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Three centuries of heavy metal pollution in Paris (France) recorded by urban speleothems

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HIGHLIGHTS

- Urban speleothems from underground aqueduct in Paris, France were studied.
- Speleothems are used to reconstruct the history of sub-surface water pollution.
- Two distinct periods of heavy metal pollution occurred during the last 300 years.
- Lead isotope ratio is used to constrain lead contamination sources.
- 18th century metal contamination originates from the use of urban wastes as fertilizer.

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ABSTRACT

The first record of urban speleothems used to reconstruct the history of heavy metal pollution of shallow groundwaters is presented. Two speleothems grew during the last 300 years in an underground aqueduct in the north-eastern part of Paris. They display high Pb, Mn V, Cu, Cd and Al concentrations since 1900 due to the urbanization of the site which triggered anthropogenic contamination of the water feeding the speleothems. Surprisingly, these heavy metal concentrations are also high in the oldest part. This early pollution could come from the use of Parisian waste as fertilizers in the orchards and vineyards cultivated above the aqueduct before urbanization. Lead isotopes were measured in these carbonates as well as in lead artifacts from the 17th–18th centuries (^{206}Pb/^{207}Pb = 1.180 +/− 0.003). The mean ^{206}Pb/^{207}Pb ratio, for one of the speleothems is 1.181 +/− 0.003 unvarying with time. These lead signatures are close to those of coal and old lead from northern European mines, lower than the natural background signature. It confirms that the high metal concentrations found come from anthropogenic pollution. Conversely, the lead isotopic composition of the second speleothem presents two temporal trends: for the oldest levels, the mean value (1.183 +/− 0.003) is similar to the first speleothem. For the youngest part, a lower value (1.172 +/− 0.005) is recorded, evidencing the contribution of a new lead source at the beginning of the industrial revolution. Pb isotopes were also measured in recent samples from a nearby superficial site. The first sample is a recent (AD 1975 +/− 15 years) deposit (^{206}Pb/^{207}Pb = 1.148 +/− 0.003), and the second, a thin subactual layer (^{206}Pb/^{207}Pb = 1.181 +/− 0.002). These data are compatible with the adding of anthropogenic sources (leaded gasoline and industrial lead from Rio Tinto ore).

1. Introduction

Current issues on water in densely populated regions focus on the use of unconventional water such as shallow groundwater, rain water management or valuation of urban wetlands.

One of the major questions in urban areas is the impact of past, present and future urban development on the water cycle. Knowledge of the hydrological system involves not only determining the zones where rainwater infiltrates and, those where it flows, in order to estimate flows and groundwater recharge trends, but also studying the relationship between the near-surface groundwater and water present in the shallow urban system (water main system, rain water, wastewater). Outsourcing of the urban water cycle in Paris (production, supply and wastewater treatment) introduced in the 19th century led to the

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abandonment of urban groundwater as a utility water for the city and its inhabitants. However, an improved knowledge of the local water quality and availability would improve urban water management and anticipate large-scale development of the region. The general question raised by the study of the groundwater in highly urbanized areas is the human impact on both quantitative and qualitative groundwater dynamics. Obtaining time-series data covering the history of groundwater during urbanization is a scientific challenge which must be addressed to develop and validate hydrological models in urban areas. The pollution of urban groundwater is strongly linked to land use and its temporal evolution (e.g., Foster, 2001). In addition, in these strongly developed zones, the sources of pollution are numerous and change frequently (Tellam, 1994). Furthermore, it is rarely possible to successfully characterize the pre-urbanization stage (Graniel et al., 1997), which is the fundamental point for studying the quality of these waters over time. This is crucial for the study of groundwater, particularly in the view of the European Water Directive (Directive 2000/60/EC, 23 October 2000), that establishes a legal framework to protect European water bodies and restore them to good ecological status to ensure long-term, sustainable water use.

In the northern part of Paris, waters from shallow aquifers have been drained since the 12th–13th centuries to supply public fountains through the construction of a network of drains and aqueducts, known as the "Northern Springs". The quantitative hydrological monitoring of these springs has been conducted since the 19th century, but geochemical study is more recent (beginning of the 20th century). A recent pioneering study (Pons-Branchu et al., 2014) demonstrated that calcareous crusts, similar to speleothems in natural caves, can develop over several centuries in these aqueducts and can be precisely dated, providing a unique natural archive of the infiltrated contamination history.

This study presents the quantitative evolution over the last 300 years of inorganic metallic contaminants recorded in these secondary calcareous deposits, with a focus on lead, vanadium and manganese. Lead pollution from anthropogenic sources is ancient, with varying historical origins but clearly identified isotopic signatures (e.g., in Seine River sediment for the past century; Ayrault et al., 2012). Here, the lead isotopic composition of the speleothems through the last 300 years is used to discuss the origin of the metallic contaminants and the impact of urban development on shallow groundwater contamination.

The first goal of this paper is to test if urban speleothems can record the trace element and lead isotope contamination of past infiltrating waters. We will not attempt to reconstruct precisely the composition of water, but will rather look at the largest and most significant historical change in contaminant levels. The second goal is to determine the origin of the contamination both in terms of sources and possibly in terms of change of groundwater pathways. Hence, it should provide constrains on the impact of the urbanization through time on the water contamination level in Paris.

2. Materials and methods

2.1. Site and samples

The Great Aqueduct of Belleville is a 1050 m long underground gallery in the Malassis plateau, in the northeastern part of Paris (Fig. 1a). It belongs to a network of drains and aqueducts known as the "Northern Springs", that drains waters from two independent groundwater levels, one within fine well sorted sands (Fontainebleau sands) and the other within limestone (Brie limestone, Fig. 1b). This network was used between the 13th and the 19th century to supply water to public fountains. Since then, it has no longer been used to supply drinking water, but water still flows from several drains. A few speleothem-like deposits develop in some parts of this underground network. Due to different possible water pathways and contamination sources, $CaCO_3$ deposits from 2 strategic portions of the Northern Springs network were sampled, 500 m apart:

- one is a large underground gallery of the middle part of the Great Aqueduct, where speleothems developing over 3 centuries provide a suitable record to test the possibility of historical reconstruction. Comparison of 2 nearby speleothems also allows the local variability of the signal.
- the other studied water system is the Saint Martin spring, upstream a historical manhole, on a hillside, where we expected to sample directly the "pristine" groundwater from the Brie limestone that drains water from the "urbanized" occidental part of the Malassis plateau (Paris).

The underground gallery of the Belleville aqueduct (Bel), oriented N/S, is approximately 5–10 m below street level. It receives both groundwater and water infiltrating directly from the surface through the roof of the gallery. Secondary $CaCO_3$ deposits grow on the wall and on the floor of this gallery. Bel 0 and Bel 2 are two speleothems that developed on the wall of the gallery. They were sampled below Levert street near the intersection of Pyrénées and Levert streets, approximately 100 m apart from each other. They are 29 mm and 45 mm thick respectively and finely laminated. A robust chronology of these deposits, based on cross dating by absolute and relative methods (U/Th and lamina counting) have been constructed (Pons-Branchu et al., 2014). They represent a 300-year-long record (between 1712 and 2012 AD) of carbonate deposit. For Bel 0, 9 samples were drilled within the growth axis for trace element (TE) analysis, and 6 for lead isotopic analysis. For Bel 2, 15 levels were selected for trace element analysis and 9 levels for lead isotopes.

