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# Urbanization impact on sulfur content of groundwater revealed by the study of urban speleothem-like deposits: Case study in Paris, France

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Speleothem-like deposits that develop underground in urban areas are an archive of the environmental impact of anthropic activities that has been little studied so far. In this paper, the sulfate content in shallow groundwater from northern Paris (France) is compared with the sulfur content in two 300-year-old urban carbonate deposits that grew in a historical underground aqueduct. The present-day waters of the aqueduct have very high sulfur and calcium contents, suggesting pollution from gypsum dissolution. However, geological gypsum levels are located below the water table. Sulfur content was measured by micro-X-ray fluorescence in these very S-rich carbonate deposits (0.5 to 1% of S). A twofold S increase during the second half of the 1800s was found in both samples. These dates correspond to two major periods of urbanization above the site. We discuss three possible S sources: anthropic sources (industries, fertilizers...), volcanic eruptions and input within the water through gypsum brought for urbanization above the studied site (backfill with quarry waste) since the middle of the 19th century. For the younger second half of the studied section, S input from gypsum brought during urbanization was confirmed by the study of isotopic sulfur composition ( $\delta^{34}\text{S} = +15.2\text{‰}$  at the top). For the oldest part, several sulfur peaks could be related to early industrial activity in Paris, that caused high local air pollution, as reported in historical archives but also to historical gypsum extraction. This study provides information on the origin and timing of the very high  $\text{SO}_4^{2-}$  levels measured nowadays within the shallow groundwater, thus demonstrating the interest in using carbonate deposits in urban areas as a proxy for the history of urbanization or human activities and their impact on water bodies.

## 1. Introduction

Water resources in densely populated areas are one of the main issues of the present century. The European Water Directive (Directive 2000/60/EC, 23 October 2000) established a framework for the protection of water bodies, including groundwater, requiring them to be restored to good ecological status. It also addressed the impact of infrastructure and anthropic activity on aquifers. To understand how increasing urbanization influences the water cycle, a diachronic comparison between the past and current state of groundwater in more or less urbanized areas is essential. The modifications induced by infrastructure can include changes in water infiltration with the construction of impervious layers or re-routing via artificial drainages, but also water quality deterioration (e.g., Foster, 2001; Wang et al., 2008; Franck-Néel et al., 2015). However, there is a lack of long-term empirical data to assess the evolution of water quality through time, and it is challenging in many zones to establish the “pre-urbanization stage” (Graniel et al., 1999). In the present paper, we focus on the shallow waterbody of the northern part of Paris, a network of drains and aqueducts known as the “Northern Springs” that drains shallow groundwater. These waters were first drained in the 1100s by religious communities, and then developed over the centuries. Although this groundwater stopped being used as drinking water during the 1800s, many of the springs are still active. Currently, these waters end up in the wastewater collection system. In two recent pioneer studies, we underlined the usefulness of the study of urban speleothems to build time records of past waters quality (Pons-Branchu et al., 2014, 2015). In these previous studies, we focused on heavy metals, rare earth elements and lead isotopic composition that provide information on pollution origin (natural vs anthropic).

A key issue that has not been addressed so far is the sulfate content of these waters, which is nowadays very high (up to 1200 mg/L, unpublished data from CEREMA), and has been reported since the first historical chemical analysis of the Belleville waters published by Boutron-Charlard and Henry (1848) in 1848. At that time, these authors already claimed that these waters were unsuitable for human consumption. However, the origin and timing of this sulfate pollution is unknown, and its historical record is lacking. Sulfur within atmosphere, soil and water is a combination of natural and anthropogenic sources. Biogenic sulfur, sea spray and large volcanic eruptions are three of the major “natural” atmospheric sources, while sulfur from host rock or minerals (mainly pyrite and evaporites such as gypsum, which is particularly abundant in Paris underground; Weaver and Bahr, 1991; Brenot et al., 2015) and deposition from atmospheric fallout represent the main natural sources in soils and waters. Anthropogenic emissions are related to industrial activities, transport, coal (a major S input) and oil burning (Smith et al., 2011), but also to the use of synthetic fertilizers rich in S for agriculture (e.g. Kopáček et al., 2014 and references therein).

Anthropogenic S is emitted as sulfur dioxide (SO<sub>2</sub>) and then oxidized to particulate sulfate (SO<sub>4</sub><sup>2-</sup>) (Rodhe, 1978; Mylona, 1996). These anthropogenic S emissions have been involved in the acidification processes that affect rain, soils and ecosystems (e.g. Odén, 1968). Historical anthropic S emissions have been reconstructed using economic data from energy and industrial statistics or official country reports (e.g. Mylona, 1996; Smith et al., 2011). The historical deposition of anthropic and natural sulfur may also be recorded in a few natural archives such as plants, ice cores or speleothems. Indeed, Frisia et al. (2005) Frisia et al. (2008) and Uchida

et al. (2013), Badertscher et al. (2014) demonstrated in pioneer studies that the sulfur content within speleothems was linked with S deposition from atmospheric fallout and recorded both anthropogenic S emissions and volcanic emissions as previous studies had shown for ice core records (e.g. Naftz et al., 1991; Laj et al., 1992). S isotopic measurement (<sup>34</sup>S/<sup>32</sup>S ratio normalized to a standard and expressed as δ<sup>34</sup>S) was used to distinguish between different S sources: natural or anthropogenic sources (McArdle and Liss, 1995) or different anthropogenic sources (power plants, coal burning, etc. see for example Forest and Newman, 1973, Querol et al., 2000). This isotopic approach has been successfully employed for the study of natural archives such as soils or plants (e.g. Zhao et al., 1998; Zhao et al., 2003; Yun et al., 2010) and also tree rings (Wynn et al., 2014). This isotopic approach has been recently applied to speleothem studies. Wynn et al. (2008, 2010, 2013) presented the first studies of sulfur isotopes within these archives, and confirmed the role of S pollution in speleothems, but also highlighted soil mediated processes.

