



## Are boron isotopes a reliable tracer of anthropogenic inputs to rivers over time?

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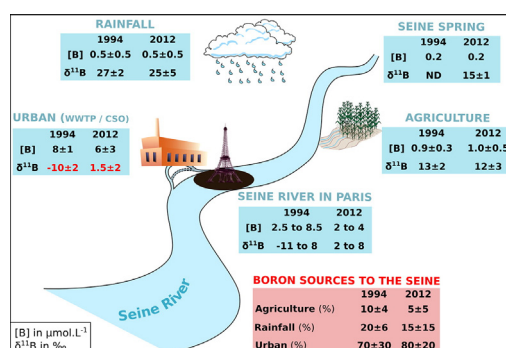
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### HIGHLIGHTS

- Boron isotope signatures and concentrations deeply evolved over 18 years in the Seine River basin.
- Urban inputs in the river were reduced and the boron isotope signature was modified.
- Boron isotopes ratio is a reliable tracer of boron sources in an anthropised catchment.
- A regular reassessment of boron end members is mandatory to interpret boron signals in rivers.

### GRAPHICAL ABSTRACT



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### ABSTRACT

This study aims at determining how the boron signal of the Seine River evolved in terms of concentration and isotopic signatures over eighteen years (1994–95 and 2006–12) and if boron isotopes can reliably trace anthropogenic inputs over time. In the anthropised Seine River watershed, boron is widely released by human activities, and even if boron concentrations ([B]) are below the potability limit, our study confirms the potential of boron isotopes (δ<sup>11</sup>B) to trace urban anthropogenic contaminations. Between 1994 and 2012, [B] have decreased across the anthropised part of the Seine River basin (and by a factor of two in Paris) while δ<sup>11</sup>B has increased. This means either that urban inputs have been reduced or that the boron signature of urban inputs has changed over time. Both hypotheses are in agreement with the decrease of perborate consumption in Europe over 15 years and are not mutually exclusive.

Results of a thorough analysis of urban effluents from the sewage network of Paris conurbation that are *in fine* released to the Seine River suggest a shift of the urban δ<sup>11</sup>B from −10‰ in 1994 to 1.5 ± 2.0‰ in 2012, in agreement with our second hypothesis. We attribute this change to the removal of perborates from detergents rather than to the modernisation of wastewater treatment network, because it does not significantly impact the wastewater boron signatures. Eighteen years after the first assessment and despite the decreased use of perborates, geochemical and isotopic mass budgets confirm, that boron in the Seine River basin is mainly released from urban activities (60–100%), especially in Paris and the downstream part of the basin. Contrastingly, in headwaters

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and/or tributaries with low urbanisation, the relative boron input to river from agricultural practices and rains increased, up to 10% and by 10 to 30%, respectively.

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## 1. Introduction

Human activities have a strong environmental impact that needs to be determined and quantified. Because they gather and integrate waters from all sub-areas of their drainage basins, rivers allow us to characterise the environmental quality of a given area. Measuring the chemical compositions of riverine materials allows to characterise their health and to trace natural versus anthropic sources (Gaillardet et al., 2003; Chen et al., 2014). To that purpose, major and trace concentrations of river constituents are useful, but isotope ratios of trace elements are even more efficient (Chen et al., 2008).

Boron concentrations ([B]) in most river waters (under  $40 \mu\text{g L}^{-1}$ ; Lemarchand et al., 2002b) are at least an order of magnitude below the  $0.5 \text{ mg L}^{-1}$  WHO (World Health Organization) recommendation. However, boron is widely used in human activities (glass industry, soap/detergent, fertiliser), and because of its high solubility, boron is enriched in anthropised catchments. Boron is present in the aqueous environment as borate ion ( $\text{B}(\text{OH})_4^-$ ) and boric acid ( $\text{H}_3\text{BO}_3$ ) (pKa of 9.23; Baes and Robert, 1976). It has two stable isotopes  $^{10}\text{B}$  and  $^{11}\text{B}$  (abundance of 20 and 80%, respectively), which are not identically distributed between the two boron aqueous species:  $\text{H}_3\text{BO}_3$  is enriched in  $^{11}\text{B}$  and  $\text{B}(\text{OH})_4^-$  in  $^{10}\text{B}$  ( $\alpha_{\text{B4-B3}}$  of  $0.974 \pm 0.001$ ; Klochko et al., 2006; Nir et al., 2015). Due to their high relative mass difference and to the boric acid – borate speciation, boron isotopes are easily fractionated during physico-chemical reactions, leading to a large range of  $\delta^{11}\text{B}$  in geological samples (–70 to 75%; Spivack, 1986; Hogan and Blum, 2003; Cary et al., 2015).

Numerous studies have addressed the global boron geological cycle (Argust, 1998; Park and Schlesinger, 2002; Kot, 2009; Schlesinger and Vengosh, 2016) and improved our understanding of boron isotopic fractionation during physico-chemical processes at the water-rock interface. During chemical weathering,  $^{10}\text{B}$  is adsorbed or incorporated on clays and secondary phases, leading to a clear modification of  $\delta^{11}\text{B}$  in water solutions ( $\Delta^{11}\text{B}_{\text{clay-water}} = -31.2\%$  in acidic conditions; Rose et al., 2000). A similar trend is observed for sorption of boron on manganese or iron oxides (Lemarchand et al., 2007), and the  $\delta^{11}\text{B}$  can fluctuate between –40 and 0‰ on goethite, depending on pH condition. Biology and organic matter also play an important role in boron isotope budgets (Cividini et al., 2010): the large amount of boron accumulated in different parts of plants ( $10$  to  $15 \mu\text{g g}^{-1}$  in spruce needles and beech leaves) indicate that boron fluxes involved in biological cycles may be four times higher than those exported out of the drainage basin. This estimation, combined with a large boron isotopic fractionation between soil and plants ( $\delta^{11}\text{B}$  in trees is 30 to 45‰ higher than in soil particles) may have important consequences on the estimation of the boron isotope budget in a non-equilibrated ecosystem like deforested environments and cultivated areas.

Because the boron global geologic cycle is relatively well constrained and equilibrated in terms of natural sources and fluxes (Lemarchand, 2001; Lemarchand et al., 2002b; Park and Schlesinger, 2002), boron isotopes are considered as suitable tracers for deciphering boron sources. In this context, rivers are of importance, because they are the major continent-to-ocean vectors, but also because they record human and natural boron sources.

Weathering constitutes a significant boron input for rivers draining evaporites ([B] above  $100 \mu\text{g L}^{-1}$ ; Lemarchand and Gaillardet, 2006), but is almost a negligible boron input in calcareous or igneous provinces. Atmospheric precipitations and aerosols, on the other hand, strongly contribute to the total boron budgets. For example, in pristine areas (like French Guyana), marine aerosols can contribute to a

significant proportion of the river dissolved boron load (Chetelat et al., 2005), decreasing with distance from the sea (Chetelat et al., 2005; Millot et al., 2010). Rainfall inputs to the boron cycle are difficult to quantify, because large temporal and spatial variations of [B] and  $\delta^{11}\text{B}$  (–0.5 to 45‰; Chetelat et al., 2005; Chetelat et al., 2009) are observed. The formation of gaseous boron from seawater evaporation is enriched in boric acid inducing a final “oceanic” rainfall enriched in  $^{11}\text{B}$  (higher  $\delta^{11}\text{B}$ ; Chetelat et al., 2009). Then, both [B] and  $\delta^{11}\text{B}$  decrease in rains through Rayleigh distillation as the air masses move inland (Rose-Koga et al., 2006; Roux et al., 2017). On the other hand, changes of wind directions provide aerosols and dusts from different areas and thus with different signatures (Millot et al., 2010; Roux et al., 2017). Seawater evaporation (Chetelat et al., 2005; Rose-Koga et al., 2006; Chetelat et al., 2009; Sakata et al., 2010; Zhao and Liu, 2010), coal (Sakata et al., 2010; Zhao and Liu, 2010) or biomass combustion (Chetelat et al., 2005; Zhao and Liu, 2010) and ashes from waste incinerators (Chetelat et al., 2009) are all other possible sources for [B] and  $\delta^{11}\text{B}$  fluctuations in rains.

In anthropised watersheds, additional boron inputs have to be considered. In Missouri American state, [B] in watershed with low natural boron increased following the use of tap water sourced from the Missouri River (Hasenmueller and Criss, 2013). Wastewaters from sewage treatment plants or industrial effluents largely impact boron in groundwater (Vengosh et al., 1994; Eisenhut et al., 1996; Eisenhut and Heumann, 1997; Barth, 1998; Pennisi et al., 2006; Venturi et al., 2015) or in rivers (Chetelat and Gaillardet, 2005; Hasenmueller and Criss, 2013). Their contribution can reach up to 90% of the boron content for the Seine River at low-water stage (Chetelat and Gaillardet, 2005). However, Neal et al. (2010) report a decrease of [B] in rivers and wastewater treatment plants effluents from 1997 to 2007 in UK, which coincides with a drop of European perborate consumption from  $421 \text{ kt yr}^{-1}$  in 1997 to  $54 \text{ kt yr}^{-1}$  in 2007 (RPA. Risk and Policy Analysts, 2008) mainly due to the replacement of perborates by percarbonates as bleaching agent in soap and detergents.

Manures and fertilisers are other important suppliers of boron to rivers draining agricultural areas. In these products, [B] (from  $0.05 \mu\text{g g}^{-1}$  in cattle-feedlot runoff to  $22.4 \mu\text{g g}^{-1}$  in ammonium nitrate; Komor, 1997) and  $\delta^{11}\text{B}$  (from –2 to 22.4‰; Komor, 1997) are highly variable, making difficult the identification of this source with boron signatures alone. Recently, isotopic approaches combining boron and nitrogen isotopes (Widory et al., 2004a; Widory et al., 2004b; Seiler, 2005; Widory et al., 2012), boron, strontium and REEs (Petelet-Giraud et al., 2009), or boron, nitrate isotopes and microbial markers (Briand et al., 2013; Briand et al., 2017) clearly contributed to distinguish agricultural signatures from urban effluents and natural sources.

The present study on the Seine River basin follows that of Chetelat and Gaillardet (2005). In this former study, [B] and  $\delta^{11}\text{B}$  measured in water samples collected during 1994–95 (over the whole Seine basin and with a monthly monitoring in Paris, Roy et al., 1999) revealed that boron was conservative in this river and was a good tracer of anthropogenic inputs. Over the basin, three sources of boron were identified: rainwaters, agriculture inputs and urban effluents. Boron from weathering was found to be negligible, as the Seine watershed lays over a sedimentary basin dominated by carbonate rocks. Here, we focus on two new sample sets from the Seine River basin collected between 2004 and 2012, and we combine them to the data of Chetelat and Gaillardet (2005) to investigate the evolution of [B] and  $\delta^{11}\text{B}$  in the Seine River between 1994 and 2012. We test the persistence of anthropogenic inputs to the river and the relevance of boron isotopes as tracer of anthropogenic inputs over almost 20 years.



