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Unusual variations of dissolved As, Sb and Ni in the Rhône River during flood events

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Abstract

Dissolved major and trace element concentrations were determined from November 2000 to December 2003 in the lower Rhône River (France). Subsurface water samples were collected about twice a month and more regularly during flood events. An unusual trend was observed for As, Sb, Ni and Ba concentrations which increased with river discharge at the beginning of the floods, in contrast with other elements. Variations of Sb/Na and As/Na molar ratios show that it is related to higher contributions of waters from western tributaries of the Rhône River enriched in As, Sb, Ni and Ba due to ancient mining activities. These unusual variations of dissolved element concentrations are thus interpreted as mark of a water mass origin within the watershed.

Keywords: Arsenic; Trace element; Rhône river; Flood events

1. Introduction

Rivers are a major link between continents and oceans for most biogeochemical cycles, and represent a major source of material to the coastal zone. Estimation of particulate and dissolved fluxes from rivers is of primary importance for a better understanding of the coastal zone system. In the framework of two national programs, major and trace element fluxes have been monitored in the Rhône River, the major source of freshwater discharge to the western Mediterranean basin. This paper is focussed on the description of a specific trend observed for some trace elements (As, Sb, Ni and Ba) which show increasing dissolved concentrations with water discharge at the beginning of three floods.

2. Study area

The Rhône River is 816 km long and has a drainage area of 98,800 km^2. Its hydrographic basin is characterized by four mountainous catchments inducing strong climatic and geological heterogeneity: the Alps, the Jura, the Cevennes, and the Vosges, with maximum heights of 4807, 1718, 1699 and 1424 m, respectively. The alpine mountains (eastern part of the watershed drained by the Rhône, Isère and Durance tributaries) consist mainly on sedimentary rocks (alluvia, sands, sandstones, conglomerates, schists, limestones, dolomite and shales) with some siliceous crystalline and metamorphic rocks (granites and gneiss). The Jura and Vosges mountains at the north (Saône tributary) are mainly calcareous, whereas crystalline siliceous rocks dominates

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in the southern Massif Central (Cevennes mountains) on the western side of the catchment (Gard, Cèze and Ardèche tributaries). The strong climatologic variations observed over the entire watershed encompass oceanic, continental and Mediterranean rainfall regimes. The Rhône hydrograph results from glacier-melt, snow-melt and rains (Vivian, 1989). Seasonal melting of glacier and snow is responsible for high river flows in spring (mainly in the Alps area), whereas high variations of discharge result from localized storms occurring most of the time in the lower part of the watershed: southern Alps or Cevennes mountains.

3. Material and methods

Subsurface water samples were collected in the Rhône River at Arles (47.5 km upstream from the river mouth) about twice a month from November 2000 to December 2003. The southern tributaries (Durance, Ouvèze, Gard, Cèze and Ardèche River) were also sampled during a flood in December 2003. Water was filtered in the laboratory, after collection, through pre-weighted 0.2-μm cellulose acetate filters. Dissolved major cations (Ca, Mg, Na and K) were determined by ICP–OES (Jobin Ybon ULTIMA C) and dissolved trace elements analyses (Li, V, Ni, Cu, Zn, As, Sr, Rb, Mo, Sb, Cs, Ba, Pb and U) were performed by ICP–MS (Perkin Elmer, Elan 5000 and 6000). An indium internal standard solution was added to each sample before analysis. The international geostandards SLRS-3 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the validity and the reproducibility of the analyses by ICP–MS. A good agreement between our values and the certified data was obtained (relative difference <5% except for Ni (7%), Mo (10%) and Zn (17%)). “Blank” tests showed a contamination less than 2% of the lowest concentration measured.

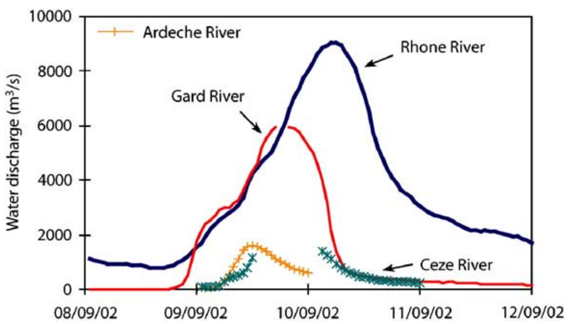

Fig. 1. Water discharge variations of the Rhône (at Arles), Gard, Cèze and Ardèche rivers during the Mediterranean flood of September 2002. Arles is located downstream of the tributaries.

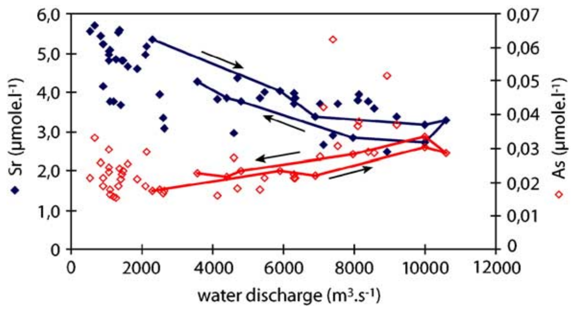

Fig. 2. Dissolved Sr and As (in μmol/l) vs. water discharge for the Rhône River (data from 05/2001 to 12/2003). As an example, anti-clockwise and clockwise hysteresis loops are highlighted for As and Sr concentrations (grey and dark lines, respectively) during the flood of December 2003.

4. Results and discussion

The liquid discharge of the Rhône River at Arles varied greatly during the sampling period, from 247 to 10 600 m^3/s. Three major floods occurred in September 2002 (9034 m^3/s), November 2002 with two successive flood events (peaks at 8250 and 9250 m^3/s) and December 2003 (10 600 m^3/s). These floods were exceptional being respectively the 4th, the 5th and the 1st largest floods recorded in Arles since 1856, with return periods of 55, 50, and 350 years, respectively. The September 2002 flood was a strong typical “Mediterranean” flood (associated to air masses from the Mediterranean sea with precipitations located generally in the southern part of the watershed) with a discharge increase of 7000 m^3/s in 24 h. It was related to a torrential rainfall affecting mainly two southern tributaries from the west bank, the Gard and the Cèze rivers (Fig. 1). Floods of November 2002 and December 2003 were also “Mediterranean floods”, with precipitations affecting all the southern part but extending up to the lower part of the northern watershed.

The usual trend of any dissolved element concentration during floods is a decrease with increasing water discharge, in relation to dilution process (Chow, 1964). Such a trend has been observed over the three study years for all the major elements as well as Li, Zn, Rb, Sr, Mo, Cs and U concentrations (example in Fig. 2 for strontium). The overall variations of V, Cu and Pb dissolved concentrations were weak. In contrast, dissolved Ni, As, Sb and Ba concentrations showed a positive relation with water discharge (Fig. 2). In fact, this relation is more precisely associated to an increase of concentrations during the flood events, i.e. for