The Saint Martin (SM) historical manhole is located in rue des Cascades, approximately 500 m away from, and slightly topographically above the first sampling site. Two secondary $CaCO_3$ deposits growing on the floor upstream of the manhole were sampled. They are located at street level and are produced by the flowing of a historical captured spring. SM 0 is a thin (~0.2 mm) $CaCO_3$ layer that forms at the surface of a little basin that collects water from the spring (it is probably not more than 5–6 years old, with an age of AD 2009 +/− 3). SM 1 is a core sampled in a flowstone, sampled upstream, 3 m away from SM 0. Water was flowing on the speleothem at the time of sampling suggesting that it is still active and indicating that the top of the flowstone is contemporaneous. The top of the core is composed of a laminated zone (0–5 mm), and a porous zone for the deepest level. In a recent study (Pons-Branchu et al., 2014), we showed that lamination is annual for urban speleothems with two laminae deposited each year. The laminated upper part of the flowstone covers 27 years (54 laminae). No laminae are visible in the porous part of the flowstone. Nevertheless, it is likely that the growth rate of the porous part is much larger than the growth rate of the laminated zone. Therefore, the age in this part of the flowstone is bracketed with 2 extreme assumptions: i) the growth rate in the porous part is identical to the growth rate in the laminated part. In this case, the level analyzed for lead isotopes, at a depth of 10 mm, is 54 +/− 2 year old (1958 AD); and ii) the growth rate in the porous part is infinitely high. In this case, the age of the same point is 27 +/− 2 years (1985). These assumptions give a mean age of 41 +/− 15 years (AD 1972 +/− 15) at 10 mm depth in the porous zone. Using the same calculation, a mean age of 32 +/−5 years (AD 1980 +/− 5) is proposed at 6.75 mm depth.

Historical lead artifacts were analyzed in order to constrain the sources of Pb used during the last few centuries:

- 2 lead artifacts from the Versailles Palace fountains water supply system: one lead gasket from the oldest system (17th century) and a piece of lead from a pipe (installed during the year 1865)
- a piece of lead pipe from a Parisian house from the 1950s.

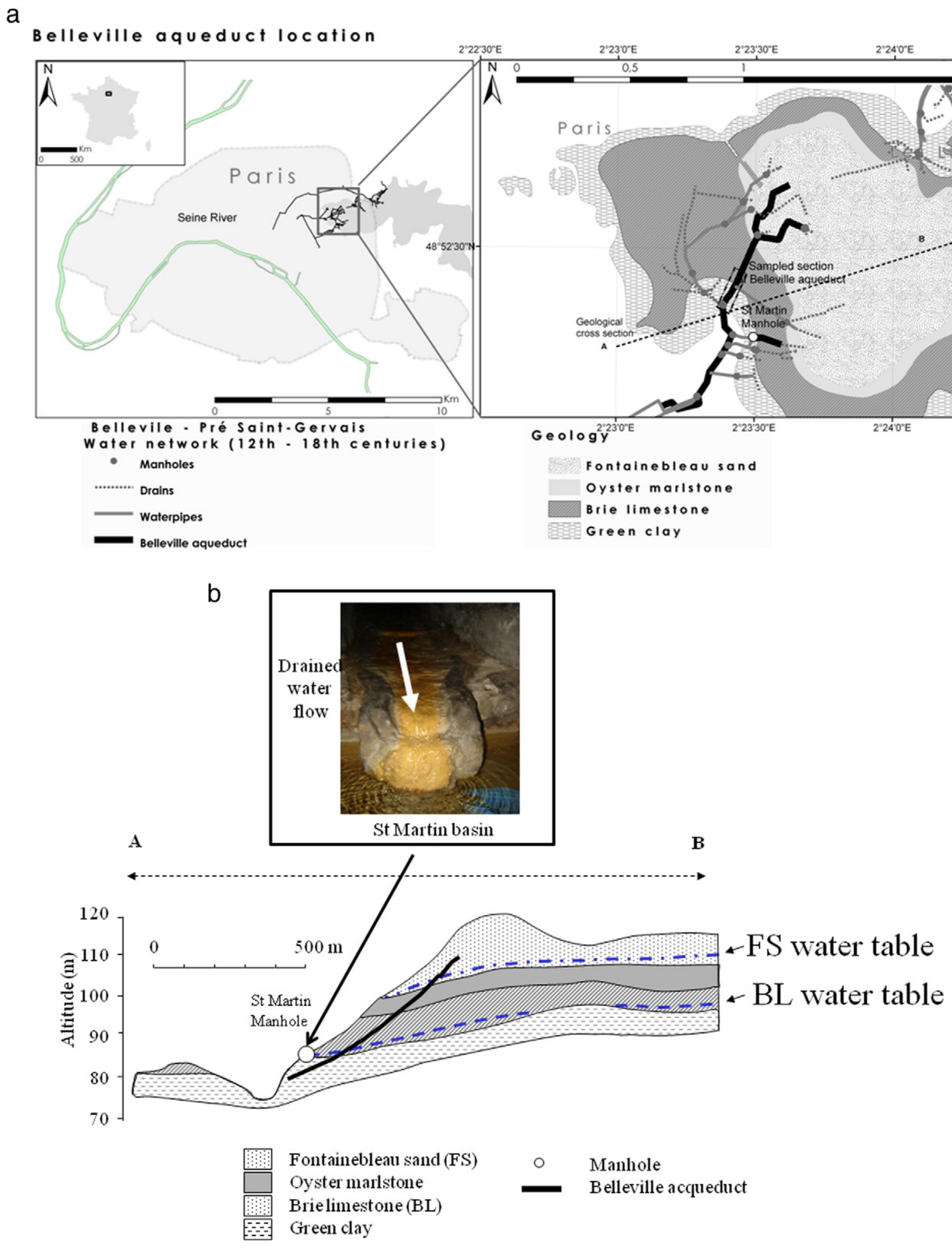

Fig. 1. Site presentation. a) location and geological map; b) schematic geological cross section. Relative locations of St Martin manhole and Belleville aqueduct are reported. NB: Bel samples are in the middle part of the Great Aqueduct, perpendicular to the drain represented in panel b.

2.2. Analytical

Between 10 and 20 mg of calcite were sampled using a stainless steel diamond microdrill along the growth axis of Bel 0, Bel 2 and SM 1. The powders were then dissolved in 0.5 N HNO_3 and the solutions adjusted to 100 mg/L of Ca (Bourdin et al., 2011).

2.2.1. Determination of trace and major element concentration

Analyses were performed with a Quadrupole ICP–MS Thermo Fischer Scientific XseriesII, at the LSCE, based on the standard addition method for Ca-100 mg/L solution (Bourdin et al., 2011) to deal with the calcite matrix effects. The accuracy and reproducibility of the elemental analyses were verified through the repeated ($n = 8$) analysis of the water reference NIST-1640a (National Institute of Standards and Technology, USA) enriched with 100 mg/L of Ca and by the analysis of a carbonate rock reference material (GSR6 from the Institute of Geophysical and Geochemical Exploration, China). The determination of Lead (Pb), Manganese (Mn), Copper (Cu), Vanadium (V), Aluminum (Al), and Thorium (Th) falls within 4% of the certified values for both reference materials. As the reproducibility of V and Cu measurements were poor for a low solution concentration (lower than 200 μg/L for V and 1000 μg/L for Cu), an external error bar of 10% for low concentrations and 5% for higher concentrations for these elements was used. Some of the samples were measured twice in order to check for drift corrections.