## 2. Environmental setting

The Seine River basin is one of the most human-impacted areas in Europe. It spans over 79,000 km<sup>2</sup> running on limestone and marl rocks of Mesozoic and Cenozoic ages. Quaternary deposits cover the basin surface (Roy et al., 1999). In headwaters, Yonne River drains Morvan igneous rocks. The average Seine water discharge is 310 m<sup>3</sup> s<sup>-1</sup> in Paris but can reach up to 1300 m<sup>3</sup> s<sup>-1</sup> during flood events (Chen et al., 2008). Average precipitations are low (700 mm an<sup>-1</sup>) with minima in summer and maxima during winter (Chetelat and Gaillardet, 2005). During the summer, suspended particulate matter (SPM) concentration is also lower (<10 mg L<sup>-1</sup> in average in Paris) and follows the water discharge trend (Chen et al., 2008). The Seine hydrology is thus characterised by two distinct periods: a low water summer stage with scattered storms and a high water winter stage with episodic floods.

The Seine watershed is split between an agricultural part with low urbanisation upstream and the Paris region with a high population density (12 million inhabitants) and intensive industrial activities downstream. The Paris conurbation concentrates around 35% of French industrial activity, creating a huge production of wastes and an important contamination potential for the Seine River. The Paris conurbation wastewaters are collected by four main Waste Water Treatment Plants (WWTP), managed by the Syndicat Interdépartemental pour l'Assainissement de l'Agglomération Parisienne (SIAAP). The main

plant ("Seine Aval" in Achères) treats 70% of these effluents and the sanitised water is rejected to the Seine River, right after Paris. The flow from Seine Aval WWTP represents up to 15% of the Seine water discharge at low water-level period. Combined sewer overflows (CSO), consisting of a physical by-pass, assist this network when abundant rainfalls risk to flood WWTP by directly discharging part of the overflowing wastewaters to the river. In this combined sewer system in Paris, domestic wastewaters, urban runoff and industrial effluents cannot be separated. Although problematic for determining the environmental impact, CSO represent a scientific opportunity to study non-treated urban wastewaters collected over a large surface area.

## 3. Sampling and analysis

Two different sample sets are analysed in this study and are compared to the data published in Chetelat and Gaillardet (2005). Their locations are represented and organised as follow in Fig. 1:

- 1994–1995 samples were collected by Roy et al. (1999) and are the corpus of Chetelat and Gaillardet's study (2005). They were obtained during two sampling sessions on the upstream part of the Seine River basin at very high (January 1994) and normal (March 1994) water stage, and from a monthly sampling in Paris during one year (1994–95). Only one sample (BP8) was collected downstream of Paris.

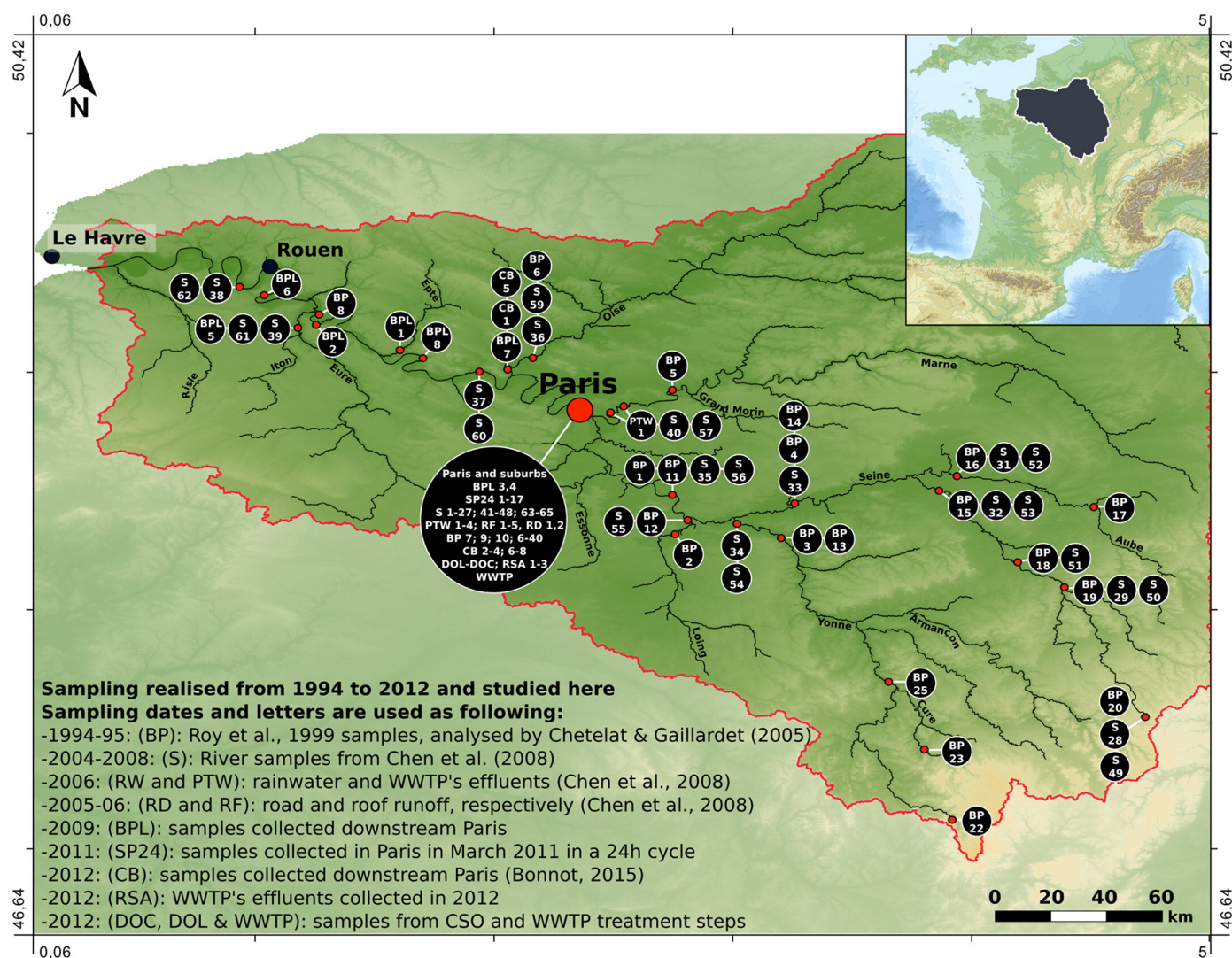


Fig. 1. Map of sampling points of waters analysed in this study.

- 2004–2007 samples were sampled by [Chen et al. \(2008\)](#) and represent the major part of the samples analysed in this study. The Seine River in Paris was sampled on a monthly basis between January 2004 and March 2007. Samples from the whole basin were collected in high- (February 2006) and low- (July 2006) water stage. Four rainwaters were also sampled in Paris during this period. Complementary samples such as WWTP effluents, roof and road runoffs allowed us to characterise the urban sources of Seine River pollution.
- 2009, 2011 and 2012 samples of the Seine River and its tributaries were taken downstream of Paris ([Bonnot, 2015](#)). Additionally, the Seine in Paris was followed-up over 24 h in March 2011 to observe the short-term variations of [B] and  $\delta^{11}\text{B}$ . We collected WWTP effluents three times in May–July 2012, and the waters from the different treatment steps (“process” samples including: raw, decanted, decarbonated, nitrified and denitrified waters) two times in Colombes WWTP (NW of Paris) ([Gasperi et al., 2011](#); [Rocher et al., 2012](#)). Finally, we sampled CSO outputs in 2012 in the cities of Clichy and La Briche. Clichy CSO drains 120 km<sup>2</sup> across Paris and its southern and eastern suburbs whereas La Briche CSO drains 52 km<sup>2</sup> in the northern industrialised part of Paris’ region.

Water samples were filtered at 0.2  $\mu\text{m}$ , acidified to pH 2 with 16 M distilled  $\text{HNO}_3$  (except the samples dedicated to anion analysis) and stored in acid-washed polypropylene bottles at 4 °C. Major elements ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ) were measured by HPLC ion chromatography (Dionex DX120) or ICP-OES (ICAP 6000 series, Thermo), and trace elements by ICP-MS (Plasma Quad II, Thermo X series II and Element II). Major and trace metals concentrations from the corpus of 2004–07 and 2011–12 samples were obtained from [Chen et al. \(2008\)](#) and [Bonnot \(2015\)](#), respectively.

Chalks and marls mostly make the Seine basin. To characterise the  $\delta^{11}\text{B}$  of boron potentially released during weathering, Jurassic limestones from Jura and a Cretaceous chalk sample from the Upper Seine River area were digested and analysed. In addition, fresh Oxfordian marls from Bure (East of Paris basin) were leached in Milli-Q water to simulate the water leaching occurring during an intense rainfall episode. We placed 0.5 g of marl in contact with 10 mL of Milli-Q water and shook it for a period of 1 h, after which we recovered water by centrifugation. This procedure was reproduced six times, each time with fresh Milli-Q. Leachates were gathered two by two (fractions 1–2; 3–4 and 5–6). Boron concentrations were determined for each fraction whereas  $\delta^{11}\text{B}$  was measured only for the fraction 1–2.

We extracted boron for isotope ratio measurements by ion exchange chromatography, following [Lemarchand et al. \(2002a\)](#) and [Paris et al. \(2010\)](#). A water sample volume of 1 to 50 mL (corresponding to  $\approx 50$  to 400 ng of B) at pH 8.5 to 9.5 (adjusted with distilled  $\text{NH}_4\text{OH}$ ) was loaded on a column loaded in water up to 50  $\mu\text{L}$  (once resin settled) with Amberlite IRA 743 resin at 200–400 mesh. Boron was eluted with 0.5 and 0.1 M  $\text{HNO}_3$  (final volume of 0.65 mL). Extraction yields, regularly checked on standard solutions and samples, were of  $100 \pm 5\%$ . Procedural blanks were below 1 ng of boron and were negligible compared to sample boron amount ( $\sim 400$  ng). After boron extraction, sample solutions were diluted to  $\text{HNO}_3$  0.05 M before MC-ICP-MS analysis.

$^{11}\text{B}/^{10}\text{B}$  isotopic ratios were measured with MC-ICP-MS Neptune (ThermoScientific) at the Institut de Physique du Globe de Paris with a demountable Direct Injection High Efficiency Nebulizer (d-DIHEN; [Louvat et al., 2010](#); [Louvat et al., 2014](#)). This sample introduction system improved stability, sensibility and reproducibility for boron isotope analysis and avoided the persistent memory effect of boron in spray chambers. For each sample, the average boron isotopic ratio was obtained after three successive sample-standard (NBS SRM 951) bracketing measurements ([Louvat et al., 2014](#)). The isotopic ratio of

boron ( $\delta^{11}\text{B}$ ) is reported relative to the international standard reference material NBS SRM 951 ([Catanzaro et al., 1970](#)):

$$\delta^{11}\text{B} = \left( \frac{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{sample}}}{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{SRM 951}}} - 1 \right) \times 1000 (\text{‰}) \quad 1$$

Repeatability (2SD calculated from the 5 individual  $\delta^{11}\text{B}$  values obtained from the three successive measurements of the same sample solution; [Louvat et al., 2014](#)) was generally better than 0.1‰, but reproducibility on up to 6 different extractions of a same sample was between 0.2 and 0.4‰.

## 4. Results and discussion

### 4.1. Boron concentrations and isotopic ratio over the whole Seine River basin

Over the whole Seine River basin, [B] ranges from 0.17 to 6.50  $\mu\text{mol L}^{-1}$ , whereas  $\delta^{11}\text{B}$  values span between  $-2.6$  and 14.9‰ (Table S1). As previously observed for this basin ([Chetelat and Gaillardet, 2005](#)), the  $\delta^{11}\text{B}$  and [B] of the whole set of samples define a hyperbolic trend ([Fig. 2A](#)). The sparsely populated and agricultural upstream region is characterised by high  $\delta^{11}\text{B}$  (up to 14.9‰) and low [B] (down to 0.17  $\mu\text{mol L}^{-1}$ ), while the downstream part of the basin, densely industrialised and populated, shows low to negative  $\delta^{11}\text{B}$  (down to  $-2.6$ ‰) and the highest [B] (up to 6.50  $\mu\text{mol L}^{-1}$ ).

