

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 (Drysedale 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 (Manginiet 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, ²⁰⁸Pb/²⁰⁴Pb = 36.6998 ± 0.0027 (2 σ), ²⁰⁷Pb/²⁰⁴Pb = 15.4930 ± 0.0010 (2σ), ²⁰⁶Pb/²⁰⁴Pb =
176 16.9376 ± 0.0010 (2 σ)]. The Pb isotope ratios of standard measurements are consistent with the
177 recommended values and are in agreement with the laboratory long term values (²⁰⁸Pb/²⁰⁴Pb
178 = 36.7156 ± 0.089, ²⁰⁷Pb/²⁰⁴Pb = 15.4970 ± 0.0066, ²⁰⁶Pb/²⁰⁴Pb = 16.9405 ± 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 ~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

216 1995 AD for S3. Aluminum concentrations display more variability between cores than the Pb (Fig. 3). In
217 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
218 S1 and $56 \mu\text{g g}^{-1}$ for S3. Higher concentrations of Al in both stalagmites (S1 and S2) occurred in three
219 periods, around 1890 AD, from 1930 to 1940 AD and around 1980 AD. For S3, the Al concentrations
220 display the highest variability from 1870 to 1920 AD.

221 **3.3. Lead isotope ratios**

222 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
223 between 2.150 and 2.072 and from 1.191 to 1.108, respectively. Our data plot well on a straight line in a
224 $^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$ diagram (Fig.5). This means that the data vary between the isotope field defined
225 by the natural sources (Upper Continental Crust and Belgian pre-industrial background) (Millot et al.
226 2004; Sonke et al., 2002) in the 18th century and the anthropogenic sources in the 20th century defined by
227 the Belgian Zn-smelter (Sonke et al., 2002, 2008), Benelux urban aerosols (Bollhöfer and Rosman, 2001),
228 and the Netherlands gasoline (Hopper et al., 1991).

229 **4. Discussion**

230 **4.1. Lead mobilization from soils to speleothems**

231 Recent studies highlight the importance of both organic and inorganic colloidal material for
232 transporting heavy metal from soil to cave (e.g., Borsato and al., 2007; Fairchild et al., 2010; Hartland et
233 al., 2012). The mobility of trace elements is mainly influenced by the soil characteristics and processes
234 (e.g., pH, organic acid content, redox conditions, leaching, ion exchange, temperature...etc). Metals can
235 be transported along the soil profile by colloids or in dissolved forms depending on the metal element
236 (Citeau et al. 2003; Zhao et al. 2009). Several researchers have suggested that organic matter in dissolved
237 or particulate form plays an important role in controlling Pb mobility in the soil (e.g., Schwab et al., 2005;
238 Kaste et al., 2005). The Pb might show different forms of mobility (in dissolved and particulate form) and
239 speeds of migration in soils, depending on soil pH and on the nature of the Dissolved Organic Carbon
240 (DOC) present in the percolating water (Temminghoff et al., 1998; Strobel et al., 2001; Gangloff et al.,
241 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

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

326 Lead isotope ratios are powerful tools to distinguish between natural atmospheric Pb (supplied
327 primarily by soil dust) and Pb from anthropogenic sources (mining, metallurgical activities, and coal
328 burning). $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are frequently used in environmental studies to track lead pollution (e.g.,
329 Bollhöfer and Rosman, 2001; Shotyk et al., 1998; Weiss et al., 1999). Natural sources of Pb over north-
330 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.,
331 1999). In the 20th century a significant shift in $^{207}\text{Pb}/^{206}\text{Pb}$ values was detected in European dust reflecting
332 the strong contribution from anthropogenic sources (Pacyna and Pacyna, 2001; Pacyna et al., 2007). The
333 largest emission of Pb during human history clearly occurred during the 20th century and especially
334 between the 1950s and the 1980s, and is very clearly expressed in archives of past Pb pollution (e.g.,
335 Cloquet et al., 2006; Shotyk et al., 2005; Sonke et al., 2002).

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

346 Crust (Milot 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

415 **Acknowledgments**

416 We thank all the persons who contribute to this work and especially Jacque Navez, Laurence
417 Monin from (LA-ICP-MS analyses), Nadine Mattielli and Ivan Petrov at ULB (MC-ICP-MS analyses),
418 and Dr Chris Ottley at Durham (ICP-MS analyses). This study was funded by the Walloon Region and the
419 FNRS. M. Allan received funding through a PhD grant from the government of Syria and Erasmus
420 Mundus EPIC. Thanks to the personal of Han-sur-Lesse caves and especially to Mme Malou, Guy Evrard
421 and the guide Etienne Lannoye for their help during sampling. The manuscript has been improved by the
422 constructive comments of the reviewers and by the editor, Dr. L Reisberg.

