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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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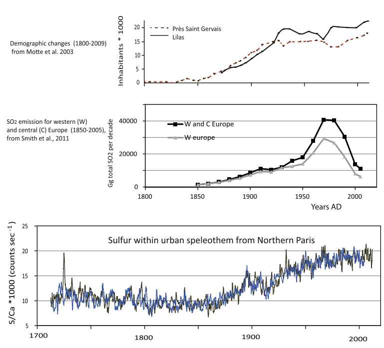
HIGHLIGHTS

- Sulfur content and $\delta^{34}S$ within an urban speleothem is studied
- $\delta^{34}S$ support natural S origin from gypsum dissolution
- Sulfur trend in speleothem suggest gypsum input within groundwater since urbanization

GRAPHICAL ABSTRACT



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ABSTRACT

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 discus 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

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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 ($\delta^{34}S = +15.2‰$ 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 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_2) and then oxidized to particulate sulfate (SO_4^{2-}) (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 ($^{34}S/^{32}S$ ratio normalized to a standard and expressed as $\delta^{34}S$) 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 $\delta^{34}S$ 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 Mallassis 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 $^{230}Th/^{234}U$ 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.

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