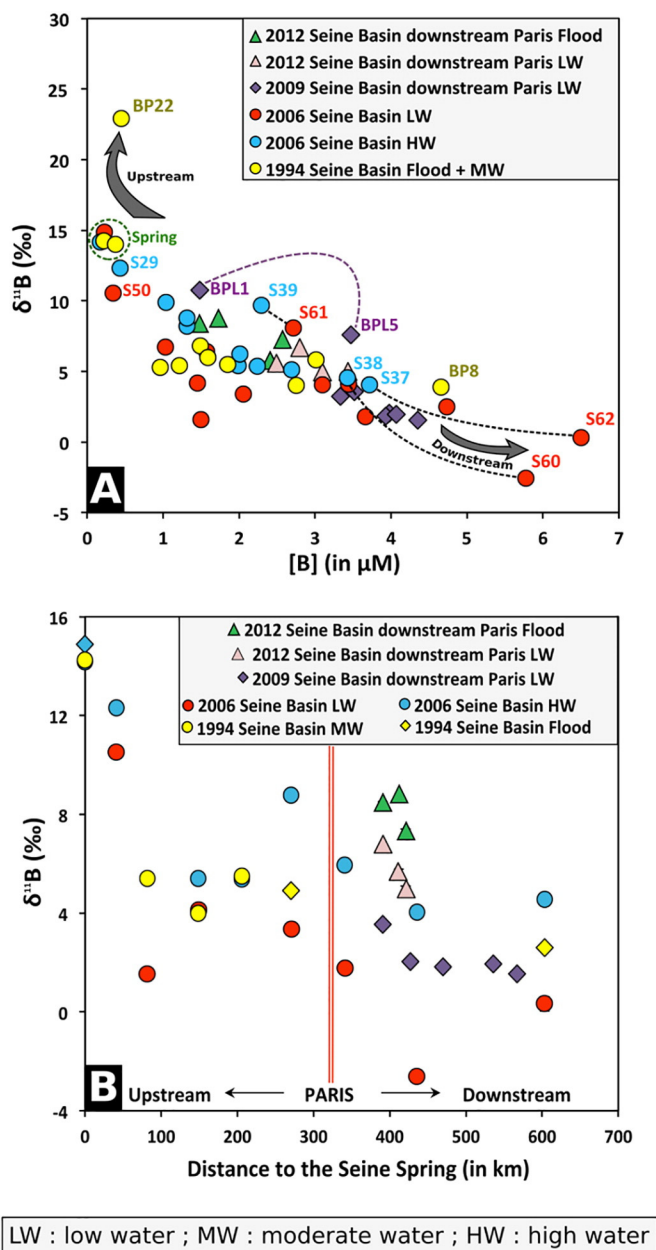
Between 1994 and 2006, [B] and  $\delta^{11}\text{B}$  remained constant through the upstream part of the Seine River basin. Only one location downstream of Paris (BP8) was collected in 1994 and analysed by [Chetelat and Gaillardet \(2005\)](#), during high water stage. The comparison of [B] and  $\delta^{11}\text{B}$  with our recent sample corpus is thus difficult in this part of the basin. Boron concentrations and  $\delta^{11}\text{B}$  for this sample are within the range reported for the 2006 downstream samples ([Fig. 2A](#)). The [B] of the locations downstream of Paris decreased between 2006 and 2009/2012 (from 5–7  $\mu\text{mol L}^{-1}$  to 3–6  $\mu\text{mol L}^{-1}$ ), without significant  $\delta^{11}\text{B}$  changes.

The hydrological regime of the Seine River and its tributaries also impact [B] and  $\delta^{11}\text{B}$ . 2006 high water stage (HW) samples (blue dots in [Fig. 2A](#)) have [B] lower than 2006 low water stage (LW) samples (red dots in [Fig. 2A](#)). In 2009 and 2012 as well, at a given sampling location within the Seine watershed, [B] are generally higher during low water stages than during flood periods. A similar observation was reported for urban areas from Benelux and the UK ([Wyness et al., 2003](#); [Neal et al., 2010](#)). A dilution effect could affect [B] during flood periods because we assume that boron behaves conservatively in the Seine River basin. Once boron is in the river water, secondary processes that could partition boron or its isotopes are negligible compared to mixing processes. Two pieces of evidence support this assumption:

- 1/ Correlations are observed between [B] and [Cl] ( $R^2 = 0.93$ ) or [B] and [Na] ( $R^2 = 0.90$ ) ([Fig. S1A](#) and [S1B](#)), two elements considered as the most conservative ones in this basin ([Chetelat and Gaillardet, 2005](#)).
- 2/ A boron mass budget at the Seine-Yonne river confluence, upstream of Paris, shows that [B] and  $\delta^{11}\text{B}$  measured 10 km after the confluence (S35) are in perfect agreement with the calculated [B] and  $\delta^{11}\text{B}$  of the two mixing tributaries (S33 and S34) taken before the confluence and weighted by their respective water discharge. This calculation might not work for every confluence in this basin, even more so if the Seine is sampled kilometres below the confluence and additional small or diffuse water inflows admix but were not sampled.

We acknowledge that the interaction between the dissolved and solid phases and the possible partitioning effects they imply could affect





**Fig. 2.** A) Boron isotope signatures as a function of boron concentrations in the Seine River and its tributaries. Sample names are reported for several points and referred to Fig. 1 and Table S1. Dashed lines link high and low water samples of a same location. A green dotted circle groups the Seine spring samples. 2SD errors on  $\delta^{11}\text{B}$  are included in data symbols. B) Evolution of  $\delta^{11}\text{B}$  along the Seine River transect from spring to mouth for all sampling cruises, including various hydrological periods.

the conservative behaviour of boron. We believe this is not the case, at least not significantly, for the following reasons:

1/ We are confident that no or little boron is released from soil, river-bank or floodplain leaching during flood events. Such a process would increase [B] in the river as it is observed for nitrate concentrations in headwaters from agricultural areas (Fig. S4), and thus induce a non-conservative behaviour. We do not observe any [B] increase. Instead, we note hints of a decrease. Moreover, the strong boron binding to soil particles (Sakata, 1987; Goldberg et al., 2000) will reduce exchanges with soil pore-waters and thus the boron flux joining the river dissolved loads during high water flows.

2/ Fig. 2B shows significantly higher  $\delta^{11}\text{B}$  during high water stages compared to low water stages for a given sampling location (2006 to 2012). During high water stage, the re-mobilisation of suspended particulate matter (SPM) by the river induces higher SPM concentrations that could bring an additional source of boron to the dissolved load of the river (as discussed above for the soils). As borate is more easily incorporated into minerals during water-rock interactions, these SPM are generally enriched in  $^{10}\text{B}$  (Rose et al., 2000). Boron exchange with more dilute river waters during rainfall events should thus result in a lowering of the dissolved  $\delta^{11}\text{B}$  but the opposite is observed in this study, rendering this SPM boron supply unlikely.

3/ Chetelat and Gaillardet (2005) reported that boron uptake by solid phases during water/sediment interaction in the river (resulting in lower [B] and higher  $\delta^{11}\text{B}$  of the dissolved load) is unlikely to occur because it would require an unrealistically high partition coefficient of boron between the SPM and the dissolved load in the Seine River. Nonetheless, this mechanism remains possible in soils, where boron would not be released from soils but adsorbed on soils from the soil solution, and would result in a soil solution depleted in boron and enriched in  $^{11}\text{B}$  that may be drained to the river during rain events. In a steady-state system as the Seine River basin, the SPM exported to the river concomitantly to the soil solution will be affected by desorption processes that erase this signal.

All the above observations support a mostly conservative behaviour of boron in the Seine River basin. The variations of  $\delta^{11}\text{B}$  observed between the Seine River and its tributaries (and through time) therefore result from the simple mixing of distinct boron sources (Fig. 2 and Fig. S2). As an example, the Epte and Eure rivers (BPL1, S61 and BPL5 in Fig. 1), join the Seine River downstream of Paris. In 2009, they display higher  $\delta^{11}\text{B}$  (10.8 and 7.6‰ for the Epte and Eure rivers, respectively) than the samples recovered downstream (1.5 to 3.5‰). Boron concentration is also lower in the Epte River ( $1.5 \mu\text{mol L}^{-1}$ ) than in the downstream Seine River ( $4 \mu\text{mol L}^{-1}$  on average). These differences reflect specific local land uses or other boron sources than those regulating boron signal in the Seine main stem. The Eure and Epte River catchments are partially preserved from urban anthropogenic impacts because the region is more sparsely industrialised than the downstream part of the basin. Higher relative contribution of boron from rainfall or agricultural practices could thus explain higher  $\delta^{11}\text{B}$  and lower [B] than in the Seine River. This small-scale complexity was also noted for Zn isotopes in another downstream tributary of the Seine River, the Oise River (Bonnot, 2015). The detailed understanding of the boron budget of these tributaries would require a specific study of their basins and of the associated human land use, which are out of the scope of this study.

In conclusion, in the Seine River basin, from upstream to downstream, the concomitant decrease of  $\delta^{11}\text{B}$  and increase of [B] are mostly due to the reinforced human pressure. The low number of Seine River samples collected downstream Paris in the 1994–95 sampling campaign makes the observation of a decrease of overall [B] between 1994 and 2012 difficult. If such a change occurred, it seems nonetheless to have had low impact on headwaters  $\delta^{11}\text{B}$  signatures of this basin, which appear relatively constant between 1994 and 2012.

#### 4.2. Boron concentrations and isotopic ratios in Paris

A diel cycle sampled in March 2011 shows the short-term evolution of boron signature in Paris (Fig. 3 and Table S2). Boron concentrations appear scattered (between  $1.7$  and  $3.2 \mu\text{mol L}^{-1}$ ), without periodicity, and roughly constant around  $2.5 \pm 0.5 \mu\text{mol L}^{-1}$ . With the exception of the first sampled point, a diurnal evolution of  $\delta^{11}\text{B}$  is observed with an increase of  $\delta^{11}\text{B}$  during the night and the following morning (up to 6.1‰) and a decrease at the end of the monitoring (5.6‰). However, the reproducibility of such an increase is not certain over several days and the amplitude of  $\delta^{11}\text{B}$  variation is relatively low ( $\approx 1\%$ ). The origin

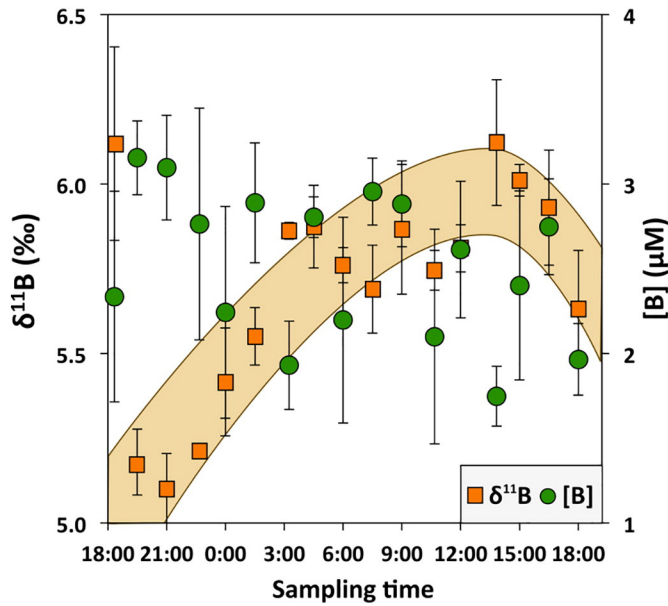


Fig. 3. Evolution of [B] and  $\delta^{11}\text{B}$  during a diel sampling in Paris (Quai Saint Bernard) in March 2011.

of these variations remains unclear. A biological effect appears unlikely due to the lack of a clear day/night  $\delta^{11}\text{B}$  contrast. Barge traffic on the Seine River might explain the [B] scattered record, but not the evolution in  $\delta^{11}\text{B}$ . Regardless, it is worth noting that the  $\delta^{11}\text{B}$  signature of the Seine River at a single location can evolve over 1‰ in just 10 h. Such high-frequency variations must be kept in mind when discussing boron behaviour in the whole Seine River basin and over long-term (few years) periods.

