Boron Isotope Variation During Flood Events in a Mediterranean Basin: Tracer of the Water Compartments (Hérault, S. France)

Emmanuelle Petelet-Giraud, Philippe Négrel, Catherine Guerrot

Available online at www.sciencedirect.com
ScienceDirect
Procedia Earth and Planetary Science 13 (2015) 203 – 206
Procedia
Earth and Planetary Science

11th Applied Isotope Geochemistry Conference, AIG-11 BRGM

Boron isotope variation during flood events in a Mediterranean basin: Tracer of the water compartments (Hérault, S. France)

Emmanuelle Petelet-Giraud[a]*, Philippe Négrel[a] and Catherine Guerrot[a]

[a]*BRGM, Laboratories Division, 3 avenue C. Guillemin, BP 36009, 45060 Orléans Cedex 02, FRANCE*

Abstract

Boron isotopes were measured during 3 flood events at the outlet of the Hérault watershed in complement with Sr isotopes. The main water sources (i.e. karst aquifer and the tributaries) were also constrained in high and low flows. Boron isotopes are controlled both by natural and anthropogenic inputs (sewage effluents and/or fertilizers) whereas Sr isotopes trace the various lithologies in the basin. The signature of the Hérault River during flood events presents isotopic variations as large as 15 delta units for boron isotopes, revealing the various contributions of the water compartments according to the rainfall intensity, duration and location.

Peer-review under responsibility of the scientific committee of AIG-11

Keywords: Boron isotopes; flood event; Mediterranean catchment

1. Introduction

The Hérault River is located in the south of France and drains a medium-sized basin of 150 km long and 2500 km². The watershed is divided into three geological compartments: (1) the upper part is mainly composed by granitic rocks, schist, metalimestone and metadolomite (Palaeozoic basement); (2) in the middle part, Triassic clay and sandstone with some evaporitic layers (anhydrite and gypsum) constitute the Mesozoic cover. The upper layers are formed by Jurassic limestone with some dolomite, clay and calcareous marl. The Jurassic and Cretaceous limestones are folded, faulted and highly karstified; (3) down to the Mediterranean Sea, the alluvial plain is composed of

* Corresponding author. Tel.: +33-2-3864-3775; fax: +33-2-3864-3711.
E-mail address: e.petelet@brgm.fr

Peer-review under responsibility of the scientific committee of AIG-11
doi:10.1016/j.proeps.2015.07.048

tertiary and quaternary deposits (Fig.1). The head of the basin is covered by oak, beech and fir trees. In the middle part of the watershed typical Mediterranean vegetation prevails, while most of the alluvial plain is covered with vineyards. The climate is typically Mediterranean and characterized by a highly irregular rainfall regime. Rainfall events are often short but very intense; causing flash floods that can be disastrous. An automatic water sampler device, located at the watershed's outlet in the Mediterranean Sea, collected samples when the river discharge reaches 35 m^3/s. Between October 2001 and December 2002 and then in January 2006, 7 flood events were automatically sampled with a maximum water discharge between 120 and 1300 m^3/s, the latter corresponding to the 10-year return flood. Three contrasted flood events were selected for both Sr and B isotopes investigation (Fig. 1).

This study presents $\delta^{11}B$ results in complement with $^{87}Sr/^{86}Sr$ during flood events to decipher anthropogenic versus natural inputs and to assess the anthropogenic impact, mainly from wastewater effluents and/or fertilizers.

