

Trace Pb, Zn, Cd, Tl contents and Pb–Sr radiogenic isotopes in the dissolved and particulate phases of a river during high-water stage: constraints on the origin(s) and transport of the metals

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Introduction

Trace elements and long-lived radiogenic isotopes such as Pb, Sr, Nd have long been used in 'solid' Earth Sciences, with much success, for both chronological and source-tracing purposes. The unique power of radiogenic isotopes for discriminating the sources of the elements in surface processes has been used only recently: e.g. for tracing anthropogenic sources of metals in our environment and in rivers, continental erosion in streams, aerosols in winds etc.

We also now know that trace elements, and particularly metals, are to a great extent present in continental waters as inorganic and organic complexes, and that the distributions of the elements between the dissolved and particulate phases are a function of many parameters: their

knowledge is therefore crucial if we want both to evaluate their origin(s), and to model their transport and behaviour downstream to the sea (desorption, precipitation...).

The purpose of the underway study reported here is to get insights in these aspects by measuring trace element (Pb, Zn, Cd, Tl) concentrations and Pb and Sr isotopic compositions (and some major elements, not discussed) in water samples from a river during heavy autumn rainfall.

Location and time of sampling

The study was conducted in a small coastal Mediterranean karstic watershed being drained by the Vène river (figure 1): the sampling site, where the Vène pours into the Thau coastal lagoon, is under continuous control for hydro-dynamic measurements by the former L.H.M. (now part of the group G.B.E.). The Thau lagoon is much studied as it is a fragile ecosystem renowned for its mussels and oysters, but surrounded by growing human activities. Two karstic sources that feed the Vène were also sampled when they were flowing.

The present detailed study on separate phases was initiated starting with September 1993 heavy rainfalls after a long period of dry summer. The river began to flow a few days after the first rainfall

Methods

Since the early discovery by Patterson (1) of Pb contamination problems, analytical geochemists have developed ultra-clean procedures in order to analyze trace elements. A wet chemical method, derived from Manhès (2) for Pb, involving chelating/anion-exchange resins separation and isotope dilution was developed (3) that allowed determination of metal concentrations both precisely (%) and at very low levels (ppb-ppt). Filtration (500 ml) was performed upon arrival at

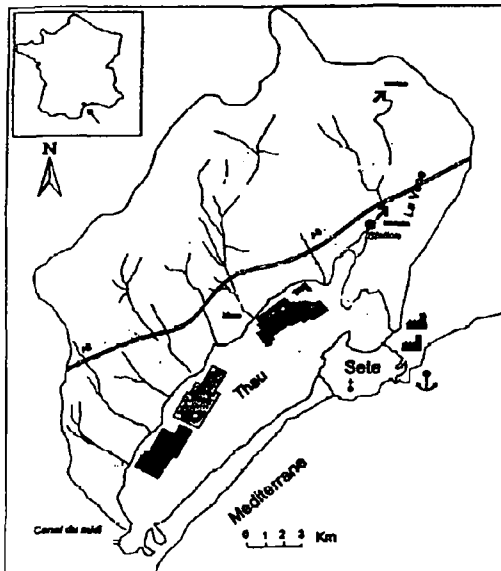


FIG. 1.

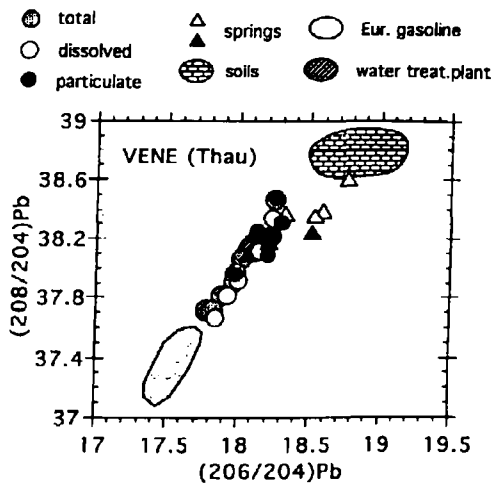


FIG. 2.

the laboratory, a few hours after sampling, on previously cleaned 0.2μ teflon filters. All the handling and chemical procedures were done in a clean lab under class 100 laminar flow. Great care was taken as to maintain contamination levels as low as possible (below 0.5 ng Pb).

Previous work

A first study had been conducted on the watershed in 1991-93 in order to characterize (metal content ratios, Pb isotopes) the main potential sources for metal pollution (4,5): the Sète industrial harbour, a large cementry, treating plants for urban effluents, the road network, vineyards, soils; 'fortunately', lead added to European gasoline has a distinctive very low isotopic composition. First order variations had been observed that were tentatively related to sequential remobilization of the metals from the various sources: however these measurements were done on long periods (2 years) and on total (dissolved + particulate) samples, obscuring a certain number of processes.

Results and discussion

Concentrations. After a general peak in concentration for all metals in the first days of flow, contents decrease rapidly, more or less regularly, for Pb and Zn. Levels in the dissolved load go down to almost natural levels – at least for Pb, Cd and Tl. Background concentrations in this area are then in the 10–50 ppt range for Pb, 5–15 ppt for Cd and Tl.

Metals present in particulate form show much more variable levels, although overall decreasing trends can also be seen. Some very heavy storm events lead to strong variations of some elements but not the same in the dissolved and particulate phases of river samples.

Isotopic compositions. An overall increase of the Pb isotopic composition inversely accompanies the concentration trend, at least when total samples are considered. Variations of Pb isotopic compositions are easily explained by a mixture of two – sometimes three – end-members: gasoline (\pm plants) characterised by low $^{206}/^{204}\text{Pb}$, more radiogenic soils, Sète harbour (this end-member has been characterised elsewhere (6)) (figure 2).

Detailed examination of data actually shows some – but not systematic – delay/decoupling between the dissolved and particulate loads, both with respect to trace element ratios and Pb isotopes.

In particular one sample from late November (heavy storm) shows that the dissolved Pb mostly comes from gasoline while Pb associated to particulates, also characterised by high Pb/Zn and Cd/Zn ratios, seems to originate at Sète harbour. Additional evidence comes from Cl content and Sr isotopes.

References

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