

Lead concentrations and isotope ratios in speleothems as proxies for atmospheric metal pollution since the Industrial Revolution

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1 Abstract

2 Lead concentrations and isotope ratios from two speleothems from the Han-sur-Lesse cave in southern
3 Belgium were measured in order to study the ability of speleothems to act as archives of atmospheric
4 pollution. To address this aim we analyzed trace elemental Al and Pb compositions by LA-ICP-MS and
5 ICP-MS as well as Pb isotopes by MC-ICP-MS. The results help to identify three intervals characterized
6 by particularly high enrichment of Pb: from 1880 to 1905 AD, from 1945 to 1965 AD, and from 1975 to
7 1990 AD. The speleothem record shows similar changes as the known historical atmospheric pollution
8 level in Belgium. Lead isotope ratios discriminate between Pb sources and confirm that coal and gasoline
9 combustion, combined with regional metallurgical activities, were the predominant Pb pollution sources in

10 the stalagmites during the last 250 years. This study opens possibilities to determine anthropogenic versus
11 natural metal sources in well-dated speleothem archives.

12 **Keywords:** Atmospheric pollution, trace metals, Pb isotopes, stalagmites, Western Europe.

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36 **1. Introduction**

37 The increase in atmospheric metal deposition compared to prehistoric levels is particularly marked in
38 Europe since at least 2000 years. Mining and metallurgical activities, and later coal burning and transport
39 emissions were the principal anthropogenic sources (Nriagu, 1979; Pacyna and Pacyna, 2001; Pacyna et
40 al., 2007). Belgium, as part of the northwestern European industrial basin, has a long industrial history.
41 To assess the extent of atmospheric contamination, it is necessary to identify the main past and present
42 sources of trace metal emissions. The isotopic ratios of Pb ($^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$) are used in
43 environmental deposits to quantify anthropogenic Pb inputs compared to the natural/local background and
44 to trace Pb emission sources (e.g., Geagea et al., 2008). Atmospheric metal pollution is directly recorded
45 by several types of environmental archives such as lake sediments (e.g., Shirahata et al., 1980; Brännvall
46 et al., 1999; Outridge et al., 2011), marine deposits (e.g., Gobeil et al., 1999), ice (e.g., Hong et al., 1994;
47 Boutron et al., 1991, 1994 Rosman et al., 1997), soils (e.g., Elless et al., 2001) and peat (e.g., Shotyk et al.,
48 2005; Allan et al., 2013). However, some areas with abundant past heavy metal pollution lack suitable
49 archives due to dating uncertainties and limited spatial occurrence of some of these archives (e.g., ice).
50 The abundance of speleothems (and stalagmites in particular) and their precise dating possibilities suggest
51 that they might make ideal archives for the reconstruction of historical metal pollution fluxes. During the
52 last decades, speleothem studies have enhanced our knowledge of continental climate and environment, in
53 particular the precise chronology of past decadal to millennial climate and environmental changes up to
54 600ka, limit of the U/Th dating method (Drysdale et al., 2009; Fleitmann et al., 2012; Genty et al., 2003;
55 Wang et al. 2008). Their amenability to radiometric dating using the U-series, mainly the U/Th method (Li
56 et al., 1989; Hellstrom et al., 1998; Kaufman et al., 1998) with a precision of better than 0.5%, combined
57 with layer counting (e.g., Genty et al., 1996, McMillan et al., 2005; Verheyden et al., 2006) in seasonally
58 layered speleothems offer a high resolution archive for reconstructions of past climate and environment
59 (e.g., Fairchild and Baker, 2012). Until now, the potential of speleothems for recording environmental
60 pollution is largely unexplored and mainly focused on quantifying aerosol contributions in touristic caves
61 (Chang et al., 2008; Dredge et al., 2013).

62 The goal of this study is to define the high Pb concentrations and Pb content variability in the upper
63 250 years of two northwest European speleothems. We verify the reproducibility of the Pb time-series in
64 and between speleothems. We discuss possible drivers for the increased Pb concentration and investigate
65 the eventual link with known anthropogenic atmospheric Pb pollution. The study therefore assesses the
66 ability of speleothems to register past atmospheric metal fall-outs despite the transfer of the signal through
67 the soil and the host rock. To address this aim we analyzed speleothem Pb and Al compositions by LA-
68 ICP-MS and ICP-MS as well as Pb isotope ratios by MC-ICP-MS. The elemental and isotopic Pb
69 signature in speleothems is compared with that of other records from the same area to establish a potential
70 link with the historical atmospheric pollution.