2.2.2. Lead isotopes

For Pb-rich levels (above 3 mg/kg), a fraction of the solution used for TE determination was evaporated and used for chemical separation. For the other samples, between 6 and 90 mg (depending on the Pb content) of powdered calcite was dissolved in diluted HCl, and the solution evaporated and dissolved in 0.3 mL 1 N HBr. They were charged into a 0.25 mL column of AG1X8 anionic resin. The Ca matrix and most of the TE were eluted by 2 mL of 1 N HBr. The lead fraction was eluted using 0.5 N HNO_3. First, a diluted aliquot of this lead purified fraction was analyzed to measure the lead concentration. Then, the purified solutions were adjusted to 12 mL (first round of analysis) or 4 mL (second round of analysis) of a 5 μg/L Pb solution (in order to reach 250,000 to 500,000 counts per second on the ^{208}Pb mass). For the Pb-rich (133.6 mg/kg) upper level of Bel 2 and for the "historical" Pb gaskets, Pb isotope analysis was performed without chemical separation or pre-concentration but with the appropriate dilutions to adjust the Ca and Pb concentrations.

The isotopic analyses were also performed on an ICP-Q MS XseriesII at LSCE using the procedure described in Ayrault et al. (2012). Briefly, the standard-sample bracketing method was used for mass bias correction, by measuring the NIST SRM-981 reference solution diluted to 5 μg/L Pb in each of the 3 samples. For the first round of analysis, a 1 mL/s nebulizer was used for sample introduction and for the second round of analysis, a 50 μL/mn nebulizer.

The blank of total procedure (including chemical separation and dilutions) was between 300 and 2600 counts per second for the ^{208}Pb peak (less than 1% of the signal), and a ^{206}Pb/^{207}Pb ratio of 1.131 +/ 0.028 (2σ). The reproducibility of the analysis was tested by the repeated (6) analysis of the Bel 2 upper level (Bel 2—1 mm) with both rounds of analysis and using 3 different aliquots (two after chemical separation and one without chemical treatment (Table 1)). The 2 sigma standard deviation for the ^{206}Pb/^{207}Pb ratio was 0.3%. This external reproducibility was therefore used as the minimum error bar on the measured values. Several replicate lead isotope analyses of sample SM 0 were also performed during different ICP–QMS sessions in order to check the reproducibility of measurements over time (see Table 1).

Table 1
Replicate analysis of Pb isotopes on Bel 2-1 and SM 0 samples.
Bel 2-1 W: analyzed without chemical separation of lead from $CaCO_3$ matrix.

Sample code	^{206}Pb/^{207}Pb ±
Bel 2-1	
3207	1.1715 ± 0.003
Bel2-1 W	1.1720 ± 0.005
3209	1.1715 ± 0.004
3209 bis	1.1676 ± 0.003
3209 [a]	1.1721 ± 0.002
4854 [a]	1.1725 ± 0.004
Mean ± 2σ	*1.1712 ± 0.004*
SM-0	
1	1.1821 ± 0.002
2[a]	1.1804 ± 0.001
3[a]	1.1810 ± 0.002
Mean ± 2σ	*1.1812 ± 0.0014*

[a] Samples run with a 50 μL/mn nebulizer. The others were run using 2 mL/mn nebulizer.

Three aliquots of the SRM-981 reference solution were passed through an ion exchange column during the sample purification sessions and analyzed as samples in order to check the validity of the total procedure including blank correction and mass bias corrections.

The values obtained for the ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios were respectively 1.0955 +/− 0.0019 and 2.163 +/− 0.006. They agree within uncertainties with the SRM-981 certified values (1.09333 ± 0.00039 and 2.1681 ± 0.0008, respectively).

3. Results

3.1. Pb stable isotope ratio

The ^{206}Pb/^{207}Pb ratio measured along the Bel 0 core is almost constant between 1.183 ± 0.002 and 1.179 ± 0.002 with a mean value of 1.182 +/− 0.003 (Table 2 and Fig. 2). This value is very similar to the ^{206}Pb/^{207}Pb ratio (1.180 ± 0.003) in the 2 samples of historical lead from the Versailles Palace fountains (from the 18th century and from the year 1865). Between the years 1710 and 1785, the ^{206}Pb/^{207}Pb ratio (1.183 +/− 0.003) of Bel 2 is similar to the value measured in Bel 0. After 1830, the isotopic ratio in Bel 2 decreases, with a mean value for the younger levels since ca 1800–1850 of 1.172 +/− 0.005.

For the Saint-Martin manhole, the ^{206}Pb/^{207}Pb ratio of the oldest (1972 +/− 15) sample is 1.148 +/− 0.003 and 1.181 +/− 0.002 for the youngest (2009 +/− 3) sample.

3.2. Trace metals

3.2.1. Belleville samples (~1700–present)

The trace metal content displays high content variation (Table 3). When plotted against the age, the Cu, Cd, Mn, Th, V, Al, and Pb concentrations in carbonate samples present different trends (Fig. 3).

Cu contents range between 1.09 and 5.23 mg/kg, with the highest content for the youngest levels (since the year 1980).

Cd (between 11.8 and 360 μg/kg, Mn (from 0.61 mg/kg in the poorest level to 10.0 mg/kg in the richest) and Pb (between 295 μg/kg and 133.7 mg/kg) have their highest concentrations between the years 1700 and 1760 and between 1950 and 2012.

Table 2
^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb signature of speleothems and historical lead gasket and pipes.

Sample name	Depth mm	Age AD	^{206}Pb/^{207}Pb ±
Bel 2-1	1	2004	1.1712 ± 0.0036
Bel2-3	8.5	1954	1.1689 ± 0.0023
Bel 2-5	14.8	1911	1.1752 ± 0.0042
Bel 2-5	14.8	1911	1.1752 ± 0.0042
Bel 2-7	20.5	1872	1.1722 ± 0.0032
Bel 2-9	26.5	1832	1.1721 ± 0.0021
Bel 2-11	33.5	1784	1.1807 ± 0.0026
Bel 2-13	40.5	1737	1.1830 ± 0.0021
Bel 2-14	44.5	1710	1.1826 ± 0.0031
Bel 2-14	44.5	1710	1.1840 ± 0.0032
B0-1	2	1991	1.1809 ± 0.0029
B0-1	2	1991	1.1812 ± 0.0023
B0-4	13	1878	1.1833 ± 0.0023
B0-5	16	1847	1.1796 ± 0.0021
B0-6	19	1816	1.1801 ± 0.0024
B0-7	21.5	1790	1.1828 ± 0.0020
B0-8	24	1765	1.1790 ± 0.0021
SM1-9-10	9.5	1972	1.1477 ± 0.0028
SM 0	0.2	2009	1.1812 ± 0.0024
Lead gasket (Versailles)		XVIIth	1.1799 ± 0.0027
Lead pipe (Versailles)		1865	1.1803 ± 0.0020
Lead pipe (Paris)		1958	1.1721 ± 0.0017