In this paper, we present the S record based on micro-X-ray fluorescence analysis of two urban speleothems-like deposits that grew during the last 300 years in a historical aqueduct from the Northern part of Paris (France), as well as δ<sup>34</sup>S measured at three positions along the speleothem length (corresponding to three different periods). The origins of sulfur in these urban speleothems and their historical variations are discussed. This paper provides a clue to the high S content of the sub-surface water table observed in the area, and the timing of this contamination.

## 2. Site description and sampling

### *The Belleville underground aqueduct*

The studied site is located in the Mallasiss plateau, in the northeastern part of Paris. In this plateau, permeable and impermeable Oligocene sedimentary strata alternate, leading to the existence of a multilayer aquifer made of two compartments, one in the Fontainebleau Sands, and the other on the Brie Limestone (Fig. 1). These groundwaters have been drained since the 12th century and form the “Northern Spring network”. Secondary drains converge to a main gallery which forms the Belleville aqueduct. In some of the subterranean galleries, carbonate deposits are found on the walls and the floor. These carbonate deposits are formed by the water dripping from the roof of the aqueduct or from lateral flows (water drained from the watershed). Rainfall is theoretically the only source of groundwater recharge, but the possible influence of water from the wastewater collection system or the modern water supply system is suggested by a negative cerium anomaly within the younger levels of the urban speleothems (Pons-Branchu et al., 2014). Bel 2 and Bel 0 are two laminated flowstones. They are 43 mm and 29 mm thick respectively, and grew during the last 300 years. The chronology is based on annual laminae counting and <sup>230</sup>Th/<sup>234</sup>U analysis (Pons-Branchu et al., 2014). These samples were collected within the main gallery of the Belleville aqueduct, one (Bel 0) below the intersection of Pyrenees and Levert streets, and the second 300 m away, below buildings in Levert street. They developed on the wall of the main gallery, by water dripping from the ceiling and water flowing laterally within the aqueduct. Drip water from the roof of the aqueduct (coming from the street) and water from the Saint Martin spring (water of the aqueduct) were also collected and analysed.

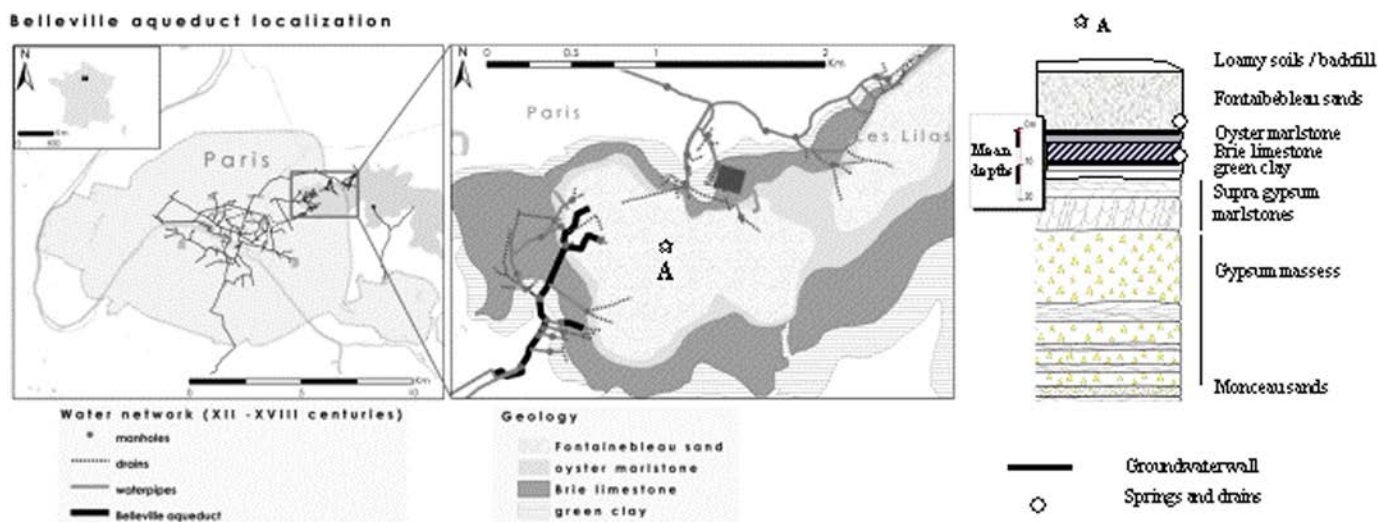


Fig. 1. Belleville aqueduct location and stratigraphic section.

### 3. Analytical methods

#### 3.1. Sulfur content analysis

##### 3.1.1. Micro-X-ray fluorescence

Micro-X-ray fluorescence ( $\mu$ -XRF) is used in this study to obtain elemental distribution, particularly the sulfur distribution.  $\mu$ -XRF analyses were performed at IFSTTAR Laboratoire Eau et Environnement (Nantes, France) on polished transverse sections of Bel 2 and Bel 0, with a Bruker M4 TORNADO laboratory instrument, equipped with an Rh X-ray tube operated at 50 kV and 300  $\mu$ A. The X-ray fluorescence was measured using a silicon drift detector. The spot size was 25  $\mu$ m and the distance between each spot is 25  $\mu$ m. Two parallel lines of analysis, covering the whole sections along the growth axis were performed for each sample. The lines were 35,000  $\mu$ m, or 1382 points. They were recorded in vacuum with an acquisition time of 50 ms/pixel. In order to test the repeatability of the analysis, a standard deviation was calculated, by comparing the S/Ca intensity ratios on two distinct transects of each sample. This value ( $\pm 2$  for S/Ca \* 1000 signals ranging from 7 to 30) represents the repeatability of the S/Ca measurement, and includes analytical reproducibility and sample heterogeneity. Accuracy of the measurements is checked in routine analysis of reference materials (BE-N, GS-N and AC-E from SARM -Service d'Analyses des Roches et des Minéraux du CRPG-centre de recherches pétrographiques et géochimiques- and NIST 2710).