71 **1.1. State of the art**

72 Speleothems such as stalagmites and flowstones are increasingly used for paleoclimatic research.
73 They contain several already well-studied climate and environmental proxies (Fairchild and Baker, 2012).
74 The oxygen isotopic composition of speleothems in tropical areas varies with changes in the monsoon
75 intensity through changes in the contribution of summer monsoon (e.g., Wang et al., 2008; Scholte and De
76 Geest, 2010). In northern latitudes the $\delta^{18}\text{O}$ seems influenced by temperature as well as rainfall amount
77 (Mangini et al., 2005; Matthey et al., 2008). The spatial variability of the $\delta^{18}\text{O}$ signature of speleothems was
78 proven to reflect the regional air circulation patterns in Europe (McDermott et al., 2011). The $\delta^{13}\text{C}$ in
79 speleothems from regions in which most types of vegetation employ the same photosynthetic pathway, as
80 in Europe, mainly reflects changes in the intensity of vegetation cover or soil bacterial activity (Genty and
81 Massault,, 1999). The relative contribution of isotopically light carbon from the soil compared to that of
82 the host limestone increases in warm periods. Genty et al. (2003) demonstrated that the $\delta^{13}\text{C}$ changes
83 recorded in the Villars speleothems from France are the equivalent of the Dansgaard-Oeschger cycles
84 identified in polar ice cores. In addition to stable isotope ratios, speleothem trace element (e.g., Mg,
85 Ba, Sr, U) compositions represent a large proportion of the studied speleothem proxies. These elements
86 seem to be influenced by the vadose hydrology in the epikarst zone above the drip-water site. They

87 therefore may give information on the paleo-recharge amounts, i.e. balance of precipitation and
88 evaporation, in speleothems (Baker et al., 1997; Fairchild et al., 2001). Variations in trace element
89 concentration in stalagmites depend on: 1) chemical mobilization of elements in the soil (Blaser et al.,
90 2000; Jo et al., 2010); 2) contributions from the surrounding limestone; 3) dry deposition of dust or tephra
91 deposition at the surface (Dredge et al., 2013); 4) the nature of the transport from the soil zone through the
92 host rock to the cave environment and 5) carbonate precipitation conditions (Fairchild and Treble, 2009;
93 Fairchild et al., 2010; Jo et al., 2010; Hartland et al., 2011; Wynn et al., 2014). Little research has studied
94 the transmission of Pb from soil to cave (e.g., Borsato and al., 2007; Baldini et al., 2012; Hartland et al.,
95 2012). Hartland et al. (2012) showed that the Pb mobilization in forest soils overlying limestone may be
96 strongly related to the presence of organic matter (colloidal transportation). They further suggested that
97 the transportation by organic colloids should be indicated by covariation of elements that are strongly
98 bound to colloids (such as Pb, Al). Borsato et al. (2007) suggested that the transport of Pb can be
99 attributed to a combination of the effects of mobile organic matter and high flow from the soil to the
100 speleothem. Recently, uranium (Siklosy et al., 2011), anthropogenic sulphate (Wynn et al., 2008; Frisia et
101 al., 2005), and lead (McFarlane et al., 2013) were detected in speleothems in a specific context of
102 pollution demonstrating their potential as archives for human impact on the environment. Wynn et al.
103 (2010) and Frisia et al. (2005) showed that the sulphate in speleothem calcite is indicative of atmospheric
104 pollution opening the possibility of speleothems to be archives of atmospheric pollution.

105 **2. Material and Methods**

106 Two speleothems from the Han-sur-Lesse cave system developing in Givetian (Devonian) limestone
107 and located in southern Belgium (Quinif and Bastin, 1986) are investigated (Fig. 1). Because the area is
108 part of the natural reserve of Han, the area was not impacted by anthropogenic pollution, other than that
109 derived from the atmosphere. The surface runoff over the cave system is close to zero (Bonniver et al.,
110 2010) indicating that most of the natural rainfall infiltrates into the soil towards the vadose zone after
111 some evapotranspiration, particularly during spring and summer. This percolation water feeds the
112 speleothems in the cave.

113 The Proserpine stalagmite is a two meter long and ~1m large stalagmite located in the Salle du Dôme
114 in the touristic part of the Han-sur-Lesse cave system. Two cores were collected in 2011 (S1) and 2001
115 (S2) and used for this study. The Proserpine stalagmite is layered (two layers per year) over the last 500
116 years. A detailed study of the stalagmite, based on the S2 core is found in Verheyden et al. (2006). The
117 chronology of the speleothem and thus of the cores is based on U-series dating, combined with layer
118 counting and on ^{14}C dating of the straw incorporated in the stalagmite (Fig.2) (Verheyden et al., 2006; Van
119 Rampelbergh et al., 2014). Layer counting was carried out on high-resolution scans using Adobe
120 Photoshop and by using a microscope. In 2011 the S1 core was taken at ~50 cm from the S2 core and
121 presented a similar sedimentological pattern. The upper 13 cm from stalagmite core S1 and the upper 10
122 cm from core S2, are presented in this paper (Fig 2). According to previous studies, a hiatus of at least 83
123 years occurred from ~1870 to 1790 AD which corresponds to a sedimentological perturbation at ~ 9 cm
124 from the top of the stalagmite when core S2 was sampled in 2001 (Verheyden et al., 2006). The calcite
125 deposition at this level is heavily disturbed with straw pieces embedded in the calcite (Verheyden et al.,
126 2006). The straw pieces are interpreted to be relics of torches used in the cave or even from fires lit on the
127 paleo-surface of the stalagmite to illuminate the Salle-du-Dôme chamber (Verheyden et al., 2006). The
128 cave has been visited since 1700 AD as indicated by first perturbations in the stalagmite (Verheyden et al.,
129 2006).