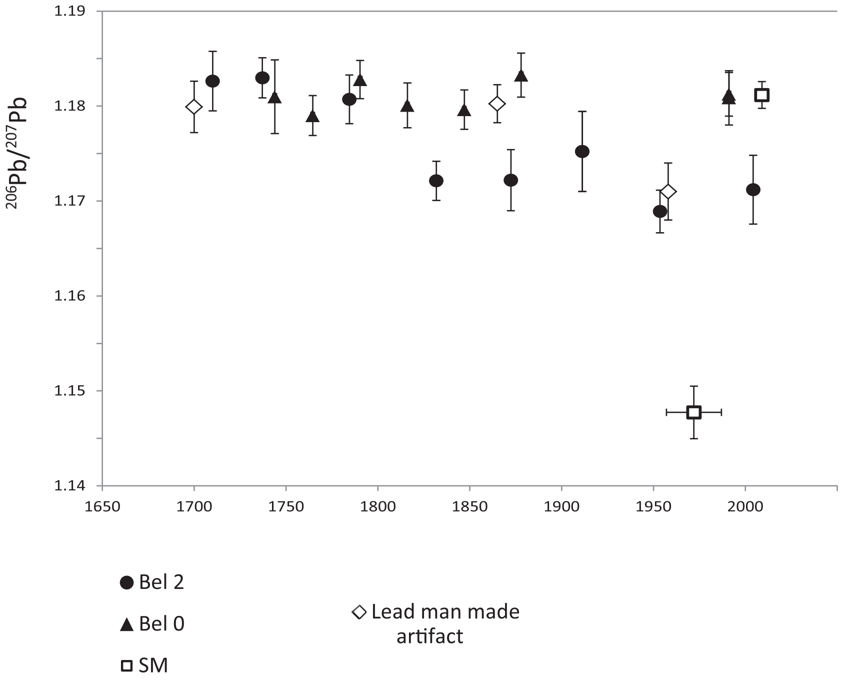

Fig. 2. ^{206}Pb/^{207}Pb signature of speleothems and historical artifacts.

Table 3
Trace element analysis in urban speleothems.

	Prof	Age	Al	V	Mn	Cu	Cd	Pb	Th
	mm	Yr AD	mg/kg	µg/kg	mg/kg	mg/kg	µg/kg	mg/kg	µg/kg
Bel 2-1	1	2004	80.1	577	4.12[a]	5.02	357	134	14.6
Bel 2-1	1	2004	83.2	580	4.25[a]	5.23	360	134	15.5
Bel 2-2	4.5	1981	91.6	713	4.72[a]	4.81	354	1.20	39.5
Bel2-3	8.5	1954	52.4	536	3.00[a]	2.00	78.0	2.18	11.5
Bel 2-4	12.75	1925	52.3	519	3.62[a]	1.62	89.9	0.37	25.5
Bel 2-5	14.75	1911	23.6	408	2.40[a]	1.41	60.5	1.15	3.35
Bel 2-5	14.75	1911	24.3	362	2.43[a]	1.36	64.8	1.19	3.84
Bel 2-6	18.25	1888	250.2	679	7.51[a]	2.33	158	1.44	53.2
Bel 2-7	20.5	1872	22.9	110	1.10[a]	1.28	55.6	0.38	4.35
Bel 2-8	24.5	1845	109.9	93.6	1.70[a]	2.07	225	0.32	14.9
Bel 2-9	26.5	1832	48.3	73.2	2.12[a]	2.29	162	0.49	12.2
Bel 2-10	30	1808	38.0	144	1.65[a]	1.87	44.3	0.47	8.81
Bel 2-10	30	1808	35.8	119	1.62[a]	1.77	46.0	0.47	9.19
Bel 2-11	33.5	1784	30.0	157	1.44[a]	1.67	68.9	0.45	9.26
Bel 2-12	37.5	1757	44.7	188	3.08[a]	1.85	62.2	2.14	13.9
Bel 2-13	40.5	1737	95.9	305	4.43[a]	2.50	180	1.84	20.3
Bel 2-13	40.5	1737	91.0	267	4.25[a]	2.36	175	1.90	22.6
Bel 2-14	44.5	1710	180.9	417	6.83[a]	2.55	340	4.07	29.8
Bel 2-15	15	1910	9.0	235	0.62[a]	1.28	42.6	0.31	1.2
Bel 2-15	15	1910	9.3	159	0.61[a]	1.19	44.9	0.30	1.73
Max/min			**27.7**	**9.7**	**12.2**	**4.4**	**8.4**	**453**	**44.3**
B0-1	2	1991	153.4	875	7.59[a]	2.55	314	3.62	27.2
B0-2	7	1940	70.5	597	3.19[a]	2.03	64.6	1.47	10.4
B0-3	10	1909	80.7	296	2.88[a]	2.12	45.8	0.64	16.8
B0-4	13	1878	36.7	54.9	3.24[a]	1.41	15.3	1.03	3.21
B0-5	16	1847	37.8	224	1.65[a]	1.40	15.9	2.57	6.18
B0-6	19	1816	65.6	556	2.26[a]	1.32	16.3	1.42	13.4
B0-7	21.5	1790	67.4	213	3.60[a]	1.20	11.8	1.33	20.3
B0-8	24	1765	52.2	178	10.0[a]	1.09	13.4	5.83	6.72
B0-9	26	1744	118.7	427	8.63[a]	1.34	27.4	1.19	27.0
Max/min			**4.2**	**15.9**	**6.1**	**2.3**	**26.6**	**9.13**	**8.5**
SM1-9–10	9.5	1972 +/− 15	39.0	144	9.19	21.2	1942	19.8	10.8
SM1 0–1.5	0.75	2008 +/− 2	95.0	259	5.70	13.0	2426	30	26.7
SM1 6–7.5	6.75	1980 +/− 15	1.2	204	12.6	17.0	1998	38	11.8
SM 0		2009 +/− 3	17.9	nd	0.70	5.84	1049	4.94	4.68

The values in bold represent the difference between the minimum and the maximum values.

[a] Mn content for Bel 0 and Bel 2 have been already published in Pons-Branchu et al. (2014).