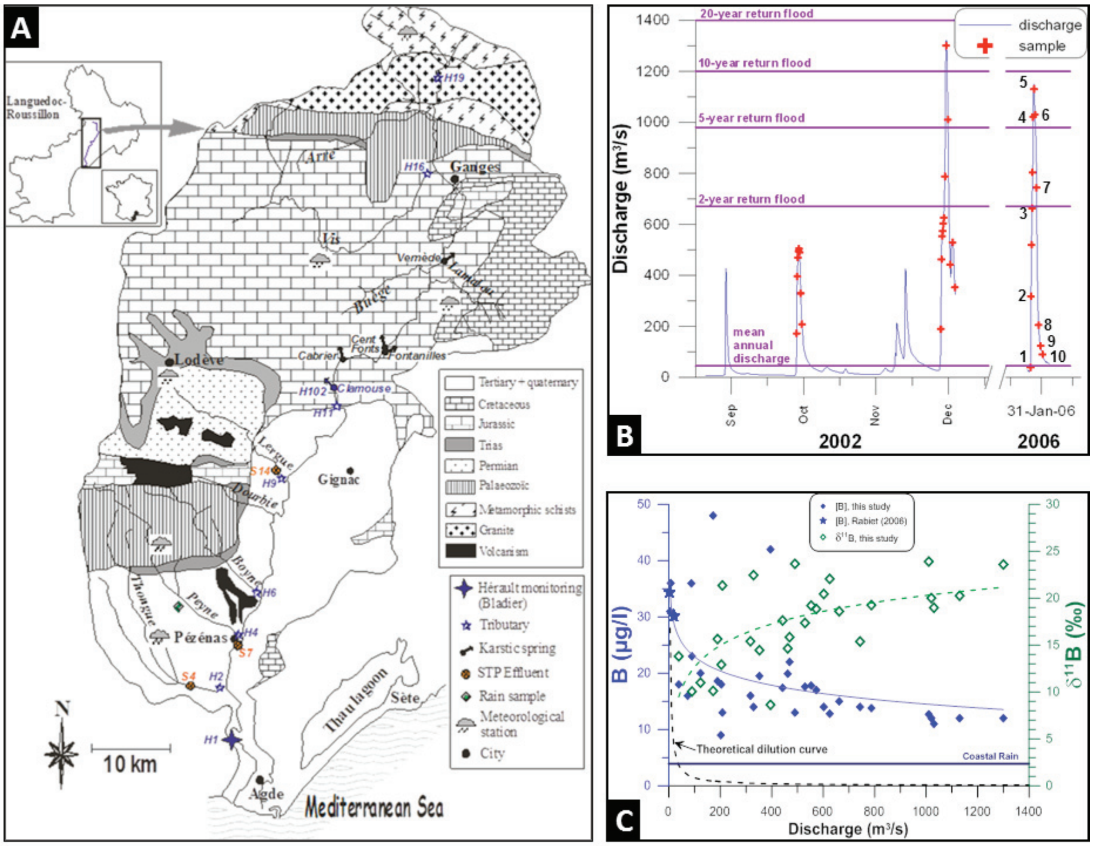


Fig. 1. (A) Simplified geological map and sampling location of the Hérault watershed; (B) Discharge at the outlet of the Hérault River and sampling points; (C) Boron concentration and $\delta^{11}B$ versus discharge at the outlet of the basin.

2. Boron concentrations and end-members characterization

The variations in dissolved species content in rivers are particularly noticeable during flood periods with a sharp decrease in concentration with increasing discharge. However, this classical dilution scheme can be highly disrupted in such basin extremely dependent on the flood events and, in a different way, on the different dissolved species considered. In the Hérault watershed, two types of behavior of dissolved species versus the river discharge were evidenced[1]: (1) conservative species like Cl decrease rapidly with increasing discharge according to a fitted logarithmic law; (2) solubility-controlled species like Ca and HCO_3 present no variation with increasing discharge. Boron behaves as a conservative element, as observed in the Seine River[2], and presents a clear decreasing content with increasing discharge according to a logarithmic law (Fig.1). It is worth noting that the fitted curve plots above the theoretical dilution line (i.e. dilution with a "zero concentration" water) and defines a plateau with a higher B content than the local rain. As demonstrated for other species[1] (Na, Mg, Sr…), this reflects another B source in addition to the simple rain water dilution. Basically in a river basin, the sources of boron mainly originate from (1) rainwater, (2) water-rock interaction and (3) anthropogenic inputs. The Hérault watershed is a coastal basin mainly recharged by marine rain, i.e. with a marine $\delta^{11}B$ signature, even if some rain event can have a continental origin with a lower $\delta^{11}B$ signature. The basin is characterized by various rock types: granite, carbonate, evaporite, clays and volcanic rocks, leading to a potential large range of $\delta^{11}B$ signature in the draining waters. The anthropogenic activities releasing boron mainly consist in treated urban effluents as boron is widely used in detergent and is not removed by classical waste water treatment and agriculture with vineyards representing about 70% of the cultivated areas[3] and requiring 150-200 g/ha/y of boron for an optimal growing, mostly available in the chemical fertilizers.

