolved trace element concentrations in the Marne and Seine Rivers near Paris

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Abstract

The concentrations of dissolved trace elements (Li, B, Mn, Cu, As, Rb, Sr, Mo, Cd, Ba, Pb) in the Marne and Seine rivers in the Paris urban area were monitored over a 2-year period. The resulting data indicated moderate contamination of waters by the most toxic elements (Cu, As, Cd and Pb). The River Marne upstream and the River Seine downstream of the city of Paris displayed similar concentrations. However higher fluxes of trace elements were observed in the Seine than in the Marne due to their different discharges.

Li, B, Rb, Sr and Ba concentrations were correlated with river discharge and concentrations were higher during high river flow. This was interpreted as a dilution by discharge from a major natural or anthropogenic source. Mn, Cu, Mo, Cd and Pb concentrations were not correlated with discharge. Dissolved Mn, Cu and Cd increased rapidly in summer, whereas the concentration of Mo decreased. These variations were attributed to redox processes. During summer when the dissolved oxygen concentrations decrease, Mn, Cu, Cd and Pb are released into solution whereas Mo is immobilised.

Like metals, variations in arsenic contents were not linked with discharge. Its similarity with phosphate distribution suggests similar controls involving phytoplankton uptake and release from sediments through organic matter mineralization.

Keywords: Dissolved trace elements; Metals; Arsenic; Biogeochemistry; Seine and Marne rivers

1. Introduction

For better control of toxic trace element discharges, it is essential to characterize the water contamination. Variations in metal concentrations as a function of time have been intensely investigated in the solid phase. Most studies demonstrated that the observed reduction in toxic trace element discharge resulted in a decrease in sediment pollution in several large European rivers (Gocht et al., 2001; Meybeck et al., 2004; Woitke et al., 2003). Accurate data on the concentrations of trace elements in solution are very scarce as results are often affected by contamination during sample handling and analysis (Shiller and Boyle, 1985; Benoit, 1994; Shiller, 1997). Despite improvements in the 1980s (Zwolsman et al., 1997 and references therein), the concentrations of dissolved trace elements in rivers and the mechanisms which control their variability generally remain poorly documented (Shiller, 1997). In Europe, the adoption of the water framework directive highlighted the difficulty

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in measuring baseline levels for priority substances in water (Coquery et al., 2005).

The potential factors controlling the variability of trace element concentrations are interrelated. According to Sherell and Ross (1999), three broad mechanisms can be distinguished: changes in the hydrological flow path at high discharge, exchanges between bed load or suspended particles and the dissolved phase, discharge of contaminants due to human activities. Hydrological processes have been shown to exert a major control in several small and large rivers (Neal et al., 1997; Sherell and Ross, 1999; Seyler and Elbaz-Poulichet, 1996; Elbaz-Poulichet et al., 2003). In contrast, they are generally of minimal importance in the Mississippi River where redox processes occurring both in the stream and in the source region play an important role in determining seasonal variations in trace elements (Shiller, 1997). For the Po River, Pettine et al. (1994) underlined the role of phytoplankton, which can disturb the cycle of trace elements through biological uptake.

Data on trace elements in water are very scarce for the Seine River basin, which includes all the major sources of contamination normally associated with a modern industrialized society, i.e. high population density, intensive agriculture, heavy industry (Horowitz et al., 1999). Garban et al. (1999) suggested that phytoplankton plays an indirect role in controlling the fate of Cu and Mn by modifying the physicochemical parameters of water during the growth phase (exudation of complexing agents, increase in pH). The data of Chiffoleau et al. (1999), although limited to two surveys at the entry of the Seine estuary, indicate significant variability of dissolved concentrations of Ni, Cu, Zn, Pb and Cd as a function of discharge. A few additional dissolved metal concentrations are given in Thévenot et al. (1998).

The objectives of this study were to provide data on dissolved trace elements in the River Seine, one of the rivers with the highest human impact in Europe, and to decipher the main processes which control the concentrations.

The paper focuses on several trace elements including metals and metalloids (Li, B, Mn, Cu, As, Rb, Sr, Mo, Cd, Ba, Pb). The relations between concentrations, river discharge, and nutrients (phosphate) were investigated in two hydrological years.

2. Study area

The Seine River basin (Fig. 1) covers an area of 68 000 km^2. It is part of the London–Paris basin which is mainly dominated by carbonate rocks. Aluminosilicate weathering is limited to the upper Yonne River basin and has no marked influence on the water chemistry of the Seine or Marne (Roy et al., 1999).

As the basin has about 17 million inhabitants, human activity obviously has a serious impact. Upstream of Paris, the Seine River and its main tributaries (Marne, Yonne) drain intensive agricultural basins (cereals, industrial crops). The Paris urban area (~2500 km^2)

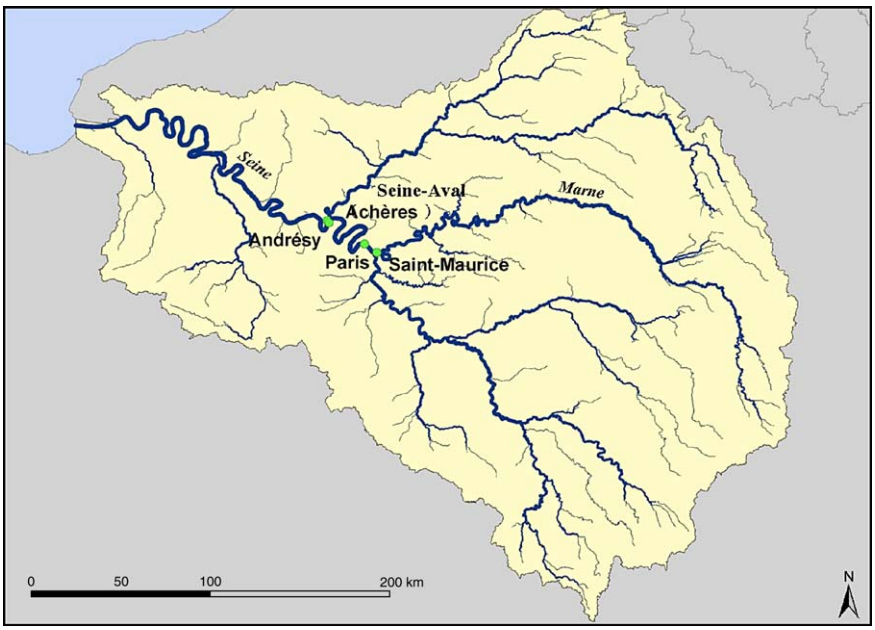

Fig. 1. Map of the Seine basin showing the location of sampling stations.