130 In addition to the Proserpine stalagmite cores, we present Pb concentration data from ‘La Timide’
131 stalagmite (S3), a 35.5 centimetre-long candle-shaped stalagmite. The stalagmite was sampled in 2004 in
132 the ‘Réseau Renversé’, a non-touristic part of the Han-sur-Lesse cave located more than 200 meters from
133 the entrance beyond a siphon that was by-passed by a tunnel opened in 1961 AD. The stalagmite was
134 therefore totally preserved from direct aerosol deposition until recently. The upper 3.5 cm, corresponding
135 to the last 250 years, is presented in this paper (Fig.2).

136 U-series dating was performed on an ICP-MS Finnigan ELEMENT mass spectrometer at the
137 University of Minnesota (USA) for core S2 (Verheyden et al., 2006) and S3 (this paper) and using a
138 Thermo NEPTUNE MC-ICP-MS at the Laboratoire Géosciences et Environnement, Toulouse (GET) for

139 S1(this paper). Uranium and thorium chemical separation and purification procedures are described in
140 Edwards et al. (1987) and Cheng et al. (2009a, 2009b). All ages are reported as years AD (Table 1).

141 The three stalagmites (S1, S2 and S3) were measured with different resolution and by somewhat
142 different methods. For S1, Al and Pb concentrations were determined using a Thermo XSeries2 ICP-MS
143 with an ESI New Wave UP-193FX Fast ExcimerArF laser of 193 nm at the Royal Museum for Central
144 Africa (Tervuren, Belgium). Spots were made of 50 μm diameter (spaced at 500-1000 μm intervals)
145 (n=205). For S1, the upper 4 cm were duplicated by continuous ablation with a scan speed of 10-30 $\mu\text{m s}^{-1}$
146 with 22 μm intervals between two measurements (Fig. 2). Total Al and Pb blanks were negligible and
147 ranged from 0.0009 $\mu\text{g g}^{-1}$ (for Pb) to 0.04 $\mu\text{g g}^{-1}$ (for Al). Both Al and Pb blanks were below their limit of
148 detection (0.01 $\mu\text{g g}^{-1}$ for Pb and 0.2 $\mu\text{g g}^{-1}$ for Al) representing usually less than 0.1% of average sample
149 concentrations.

150 Seventy-five sample powders were obtained from core S2, by microdrilling using a 700-micron
151 tungsten carbide drill bit at 1.200 micron mean spatial resolution. The powders were dissolved in nitric
152 acid and Al and Pb concentrations determined using a Thermo XSeries2 ICP-MS in the Department of
153 Earth Sciences, Durham University (Durham, UK).

154 For S3, concentrations (n=140) were measured by LA-ICP-MS (CETAC LSX-213) at Union College,
155 Schenectady (NY, USA). Spots of 50 μm diameter were made spaced at 250 μm intervals. Blank
156 concentrations represent usually less than 0.0008 $\mu\text{g g}^{-1}$ for Pb and <0.03 $\mu\text{g g}^{-1}$ for Al and therefore are
157 considered negligible. The limits of quantification were calculated from the intensity and standard
158 deviation measurements of 20 blanks. For all stalagmite cores, with each series of samples, four certified
159 reference materials (NIST 610, NIST 612, MACS-1, and MACS-3) were analyzed in order to determine
160 the precision and accuracy of analytical procedures. Comparison between reference values and measured
161 values shows that the reproducibility was satisfactory (more than 70%). Calcium was used as internal
162 standard and assumed to be 40% of the rather pure speleothem CaCO_3 . The different spatial resolutions
163 handled and slight lateral variations in the Proserpine stalagmite may explain observed differences in
164 metal concentrations between both cores S1 and S2.

165 Lead isotope ratios were determined in core S1 (Table. 2). After cleaning of the speleothem surface
166 with ethanol and HCl, dried calcite samples (200-400 mg taken by a micro-drill) were dissolved in HNO₃
167 at 125°C for 48 h. After evaporation, 2 ml of 6 M HCl were added to ensure complete digestion and the
168 solutions were evaporated. The Pb fraction was extracted after sample dissolution in 0.8 M HBr using
169 AG1-X8 resin in a Teflon column (Weis et al., 2005). Lead isotopic ratios were measured by a Nu
170 Instruments MC-ICP-MS at the Department of Earth and Environment Sciences (Université Libre de
171 Bruxelles, Belgium). Total procedural Pb blanks were ≤ 0.4 ng and considered as negligible relative to Pb
172 contents in the individual samples (Pb content > 40 ng). Mass fractionation for Pb was corrected by using
173 Tl as an internal standard. NBS981 standard was repeatedly measured in alternation with samples to
174 correct for instrumental drift. The isotope ratios of the NBS981 standard were stable during the analysis
175 session [$n = 50$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.6998 \pm 0.0027$ (2σ), $^{207}\text{Pb}/^{204}\text{Pb} = 15.4930 \pm 0.0010$ (2σ), $^{206}\text{Pb}/^{204}\text{Pb} =$
176 16.9376 ± 0.0010 (2σ)]. The Pb isotope ratios of standard measurements are consistent with the
177 recommended values and are in agreement with the laboratory long term values ($^{208}\text{Pb}/^{204}\text{Pb}$
178 $= 36.7156 \pm 0.089$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4970 \pm 0.0066$, $^{206}\text{Pb}/^{204}\text{Pb} = 16.9405 \pm 0.0037$, $n = 1630$). Mass
179 fractionation for Pb was corrected by using Tl as an internal standard.