##### 3.1.2. Sulfur content

For tie points, S contents were also analysed on 400 mg of powdered samples at the base and the top of the samples at the SARM laboratory (Centre de Recherches Pétrographiques et Géochimiques, CNRS Analytical Research facility, Nancy, France) by an SC-144DR Sulfur and Carbon Analyser (induction furnace combustion, LECO). Briefly, the sample is placed in a pure oxygen environment at 1350 °C, then undergoes complete combustion, releasing the sample's sulfur as sulfur dioxide. The SO<sub>2</sub> is then measured by infra-red cells. Calibrations and quality controls are made with standard materials at SARM. The values are given with error bar <5%.

#### 3.2. Isotopic sulfur signature ( $\delta^{34}\text{S}$ )

Three samples of ca 500 mg were extracted using a diamond microdrill at the base, the middle and the top of Bel 2 speleothem. The samples were analysed at the GNS National Isotope Centre (New Zealand). The carbonate samples were soaked with sodium hypochlorite for 24 h to remove any surface sulphide material. The solutions

were filtered and the filtrates dried. 50% HCl was then added under nitrogen atmosphere to remove the carbonates. The solution was filtered and warmed at 80 °C and a 5% solution of Barium chloride was added and left over night for any sulfate to precipitate. After filtration on a 45  $\mu$ M cellulose nitrate filter paper, the filtrate was rinsed with de-ionised water and then dried. The filter paper was then combusted in a platinum crucible. The remaining sulfates were then weighed out for isotopic analysis. Each sample was measured for isotopic content using tin capsules with equal amounts of V<sub>2</sub>O<sub>5</sub> on a EuroVector Elemental Analyser connected to a GVI IsoPrime mass spectrometer. All results are reported with respect to VCDT, normalized to internal GNS standards: R18742 (BaSO<sub>4</sub>), R2268 (Ag<sub>2</sub>S), and R2298 (BaSO<sub>4</sub>) with accepted  $\delta^{34}\text{S}$  values of -32.75‰, +3.25‰ and +8.6‰, respectively. The external precision for this instrument is better than 0.3‰ for  $\delta^{34}\text{S}$  value.

#### 3.3. Sr content

Sr contents were analysed in 14 spot samples (ca 5 mg) extracted from along the central growth axis of Bel2, using ICP-Q-MS (XseriesII, Thermo Fischer Scientific) at the Laboratoire des Sciences du Climat (LSCC, France). Repeat aliquots were also analysed. In order to check for analytical precision (standard deviation is <2%). The detailed protocol is described in Bourdin et al. (2011).

#### 3.4. Water analysis

SO<sub>4</sub> and Ca concentrations were measured at the CEREMA laboratory, Trappes (France). Waters were first filtered using a 0.45  $\mu$ m cellulose nitrate filters.

Ca analyses were undertaken using Flame - atomic absorption spectrometer (Varian - AA 280 FS), following the standardized method EN ISO 7980 (Water quality determination of calcium and magnesium - Atomic absorption spectrometry method). Limit of quantification is 10 mg/L (determined following the French standardized method NFT T 90-210 - Water quality; Initial assessment protocol of laboratory method

**Table 1**

S content on the top and the base of the Bel 2 and Bel 0 samples (SARM analysis).

Sample	S total %
Bel 2 34-38 mm	0.56
Bel 2 2-5 mm	0.95
Bel 0 base	0.40
Bel 0 top	0.86

**Table 2**

Water composition for water dripping from the roof of the aqueduct and for the Saint-Martin spring (aqueduct water). Samples taken in August 2010.

Location	SO <sub>4</sub> mg/l	Ca mg/l	Ca/S (mol/mol)
Drip water (roof)	775	451	1.40
Water flow (aqueduct)	1086	469	1.04

performances) and results are associated to an uncertainty of 10% (determined following the standardized method ISO 11352 - Water quality; Estimation of measurement uncertainty based on validation and quality control data).

SO<sub>4</sub> contents were determined using a spectrophotometer Uviline 9400 Secomam following the French standardized method NPT 90-040 (Water Quality - Determination of sulfate ions - nephelometric method). Briefly, after precipitation of sulfate ion by barium chloride in hydrochloric acid medium, the measurements were undertaken on a spectrophotometer (at 650 nm). Limit of quantification is 15 mg/L, and results are associated to an uncertainty of 15%.