In Paris, the two sessions of monthly monitoring (1994–1995 and 2004–2007) of the Seine River waters are compared in Fig. 4. Chetelat and Gaillardet (2005) measured [B] between 2.4 and 8.4  $\mu\text{mol L}^{-1}$  and a large variation of  $\delta^{11}\text{B}$  between  $-10.6$  and 8.1‰ for the 1994–95 samples, while 2004–07 samples have half as much boron (1.5 to 4.2  $\mu\text{mol L}^{-1}$ ) and a much narrower range of  $\delta^{11}\text{B}$  (2.1 to 8.6‰). The negative to very negative  $\delta^{11}\text{B}$  values observed in 1994 for low water discharges are no longer found 10 years after.

In both cases, [B] and  $\delta^{11}\text{B}$  are correlated to the Seine water discharge  $Q_w$  (Fig. 4A and 4B, respectively), with a power law fit for [B], under the form  $[B] = \alpha Q_w^\beta$ . Exponent  $\beta$  of the power laws is  $-0.56$  and  $-0.42$ , and coefficient  $\alpha$  of 133 and 28, for 1994–95 and 2004–07, respectively (Fig. 4A). The 50% drop of [B] between 1994–95 and 2006–07 could testify for the boron “decontamination” of the Seine River. The decrease of [B] is most likely explained by replacement of perborates by percarbonates in detergent/soap formulation since the 1990’s in Europe (the European perborate consumption was reduced by 90% between 1997 and 2007, RPA. Risk and Policy Analysts, 2008; Neal et al., 2010).

The highest  $\delta^{11}\text{B}$  values (Fig. 4B), (for high water discharge) are almost the same for both monitoring sessions (around 8‰). During high-water stage, a higher share of upstream waters accounts for the Seine waters in Paris. Therefore, upstream boron sources (agricultural inputs and rains, Chetelat and Gaillardet, 2005) must have remained constant since 1994. By contrast, at low water stage,  $\delta^{11}\text{B}$  values are up to 12‰ higher in 2004–07 than in 1994–95. According to previous studies (Lemarchand et al., 2002b; Chetelat and Gaillardet, 2005; Pennisi et al., 2006), high [B] and low  $\delta^{11}\text{B}$  are typical of urban effluents. Indeed, Ca or Na borate ores constitute the main source of boron in human activities. The associated  $\delta^{11}\text{B}$  is highly variable, but negative for Turkey (from  $-25.4$  to  $-1\%$ ; Palmer and Helvacı, 1995; Palmer and Helvacı, 1997) and USA (from  $-8.6$  to 2.3‰; Swihart et al., 1996) deposits. Additionally, the manufactured Na-perborate products, used

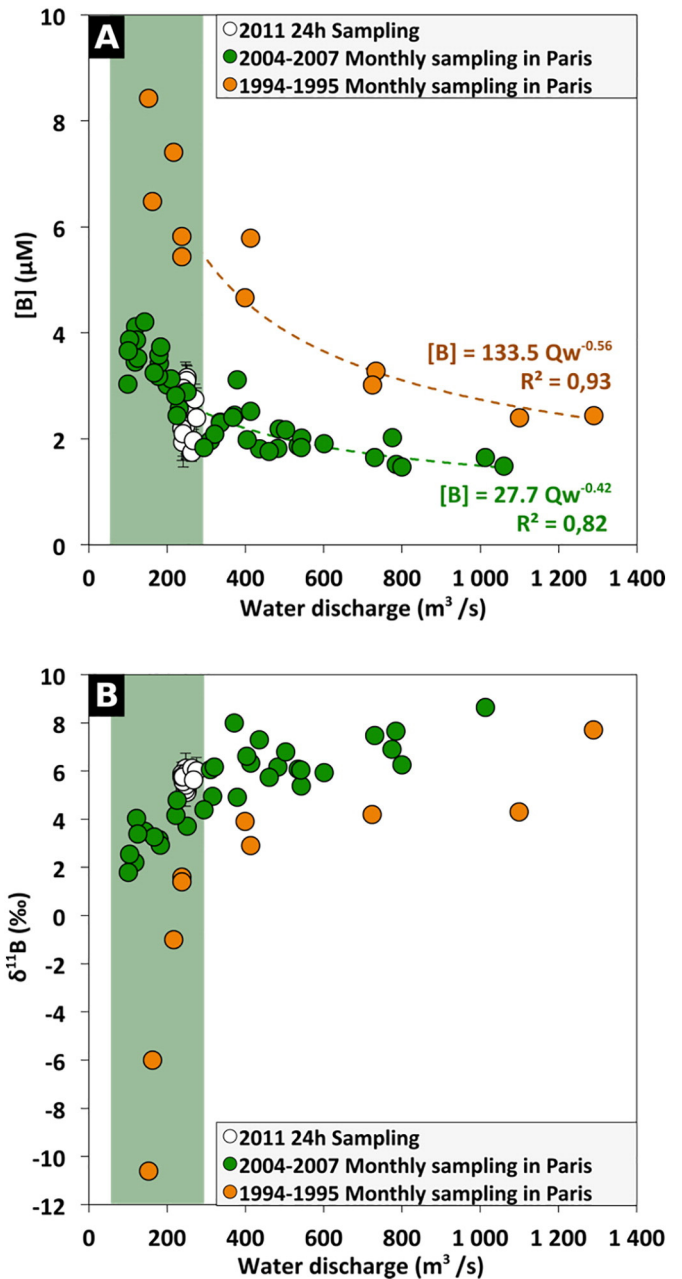


Fig. 4. Evolution of [B] (A) and  $\delta^{11}\text{B}$  (B) with water discharge in Paris (Quai Saint-Bernard) between 1994–95 and 2004–07 monthly monitoring and for a diel sampling in May 2011. The green area emphasizes the main modification observed between the two sampling campaigns.

in detergents and washing products, present a narrow, yet negative overall,  $\delta^{11}\text{B}$  range (from  $-6.3$  to 3.1‰; Eisenhut et al., 1996; Barth, 1998; Chetelat and Gaillardet, 2005) and can result from a mixture of the Turkish and American borate ores. The lowering of [B] and increase of  $\delta^{11}\text{B}$  between 1994–95 and 2004–07 in Paris can thus possibly reflect either: 1/ a decrease of urban boron use and rejection to the Seine River, or 2/ a change of the  $\delta^{11}\text{B}$  signature of the urban boron.

In the first case, the average urban relative contribution has been reduced from 90% in 1994–95 (Chetelat and Gaillardet, 2005) down to 65% in 2006, with an associated average  $\delta^{11}\text{B}$  for the Seine in Paris at low-water stage of 2.9‰, in agreement with the measured values. This calculation assumes that the  $\delta^{11}\text{B}$  and Cl/B ratio of the urban end member remained constant between 1994–95 and 2004–07 ( $-10\%$  and 23, respectively), based on the measured Cl/B ratio for low water stage in Paris. In the second case, the  $\delta^{11}\text{B}$  signature of the urban inputs should

range between  $-0.6$  and  $0.8\%$ , given the  $\delta^{11}\text{B}$  value at low water stage in 2006 (around  $2.5\%$ , cf. Fig. 3B), if we assume that the urban inputs in 2004–07 still represent 90% of the boron signal at low water stage, as in 1994–95 (Chetelat and Gaillardet, 2005). The  $\delta^{11}\text{B}$  of the urban boron inputs would thus have increased by  $10\%$  between 1994–95 and 2004–07 (it was estimated at  $-10 \pm 2\%$  in 1994–95, Chetelat and Gaillardet, 2005). In order to determine which of the two hypotheses is the most realistic or if we observe a combination of both, we need to define the boron signature of the current urban end member. To do so, we focus on the wastewater treatment network in Paris that integrates waters heavily contaminated and influenced by detergents and other urban boron-sources.

#### 4.3. Determination of the urban anthropogenic end member

Urban anthropogenic boron could be delivered to the Seine River by the Combined Sewer Overflows (CSO) during flood events or by the Waste Water Treatment Plant (WWTP). To identify the boron signature of the urban end member as accurately as possible, CSO effluents were first analysed as a system typical of untreated urban waters before focusing on the WWTP releases in the Seine River.

##### 4.3.1. Combined sewer overflows

The two CSOs of La Briche and Clichy drain the North and the South-east areas of Paris conurbation, respectively. In CSO's effluents, [B] fluctuate and lie on the upper part of the range observed for the Seine River waters (from  $3$  to  $7 \mu\text{mol L}^{-1}$ , Table S3 and Fig. 5). Similarly to metallic trace element concentrations, e.g. Cu and Zn (not shown here), these [B] are lower than previously observed in WWTP plants effluents (Hasenmueller and Criss, 2013; Briand et al., 2017). Dilution by abundant rain waters can in part explain these low [B] in CSOs, while reduction of [B] in urban effluents may account for another part (Neal et al., 2010). The CSO  $\delta^{11}\text{B}$  values are systematically lower in La Briche ( $0.1$  to  $1.9\%$ , average  $0.7 \pm 0.8\%$ ) compared to Clichy ( $0.7$  to  $3.6\%$ , average  $2.1 \pm 1.0\%$ ) (Fig. S3), while [B] are higher for La Briche ( $5.4$  to  $7.1 \mu\text{mol L}^{-1}$ )

than for Clichy ( $3.2$  to  $5.8 \mu\text{mol L}^{-1}$ ). As the two CSO networks are totally disconnected, these differences in  $\delta^{11}\text{B}$  and [B] cannot be explained by additional boron inputs to La Briche compared to Clichy, but rather by contrasted urban land uses. Indeed, Clichy CSO mostly drains Paris City and integrates both domestic wastewaters and urban effluents, while La Briche CSO collects waters from a more industrial area. As such, both CSO waters represent an “end member” for the raw urban releases of boron to the river. However, and so much the better, apart from heavy rain periods when the wastewater network overflows, most of the wastewaters rejected to the river are not raw waters but have been treated in WWTP.