180 3. Results

181 3.1. Chronology

182 The chronology of the Proserpine stalagmite is well established (Verheyden et al., 2006; Van
183 Rampelbergh et al, 2014). Based on the seasonal layering with deposition of one dark and one light layer
184 every year in the stalagmite we can easily count back the layers from the surface to the sedimentological
185 perturbation at ~10 cm from the top where straw was found in the stalagmite. For S1, counting back from
186 the upper layer (end 2010 AD), 145 ± 3 layer alternations are visible corresponding to the period from 1870
187 to 2010 (~upper 10 cm). The number of years obtained by layer counting is then compared with
188 the number of years suggested by U/Th dates. For S2, the age was constructed based on layer counting,
189 U/Th dates and one ¹⁴C date (Verheyden et al., 2006). Layer counting from the top (2001 AD) down to ~9

190 cm (133 ± 10 layer couples) places the restart of layering at 1870 AD above the perturbation (Fig.2). The
191 growth rate in S1 and S2 is commonly 1 mm/year. The upper 230 years (~ 10 cm) of Proserpine stalagmite
192 consist of greyish calcite (Fig. 2) because of incorporation of black carbon from torches and graphite
193 lamps used until 2001 in this touristic part of the cave. The U/Th results of the S2 core not yet published
194 are given in Table 1.

195 Table 1 gives the U/Th dating results for the candle shaped Timide stalagmite (S3). Based on the ages
196 and height of the samples that were dated, we can calculate average growth rate in mm/year. The average
197 growth rate varies throughout the core ranging from 0.03 to 0.17 mm/yr. The average growth rate in the
198 Timide stalagmite is notably highest (0.17 mm/yr) since ~ 1815 AD. The age model resolution in this
199 stalagmite (S3) is less good than those S1 and S2 because there is no visible laminae and it is not possible
200 to count them. However, the stalagmite was incorporated in this paper because a change in Pb content
201 similar to that seen in cores S1 and S2 was observed, despite the fact that S3 was collected from another
202 part of the cave.

203 **3.2. Pb and Al concentrations**

204 Lead concentrations of S1 range between 0.01 and $17 \mu\text{g g}^{-1}$, between 0.007 and $3 \mu\text{g g}^{-1}$ for S2 and
205 between 0.001 and $0.4 \mu\text{g g}^{-1}$ for S3 (Fig. 2, see supplementary data). The Pb content of core S3 is \sim ten
206 times less than in S1 and S2. Both analytical techniques used for Pb measurements in speleothem cores S1
207 (LA-ICP-MS) and S2 (ICP-MS) produced very similar results. The reproducibility of the Pb curve in
208 Proserpine stalagmite cores S1 and S2, although measured with different methods and in different cores,
209 demonstrates the robustness of the lead signal in speleothems. At approximately 1820 AD, increased Pb
210 concentrations were detected in S3 but cannot be visible in S1 and S2 because a growth hiatus of at least
211 83 years occurred from 1790 to 1870 AD in the Proserpine stalagmite. Mean Pb concentrations since 1870
212 AD are more than twice those observed before 1780 AD for the three records. Higher Pb concentrations
213 recorded in the stalagmite cores (S1, S2, and S3) are observed at depths corresponding in each stalagmite
214 to the periods from ~ 1880 to 1905 AD and from 1945 to 1965 AD, and a third Pb peak is found around
215 1980 AD in cores S1 and S2). The Pb values decrease toward the surface of S1 and S2 after 1980 and after

1995 AD for S3. Aluminum concentrations display more variability between cores than the Pb (Fig. 3). In
the lower part of S1 and S3 (from 1740 to 1780 AD) the Al concentrations averaged around $5.6 \mu\text{g g}^{-1}$ for
S1 and $56 \mu\text{g g}^{-1}$ for S3. Higher concentrations of Al in both stalagmites (S1 and S2) occurred in three
periods, around 1890 AD, from 1930 to 1940 AD and around 1980 AD. For S3, the Al concentrations
display the highest variability from 1870 to 1920 AD.

3.3. Lead isotope ratios

The Pb isotope ratios analyzed in core S1 are displayed in Table 2. In S1, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ranges
between 2.150 and 2.072 and from 1.191 to 1.108, respectively. Our data plot well on a straight line in a
 $^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$ diagram (Fig.5). This means that the data vary between the isotope field defined
by the natural sources (Upper Continental Crust and Belgian pre-industrial background) (Millot et al.
2004; Sonke et al., 2002) in the 18th century and the anthropogenic sources in the 20th century defined by
the Belgian Zn-smelter (Sonke et al., 2002, 2008), Benelux urban aerosols (Bollhöfer and Rosman, 2001),
and the Netherlands gasoline (Hopper et al., 1991).