## 4. Results

### 4.1. Sulfur content in water and carbonate deposits

S content of the carbonate powdered samples, is 0.56% at the base and 0.95% at the top of Bel 2 and 0.4% at the base and 0.86% at the top of Bel 0 (Table 1). The present-day waters (Saint Martin Spring and water from the roof of the gallery) display high SO<sub>4</sub> (775 and

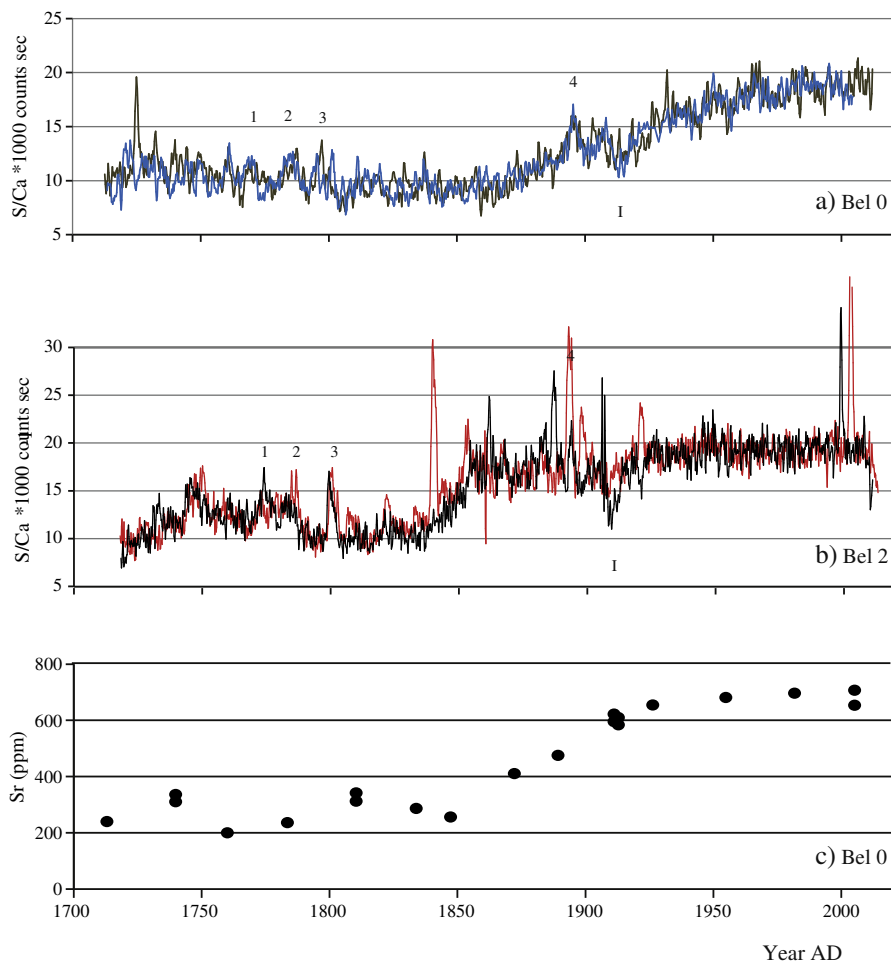
1086 mg/L, respectively) and Ca (451 and 469 mg/L respectively) contents, and a Ca/S molar ratio of 1.4 and 1 respectively (Table 2).

### 4.2. Micro-X-ray-fluorescence sulfur/calcium profiles in carbonate deposits

The intensity measured by *Micro-X-ray fluorescence* is relatively constant along the transects for several elements such as P, K and Ca, with low variations for P. Only the intensity of S varies significantly. The relative S intensity ( $S/Ca * 1000$ ) varies from  $7 \pm 2$  to  $30 \pm 2$ . The mean  $S/Ca$  intensity ratio increases by a factor of 2 between the base and the top for each sample, with most increase occurring roughly in the middle of the sequences. These S trends were replicated on the parallel lines analysed.

We used the recently published chronology of this carbonate deposit (based on both annual laminae counting and <sup>234</sup>U/<sup>230</sup>Th analysis, see Pons-Branchu et al., 2014 for details) to convert the depth along the growth axis into calendar years. The chronology was given in this previous study with an uncertainty of  $\pm 15$  years. Taking into account the mean growth rate, one single analysis point represents approximately 0.2 year (5 points per year). To smooth the high frequency variability of the  $S/Ca$  ratio, the moving average of order 3 was calculated over the two transects taken along the speleothem's growth axis (Fig. 2a and b). With the calendar scale, the twofold increase in  $S/Ca$  ratio occurred rapidly between the years 1850 and 1860 for Bel 2, and a little later (1860–1890) and more progressively for Bel 0 with an acceleration at ca 1910 CE.

Several positive and negative peaks (deviations from the mean trend) were present in the two transects of each sample. Peaks that were not replicated in each transect and in the two samples were not considered.



**Fig. 2.** Evolution of the composition along Bel 0 and Bel 2 samples. (a)  $S/Ca * 1000$  along the Bel 0 growth axis; (b)  $S/Ca * 1000$  along the Bel 2 growth axis. c) Sr content measured along the Bel 2 speleothem.

**Table 3**  
 $\delta^{34}\text{S}$  (vs CDT) measured in levels a, b and c of the Bel 2 speleothem.

Lab-code	Sample	Mm/Top	$\delta^{34}\text{S}$ extracted (‰)
S-1300294	Bel 2 S-a-5	9–12	15.2
S-1300295	Bel 2 S-b	32–34	12.1
S-1300296	Bel 2 S-c	41–44	11.9

They are labelled from 1 to 5 for positive peaks and I for the only negative peak and drawn within Fig. 4.

#### 4.3. Sulfur isotopic composition

The isotopic S composition ( $^{34}\text{S}/^{32}\text{S}$ ), expressed as  $\delta^{34}\text{S}$  are +11.9‰, +12.1‰ and +15.2‰ V-CDT at the base, the middle and the top of the Bel 2 speleothem (Table 3).