##### 4.3.2. WWTP effluents

Achères WWTP is the main water treatment plant of Paris conurbation and accounts for up to  $15\%$  of the Seine water discharge at low-water stage, based on its water treatment capacity of  $1.5 \cdot 10^6 \text{ m}^3 \text{ d}^{-1}$ . The Achères WWTP outlet was sampled once in 2006 and thrice in 2012. Highly variable [B] ( $3.1$  to  $10.0 \mu\text{mol L}^{-1}$ ) are measured, associated with a rather narrow range of  $\delta^{11}\text{B}$  ( $-2.4\%$  in 2006 and  $0.7 \pm 1.5\%$  ( $n = 3$ ) in 2012). The urban effluent end member, defined for the 1994–95 monitoring of the Seine in Paris with a  $\delta^{11}\text{B}$  value of  $-10\%$  (Chetelat and Gaillardet, 2005), had thus increased by  $8\%$  by 2006 ( $-2.4\%$ ) and then again by  $2\%$  by 2012 (around  $0\%$ ) (Fig. 5). The combined reduced use of perborates in detergents since the 90's and increased average  $\delta^{11}\text{B}$  released by urban effluents between 1994 and 2012 reveal that boron in detergents had negative  $\delta^{11}\text{B}$  as reported elsewhere (from  $-6.3$  to  $3.1\%$ ; Eisenhut et al., 1996; Barth, 1998; Chetelat and Gaillardet, 2005) and that a change of the main urban boron source (with a different  $\delta^{11}\text{B}$ ) occurred between 1994–95 and 2006–12 (Fig. 5).

Independently, the  $\delta^{11}\text{B}$  of Achères WWTP outlet is significantly variable (over a few ‰) at the scale of only a few months. Defining the origin of this variability would require a much more extensive study of the wastewaters collected in the Parisian sewage network. Roughly, it would necessitate to identify the respective  $\delta^{11}\text{B}$  signatures for domestic or industrial wastewaters as well as for urban runoffs, both in terms of [B] and  $\delta^{11}\text{B}$ , and their relative fluxes. However, these signatures would probably also be quite variable, depending on the manufactured B-containing products, uses and amounts that are used, and one would need to go one step further to decipher the origin of each boron input. Such a detailed study would require a large amount of additional work.

Finally, the WWTP effluents hold a  $\delta^{11}\text{B}$  approximately  $0.5$  to  $2\%$  lower than CSO effluents. Such a difference could be explained by the wastewater treatment itself.

##### 4.3.3. Boron isotope fractionation during purification processes of a WWTP

We sampled twice the different water treatment steps of the most recent Paris WWTP (Seine Centre in Colombes, downstream of the two sampled CSOs) within an interval of two weeks in May–June 2012. After screening the raw waters, purification processes include: 1/ physico-chemical settling to suppress part of carbonaceous and phosphorus matters; 2/ biological decarbonation using an aerobic heterotroph bacteria that fixes carbon; 3/ biological nitrification to remove total nitrogen to nitrate; 4/ biological denitrification with carbon addition to reduce nitrate into diazote. All samples are 24 h samples, i.e. hourly subsamples gathered over 24 h.

Along the purification, [B] barely changes (by  $<1 \mu\text{mol L}^{-1}$ , Fig. 6), which confirms that boron is not importantly removed by WWTP processes, in agreement with previous studies (Fox et al., 2002; Hasenmueller and Criss, 2013). Boron isotope signature values are significantly different between the two sample sets: there is a  $-2$  to  $3\%$  drop between the raw wastewaters (at  $3\%$ ) and the two last steps of nitrification and denitrification ( $0.8$  and  $0.3\%$ , respectively) for the first series of samples, while for the second series  $\delta^{11}\text{B}$  remains constant ( $3.3 \pm 0.5\%$ ) throughout the purification procedure.

The slight [B] increase and  $\delta^{11}\text{B}$  decrease for the last two treatment steps in the first sample set could be explained by an addition of

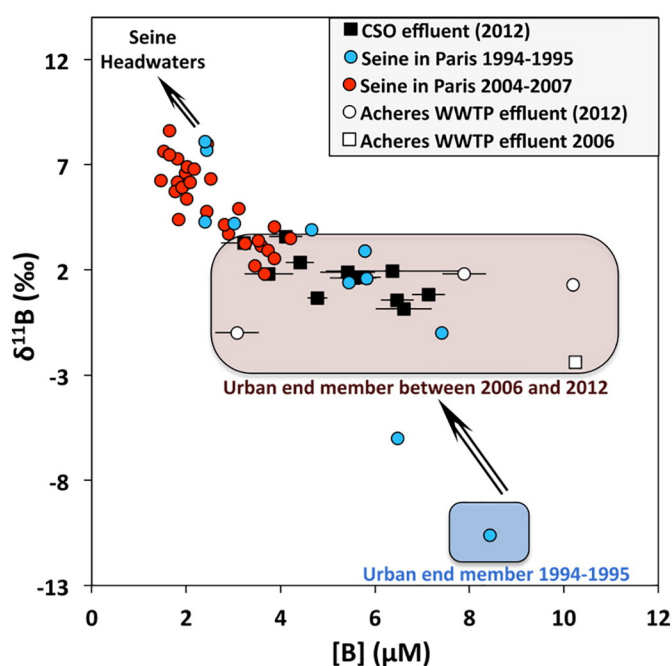


Fig. 5. Modification of the urban end member in Paris between 1994–1995 and the 2004–2012 period. Blue area represents the former estimation of urban pool by Chetelat and Gaillardet (2005). The brown area, larger because of highly variable [B], corresponds to the more recent (2006–2012) urban signature based on WWTP and CSO effluents.



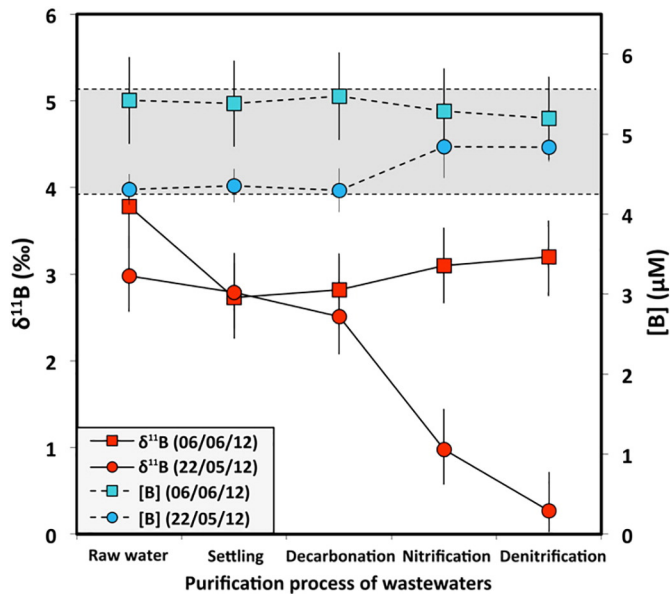


Fig. 6. Monitoring of [B] and  $\delta^{11}\text{B}$  during purification process in Seine Centre WWTP in May and June 2012 (2 sets of samples collected at 2 weeks interval).

boron with much lower  $\delta^{11}\text{B}$ . Alternatively, there might be some chemical variations recorded at short timescale, as the waters at each purification step are not synchronous and because these samples integrate hourly sampled waters over 24 h. Sorption/desorption, changes in boron speciation with pH modification (Spivack, 1986) or thermodynamic exchanges between solid sludge and dissolved wastewaters might also be potential processes favouring boron isotope fractionation. Regardless of its origin, the shift of  $\delta^{11}\text{B}$  (0 to 3‰) between the raw and treated wastewaters could partially explain the difference of  $\delta^{11}\text{B}$  signatures observed between the raw waters collected by the CSOs and the filtered waters rejected by the WWTP in the river ( $\Delta^{11}\text{B}_{\text{CSO-WWTP}} = \delta^{11}\text{B}_{\text{CSO}} - \delta^{11}\text{B}_{\text{WWTP}}$  from 0 to 2‰).

Seine-Centre WWTP benefits from the most recent technologies in its field and an assessment of boron isotope fractionation during the depollution processes for older water treatment plants is needed; in particular for Achères WWTP that receives 70% of Paris conurbation wastewaters. Indeed, between 1994 and 2012, treatment technologies may have changed, and associated boron isotope fractionation as well. Actually, the complexity of the sewage network and of the wastewater treatments (WWTP age, treatment protocol, sludge removal and use) in the Paris conurbation, and the absence of a collective network in some parts of the basin must be taken into account in the human impact upon boron geochemical cycle in the Seine River basin. Non-collective network in less populated areas may become additional pollution sources. Their contribution is difficult to assess without very local studies.

To conclude, the wastewater treatment steps do not affect systematically [B] and  $\delta^{11}\text{B}$ . Within the observed 3‰ range, both WWTP and CSO effluents can be considered part of the current urban end member in the Seine River basin. We can thus propose an average  $\delta^{11}\text{B}$  of  $1.5 \pm 2\%$  for the urban end member in Paris conurbation in 2012, 12‰ higher than the estimate done for 1994–95 samples by Chetelat and Gaillardet (2005). In absence of a better determination of other anthropogenic boron inputs, this value can be used to constrain the proportion of urban boron input to the Seine River basin.

#### 4.4. Other contributing sources of boron

##### 4.4.1. Rainfall

Four new rainfalls sampled in 2006 complete the previous extensive study of boron budget in Parisian rainfalls (Chetelat et al., 2009). Boron concentrations lie between 0.1 and 0.2  $\mu\text{mol L}^{-1}$  with highly variable

$\delta^{11}\text{B}$  (from 12.9 to 29.6‰, Table S1). Both [B] and  $\delta^{11}\text{B}$  are in the range of previously published values (Chetelat et al., 2009), which suggest that there has been no significant evolution of boron atmospheric budget in Paris between 2001 and 2006. In the literature, dry deposition of boron is assumed to be at most as important as wet deposition (Park and Schlesinger, 2002). As boron solubility is not well known in these particles, we can assume that this input will not drastically change the atmospheric boron budget. The high variability of  $\delta^{11}\text{B}$  results from a mixing of boron from marine (high  $\delta^{11}\text{B}$ ) and anthropogenic emissions (e.g. dissolution of fly ash with low  $\delta^{11}\text{B}$ ; Chetelat et al., 2009). With an average [B] of 0.15  $\mu\text{mol L}^{-1}$  (Chetelat et al., 2009), precipitation input to the boron budget represents 2 to 10% of the total [B] for the Seine River in and downstream of Paris between 2004 and 2012 ([B] from 1.5 to 6.5  $\mu\text{mol L}^{-1}$ ). For the Seine and tributaries upstream of Paris, low [B] and high  $\delta^{11}\text{B}$  in some sub-catchments (Yonne, Aube or Seine Spring) indicate that the rainfall impact can be higher (up to 20%).

##### 4.4.2. Chemical weathering

Another possible source of boron is through substratum weathering. The five analysed limestones from the Jura Mountains and from the Seine River basin present low [B] and  $\delta^{11}\text{B}$  around 10‰ (0.3 to 1.5  $\mu\text{g g}^{-1}$  and 9.1 to 12.2‰, Tables S4 and S5). If congruent dissolution of these rocks occurred during weathering, without any secondary processes, waters draining these rocks would have the same  $\delta^{11}\text{B}$ . Boron concentrations released by chalk weathering in river waters is estimated at 0.02  $\mu\text{mol L}^{-1}$ , based on the average  $[\text{Ca}^{2+}]$  measured in upstream region waters (2  $\text{mmol L}^{-1}$ ) and on a molar Ca/B ratio in these rocks of 9.10<sup>6</sup> (Chetelat and Gaillardet, 2005). It is 10 times lower than [B] in the headwaters of the basin (0.2  $\mu\text{mol L}^{-1}$ ) and can be considered as negligible for the boron budget of the whole Seine River basin waters.