4. Discussion

4.1. Lead mobilization from soils to speleothems

Recent studies highlight the importance of both organic and inorganic colloidal material for
transporting heavy metal from soil to cave (e.g., Borsato and al., 2007; Fairchild et al., 2010; Hartland et
al., 2012). The mobility of trace elements is mainly influenced by the soil characteristics and processes
(e.g., pH, organic acid content, redox conditions, leaching, ion exchange, temperature...etc). Metals can
be transported along the soil profile by colloids or in dissolved forms depending on the metal element
(Citeau et al. 2003; Zhao et al. 2009). Several researchers have suggested that organic matter in dissolved
or particulate form plays an important role in controlling Pb mobility in the soil (e.g., Schwab et al., 2005;
Kaste et al., 2005). The Pb might show different forms of mobility (in dissolved and particulate form) and
speeds of migration in soils, depending on soil pH and on the nature of the Dissolved Organic Carbon
(DOC) present in the percolating water (Temminghoffet al., 1998; Strobel et al., 2001; Gangloff et al.,
2014).

242 A few studies have investigated the migration of Pb from forest soil to cave (e.g.,
243 Borsato et al., 2007; Baldini et al., 2012; Fairchild et al., 2010; Hartland et al., 2012). They suggested
244 that an increased transport of Pb to the speleothem can be attributed to a combination of the effects of a
245 higher presence of mobile organic matter and higher water flow from the soil to the speleothem during
246 periods of more intense rainfall. They further suggested that when Pb is principally transported by organic
247 colloids, this would be indicated by covariation of elements that are strongly bound to colloids (such as Pb
248 and Al). In this study, there is no significant covariation between Pb and Al ($0.04 < r > 0.3$, $0.002 < R^2 > 0.08$)
249 in the 3 available records that would suggest any colloidal transport (Fig. 3). In absence of covariation
250 between Pb and Al, even if part of the Pb and Al was transported as organic matter metal complexes an
251 important part seems to have been transported in a form bound to inorganic particles. The transfer of Pb
252 signals from the forest soil to the speleothem requires further investigation, but is beyond the scope of the
253 present study.

254 **4.2. Lead content in S1, S2 and S3 speleothem cores**

255 Lead concentrations of the last 250 years in the stalagmite cores S1 and S2 display similar changes
256 with similar timing (Fig.4). The lead content of stalagmite S3 is ~ten times less than in S1 and S2. This
257 difference in Pb content between S1/S2 and S3 may be attributed to possible differences in chemical
258 composition (Pb/Ca ratio and saturation state) of the initial seepage water in the Salle du Dôme and in the
259 “Réseau renversé” respectively. Chemical monitoring of both dripping places would give more
260 information on the initial state of the water. Unfortunately the Timide (S3) dripping site is extremely
261 slowly nowadays and sampling of sufficient water for a chemical measurement has failed until now. High
262 spatial variability in trace elemental composition of seepage waters in the cave system of Han-sur-Lesse
263 was demonstrated for Mg and Sr in Verheyden et al. (2008). Other studies showed that stalagmites from a
264 same cave may exhibit different trace element patterns (Roberts et al., 1999 and Fich et al., 2003, Baldini
265 et al., 2006), suggesting that different drip sites preserve distinct components of the climate signal.
266 Therefore, a more comprehensive characterization of the spatial hydrochemical variability of several drips
267 from the same cave is essential to understand the causes for observed differences in stalagmite trace

268 element records. The two stalagmites, Proserpine (S1 and S2) and Timide (S3) have different settings and
269 are fed by different hydrological fissure systems. The Proserpine stalagmite is continuously fed by highly
270 saturated seepage water (Van Rampelbergh et al., 2014) and the presented upper 10 cm grew with a rather
271 high rate of ~0.6 mm/yr (Verheyden et al., 2006; Van Rampelbergh et al., 2014). The Timide stalagmite
272 (S3) is fed by a slow drip, and grew at 0.17 mm/year. The difference in Pb values between S1-S2 and S3
273 is most probably due to differences in the hydrological feeding system and residence time of the seepage
274 water. However, the changes observed in S3 over the last 200 years seem to roughly follow the changes
275 observed in the Proserpine stalagmite (S1 and S2 cores) with the occurrence of three periods of higher lead
276 content. The three intervals characterized by particularly high enrichment of Pb were: from 1880 to 1905
277 AD, from 1945 to 1965 AD, and from 1975 to 1990 AD. The similar timing of occurrence of higher Pb
278 content in cores S1 and S2 of the Proserpine stalagmite and in the S3 stalagmite, despite very different
279 hydrologies and locations, demonstrates the robustness of the Pb signal in a single speleothem and
280 suggests a reproducible Pb variability, but not necessarily Pb amount, in different speleothems from the
281 same cave.

282 Much lower Pb values are observed before 1760 AD in S1 and are interpreted as background values
283 from a pristine environment compared to the higher lead values after 1760 AD. Early visitors using
284 torches entered the Salle du Dôme since at least ~1700 AD (Timperman, 1989, Verheyden et al., 2006) as
285 indicated by the deposition of grey to brown calcite, but the ash from the torches likely did not affect
286 significantly the Pb record during this period. The S3 stalagmite is located in another part of the cave, cut
287 off by a siphon, preventing direct massive air exchange between both parts. If air-transported aerosols
288 were at the origin of the lead changes in the stalagmites, the Proserpine would have lower Pb content than
289 Timide because Proserpine is continuously washed by dripwater while Timide is relatively ‘dry’ with long
290 periods between two drips (slow growth) which would enable more aerosols to accumulate on the
291 stalagmite. The reproducibility of lead changes between the two stalagmites, despite being completely
292 different ‘local systems’ and with different exposure to possible direct anthropogenic contamination
293 suggests the seepage water as the main sources of the Pb in the stalagmite.