#### 4.4. Sr content

Sr content within Bel 2 sample varied from 200 ppm at the base of the speleothem (oldest level) to 706 ppm at the top (youngest level) of the speleothem. The general trend shows a strong increase (2.5 to 3 fold increase between the older and the younger part) starting at the levels corresponding to the interval 1850–1870 CE (Fig. 2c). The mean S/Ca intensity ratio doubled during this interval.

### 5. Discussion

#### 5.1. Isotopic evidence for sulfur sources

The major feature of the S trends in Bel 0 and Bel 2 is the twofold increase at the end of the 19th century with a ca 10–20 years delay between the two records. We aim to determine the origin of this increase. The sulfur sources in natural archives (tree rings, soils, speleothems, etc.) can be identified by their isotopic composition noted as  $\delta^{34}\text{S}$  (Nova'k et al., 1995; Frisia et al., 2008; Wynn et al., 2014; Bern et al., 2015; Rivas et al., 2014)). In karstic systems, S biological cycling may result in a slight isotopic fractionation between  $\delta^{34}\text{S}$  of S source and  $\delta^{34}\text{S}$  in speleothems, and in a delay between S atmospheric fallout and the S recorded by stalagmites (Borsato et al., 2015; Wynn et al., 2013). In these environments, the S time transfer increases with the vegetation cover, but in particular environment such as Acquasante spring (Italy) for instance, where there is little or no S retention through biological activity, the water pathway through the karst system is rapid (Borsato et al., 2015). In Belleville, the sulfur isotopic composition should not be modified between the source and the secondary carbonate deposits as fractionation of sulfur is very limited under oxidizing conditions and in the absence of vegetation cover.

The S content in Bel 0 speleothem is very high compared to all previously published values for speleothems, by a factor of several tens to

hundreds (Table 4). Regarding S isotopes, most previously published values are lower than the  $\delta^{34}\text{S}$  measured in the Bel 2 sample. Relatively high  $\delta^{34}\text{S}$  values (up to +19.1‰ V-CDT) reported for a speleothem from SW Ireland were attributed to partial sulfate reduction along the drip water flow paths that registered extensive fractionation processes (Wynn et al., 2008). Trace element analysis (Ce anomalies, see Pons-Branchu et al., 2014) and Eh values of drip waters (70 mV, unpublished data from CEREMA) do not support evidence of reducing conditions within the overlying regolith. This suggests that sulfur isotope values enriched in  $^{34}\text{S}$  cannot be accounted for by reducing conditions (Cf. Wynn et al., 2008).

$\delta^{34}\text{S}$  signatures of sulfur in the local environment present a large range of values (Table 5). Natural sources range from low  $\delta^{34}\text{S}$  in pyrite-derived S (e.g.  $\delta^{34}\text{S} = +4\%$  for the Oligocene Fontainebleau sand in which part of the groundwater flows, Le Pape et al., 2013), whereas S from oceanic origin has a higher signature ( $\delta^{34}\text{S} = +20.99\% \pm 0.24$  for sea salt, see Rees et al., 1978 and  $\delta^{34}\text{S} = +15\%$  to ca +22‰ in the Eocene gypsum, Le Pape et al., 2013, Fontes and Letolle, 1976). Anthropogenic atmospheric signatures are marked by low  $\delta^{34}\text{S}$  values, derived from different sources, including pyrite within coal (see Table 5). They are consistent with the values published for sulfur in local rainwater during the 1970s,  $-3$  to  $+7\%$  (Mégien, 1976), or those for Northern Italy for the period 2005–2007,  $-1.4$  to  $+7.3\%$  (Wynn et al., 2013).

In the Belleville sample, the high  $\delta^{34}\text{S}$  observed (+11.9‰ at the base, +12.1‰ in the middle and +15.2‰ at the top, see Fig. 3) indicate a sulfur isotope source enriched in  $^{34}\text{S}$  is dominating the sulfur isotopic composition of the speleothem. However, the very high sulfur content in the speleothem-like deposits, the aqueduct water and the dripping water from the roof, and the Ca/S molar ratio close to 1 in present-day waters point to gypsum dissolution as a main source of sulfates and calcium (gypsum:  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

In order to determine the source of the additional sulfate producing the S content step around 1860, we considered that the S after 1860 (9500 ppm  $\delta^{34}\text{S} = +15.2\%$ ) resulted from mixing of S incorporated before 1860 ( $S_{\text{before 1860}} = 5600$  ppm and  $\delta^{34}\text{S}_{\text{before 1860}} = +12.1\%$ ) and S derived from the Eocene gypsum ( $\delta^{34}\text{S} = +20.0\%$ ). The expected  $\delta^{34}\text{S}$  of the mixture is given by:

$$\delta^{34}\text{S}_{\text{mix}} = \frac{S_{\text{before 1860}} \times \delta^{34}\text{S}_{\text{before 1860}} + S_{\text{gypsum}} \times \delta^{34}\text{S}_{\text{gypsum}}}{S_{\text{before 1860}} + S_{\text{gypsum}}} = 15.3\%$$

This value is in good agreement with the  $\delta^{34}\text{S}$  measured in the sample after 1860, supporting the contribution of the Eocene gypsum as the source of additional S in the sample. The involvement is further confirmed by the strong increase in the Sr concentration in the sample at the same period (see Fig. 2), because Sr is very common within gypsiferous rocks.

The origin of the S before 1860 is more difficult to be precisely determined. S isotopes in the first part of the sample ( $\delta^{34}\text{S} = +12.1\%$ ) are consistent with approximately equivalent contributions of S from the

**Table 4**  
Sulfur content and  $\delta^{34}\text{S}$  reported for previous studies in speleothems and drip water for the last 300 years compared with Bel 2 data (this study).