However, the Parisian basin also contains some marls. During the leaching experiment, [B] in the first leachate is around 20  $\mu\text{mol L}^{-1}$  with a negative  $\delta^{11}\text{B}$  of  $-20\%$ . This huge amount of boron is extracted from the clay interlayers of the marls and the very negative  $\delta^{11}\text{B}$  of leachate is in agreement with a preferential desorption of <sup>10</sup>B from phyllosilicates (Rose et al., 2000). The two following leachates (F3–4 and F5–6) were much less enriched in boron (6 and 3  $\mu\text{mol L}^{-1}$ , respectively). Therefore, the impact of marl weathering in the boron budget of Seine basin waters may be significant for freshly exposed marls but not for rocks already altered. Besides, the proportion of marls within the basin is very small. Altogether, in the calcareous Seine River basin, chemical weathering of carbonates is a negligible source of boron.

##### 4.4.3. Agricultural inputs

Agricultural activities are quite developed in the Seine River basin but their impact on boron geochemistry is not obvious, and is in part hidden by other anthropogenic boron inputs, in particular in the downstream part of the basin. Boron is an essential nutrient (Carpena et al., 2000) and its application in fertilisers during flowering periods of crops (wheat, corn, rapeseed) or fruit trees is reported in literature (Perica et al., 2001). However, the amounts of boron amendment are limited (7.5  $\text{kg km}^{-2}$  for corn; Oost, 1999), as it becomes toxic at high concentrations, and it is still uncertain how boron transits from the soils to the rivers. Nitrates are commonly used to constrain agricultural inputs to the rivers (Widory et al., 2004a; Widory et al., 2004b; Seiler, 2005; Widory et al., 2012), because they are largely released by manures or fertilisers. Several studies showed that high  $\text{NO}_3/\text{Na}$  and  $\text{Cl}/\text{Na}$  ratios are characteristic of these agricultural inputs (namely in Seine River basin; Roy et al., 1999; Chetelat and Gaillardet, 2005; Chen et al., 2008) and could be used to determine the co-migration of other elements from the agricultural surfaces to the rivers. Here we used  $\text{NO}_3/\text{B}$  ratios measured in the Seine River basin to constrain the agricultural boron end member (Fig. 7).

Intensive cropping is developed over the whole Seine River basin, but only the headwater areas are relatively preserved of urban and industrial activities and will enable to trace agricultural boron inputs.



Headwaters samples, especially during flood regime, present high  $\text{NO}_3^-/\text{B}$  ratio (up to 1500) and  $\delta^{11}\text{B}$  (around 12‰). It concerns the headwaters of the Seine River (samples S29/S50) and all the Seine tributaries located upstream of Paris (S31, S34 and S35). Therefore, boron inputs from agriculture may be featured by  $\delta^{11}\text{B}$  around  $12 \pm 2\%$  and  $\text{NO}_3^-/\text{B}$  ratio around 1500. Such a  $\delta^{11}\text{B}$  signature is not clearly distinct from weathering or even rain  $\delta^{11}\text{B}$ , and together with the  $\text{NO}_3^-/\text{B}$  ratio, is identical to that previously defined as the agriculture end member for the 1994 samples ( $14 \pm 4\%$  and  $1200 \pm 500$ ; respectively; Chetelat and Gaillardet, 2005).

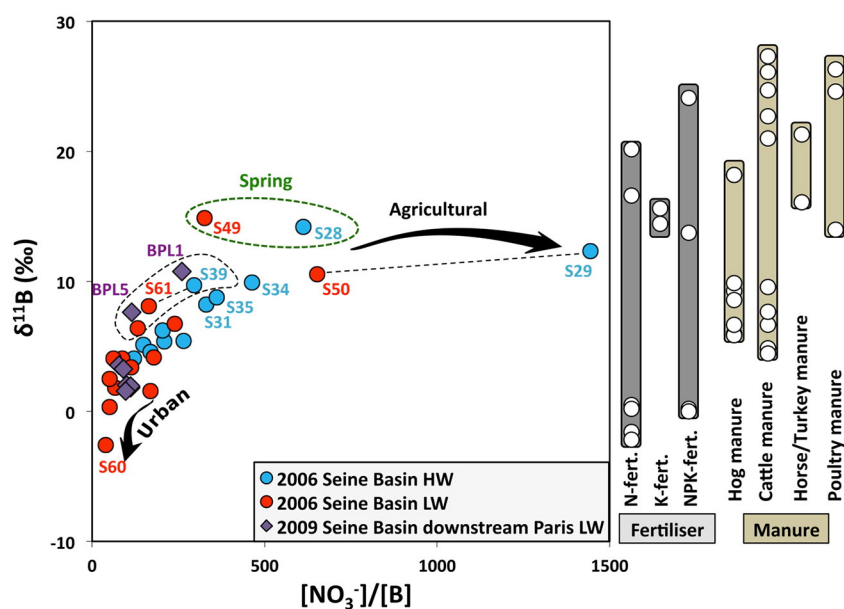
Fertiliser and manure [B] and  $\delta^{11}\text{B}$  published in literature are again highly variable. In fertilisers, [B] range from a few  $\text{ng g}^{-1}$  to  $22 \mu\text{g g}^{-1}$  (Komor, 1997; Widory et al., 2012), and  $\delta^{11}\text{B}$  from  $-8$  to  $25\%$  (Widory et al., 2004a; Widory et al., 2012). In manure, [B] range from 10 to  $8000 \text{ ng g}^{-1}$  and  $\delta^{11}\text{B}$  from 5.8 to  $28.6\%$  (Komor, 1997; Widory et al., 2004a; Widory et al., 2004b; Widory et al., 2012). The variation is related to the different diets, according to breeding regions and animal types (hog, cattle or poultry). In the Seine basin, cropping largely dominates over breeding and the manure impact upon the river geochemistry must be negligible. Intensive wheat and rapeseed crops cover the upstream plains and excess boron inputs from fertiliser might explain the  $\delta^{11}\text{B}$  signal recorded in upstream Seine basin rivers. Most N and NPK (Nitrate, Phosphorus and Potassium) fertilisers have very low  $\delta^{11}\text{B}$  (from  $-2$  to  $0.4\%$ ; Widory et al., 2012), which cannot explain our measured values. In majority, they also have low [B] and cannot be a major source of boron to the rivers. K-fertilisers and some N or NPK fertilisers have  $\delta^{11}\text{B}$  in the range of those measured in the Seine headwater areas (around 15–20‰) and high [B] ( $13 \mu\text{g g}^{-1}$  in a K-fertiliser; Komor, 1997). Application of such fertiliser could easily explain the  $0.5 \mu\text{g L}^{-1}$  [B], the high  $\text{NO}_3^-/\text{B}$  ratio and the  $\delta^{11}\text{B}$  measured in headwaters. Similarly, high  $\text{NO}_3^-/\text{Na}$  and  $\text{Cl}/\text{Na}$  ratios in upstream samples (not shown here) are typical of agricultural inputs as previously noted (Roy et al., 1999) and reinforce identification of such inputs in the upstream part of the Seine River basin.

Some of the upstream water samples present a  $\text{NO}_3^-/\text{B}$  ratio higher for flood than for low water stage (e.g. Buncey for S29 and S50, see Table S1, Fig. 7), which indicate that agricultural inputs are proportionally higher for high water periods, and thus the soluble nitrate released to the river when the soils are leached by intensive rainwater.

Application on a same crop of distinct fertilisers, containing boron or not, depending on the season (flowering or not) and on the plant needs, could also potentially explain these seasonal variations in the  $\text{NO}_3^-/\text{B}$  measured in the rivers impacted by agricultural inputs. Moreover, a preferential boron adsorption could induce lower input of boron than nitrates, the latter being added to crops in extreme excess. Several studies report a control of boron adsorption in various types of soils by mineralogy or by soil characteristics (e.g. the cation exchange capacity, the organic and inorganic content or the surface area) (Goldberg and Glaubig, 1985; Sakata, 1987; Goldberg et al., 2000). Finally, boron is incorporated in plants (e.g. several  $\mu\text{g g}^{-1}$  in corn or wheat leaves and roots; Vanderpool and Johnson, 1992) with a better efficiency than nitrates and the geochemical boron budget over the basin could be unbalanced if part of the harvest is exported out of the basin as cereals.

#### 4.5. Estimation of the relative proportion of boron sources in the Seine River basin

The proportion of each boron source to the total boron budget was calculated for each sample through a set of mixing equations, resolved by an inverse method (e.g. Négrel et al., 1993; details in S.I.7). Similarly to Chetelat and Gaillardet (2005), each boron source (natural boron from weathering is neglected) is characterised by its own  $\text{NO}_3^-/\text{B}$ ,  $\text{Cl}/\text{B}$  and  $\text{Na}/\text{B}$  ratios as well as  $\delta^{11}\text{B}$  signature. The agricultural end member was based on sample S29 (see Section 4.4.3) with  $\text{NO}_3^-/\text{B}$ ,  $\text{Cl}/\text{B}$  and  $\text{Na}/\text{B}$  ratios of  $1500 \pm 200$ ,  $825 \pm 100$  and  $450 \pm 120$ , respectively and an associated  $\delta^{11}\text{B}$  of  $12 \pm 3\%$ . Atmospheric boron input is highly variable with time. The study of Chetelat et al. (2009) integrated Parisian rainfalls over a year between 2001 and 2002, with average  $\text{NO}_3^-/\text{B}$ ,  $\text{Cl}/\text{B}$  and  $\text{Na}/\text{B}$  ratios of  $150 \pm 50$ ,  $200 \pm 100$  and  $160 \pm 100$ , respectively, and an average  $\delta^{11}\text{B}$  of  $25 \pm 5\%$ , consistent with the four rainwaters values measured in this study. Finally, the urban (wastewaters) boron inputs, accurately defined in this study based on CSO and WWTP outputs, are characterised by higher and more variable  $\text{NO}_3^-/\text{B}$ ,  $\text{Cl}/\text{B}$  and  $\text{Na}/\text{B}$  ratios than in 1994–95:  $100 \pm 100$ ,  $430 \pm 300$  and  $330 \pm 200$ , respectively. Contrarily, the urban  $\delta^{11}\text{B}$  is relatively well constrained at  $1.5 \pm 2\%$  in the 2006–2012 period, 12‰ higher than in 1994–95.