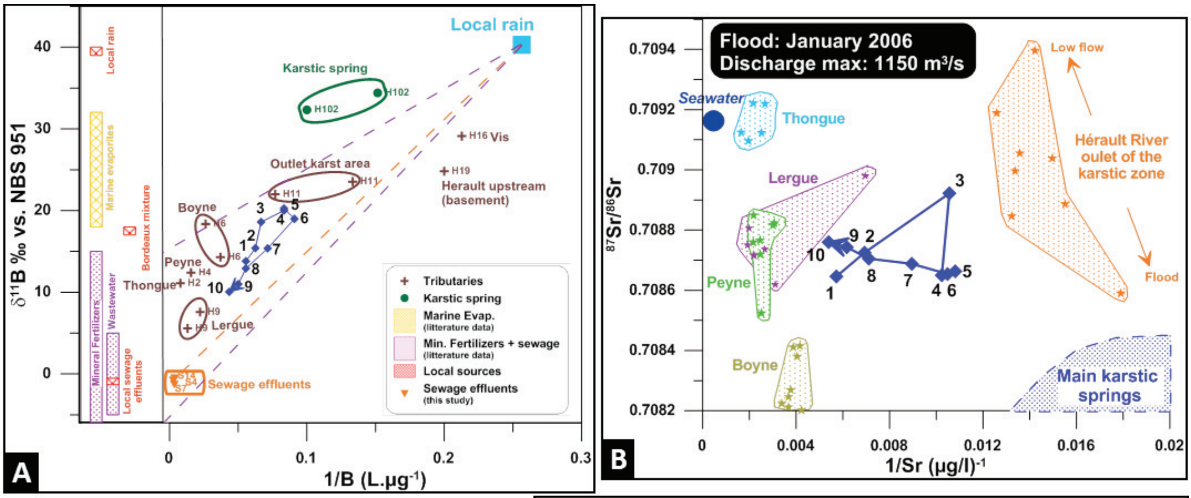
At the catchment scale, boron isotopic compositions vary from 5 to 35 ‰ in surface and groundwater, while boron contents vary from 4.7 to 127 $\mu g.L^{-1}$ (Fig.2). The local rainwater signature ($\delta^{11}B$=40.3‰; [B]=3.9$\mu g.L^{-1}$) is typical of coastal rainwater[4]. The main karstic spring (H102) and the Vis river (H16) draining carbonates present a slight evolution from rain input both for B content and isotopic signature. From the upstream of the Hérault River down to the outlet of the karst area, the B content is lower than 10 $\mu g.L^{-1}$ with a $\delta^{11}B$ between 22 and 25‰. The tributaries of the alluvial plain present lower $\delta^{11}B$ together with increasing B contents, that can be related either to anthropogenic inputs with sewage effluents and/or fertilizers, or to natural input, i.e. drainage of argillaceous sediments and evaporites. Three waste water treatment plant effluents were sampled in the alluvial plain which concentrates most of the population. These samples present homogeneous $\delta^{11}B$~0‰ typical of sewage effluents with [B]=320±60$\mu g.L^{-1}$.

The Lergue river presents the lowest $\delta^{11}B$ (5.5‰) and [B]=76$\mu g.L^{-1}$ in low flow period (0.95 $m^3.s^{-1}$), i.e. a boron flux equal to 72$mg.s^{-1}$. Two main WWTPs are present in the Lergue basin, S14 releases about 6 $mg.s^{-1}$ of boron, considering a mean entering discharge[5] of 2000 m^3/day assumed to represent the output discharge with a [B]=379$\mu g.L^{-1}$, in the same way the second WWTP releases about 10 $mg.s^{-1}$ of boron. Thus in low flow period (<1$m^3.s^{-1}$), assuming that all the WWTP effluents reach the river, the B from WTTP can represent a maximum of 20% of the boron flux of the Lergue river. Note that the Lergue River also drains Triassic evaporites that can release B in solution with a $\delta^{11}B$ > 20‰. The Thongue River presents the highest B concentration with 127 $\mu g.L^{-1}$ and $\delta^{11}B$ = 11.1‰. The Boron flux from the S4 WWTP is about 3 $mg.s^{-1}$ but cannot be compared to that of the river that is not gauged. Nevertheless, it was demonstrated that this river is impacted by WWTP effluents using the Gd anomaly[3]. The Peyne River was also evidences to be impacted by WWTP effluents[3].