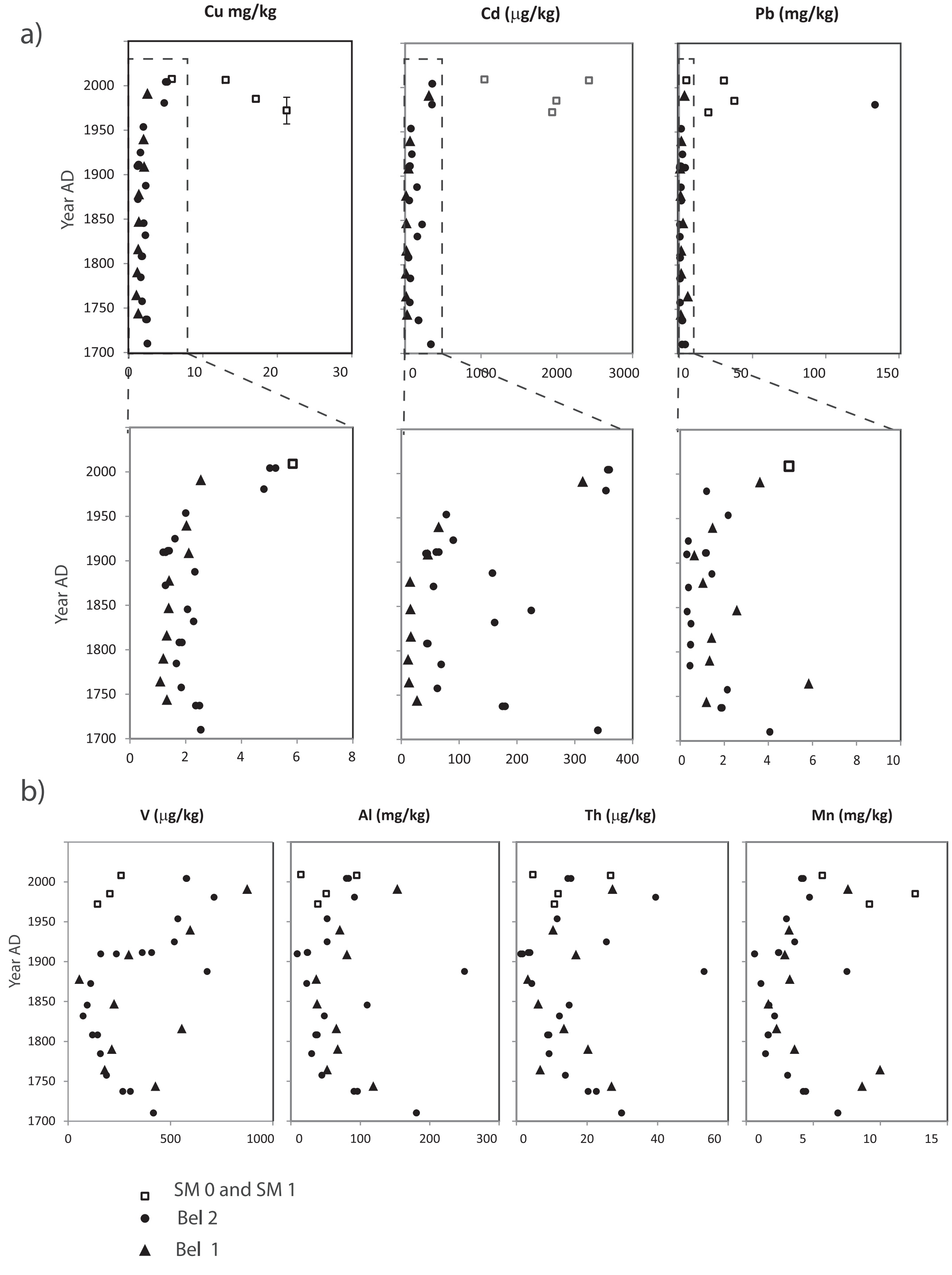

Fig. 3. Trace elements in Belleville and Saint-Martin samples. a) Cu, Cd and Pb. b) V, Al, Th, and Mn.

V (between 55 and 875 μg/kg), Th (between 1.2 and 53.2 μg/kg) and Al (between 9 and 250 mg/kg) show their highest concentrations between 1700 and 1760 and then between 1900 and the more recent levels.

3.2.2. Saint-Martin samples (1972–present)

The Cu and Cd contents are significantly higher in Saint Martin deposits than in Belleville ones (between 5.8 and 21.2 mg/kg for Cu and between 1049 and 2426 μg/kg for Cd).

Mn (between 0.7 mg/kg to 12.6 mg/kg), V (between 144 and 259 μg/kg), Th (between 4.7 and 26.7 μg/kg) and Al (between 17.9 and 95 mg/kg), present the same range of levels in Saint Martin and Belleville samples.

Pb content is high for all levels, between 38 mg/kg and 4.9 mg/kg.

4. Discussion

4.1. Pb sources

Pb stable isotopes (hereafter expressed as the ^{206}Pb/^{207}Pb ratio) are used to reconstruct the Pb sources in the environment because each lead ore has a ^{206}Pb/^{207}Pb ratio that reflects the geological history of the lead. Three main sources of Pb have been identified in Seine River sediments sampled downstream of Paris and covering the period 1925–2003 (Ayrault et al. 2012):

(1) The lead ($^{206}Pb/^{207}Pb = 1.163 \pm 0.01$) that has accumulated in the Seine basin since the 19th century from paint, leaded roofs and balconies … (hereafter called "historical" Pb) that ultimately originates from the Rio Tinto mine in Spain ($^{206}Pb/^{207}Pb \approx 1.1634 \pm 0.0001$; Marcoux, 1998).
(2) The local natural background lead, whose signature is $^{206}Pb/^{207}Pb = 1.202 \pm 0.001$ (Elbaz-Poulichet et al. 1986; Semlali et al. 2004).
(3) Pb used in additives to gasoline ($^{206}Pb/^{207}Pb = 1.08 \pm 0.02$) that contains high proportions of old Australian lead from the Broken Hill mine ($^{206}Pb/^{207}Pb \approx 1.040 \pm 0.001$), Octel Ltd being the only leaded additive provider for French gasoline (Véron et al. 1999).

A fourth source of lead to Parisian soils has been proposed ($^{206}Pb/^{207}Pb \sim 1.183$, Semlali et al. 2004) as a mixture between natural Pb and Pb derived from coal combustion ($^{206}Pb/^{207}Pb \sim 1.17$). This signature was detected in Versailles soils during the 20th century (Semlali et al., 2004) and in upstream sediment of a Seine River sub-basin (Ayrault et al., 2014), but it was not detected in the downstream core sediments (Ayrault et al., 2012) where it may be hidden by the first three sources.

Over the years, mixing between "historical" and "gasoline" Pb has yielded a composite "urban" Pb signature ($^{206}Pb/^{207}Pb = 1.154 \pm 0.002$), determined by analyzing wastewater treatment plant (WWTP) effluents collected in 2006 (Ayrault et al. 2012) and the three main Parisian municipal solid waste incinerators in 2001 (1.1550 ± 0.0005; Widory, 2006).

During the 19th century, most lead was imported into France (the main supplier being Rio Tinto, Ayrault et al, 2012) and French mines probably represented only a small fraction of the production (Lestel, 2007). For the 17th and 18th centuries, to our knowledge, there is little/no data available concerning the origin of the Pb used in France.

4.1.1. Belleville samples

Results obtained on Bel 0 and Bel 2 suggest that at the beginning of the 18th century, the Pb used in Paris was dominated by a source characterized by $^{206}Pb/^{207}Pb \sim 1.18$. This signature is similar to the $^{206}Pb/^{207}Pb$ measured for the Pb gasket from Versailles (1.180 +/− 0.003) and for the putative "coal source" mentioned by Semlali et al. (2004). Coal was seldom used in France until the mid-19th century, where its use strongly increased with the industrial revolution. Hence for the earliest part of the record (18th century), Pb used for artifacts is the most likely source for the signature observed in Bel 0 and Bel 2. The anthropogenic imprint of lead within water and secondary calcareous deposits is therefore old in this part of Paris.

While the $^{206}Pb/^{207}Pb$ ratio of Bel 0 remains constant over time (1.181 +/− 0.004), the lead isotopic composition of Bel 2 presents two trends: for the oldest level, a composition close to that of the historical lead, and for the youngest part, since the middle of the 19th century, a lower value with a mean at 1.172 +/− 0.005. These data reveal that Pb incorporated in the carbonates originates mainly from an old anthropogenic source, with a second input with a different signature at the beginning of the industrial revolution during the 19th century. This second source could be either coal, Pb from Rio Tinto ore or a mix of the different sources. We note that the water pipe from a mid-20th century house has the same signature as the recent signatures recorded in Belleville (Fig. 4). The contribution of leaded gasoline is insignificant. This suggests that the Pb contamination recorded at the Belleville site accumulated over a long period and is not sensitive to the recent leaded gasoline spike registered in atmospheric dust and Seine River sediments. However, for the most recent period, the Bel 2 signature is consistent with the river sediment data (see Fig. 4). More data are required to determine the precise involvement of each Pb source. Another unanswered question is why 2 nearby speleothems located in the same gallery display significantly different signatures since the mid-19th century. Information on local hydrology and its evolution will be required to answer this question.