Author	Location	Sample name	Age (year CE)	SO <sub>4</sub> water mg/kg	Ca/SO <sub>4</sub> water (mol/mol)	S ppm	$\delta^{34}\text{S}$ ‰ CDT	Main S sources
Wynn et al., 2008	SW Ireland	CC-Bill crag cave	1765–2002	7.9–8.2	13.8–23.1	107–184	16.8–19.1	Sulfate reduction
Wynn et al., 2008	UK	BFM-Boss Brown Folly Mine	1915–1995	11	9	130–264	3.5–5.5	Anthropogenic S
Borsato et al., 2015	NE Italy	ER78-Ernesto Cave	1890–2014			45–200	ND	Anthropogenic S + volcano
Uchida et al., 2013	Japan	Ryuo-do Cave	1600–2000	0.7–16.1		170	1.1–1.7	Sea salt, pyrite oxidation linked with anthropogenic S emissions
Uchida et al., 2013	Japan	Shimizu-do Cave stmA, B	1700–2000	0.4–10		28	5	Sea salt- anthropogenic S
Wynn et al., 2010	Austria	Obi84-Orbi Cave	1967–2002			53 (mean)	8.4 (mean)	Anthropogenic S + Bedrock
Wynn et al., 2010	Austria	Obi84-Orbi Cave	1900–1967			14	nd	Bedrock
Frisia et al., 2008	NE Italy	ER78-Ernesto Cave						Anthropogenic S + volcano
Frisia et al., 2005	NE Italy	ER78-Ernesto Cave	1850–2000					Anthropogenic S + volcano
Wynn et al., 2013	NE Italy	ER78/st1-Ernesto Cave	Actual water	0.8–1.5				
This work	N France	Bel 2	1700–2012	775–1086	1–1.4	5600–9500	12.4–15.8	

**Table 5**  
 $\delta^{34}\text{S}$  signature of possible sulfur sources.

Sources	Range value ( $\delta^{34}\text{S}$ )	Reference
<i>Natural sources</i>		
Sea salt aerosols	$+20.99 \pm 0.24\%$	Rees et al., 1978
Dimethylsulphides from Sea	$+15.6 \pm 3.1\%$	Calhoun et al., 1991
Eocene Gypsum from the Paris basin	$+22 \pm 2\%$ (*)- $+17 \pm 3.2\%$ (**)	Le Pape et al., 2013 (*); Fontes and Letolle, 1976 (**)
Fontainebleau sands	$4.2 \pm 2\%$	Le Pape et al., 2013
<i>Anthropic signatures</i>		
Regional background rainwater in northern Spain:	$+7.2\%$	Puig et al., 2008
Coal-fired plant in northern Spain:	$-2.8 \pm 0.25\%$	Puig et al., 2008
Coal in United Kingdom	$-6$ to $-10\%$	Zhao et al., 2003
Atmospheric signature - central Europe:	$+4$ to $+5\%$	Querol et al., 1998
Atmospheric signature, Bologna, N Italy (industrialized area)	$+0.4$ to $+6.2\%$	Panettiere et al., 2000

Fontainebleau sands and from gypsum (respectively  $+4.2 \pm 2\%$  and between  $+22 \pm 2$  and  $17 \pm 3.2\%$ , values from Le Pape et al., 2013 and from Fontes and Letolle, 1976).

Anthropogenic sources (e.g. fertilizers, waste waters and atmospheric pollution from industrial activity) have  $\delta^{34}\text{S}$  in the same range than Fontainebleau sands (e.g. Vitòria et al., 2004; Gázquez et al., 2015 and references there in) and could also contribute for this high sulfur content within the oldest part of the speleothem-like deposits.

However, the contribution of Fontainebleau sands could be minor regarding the very high S content within Bel 0 and Bel 2 sample, that implies a contribution of S-rich sources such as gypsum.

### 5.2. Exploring the possible role of S atmospheric emissions, and climate variability

Potential sources of  $\text{SO}_x$  pollution to the Parisian atmosphere includes i) 20th century industrial emissions (e.g. Mylona, 1996; Smith

et al., 2011) recorded in natural archives such as ice cores, (Laj et al., 1992), speleothems (e.g. Frisia et al., 2005) or soils and plants (Zhao et al., 1998; Yun et al., 2010); ii) 19th–18th century manufacturing of gunpowder, sulfuric acid, and plaster (Guillerme, 2007, 2012), with a maximum around the years 1810, that already caused concern during the 18th century on air and water quality in Paris (Beretta, 2000, and Parmentier in Le Roux, 2011); iii) the burning of hard coal since 1810 to replace wood and charcoal due to the scarcity of wood at the end of this period and the increasing demand for domestic and industrial uses; iv) large volcanic eruptions that inject sulfur gases into the stratosphere such as the Laki eruption (Iceland) in 1783 that affected northern Europe (Palais and Sigurdsson, 1989; Thordarson and Self, 2003) and caused persistent fog in Europe with human sickness and death in Europe (Stothers, 1999; Garnier, 2011; Grattan et al., 2005).