294 Speleothems display Pb enrichments (from 1880 to 1905 AD, from 1945 to 1965 AD, and from 1975
295 to 1990 AD) which seem to roughly track atmospheric lead deposition curves as documented in other
296 archives (Fig.4). Lead content in a nearby peat bog reconstructed using a core (the Misten bog core, Allan
297 et al., 2013) displays high Pb concentrations from 1770 to 1990 AD. The Misten peat bog is an
298 ombrotrophic peat, i.e. it receives input directly from the atmosphere. Therefore, the recent additional Pb,
299 found in the peat core was of atmospheric origin. This lead was demonstrated in Allan et al. (2013) to
300 have anthropogenic sources. Because of the important difference in chronological resolution of the Pb
301 values in the Misten peat bog and the studied stalagmites it is difficult to compare the two records.
302 However, the fact that higher Pb values are found in the Misten peat between 1770 and 1990,
303 demonstrates that Belgian soils received indeed more lead of anthropogenic origin during these years.
304 Despite the different sampling resolution, the correlation between Pb concentrations in stalagmite cores
305 (S1 and S2) and peat core (M1) is significant. Greenland ice (ice core ACT2) shows an increase in Pb
306 between 1880 and 1915 AD, a higher amount between 1950 and 1970 and a decrease since the 1980s
307 (Fig.4; McConnell et al., 2006). Likewise a marine record from the *sclerosponge Ceratoporella nicholsoni*
308 (Lazareth et al., 2000) showed a Pb concentration increase occurring between 1840 and 1920 AD and
309 between 1950 and 1990 AD and associated with the global anthropogenic Pb fall-out. The similarity of the
310 global atmospheric lead curves in continental (peat, ice) and marine archives and the speleothem Pb-
311 curves suggests that speleothems recorded at least partly the global anthropogenic atmospheric Pb fall-out.
312 We conclude that Pb concentrations recorded in the S1, S2 and S3 cores may reflect human activities and
313 consequent pollution over the last 250 years.

314 **4.3. The origin of the lead in the stalagmites.**

315 Several studies highlight the possible sources of metal content in speleothems, such as the chemical
316 dissolution and mobilization of elements in the soil (Blaser et al., 2000; Jo et al., 2010), or from the
317 surrounding limestone, and aerosol deposition on the stalagmite surface (Dredge et al., 2013). Cave
318 aerosols are sourced from both natural and anthropogenic processes. Aerosol deposition within the cave
319 may also influence speleothem chemistry and may have contributed significantly to speleothem trace

element concentrations at some sites (Fairchild et al., 2010). However, Dredge el al. (2013) showed that the aerosol deposition contributions to speleothem surfaces may not be sufficient to influence the speleothem chemistry in many cases. Among the 3 studied speleothem cores, S3 is more exposed to aerosols (open cave) but it contains the lower amount of Pb. The trace metal content in our speleothems is not affected by cave aerosols and more likely reflects the natural and anthropogenic metal coming from surrounding soil layers.

Lead isotope ratios are powerful tools to distinguish between natural atmospheric Pb (supplied primarily by soil dust) and Pb from anthropogenic sources (mining, metallurgical activities, and coal burning). $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are frequently used in environmental studies to track lead pollution (e.g., Bollhöfer and Rosman, 2001; Shotyk et al., 1998; Weiss et al., 1999). Natural sources of Pb over north-western Europe have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios that vary between 1.19 and 1.21 (Shotyk et al., 1998; Weiss et al., 1999). In the 20th century a significant shift in $^{207}\text{Pb}/^{206}\text{Pb}$ values was detected in European dust reflecting the strong contribution from anthropogenic sources (Pacyna and Pacyna, 2001; Pacyna et al., 2007). The largest emission of Pb during human history clearly occurred during the 20th century and especially between the 1950s and the 1980s, and is very clearly expressed in archives of past Pb pollution (e.g., Cloquet et al., 2006; Shotyk et al., 2005 Sonke et al., 2002).

Before 1800, all samples in S1 have a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio higher than 1.172. After 1880, the samples have ratios below 1.162 indicating an increased anthropogenic origin of the lead. This variety of isotopic signatures allows to distinguish the relative impact of different sources on Pb input from a specific local or regional area. To constrain the anthropogenic sources a binary diagram based on $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios was used (Fig. 5). The S1 core data plot between the isotope field defined by the Upper Continental Crust (UCC, Millot et al. 2004, through Belgian coal and ores (Cauet and Herbosh, 1982; Dejonghe, 1998) and finally toward a signature of modern Benelux urban aerosols (Bollhöfer and Rosman, 2001) and Belgian smelters (Sonke et al., 2002, 2008). Lead isotope ratios measured in stalagmite samples dated between 1750 and 1780 AD correspond to the Pb isotopic composition of the Belgian Pb-Zn ores (Durali-Mueller et al., 2007) with a minor contribution from the natural sources defined by the Upper Continental

346 Crust (Millot et al. 2004) and Belgian pre-industrial background (Sonke et al., 2002). The samples located
347 between 1880 and 1961 AD have isotope ratios close to the values of the Belgian Zn-smelter, steel plant
348 dust and Benelux aerosols. In 1961 AD, a particularly important decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios is consistent
349 with an increase in the Belgian smelter contribution and consumption of leaded gasoline inset (Fig. 5).
350 This sample has the isotope ratios nearest to the values of the Belgian Zn-smelter and Netherlands
351 gasoline (Hopper et al., 1991), which reflected the impact of leaded gasoline used in Europe. This
352 observation agrees with the observation of Von Storch et al. (2003), who proposed that Pb from
353 gasoline was the dominant anthropogenic source of Pb in 1965 AD. The use of leaded gasoline
354 increased from 1930 to a maximum in the 1970's. The progressive reduction of lead in gasoline
355 started in 1972 (Von Storch et al., 2003).