Boron release from chemical fertilizers is particularly difficult to assess in the catchment as it depends on plant uptake, delay between application period and rain…, nevertheless such an input cannot be excluded and would lead to lower the $\delta^{11}B$ signature of the main river as $\delta^{11}B$ of chemical fertilizers are generally between -5 and +15‰.

3. δ^{11}B evolution during a flood event

The flood event of January 2006 was sampled 10 times, including the flood pic at 1150 m^3/s (Fig. 1B). Sr isotopes were also measured and compared to previous studied flood events[1]. The initial signature of the Hérault River at the outlet rapidly evolves when the discharge increases towards that of the upstream carbonated compartment. At the maximum flow (samples 4, 5 and 6, Fig. 2B) the influence of the karstic springs is maximum and then the Hérault signature moves back towards the signature of the alluvial tributaries Lergue and Peyne when the discharge decreases. This behavior is very similar to that observed for previous flood events[1]. Similarly to Sr isotopes, the initial $\delta^{11}B$ signature of the Hérault evolves towards that of the carbonated compartment, i.e. an increase of $\delta^{11}B$ and decrease of B concentration (Fig.2C). At the flood pic, all the dissolved boron seems related to the outlet of the karstic area (H11). When the discharge decreases, the $\delta^{11}B$ decreases again together with an increase of the B concentration, reflecting the contribution of the alluvial tributaries, dominated by the Lergue River. It is worth noting that during the flood, the $\delta^{11}B$ signature of the alluvial tributaries, especially the main one (Lergue), have to remain low (<10‰) to explain the measured $\delta^{11}B$ of the Hérault. This thus implies that the natural $\delta^{11}B$ of the Lergue must be relatively low as the proportion of boron from WWTP inputs becomes very limited (max 200 $mg.s^{-1}$) during high water stages compared to >10 000 $mg.s^{-1}$ exported at the outlet of the Hérault River.



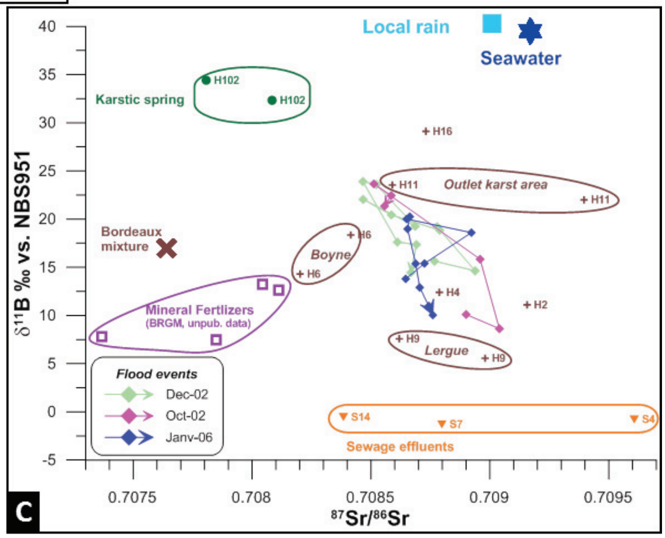


Figure 2: (A) $\delta^{11}B$ vs. 1/B, end-member characteristics and Jan-2006 flood, (B) $^{87}Sr/^{86}Sr$ vs. 1/Sr during the Jan-2006 flood, (C) δ11B vs. $^{87}Sr/^{86}Sr$ for 3 flood events

When coupling B and Sr isotopes for 3 flood events (Fig.2D), both isotopes systematics discriminate the various water compartments of the basin, i.e. the karstic aquifer and the various tributaries of the alluvial plain. During floods, the anthropogenic contributions (flux from WWTP) are negligible compared to natural inputs related to water-rock interaction.

Acknowledgements

This study was funded by the BRGM Research Division. J. Cubizolles, J-C. Foucher and M. Brach are warmly thanked for their technical support for the conception, installation and maintenance of the automatic sampling device. The authors also thank J.L. Seidel for providing a cumulative rain sample from the studied site.

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