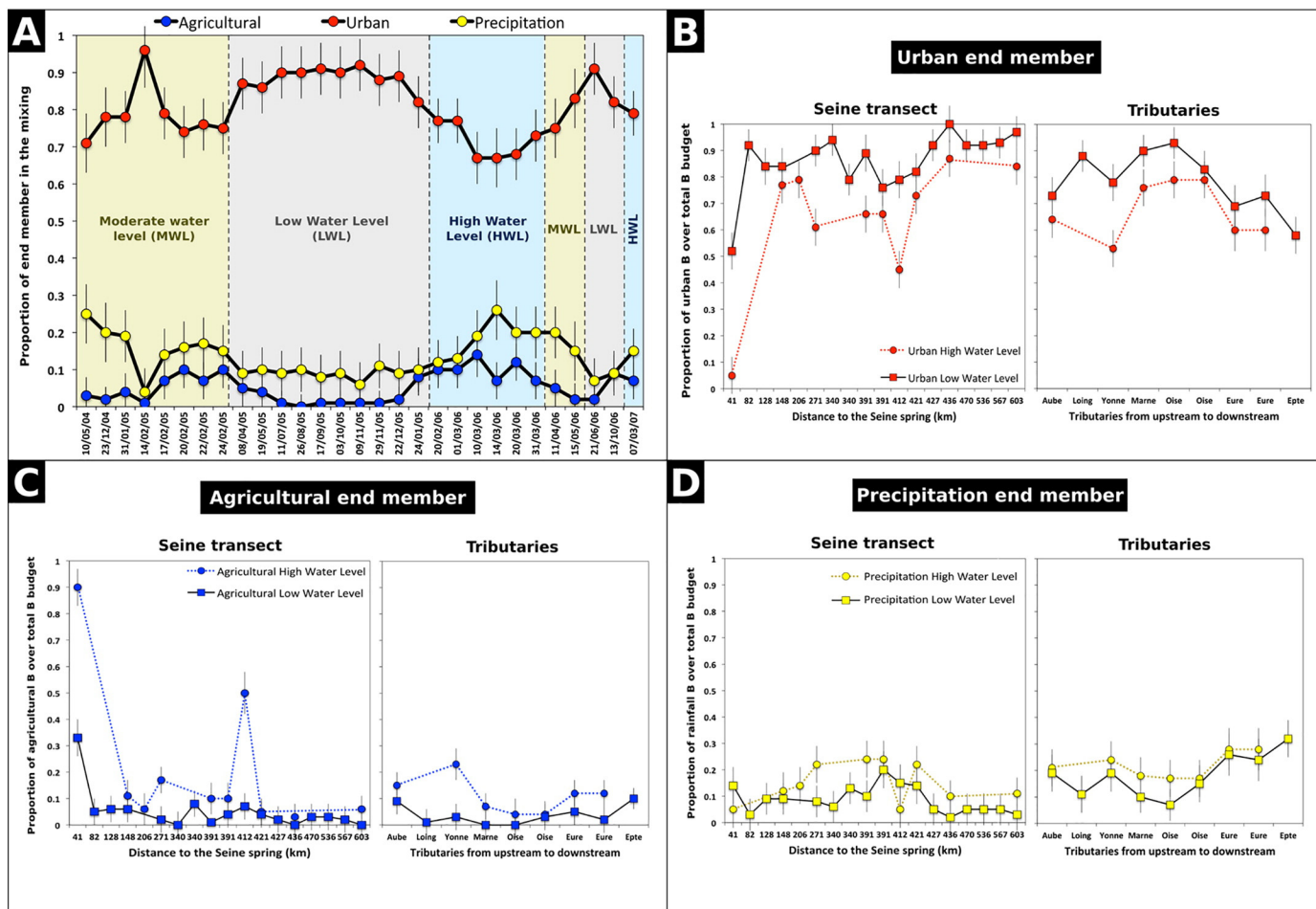
**Fig. 7.** Characterisation of boron agriculture inputs from the  $\text{NO}_3^-/\text{B}$  ratios and  $\delta^{11}\text{B}$  of the 2006–2012 samples. Dashed lines (between S50 and S29 or S61 and S39) refer to a same location at different hydrological periods. The delimited area depicts Eure and Epte River samples (BPL1, BPL5, S39 and S61), which have singular evolution compared to the Seine main stem. (Manure and fertiliser  $\delta^{11}\text{B}$  data are obtained from Komor, 1997; Widory et al., 2004a; Widory et al., 2004b; Chetelat and Gaillardet, 2005; Seiler, 2005; Widory et al., 2012).

The calculated proportions of each boron source are reported in Fig. 8 and in Table S6. In Paris (Fig. 8A) and in the whole Seine River basin (Fig. 8B), urban effluents represent between 60 and 100% of the total boron, which is similar to the proportion calculated for 1994–95 by Chetelat and Gaillardet (2005), and peak during low water levels. Except in the first kilometres of the Seine River (Fig. 8C), agricultural boron does not exceed 25% of the total boron budget in the basin and is mostly <10%, even in weakly anthropised catchments (Aube or Yonne tributaries). The atmospheric boron released throughout the basin fluctuates between 10 and 30% of the total boron budget (Fig. 8D) and is proportionally more variable than agricultural or urban boron sources. Counterbalancing urban effluents, its proportion increases during high water level, together with boron agricultural outputs due to leaching of the land fields. In detail, the Seine Spring (S28 and 249) was not considered in this calculation because the low  $\text{NO}_3^-$ ,  $\text{Na}^+$  or  $\text{Cl}^-$  concentrations indicate that boron likely originates from groundwater. In the downstream part of the basin, while the Seine River is dominated by urban boron releases, Epte and Eure tributaries are partially preserved from urbanisation but also from agricultural practices and exhibit 30 to 40% of atmospheric boron, validating the particular behaviour of boron observed in these watersheds in Fig. 2 and Fig. 7. In contrast, at low water stage, the most downstream Seine River sample (S62) exhibits slightly lower  $\delta^{11}\text{B}$  ( $-2.6 \pm 0.2\text{‰}$ ) than the value used to define the urban end member ( $1.5 \pm 2.0\text{‰}$ ), due presumably to local inputs of more negative urban  $\delta^{11}\text{B}$  in this zone. Altogether, this boron mass budget reveals that even if [B] have decreased for the Seine River between 1994–95 and 2004–2012, urban effluents in the basin remain

the dominant boron input, accounting for 60 to 100% of the boron in the river waters.

**5. Conclusion**

This study performed one decade after the pioneering work of Chetelat and Gaillardet (2005) on boron in the Seine River basin confirms that boron isotopes are still an appropriate tracer of anthropogenic releases in the environment. However, between 1994 and 2012, urban effluents have undergone a drastic reduction of their [B], probably linked to the replacement of perborates by percarbonates in detergents since the 1990's. In the same time, urban boron effluents have changed their  $\delta^{11}\text{B}$  by ~12‰, increasing from  $-10\text{‰}$  to  $1.5 \pm 2\text{‰}$ . Nonetheless, after characterisation of the rainfall, urban and agricultural source end members on the most recent 2006–12 sample set, the determined source proportions indicate that urban boron still represents 60 to 100% of the total boron budget of the Seine River, which is similar to what was previously calculated for 1994–95. Atmospheric boron fluctuates between 10 and 30% and agricultural boron does not exceed 15%, except in the first kilometres of the upstream basin. The drop of [B] in the Seine in Paris by a factor of 2 over 11 years emphasizes the fast “remediation” occurring in this watershed and thus the possibility of a quick recovery of a human-impacted environment relatively to dissolved elements such as boron. On the other hand, the important and quick shift of the  $\delta^{11}\text{B}$  signature observed for boron exported by urban effluents makes it mandatory to precisely and regularly characterise



**Fig. 8.** Proportion of boron inputs by urban, agricultural outputs and rainfall events in the Seine in Paris over a monthly sampling (A) and in the whole basin (B–D). The variations of contribution for a same sampling site in two distinct hydrological periods are also presented for each end member (urban in 8B; agriculture in 8C and precipitation in 8D). Reported uncertainties are the a posteriori errors calculated by the inverse method.

this urban source, in order to better trace human-derived sources using boron isotopes to the environment and quantify their inputs. Because the urban and agricultural boron sources also carry other boron-like soluble species, among which recognised contaminants (e.g. metallic oxyanions), boron isotopes do not only trace anthropogenic boron but more generally anthropogenic inputs to the rivers.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.01.159>.