356 The samples located in the upper part of the stalagmite (1970-2004 AD) have isotope ratios close to
357 the Belgian Zn-smelter and the modern aerosols collected above Benelux and Germany. Our results are
358 consistent with previous data recorded in the Misten peat bog core (Allan et al., 2013- Fig. 5). In Misten
359 core (M1), $^{206}\text{Pb}/^{207}\text{Pb}$ ratios decreased from 1.175 to 1.155 (between 1748 and 1953 AD) corresponding
360 to the isotopic fields representing Belgian coal and Pb-Zn ores. The sample located in the upper part of the
361 Misten core (1969-1977) has isotope ratios nearest to the values of the Belgian Zn-smelter and Benelux
362 aerosols. The youngest samples (from 1994 to 2007 AD) are characterized by an increase in isotopic ratios
363 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (from 1.151 to 1.169). This increase is linked to the increased Belgian smelter and
364 refinery activity during that period. The Pb isotope ratios of this study strongly suggest that the Han-sur-
365 Lesse stalagmites are influenced by a mixture of local and regional anthropogenic Pb sources, and track
366 increases in anthropogenic Pb pollution through time..

367 **4.4. Human activity and Pb atmospheric pollution records**

368 Following the advent of the Industrial Revolution in the mid-1700s, anthropogenic emissions of trace
369 elements (e.g., Pb) to the atmosphere largely dominated the natural inputs (e.g., Nriagu, 1989). Trace
370 metal concentrations in the Han-sur-Lesse cave stalagmites increase markedly in calcite deposited after

371 1880 AD, and this increase is indirectly attributable to increased anthropogenic trace element emissions at
372 both regional and global scales. These Pb/Al profiles are similar to those observed in the Misten peat bog
373 core (Fig. 6; Allan et al., 2013).

374 Around 1770 AD, the Pb/Al values in S1 begin to increase, synchronous with a decrease in $^{206}\text{Pb}/^{207}\text{Pb}$
375 ratios, and reach high values between 1770 and 1790 AD. This trend is attributable to the Industrial
376 Revolution (Fig. 6). From 1880 to 1907 AD, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio shows lower values ($^{206}\text{Pb}/^{207}\text{Pb}$ up to
377 1.139 at 1883 and to 1.152 at 1907 AD) reflecting an increase in Pb/Al values in all stalagmite cores,
378 which is probably the result of the inception of the Belgian metal industry (Pb at around 1830) (Dejonghe,
379 1998; Schmitz, 1979). Coal production started in Belgium in 1830 AD (Rutledge, 2011) and increased
380 significantly to reach its maximum (~ 30 million metric tons yr^{-1}) between 1927 and 1955 AD. During
381 WWI and WWII, the cave was closed, explaining the whiter calcite deposited around 1917 AD and
382 between 1940 and 1945 AD (Fig. 2).

383 Since 1945 AD, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios drop towards 1.107 (1961 AD) reflecting increasing gasoline Pb
384 contributions. The maximum Pb/Al values (between 1945 and 1990 AD) reflect peak Belgian smelter and
385 refinery activity (Schmitz, 1979; USGS). The maximum anthropogenic emissions of Pb occurred between
386 1955 and 1990 AD (Fig.6- Nriagu, 1996) and varied between 3600 and 4800 metric tons per year (p.a.) in
387 Belgium (Von Storch et al., 2003), while coal consumption was at its maximum in Europe. This
388 substantial increase in atmospheric pollution is recorded in Han-sur-Lesse stalagmites as increased Pb/Al
389 values, associated with a small decrease of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.157).

390 The samples located in the upper part of the core S1 (1995-2004) have isotope ratios nearest to the values
391 of the steel plant dust and Benelux aerosols. The Pb/Al values in S1 decrease from 1995 to the date of
392 sampling of 2011, coincident with increasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, consistent with results obtained from
393 Misten bog (Allan et al., 2013). This reduction in trace element pollution reflects progressive phasing out
394 of coal combustion in Belgium, decreases in global emission of heavy metals and also results from the
395 disappearance of leaded gasoline. However, despite the reduction of atmospheric pollution during recent
396 years, the dominant sources of trace metals measured in our stalagmites remain anthropogenic.