4.1.2. Saint Martin

In contrast to Belleville, a low $^{206}Pb/^{207}Pb$ ratio (1.148 +/− 0.003) was found in Saint Martin in the porous level, for a growth period of the speleothem bracketed between 1957 and 1987, with the most probable value being in the upper part of this range (see Section 2). As a matter of fact, this time corresponds to the period of low $^{206}Pb/^{207}Pb$ ratio recorded in the Seine River sediments downstream of Paris (Ayrault et al., 2012) between the years 1970–2000 (see Fig. 4). Conversely, the low $^{206}Pb/^{207}Pb$ signature of leaded gasoline was not detected in the only results reported for Paris gasoline and the environment in the 1960s (Chow et al., 1975). It clearly highlights the arrival of a "leaded gasoline" contamination at this site. However, as in the Seine River sediments (Ayrault et al., 2012, see Fig. 4), the most recent (2009) sample of Saint Martin lacks this low signature due to the phasing out of leaded gasoline in the decades 1980–1990. The great variability in the Pb isotopic signature in Saint-Martin compared to Belleville could be due to the relative depth of the 2 sites. As explained in Section 2, the Saint Martin site is at street level and thus more prone to contamination by leaded gasoline. Conversely, although Belleville receives some water from street runoff, Pb marked by the gasoline signature does not reach the aqueduct (or is overprinted by another source).

The parallel evolution of the $^{206}Pb/^{207}Pb$ ratio since 1945 between the speleothems and the Seine sediments is largely driven by the low $^{206}Pb/^{207}Pb$ ratio recorded by the oldest sample of Saint Martin. It clearly marks the connection with surface water that collected gasoline derived Pb in the 1970s to 1990s and highlight a similar evolution of the $^{206}Pb/^{207}Pb$ ratio of the Saint Martin (Paris) runoff water and the one of the Seine sediments over the last decades at least.

4.2. Metal recording in speleothems

Our goal is to use urban speleothems to assess the temporal evolution of the past groundwater quality. However, before drawing conclusions, it is necessary to gain insight into how TEs are incorporated in speleothems and into the parameter that may control the relation between the TE content in groundwaters and calcite precipitates. The study of TE concentrations in speleothems free of human impact is widely used to monitor climatic or environmental changes (Fairchild and Treble, 2009). It has been shown that the TE/Ca or TE/TE ratio may vary with climatic or hydrological conditions in relation with water sources or pathways within the host rock. TE can be transported as dissolved phase or adsorbed on particles or colloids. The present study discusses that the potential sources of TE in the speleothems are discussed in urban context and the possible changes over time in their incorporation processes from the water.

4.2.1. TE incorporation in speleothems

The measurement of trace elements in secondary $CaCO_3$ does not exactly reflect the composition of the water because TEs are incorporated within the lattice depending on their water/calcite partition coefficient, which can vary with environmental factors. For past periods, Bourdin et al. (2011) suggested that climatic changes can modify the stalagmite growth rate which can induce a change in the major or trace element incorporation in the calcite lattice and produce concentration variations of Mg, Ca, Sr, Ba, U and REE-Y (Rare Earth Elements and yttrium), controlled by the ionic radius of each element. The comparison between TE in drip water (in both dissolved inorganic fraction and NOM — natural organic matter fraction) and speleothem deposits underlines and confirms the effect of the precipitation rate on the metal incorporation

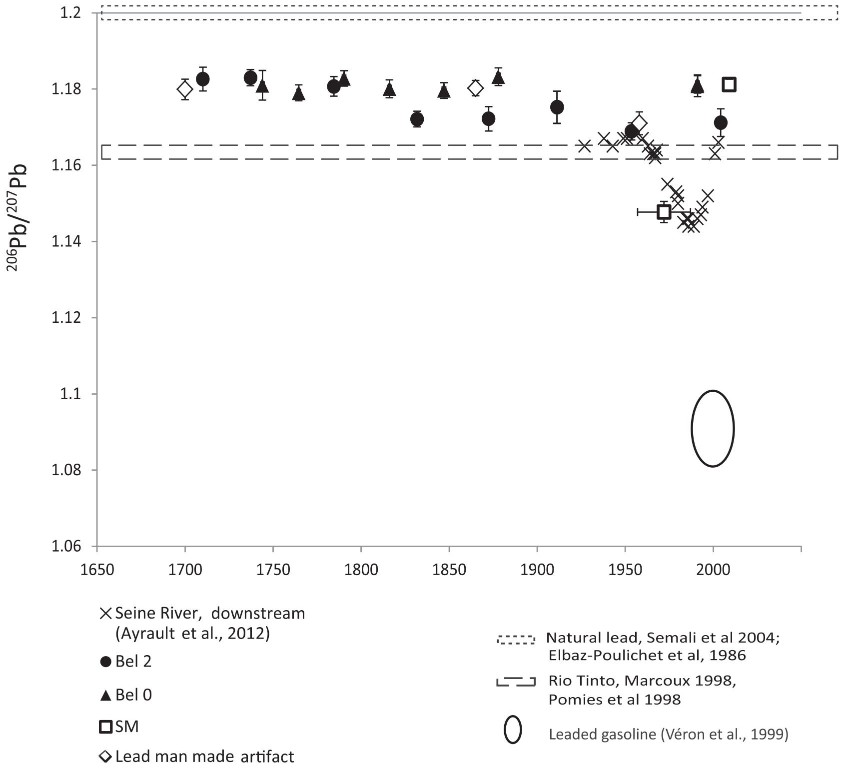

Fig. 4. Comparison of ^{206}Pb/^{207}Pb lead isotopic composition in speleothem and lead artifacts with Seine sediments (Ayrault et al., 2012) and potential sources of lead: leaded gasoline (Véron et al., 1999), Rio Tinto Ore (Marcoux, 1998; Pomiès et al., 1998), natural lead background (Elbaz-Poulichet et al., 1986; Semlali et al., 2004).

rates (Hartland et al., 2014). In particular, these authors suggest that it accounts for the depletion in Co and V carried by small colloids and NOM at high precipitation rate.

Part of the fractionation between TE and Ca could also be due to temperature changes because the water/calcite partition coefficient of some elements (particularly Mg and Cd) is temperature-dependent (Tsusue and Holland, 1966; Gascoyne, 1983). However, this temperature effect should be low compared to the other processes (e.g., change in source hydrological change or precipitation rate variation) affecting TE variations in speleothems (Day and Henderson, 2013).

For the present study, no drastic climate variability occurred during the last 300 years which is the growth period of the Bel 0 and Bel 2 speleothems. The water that feeds the speleothems originates partly from rainfall that flows directly through the soil and the aqueduct (the aqueduct could act as a karstic system) and partly from waters from the water table (older precipitations which interacted with calcareous host rock). Each speleothem has a constant growth rate: 0.1 mm/y for Bel 0 and 0.15 mm/years for Bel 2 (Pons-Branchu et al., 2014). Thus, temperature, water chemistry and growth rate effects should not induce major changes in the water/calcite partition coefficient of trace elements. Therefore, the large changes in trace element concentration observed in the speleothems are expected to reflect mainly a trace element concentration change in the water from which the speleothem precipitates, a change in water infiltration rate and exchange with host rocks or change in redox condition and organic matter content. Recently, it was demonstrated that heavy metal in foraminiferal calcite can be used to reconstruct past heavy metal concentrations in sea water, although antagonistic effects between certain metals may obscure the relationship between TEs in seawater and in calcite (Munsel et al, 2011).