## References

- Argust, P., 1998. Distribution of boron in the environment. *Biol. Trace Elem. Res.* 66 (1), 131–143.
- Baes, C.F.M., Robert, E., 1976. *The Hydrolysis of Cations*. Wiley, New York.
- Barth, S., 1998. Application of boron isotopes for tracing sources of anthropogenic contamination in groundwater. *Water Res.* 32 (3), 685–690.
- Bonnot, C., 2015. L'origine des métaux et la dynamique du zinc dans le bassin de la Seine. Institut de Physique du Globe de Paris, Paris 291 pp.
- Briand, C., Plagnes, V., Sebilo, M., Louvat, P., Chesnot, T., Schneider, M., Ribstein, P., Marchet, P., 2013. Combination of nitrate (N, O) and boron isotopic ratios with microbiological indicators for the determination of nitrate sources in karstic groundwater. *Environ. Chem.* 10 (5), 365–369.
- Briand, C., Sebilo, M., Louvat, P., Chesnot, T., Vauy, V., Schneider, M., Plagnes, V., 2017. Legacy of contaminant N sources to the NO<sub>3</sub><sup>-</sup> signatures in rivers: a combined isotopic ( $\delta^{15}\text{N-NO}_3^-$ ,  $\delta^{18}\text{O-NO}_3^-$ ,  $\delta^{11}\text{B}$ ) and microbiological investigation. *Sci. Rep.* 7, 41703.
- Carpena, R.O., Esteban, E., Sarro, M.J., Peñalosa, J., Gárate, A., Lucena, J.J., Zornoza, P., 2000. Boron and calcium distribution in nitrogen-fixing pea plants. *Plant Sci.* 151 (2), 163–170.
- Cary, L., Petelet-Giraud, E., Bertrand, G., Kloppmann, W., Aquilina, L., Martins, V., Hirata, R., Montenegro, S., Pauwels, H., Chatton, E., Franzen, M., Aurouet, A., 2015. Origins and processes of groundwater salinization in the urban coastal aquifers of Recife (Pernambuco, Brazil): a multi-isotope approach. *Sci. Total Environ.* 530–531 (Supplement C), 411–429.
- Catanzaro, E., Champion, C., Garner, E., Marinenko, G., Sappenfield, K., Shields, W., 1970. Standard reference materials: boric acid; isotopic and assay. *Standard Reference Materials* 266–17.
- Chen, J., Gaillardet, J., Louvat, P., 2008. Zinc isotopes in the Seine River waters, France: a probe of anthropogenic contamination. *Environ. Sci. Technol.* 42 (17), 6494–6501.
- Chen, J.B., Bouchez, J., Gaillardet, J., Louvat, P., Wang, Y.N., 2014. Anthropophile elements in river sediments: clues from the Seine River, France. *Geochem. Geophys. Geosyst.* 15, 4526–4546.
- Chetelat, B., Gaillardet, J., 2005. Boron isotopes in the Seine River, France: a probe of anthropogenic contamination. *Environ. Sci. Technol.* 39 (8), 2486–2493.
- Chetelat, B., Gaillardet, J., Freyrier, R., Négrel, P., 2005. Boron isotopes in precipitation: experimental constraints and field evidence from French Guiana. *Earth Planet. Sci. Lett.* 235 (1–2), 16–30.
- Chetelat, B., Gaillardet, J., Freyrier, R., 2009. Use of B isotopes as a tracer of anthropogenic emissions in the atmosphere of Paris, France. *Appl. Geochem.* 24 (5), 810–820.
- Cividini, D., Lemarchand, D., Chabaux, F., Boutin, R., Pierret, M.C., 2010. From biological to lithological control of the B geochemical cycle in a forest watershed (Strengbach, Vosges). *Geochim. Cosmochim. Acta* 74 (11), 3143–3163.
- Eisenhut, S., Heumann, K.G., 1997. Identification of ground water contaminations by landfills using precise boron isotope ratio measurements with negative thermal ionization mass spectrometry. *Fresenius J. Anal. Chem.* 359 (4–5), 375–377.
- Eisenhut, S., Heumann, K.G., Vengosh, A., 1996. Determination of boron isotopic variations in aquatic systems with negative thermal ionization mass spectrometry as a tracer for anthropogenic influences. *Fresenius J. Anal. Chem.* 354 (7–8), 903–909.
- Fox, K.K., Cassani, G., Facchi, A., Schröder, F.R., Poelloth, C., Holt, M.S., 2002. Measured variation in boron loads reaching European sewage treatment works. *Chemosphere* 47 (5), 499–505.
- Gaillardet, J., Viers, J., Dupré, B., 2003. Trace elements in river waters. In: Heinrich, D.H., Karl, K.T. (Eds.), *Treatise on Geochemistry*. Oxford, Pergamon, pp. 225–272.
- Gasperi, J., Rocher, V., Moilleron, R., 2011. Priority substances in combined sewer overflows: case study of the Paris sewer network. *Water Sci. Technol.* 63 (5), 853–858.
- Goldberg, S., Glaubig, R.A., 1985. Boron adsorption on aluminum and iron oxide minerals. *Soil Sci. Soc. Am. J.* 49 (6), 1374–1379.
- Goldberg, S., Lesch, S.M., Suarez, D.L., 2000. Predicting boron adsorption by soils using soil chemical parameters in the constant capacitance model. *Soil Sci. Soc. Am. J.* 64 (4), 1356–1363.
- Hasenmueller, E.A., Criss, R.E., 2013. Multiple sources of boron in urban surface waters and groundwaters. *Sci. Total Environ.* 447, 235–247.
- Hogan, J.F., Blum, J.D., 2003. Boron and lithium isotopes as groundwater tracers: a study at the fresh kills landfill, Staten Island, New York, USA. *Appl. Geochem.* 18 (4), 615–627.
- Klochko, K., Kaufman, A.J., Yao, W., Byrne, R.H., Tossell, J.A., 2006. Experimental measurement of boron isotope fractionation in seawater. *Earth Planet. Sci. Lett.* 248 (1–2), 276–285.
- Komor, S.C., 1997. Boron contents and isotopic compositions of hog manure, selected fertilizers, and water in Minnesota. *J. Environ. Qual.* 26 (5), 1212–1222.
- Kot, F.S., 2009. Boron sources, speciation and its potential impact on health. *Rev. Environ. Sci. Biotechnol.* 8 (1), 3–28.
- Lemarchand, D., 2001. Géochimie isotopique du bore: érosion continentale, bilan océanique et paleo-pH (364 pp).
- Lemarchand, D., Gaillardet, J., 2006. Transient features of the erosion of shales in the Mackenzie basin (Canada), evidences from boron isotopes. *Earth Planet. Sci. Lett.* 245 (1–2), 174–189.
- Lemarchand, D., Gaillardet, J., Göpel, C., Manhès, G., 2002a. An optimized procedure for boron separation and mass spectrometry analysis for river samples. *Chem. Geol.* 182 (2–4), 323–334.
- Lemarchand, D., Gaillardet, J., Lewin, É., Allègre, C.J., 2002b. Boron isotope systematics in large rivers: implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic. *Chem. Geol.* 190 (1–4), 123–140.
- Lemarchand, E., Schott, J., Gaillardet, J., 2007. How surface complexes impact boron isotope fractionation: evidence from Fe and Mn oxides sorption experiments. *Earth Planet. Sci. Lett.* 260 (1–2), 277–296.
- Louvat, P., Bouchez, J., Paris, G., 2010. MC-ICP-MS isotope measurements with direct injection nebulisation (d-DIHEN): optimisation and application to boron in seawater and carbonate samples. *Geostand. Geoanal. Res.* 35 (1), 75–88.
- Louvat, P., Moureau, J., Paris, G., Bouchez, J., Noireaux, J., Gaillardet, J., 2014. A fully automated direct injection nebulizer (d-DIHEN) for MC-ICP-MS isotope analysis: application to boron isotope ratio measurements. *J. Anal. At. Spectrom.* 29 (9), 1698–1707.
- Millot, R., Petelet-Giraud, E., Guerrot, C., Négrel, P., 2010. Multi-isotopic composition ( $\delta^7\text{Li-}\delta^{11}\text{B-}\delta^8\text{O}$ ) of rainwaters in France: origin and spatio-temporal characterization. *Appl. Geochem.* 25 (10), 1510–1524.
- Neal, C., Williams, R.J., Bowes, M.J., Harrass, M.C., Neal, M., Rowland, P., Wickham, H., Thacker, S., Harman, S., Vincent, C., P., J.H., 2010. Decreasing boron concentrations in UK rivers: insights into reductions in detergent formulations since the 1990s and within-catchment storage issues. *Sci. Total Environ.* 408 (6), 1374–1385.
- Nir, O., Vengosh, A., Harkness, J.S., Dwyer, G.S., Lahav, O., 2015. Direct measurement of the boron isotope fractionation factor: reducing the uncertainty in reconstructing ocean paleo-pH. *Earth Planet. Sci. Lett.* 414, 1–5.
- Oost, J.F., 1999. *La fertilisation en culture de maïs. Soil and Applied Boron*. University of Wisconsin.
- Palmer, M.R., Helvacı, C., 1995. The boron isotope geochemistry of the Kirka borate deposit, western Turkey. *Geochim. Cosmochim. Acta* 59 (17), 3599–3605.
- Palmer, M.R., Helvacı, C., 1997. The boron isotope geochemistry of the neogene borate deposits of western Turkey. *Geochim. Cosmochim. Acta* 61 (15), 3161–3169.
- Paris, G., Bartolini, A., Donnadiou, Y., Beaumont, V., Gaillardet, J., 2010. Investigating boron isotopes in a middle Jurassic micritic sequence: primary vs. diagenetic signal. *Chem. Geol.* 275 (3–4), 117–126.
- Park, H., Schlesinger, W.H., 2002. Global biogeochemical cycle of boron. *Glob. Biogeochem. Cycles* 16 (4), 1072.
- Pennisi, M., Gofiantini, R., Grassi, S., Squarci, P., 2006. The utilization of boron and strontium isotopes for the assessment of boron contamination of the Cecina River alluvial aquifer (central-western Tuscany, Italy). *Appl. Geochem.* 21 (4), 643–655.
- Perica, S., Brown, P.H., Connell, J.H., Nyomora, A.M.S., Dordas, C., Hu, H., Stangoulis, J., 2001. Foliar boron application improves flower fertility and fruit set of olive. *Hortscience* 36 (4), 714–716.
- Petelet-Giraud, E., Klaver, G., Négrel, P., 2009. Natural versus anthropogenic sources in the surface- and groundwater dissolved load of the Dommel river (Meuse basin): constraints by boron and strontium isotopes and gadolinium anomaly. *J. Hydrol.* 369 (3–4), 336–349.
- Rocher, V., Paffoni, C., Gonçalves, A., Guérin, S., Azimi, S., Gasperi, J., Moilleron, R., Paus, A., 2012. Municipal wastewater treatment by biofiltration: comparisons of various treatment layouts. Part 1: assessment of carbon and nitrogen removal. *Water Sci. Technol.* 65 (9), 1705–1712.
- Rose, E.F., Chaussidon, M., France-Lanord, C., 2000. Fractionation of boron isotopes during erosion processes: the example of Himalayan rivers. *Geochim. Cosmochim. Acta* 64 (3), 397–408.
- Rose-Koga, E.F., Sheppard, S.M.F., Chaussidon, M., Carignan, J., 2006. Boron isotopic composition of atmospheric precipitations and liquid–vapour fractionations. *Geochim. Cosmochim. Acta* 70 (7), 1603–1615.
- Roux, E., Turpault, M.P., Kirchen, G., Redon, P.-O., Lemarchand, D., 2017. Boron dissolved and particulate atmospheric inputs into a forested ecosystem (Northeastern France). *Environ. Sci. Technol.* 51 (24), 14038–14046.



- Roy, S., Gaillardet, J., Allègre, C.J., 1999. Geochemistry of dissolved and suspended loads of the Seine River, France: anthropogenic impact, carbonate and silicate weathering. *Geochim. Cosmochim. Acta* 63 (9), 1277–1292.
- RPA. Risk and Policy Analysts, 2008. Assessment of the Risk to Consumers from Borates and the Impact of Potential Restrictions on their Marketing and Use.
- Sakata, M., 1987. Relationship between adsorption of arsenic(III) and boron by soil and soil properties. *Environ. Sci. Technol.* 21 (11), 1126–1130.
- Sakata, M., Natsumi, M., Tani, Y., 2010. Isotopic evidence of boron in precipitation originating from coal burning in Asian continent. *Geochem. J.* 44 (2), 113–123.
- Schlesinger, W.H., Vengosh, A., 2016. Global boron cycle in the Anthropocene. *Glob. Biogeochem. Cycles* 30 (2), 219–230.
- Seiler, R.L., 2005. Combined use of  $^{15}\text{N}$  and  $^{18}\text{O}$  of nitrate and  $^{11}\text{B}$  to evaluate nitrate contamination in groundwater. *Appl. Geochem.* 20 (9), 1626–1636.
- Spivack, A.J., 1986. *Boron Isotope Geochemistry*. Woods Hole Oceanographic Institution.
- Swihart, G.H., McBay, E.H., Smith, D.H., Siefke, J.W., 1996. A boron isotopic study of a mineralogically zoned lacustrine borate deposit: the Kramer deposit, California, U.S.A. *Chem. Geol.* 127 (1–3), 241–250.
- Vanderpool, R.A., Johnson, P.E., 1992. Boron isotope ratios in commercial produce and boron-10 foliar and hydroponic enriched plants. *J. Agric. Food Chem.* 40 (3), 462–466.
- Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R., 1994. Boron isotope application for tracing sources of contamination in groundwater. *Environ. Sci. Technol.* 28 (11), 1968–1974.
- Venturi, S., Vaselli, O., Tassi, F., Nisi, B., Pennisi, M., Cabassi, J., Bicocchi, G., Rossato, L., 2015. Geochemical and isotopic evidences for a severe anthropogenic boron contamination: a case study from Castelluccio (Arezzo, central Italy). *Appl. Geochem.* 63, 146–157.
- Widory, D., Kloppmann, W., Chery, L., Bonnin, J., Rochdi, H., Guinamant, J.-L., 2004a. Nitrate in groundwater: an isotopic multi-tracer approach. *J. Contam. Hydrol.* 72 (1–4), 165–188.
- Widory, D., Petelet-Giraud, E., Négrel, P., Ladouche, B., 2004b. Tracking the sources of nitrate in groundwater using coupled nitrogen and boron isotopes: a synthesis. *Environ. Sci. Technol.* 39 (2), 539–548.
- Widory, D., Petelet-Giraud, E., Brenot, A., Bronders, J., Tirez, K., Boeckx, P., 2012. Improving the management of nitrate pollution in water by the use of isotope monitoring: the  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and  $\delta^{11}\text{B}$  triptych. *Isot. Environ. Health Stud.* 49 (1), 29–47.
- Wyness, A.J., Parkman, R.H., Neal, C., 2003. A summary of boron surface water quality data throughout the European Union. *Sci. Total Environ.* 314–316 (0), 255–269.
- Zhao, Z.-Q., Liu, C.-Q., 2010. Anthropogenic inputs of boron into urban atmosphere: evidence from boron isotopes of precipitations in Guiyang City, China. *Atmos. Environ.* 44 (34), 4165–4171.