397 **5. Conclusion**

398 High resolution records of Pb concentrations coupled with Pb isotope ratios from the Han-sur-Lesse
399 cave stalagmites in southern Belgium provide a record of changing inputs of trace elements to the region
400 over the last 250 years. The geochemical results presented here recorded natural processes prior to the
401 Industrial Revolution, but have since predominantly reflected shifting sources of anthropogenic pollution.
402 Intervals characterised by Pb enrichment exist in the speleothems and represent the intervals from 1880 to
403 1905 AD, from 1945 to 1965 AD, and from 1975 to 1990 AD. Lead isotope ratios indicate diverse sources
404 of atmospheric contamination (coal, industrial, steel production, road dust) which change through time.
405 The history of Pb pollution revealed by both Han-sur-Lesse speleothems shows some agreement with
406 other Pb records, and clearly reflects the increasing influence of atmospheric metal pollution since the
407 advent of the Industrial Revolution. These changes confirm that stalagmites are sensitive to external
408 anthropogenic atmospheric pollution. This paper therefore highlights their potential as an alternative
409 archive in continental settings to reconstruct atmospheric contamination, e.g., pollution, volcanic fall-out,
410 dust deposits, with an accurate time frame based on independent chronological tracers (U/Th, ^{14}C , and
411 lamination). This research underscores the importance of speleothems as a valuable tool for the
412 discrimination between anthropogenic and natural lead contributions in the environment and consequently
413 for quantifying the anthropogenic contribution or determining natural background values

414

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699 **Figure captions**

- 700 1: A-Map of Belgium, displaying sample sites (black dot) for Han-sur-Lesse cave and Mistenpeatbog. B-
- 701 Map of the Han-sur-Lesse cave system, from which Proserpine 2010 (S1), Proserpine 2001 (S2) and La
- 702 Timide (S3) stalagmite cores were collected.
- 703 2: Profiles of Pb (dark blue curve; in $\mu\text{g g}^{-1}$) vs core depth (in mm) measured in three stalagmite cores (S1,
- 704 S2 from the Proserpine stalagmite and S3 from the La Timide stalagmite). Light blue color corresponds
- 705 to the upper 4 cm of the S1 core, for which Pb concentrations were measured by LA-ICP-MS operated
- 706 in continuous mode with a scan speed of $10\text{-}30 \mu\text{m s}^{-1}$ with $22 \mu\text{m}$ intervals between measurements.
- 707 The red stars represent the levels which have been dated by U series techniques. Straw found in core
- 708 S2 at the level corresponding to a sedimentary hiatus was dated by ^{14}C .
- 709 3: Pb and Al concentrations ($\mu\text{g g}^{-1}$) vs age in S1, S2 and S3 stalagmites.
- 710 4: The correlation of Pb concentration profiles recorded from the three stalagmite cores (S1, S2 and S3),
- 711 Misten peat bog core (M1) from Belgium (Allan et al., 2013), and ice core (ACT2) from Greenland
- 712 (McConnell et al., 2006). The three light-gray bars show the maximum concentrations of Pb.
- 713 5: $^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$ ratios with composition fields of different possible source materials. The age
- 714 plotted presents the mean age of the interval from which the sample was taken. Stalagmite samples (red
- 715 dots), Misten bog (blue dots), Upper Continental Crust from Millot et al., (2004), Belgian pre-
- 716 industrial sediment from Sonke et al. (2002), Belgian coal and ores (blue and black diamond) from
- 717 Cauet and Herbosh (1982), Dejonghe (1998), Benelux urban aerosols from Bollhöfer and Rosman
- 718 (2001) and Belgian smelter (orange squares) from Sonke et al., (2008). The signature for steel plant
- 719 dust (grey triangles – data from Geagea et al., 2007), French diesel and gasoline (green squares - from
- 720 Geagea et al., 2008), and Netherlands gasoline (Hopper et al., 1991) are plotted for comparison.
- 721 6: Comparison between the Pb/Al ratio in all stalagmites cores and M1 peat core, Pb isotopic record in S1
- 722 and M1 with the Belgian production of coal (Rutledge, 2011), smelter and refinery production (Pb) in
- 723 Belgium (Rutledge, 2011), and with global production and emissions of Pb (Nriagu, 1996; USGS).

724

725 **Table captions**

726 1: Mass spectrometric U-Th age data for speleothems from Han-sur-Lesse cave. Decay constants used to
727 calculate activity ratios from measured atomic ratios are as follows; $\lambda^{238}\text{U}=1.551*10^{-10}$, $\lambda^{234}\text{U} =$
728 $2.835*10^{-6}$, $\lambda^{230}\text{Th} = 9.915*10^{-6}$, $\lambda^{232}\text{Th} = 4.948*10^{-11}$. Age uncertainties are reported at the 2σ level. The
729 U-Th age data for S2 is given in Verheyden et al. (2006) and Van Rampelbergh et al. (2014).

730 2: Pb isotopic ratios measured in S1 by MC-ICP-MS Nu Plasma and standard deviations.

731 **Supplementary data**

732 S1-1 : Sample depth, age, geochemical elementary content (Al and Pb) measured in core S1. Spots were
733 made of 50 μm diameter (spaced at 500-1000 μm intervals).

734 S1-2: Sample depth, age, geochemical elementary content (Al and Pb) measured in core S1. The upper 4
735 cm were duplicated by continuous ablation with a scan speed of 10-30 $\mu\text{m s}^{-1}$ with 22 μm intervals
736 between two measurement

737 S2 : Sample depth, age , geochemical elementary content (Al and Pb) measured in core S2.

738 S3 : Sample depth, age, geochemical elementary content (Al and Pb) measured in core S3.

739