As the mode of transport of TE (bound in particles or colloids, or dissolved) is unknown, the mode of incorporation of TE in an urban environment is poorly constrained. In addition, the water/calcite partition coefficient is different for each TE and it differs in field observations and laboratory experiments (Hartland et al., 2014; Tremaine and Froelich, 2013). Therefore, we will not attempt to reconstruct precisely the composition of the water, but will rather look at the largest and most significant historical changes in contaminant levels, since the concentration changes for some of the transition metals studied here show changes of several orders of magnitude within the calcite.

4.2.2. Transport of TE: clays, colloids and organic matter

Speleothems can incorporate clay minerals and colloids during their growth (Fairchild and Treble, 2009). In surface waters, a very insoluble element such as Al is mainly associated with clay minerals and can be therefore used to determine the clay contribution to a given sample (Ayrault et al., 2014). The clay composition can be estimated with the natural background levels in the particulate matter from the Seine River basin (Thévenot et al., 2007) or, when these data are not available, from the upper crust composition (Taylor and McLennan, 1995). For example, in Bel 0 and Bel 2, thorium (Th) another reactive element (with almost no anthropogenic sources) is correlated (Fig. 5, $r^2 = 0.76$) with Al, with a mean Th/Al ratio close to the crustal value (0.14 μg/mg), supporting a common origin due to the presence of clays or colloids in the speleothem. By contrast, for the other TE such as V, Cu, Mn, Cd and Pb (Fig. 5), the TE/Al ratios in the speleothems are much higher than in clays suggesting that the contribution of clays to the total trace element content of the speleothems is low.

Nevertheless, in some cases (e.g., Mn vs Al) TEs are correlated with Al although the TE/Al ratio is much higher than what is expected for clays. This indicates that the TE carriers and Al are correlated, either because they are carried by the same phase or because they are carried by 2 distinct phases in the same size range (Fairchild and Treble, 2009). This is also the case for V, although two different trends are evidenced with a significantly higher V/Al ratio than the crustal ratio, the first one for SM samples and the oldest levels of Bel 0 and Bel 2 (between 1700 and 1900) with a V/Al ratio of 2.7 and the second for the youngest samples of Bel 0 and Bel 2 with a V/Al ratio of 5.7 (Fig. 5). This suggests two sources of V through time, with a source with higher V since the beginning of the 20th century in Belleville. The different behavior in the recent period for the Belleville site (that receives groundwater and

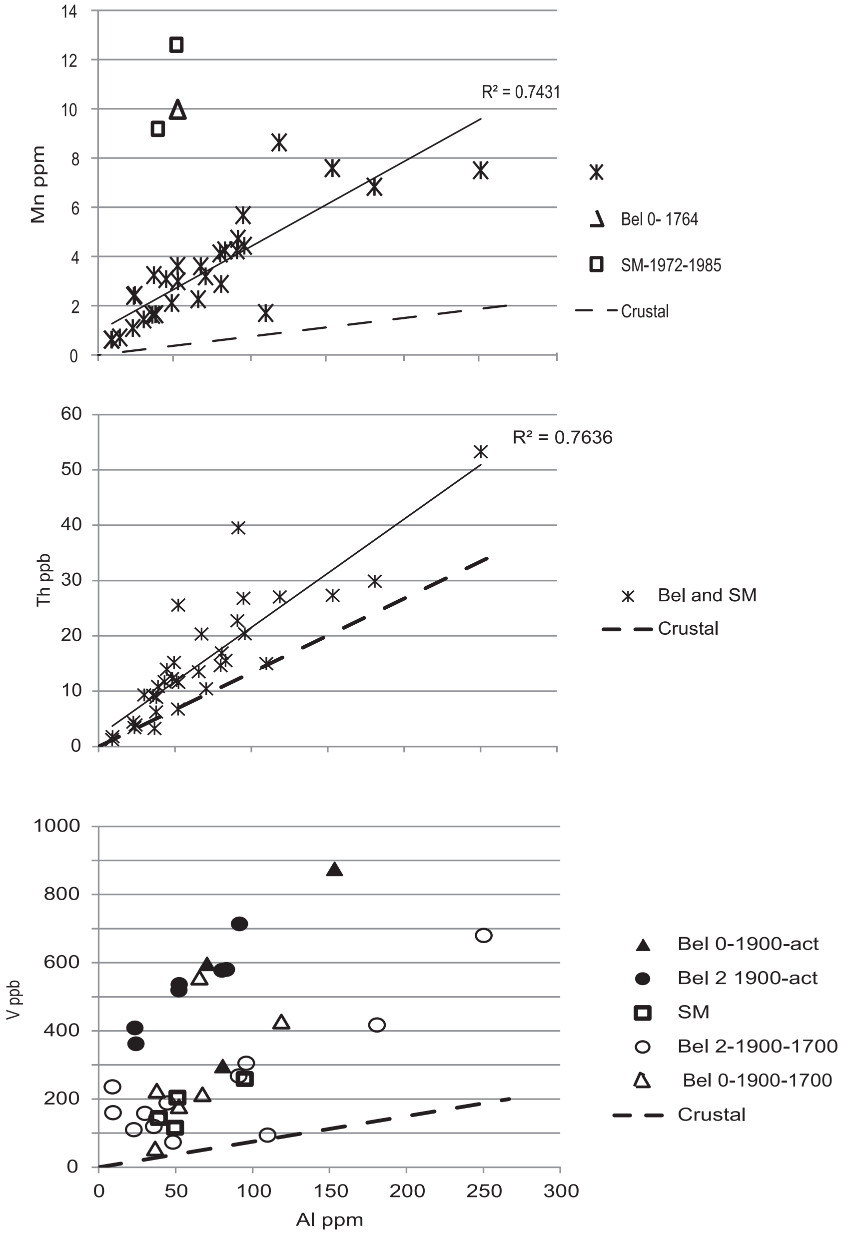

Fig. 5. Al vs V, Th and Mn concentrations in Belleville and Saint-Martin samples. The dashed line represents the concentration ratio in upper continental crust (Taylor and McLennan, 1995).

water percolating from the street above) and Saint Martin samples (fed mainly by groundwater) suggests that (1) the source or carrier of V in the groundwater has not changed over the last 300 years (similar V/Al ratio), and (2) the street runoffs and water from the wastewater collection system or modern water conveyances (Pons-Branchu et al., 2014) are a new V source for Belleville samples since the beginning of the 20th century.

In recent studies, several authors highlighted the predominant role of organic colloids in TE transport from soil to drip water in caves. Elements such as Y, Zn, Cu, Pb and Br could be associated and transported through karstic systems by colloids flushed from the soil during autumnal rainfall (Borsato et al., 2007). In addition, there is a correlation between colloidal or dissolved natural organic matter (NOM) and metal content (especially V, Co, Cu and Ni) in drip waters sampled in caves feeding speleothems (Hartland et al., 2012). This suggests that metal content in drip waters may reflect the soil organic matter content. The role of organic matter has also been underlined for the study of Rare Earth Elements (REE) in speleothems. Several authors suggested that a correlation between Mn and REE (seasonal variations) could be related to the presence of organic matter and on a longer time scale to the importance of host rock weathering with different rock/soil sources (Richter et al., 2004; Zhou et al., 2012).