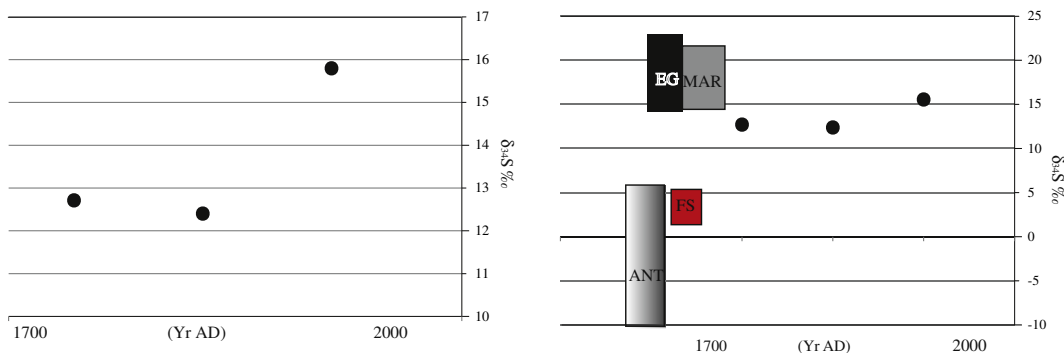
The lack of clear correlation between the sulfur trend within carbonates deposits of Belleville and between the emission history of anthropogenic S in the atmosphere, or between volcanic events as recorded in ice cores (see Fig. 4), suggests that these S emissions are not the main S sources here.

Climate variability (temperature and precipitation amount) could affect sulfur content within the water (dissolution rates for S from soil and host rocks or dilution with increasing water flux) but also partition between calcite and water as observed for other elements such as Mg or Sr (e.g. Oomori et al., 1987). However, no correlation is observed between the sulfur record and the historical temperature and precipitation trends (see Fig. 4), meaning that climatic parameters have no influence in this case or that they are totally masked by an important sulfur contributions.

### 5.3. Impact of urbanization on sulfate content in water and urban speleothems

#### 5.3.1. Historical evolution

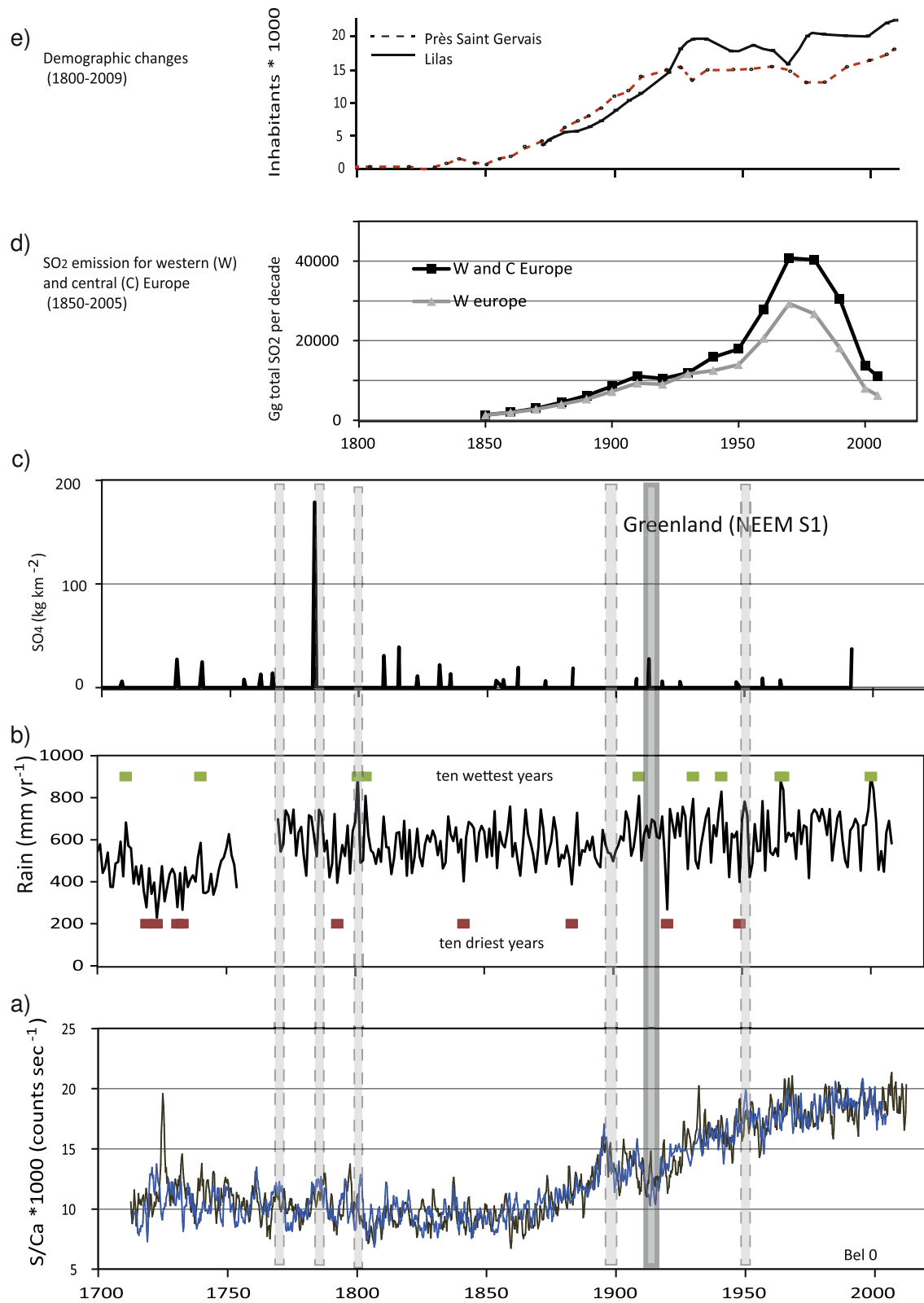
In the NE Paris region, gypsum extraction for plaster production had flourished in the north-eastern part of Paris and surrounding areas (Belleville, Mesnil Montant, Charonne) since at least the 17th century, as quarries are represented by Jouvin de Rochefort (1870) on his map of Paris in 1672. With the development of Paris city and neighbouring townships, these quarries were disused and filled. This extraction