However, in Bel 0 and Bel 2 speleothems, there is no correlation between Mn and REE content (Pons-Branchu et al., 2014). The strong increase in the REE content of these speleothems should be attributed to a large release of REE in the environment since the middle of the 20th century, with a sharp increase between 1940 and 1955. The negative Ce anomaly (Ce normalized to the NASC reference material and compared with its closest neighbors La and Pr; Pons-Branchu et al., 2014) in Bel 0 and Bel 2 indicates oxidizing conditions and Ce^{4+} precipitation before the water reaches the aqueduct. In this previous study, the increase in the Ce anomaly occurring since the 1850s AD is not correlated with Mn content. It could highlight a new source of water for Bel 0 and Bel 2 speleothems, maybe in relation with water from the wastewater collection system or modern water conveyances. Thus, Mn change over time within the speleothems does not mainly reflect here change in organic content but is attributed to a significant change in the water composition feeding the speleothems over time.

4.3. Heavy metal pollution over time

The heavy metal concentrations measured in the Belleville and Saint Martin speleothems reveal two episodes of pollution, one in the 18th century and the other in modern times.

4.3.1. Modern TE contamination

Bel 0 and Bel 2 display high Pb, Mn V, Al, Cu, Cd and Al contents since 1900 (Fig. 3). Saint-Martin samples, which grew during the last thirty years display the same concentration range as the Belleville samples, with higher Cu and Cd contents. There is no doubt that this is due to anthropogenic contamination of the water that feeds the speleothems. In this area, urbanization started around 1850–1870 (Alphand, 1889) with the embankments of the area followed in the next thirty years by the construction of the district (Sander, 2008). Metal release within the environment has increased since then. V content, especially, shows a rapid increase since the beginning of the 20th century with a new source evidenced by the V/Al ratio at this time (see Section 4.2.2). This modern V source could originate from the newly constructed street above the aqueduct, and is consistent with the reuse of steel slag in road construction (Chaurand et al., 2007). Another hypothesis for this V increase is the use of coal and later heavy fuel oil for domestic heating that produce ashes or black carbon with high V content (Montiel, 1972). This abrupt and marked effect could be due to the rapid increase of the population within the area at the beginning of the 20th century.

For Cu, Cd, Pb and Mn, the increasing trend is more marked in recent decades, with increasing concentrations since the years 1960–70, and a higher (Mn) or several orders of magnitude higher (Cd, Cu and Pb) content in Saint Martin samples compared to Belleville samples. This suggests a recent source of contamination, more pronounced in Saint-Martin samples fed by shallow water than in Belleville samples fed by both groundwater (mostly during the earliest period) and water dripping directly from the surface above the aqueduct (the main source at the present time).

To conclude, Pb isotopes reveal that Pb sources varied over time: an old source already present during the 18th century for Bel 0 and Bel 2, whereas Bel 2 probably recorded the increasing influence of “modern” Pb with a possible influence of Pb from the Rio Tinto mine (although the Rio Tinto signature is not reached). There is no evidence that gasoline derived-Pb has reached Bel 0 or Bel 2. While it suggests a slow contamination rate of the water that reaches the great gallery, however, it must be kept in mind that Pb from leaded gasoline represents only a small fraction (less than 5%) of the Pb imported and stored in the Paris region (Meybeck et al., 2007).

The distinct lead signatures of Bel 0 and Bel 2 since the middle of the 19th century raise 2 questions:

- What is the origin of these different signatures? Do they reflect different circulation pathways of the groundwater or different inputs from the outside (water or sources)?
- Do other trace metals recorded in Bel 0 and Bel 2 over the 20th century have different sources reflecting the persistence of contaminant inputs of different ages?

For Th and Mn, the linear trends observed with Al suggest a unique source over time, with a Th/Al ratio close to crustal values and a Mn/Al ratio significantly higher than crustal ratios.

4.3.2. 18th century contamination

Surprisingly, the concentrations of Pb, Cd, Al and Mn and to a lesser extent Cu are also high in the oldest part of Bel 2 and Bel 0 speleothems, approximately between 1700 and 1770 (Fig. 3). At that time, the area above the Belleville aqueduct was not urbanized and was sparsely populated. Moreover, the area was covered by orchards and vineyards (Huard, 2011; DelaGrive, 1870). Yet the Pb, V, Cu and Cd (and Al) contents for this early period reach those found for the post-urbanization period (1900–1970). This early marked pollution is consistent with the lead isotopic composition measured within the carbonates which have an isotopic composition different from the natural background and in agreement with lead artifacts. This early anthropogenic metallic imprint of the carbonates could be related to enhanced transport by organic matter as discussed for metal content variations within the speleothems, but this enhanced transport fails to explain the metal-rich source for these elements, well above the natural background and above the speleothems' lead content recorded for the 1750–1900 period.

At the beginning of the 18th century, waste in Paris (including wastes from rendering, manure, and “industrial” waste from pottery factories or slag) was directly dumped in the street or in the river. Part of the waste was collected and stored in different locations, called the “voiries”. During the 18th century, the “Voirie de Montfaucon” located 1 km downstream from the sampling sites, was the main site for Parisian waste (Le Roux, 2011). Once deposited a part of these collected wastes were used as fertilizer in the vicinity. At the same time, laborers were also ordered to collect directly waste from Paris and transport it to their fields (Delamare, 1722–1738; Barles, 1999). This practice has continued along the 18th century.

5. Conclusion

The analysis of heavy metals and lead isotopes in urban speleothems that grew during the last 300 years in an underground aqueduct and in a spring from a nearby surficial site from the north-eastern part of Paris allowed reconstructing the history of shallow groundwater pollution in relation to human activity and urban development. As expected, the most recent period (1900 to present) displays high heavy metal contents. Surprisingly, a second period with high heavy metals occurred between the years 1700 and ca 1750, when land cover was vineyards and orchards. This early contamination was linked with the use of domestic and industrial waste from Paris as fertilizer during the 18th century in the fields surrounding Paris.

The lead isotopic composition measured in these carbonates revealed that the lead present in the oldest part of the speleothems displays an anthropic imprint, with a $^{206}Pb/^{207}Pb$ ratio of ca ~1.180, lower than the natural background and similar to the artifacts from the 17th and 19th centuries. This lead isotopic signature remains constant until the present time within one of the samples, while for the other, the $^{206}Pb/^{207}Pb$ ratio changes from the middle of the 1800s to the present ($^{206}Pb/^{207}Pb$ ratio ~1.172), indicating a new lead source (possibly coal or lead from Rio Tinto ore). It suggests that the lead contamination at the Belleville site is accumulated over a long period and is not sensitive to the recent leaded gasoline signature (1.080 ± 0.001). In the more superficial site of SM fed by the spring, a lead isotopic composition influenced by leaded gasoline, ($^{206}Pb/^{207}Pb = 1.148 +/- 0.003$) was present in the 1972–1986 AD level. All these data suggest that waters from urban watershed that infiltrate within the soil are strongly influenced by land use. They also suggest that lead contamination in infiltrating waters has an old anthropogenic imprint, with a local low influence of leaded gasoline, and thus heterogeneity of the pollution infiltration on a small scale, but with a general trend linked to urban development in the whole area.

This study and Pons-Branchu et al. (2014) demonstrate the possibility of using speleothems as archives of past environmental conditions in relation with urban and industrial development. Until now, the only tools available to monitor past urban water pollution were (rare) undisturbed river sediments. As urban speleothems grow over decades to centuries, they enable much longer time periods to be explored than the other archives. By growing from shallow water deposits, they also give access to a different environment. In a city built on and with limestone like Paris, urban speleothems are abundant and they provide a wealth of data on pollution, paleohydrology and urbanization history at different scales of space and time.

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