### Potential Sources

- ES Fontainebleau Sand (from Le pape et al., 2013)
- ANT Anthropic sources : coal, plant S in rain or atmospheric particles (from Querol et al., 1998, Puig et al., 2008, Zhao et al., 2003, Panettiere et al., 2000)
- EG Eocene gypsum in Paris (from Le pape et al., 2013; Fontes and Letolle, 1976)
- MAR Marine sources (from Rees, 1978; Calhoun et al., 1998)
- Bel 2 (Belleville Aqueduct)

**Fig. 3.**  $\delta^{34}\text{S}$  in Bel 2 speleothem compared with potential natural and anthropogenic S sources.



**Fig. 4.** Comparison between S/Ca \* 1000 evolution through time for Bel 0 speleothem (a) with other environmental parameters, precipitations recorded in Paris, after Slonosky, 2002) (b), Volcanic SO<sub>4</sub> emissions as reconstructed by Greenland ice cores (Sigl et al., 2013) (c), SO<sub>2</sub> emissions (in Gg per decade), after Smith et al., 2011 (d), demographic evolution, data from Motte et al., 2003 (e). Light and dotted shades are the positives peaks observed within the two samples (only Bel 0 is presented here) and the dark one is the negative peak also repeated within the two samples.



could have produced quarry residues in the Belleville waters watershed, and early sulfur input (albeit to a lesser extent than the post-urbanization stage) from gypsum within the water of the aqueduct.

Urbanization of this area during the 19th century involved the construction of several blocks of houses such as those in Levert street in the year 1837 or the development of Pyrénées street during the 1860–70s, and the sale of plots of land for building during the 1870–90s (Huard, 2013: *Atlas Historique de Paris* and references therein; Sellali, 1996, Sander, 2008). Demographic change in two nearby municipalities is illustrated in Fig. 4 and is compared to the sulfur evolution trend. This urbanization included refilling of former gypsum quarries and backfilling of the zones to be constructed using quarry waste. In Bel 2, the two-fold S increase corresponds to the construction of the subdivision above the zone (Levert street) and could be directly related to the gypsum input by backfilling of the zone. The delayed S increase in Bel 0 could likewise be attributed to the development of Pyrenees street. This apparent delay could also be due to a shift on the chronology (error bar is about 15 years for each record). After this high S increase, S variations in the Belleville deposits appear to be very low. For the period before urbanization, scattered gypsum deposits in the watershed from quarry waste could explain the high mean S content (ca 0.5%), well above (ca 50 to 1000 times) previous sulfur content reports in speleothems, and the high isotopic S signatures ( $\delta^{34}\text{S} \sim +12\text{‰}$ ).

Urbanization could also impact the water sulfur content by leak of sewage as suggested by a previous study (Pons-Branchu et al., 2014 for Belleville, or Gázquez et al., 2015 for northern Spain region). The sulfur content trend for the youngest levels (after 1850–1880) is however very homogeneous and isotopic data implies that the main additional S source is derived from gypsum. The same argument can be evoked for rejecting recent sulfur input from fertilizers (however unlikely in this highly urbanized area).

### 5.3.2. Implication for the knowledge of water quality

As mentioned in a large number of studies, major or trace element variations within speleothems do not strictly reflect their variation within the water from which they precipitate. Indeed, partition coefficients between water and calcite may vary with environmental parameters such as temperature or pH. However, as mentioned above, in this study, no clear correlation is observed between climatic parameters and sulfur trend, these effects being potentially totally masked by the important contribution of sulfates from gypsum dissolution. We noted a clear correlation between the very high sulfate levels within the present-day waters and the unusually high S content within the urban speleothems. The two-fold increase during the second half of the 19th century, has been linked here with gypsum input during a major period of urbanization of the Northern Spring watershed. However, before urbanization, the sulfur content was very high, and could reflect even at that time high sulfate content in the water, linked with gypsum quarries present in the area, and their waste brought to the surface. These waters were described as “the most loathsome” by Figuier (1873), in the year 1873. Henry and Boutron-Charlard (1848) published a study of the quality of northern spring waters in 1848, and reported high “salt and sulfate” contents in water from the northern springs, that ceased to be used as drinking water at that period. In fact, Belgrand (1877) reported that these waters were no longer used for human consumption because of their high sulfate and magnesium content, but had been restricted to washing for several tens of years.

New investigations in order to collect older carbonate deposits in this aqueduct or in other Parisian underground aqueducts are now necessary to determine a “pre-anthropogenic” stage of these waters and complete the diachronic study of past waters.

## 6. Conclusion

Sulfur content measured within two 300-year-old urban speleothem-like deposits has provided insight for the temporal

evolution of sulfur. The major features are a generally high S content with a doubling of sulfur content, contemporaneous with the urbanization above the aqueduct. Isotopic analyses enabled the high  $\delta^{34}\text{S}$  measured within the younger part of one of the samples to be linked with gypsum input since the second half of the 19th century. However, since geological gypsum levels are located below the water table on which the speleothem-like deposits grew, an anthropic supply of this mineral has to be considered. The development of the zone included the refilling of former gypsum quarries exploited in the neighbourhood and the backfill of the zones to be constructed using material such as waste from the gypsum quarries.

This paper has thus provided important information about the timing of sulfur contamination of the waters that permitted the urban speleothems deposition, and explains the very high sulfate levels measured in present-day shallow groundwater of the northern spring of Paris. It demonstrates the potential of the study of urban speleothems to build a diachronic comparison at different periods and stages of urbanization. Thus, these archives help to better understand the impact of urbanization on water bodies, and could thereby help to protect or restore them.

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