423 **References**

- 424 Allan, M., Le Roux, G., De Vleeschouwer, F., Mattielli, N., Piotrowska, N., Sikorski, J., Fagel, N., 2013.
425 Reconstructing historical atmospheric mercury deposition in Western Europe using: Misten peat bog
426 cores, Belgium. *Environ. Pollut.* 178, 381-394.
- 427 Baker, A., Ito, E., Smart, P.L. and McEwan, R.F., 1997. Elevated and variable values of C-13 in
428 speleothems in a British cave system. *Chem. Geol.* 136, 263-270
- 429 Baldini, J., McDermott, F., and Fairchild, I., 2006. Spatial variability in cave drip water hydrochemistry:
430 implications for stalagmite paleoclimate records. *Chem. Geol.* 235, 390–404.
- 431 Baidini, J.U.L., McDermott, F., Hoffmann, D.L., Richards, D.A. and Clipson, N., 2008. Very high-
432 frequency and seasonal cave atmosphere P-CO₂ variability: Implications for stalagmite growth and
433 oxygen isotope-based paleoclimate records. *Earth Planet. Sci. Lett.* 272, 118-129.
- 434 Baldini, J.U.L., McDermott, F., Baldini, L.M., Ottley, C.J., Linge, K.L., Clipson, N. & Jarvis, K.E., 2012.
435 Identifying short-term and seasonal trends in cave drip water trace element concentrations based on a
436 daily-scale automatically collected drip water dataset. *Chem. Geol.* 330-331, 1-16.
- 437 Balswin, M., and Frappier, A.B., 2008. Toward speleothem tephrochronology: Experimental simulation of
438 volcanic ash weathering in a karst setting. American Geophysical Union, Fall Meeting 2008, abstract
439 #V11C-2075.
- 440 Bastin N. and Dulière J., 1995. Les Grottes de Han S.A., 100 ans. Press Bourdeau-Capelle, Dinant,
441 Belgium, 79p.
- 442 Blaser, P., Zimmermann, S., Luster, J., and Shotyk, W., 2000. Critical examination of trace element
443 enrichments and depletion in soils: As, Cr, Cu, Ni, Pb and Zn in Swiss forest soils. *Sci. Total Environ.*
444 249, 257–280.
- 445 Borsato, A., Frisia, S., Fairchild, I.J., Somogyi, A., Susini, J., 2007. Trace element distribution in
446 annual stalagmite laminae mapped by micrometer-resolution X- ray fluorescence: Implications for
447 incorporation of environmentally significant species. *Geochim.Cosmochim.Acta* 71, 1494–1512.
- 448 Bollhöfer, A., Rosman, K.J.R., 2001. Lead isotopic ratios in European atmospheric aerosols. *Phys. Chem.*
449 *Earth. Pt. B.* 26(10), 835-838.
- 450 Bonniver, I., 2011. Etude hydrogéologique et dimensionnement par modélisation du système traçage du
451 réseau karstique de Han-sur-Lesse (Massif de Boine – Belgique). Faculté des Sciences, Département de
452 Géologie, Faculté Notre-Dame de Namur (FUNDP), unpublished PhD thesis. 349p.
- 453 Boutron, C. F., Görlach, U., Candelone, J. P., Bolshov, M. A., Delmas, R. J., 1991. Decrease in
454 anthropogenic lead, cadmium and zinc in Greenland snows since the late 1960s. *Nature* 353, 153–156.

455 Boutron, C. F., Candelone, J. P., Hong, S., 1994. Past and recent changes in the large scale tropospheric
456 cycles of lead and other heavy metals as documented in Antarctic and Greenland snow and ice: a
457 review. *Geochim.Cosmochim.Acta.* 58, 3217–3225.

458 Brännvall, M.-L., Bindler, R., Renberg, I., Emteryd, O., Bartnicki, J., Billström, K., 1999. The medieval
459 metal industry was the cradle of modern large-scale atmospheric lead pollution in northern Europe.
460 *Environ. Sci. Technol.* 33, 4391–4395.

461 Bronk Ramsey, C., 2001. Development of the Radiocarbon Program OxCal. *Radiocarbon*, 43 (2A),
462 355-363.

463 Candelone, J.P., Hong, S., Pellone, C., Boutron, C.F., 1995. Post-industrial revolution changes in large-
464 scale atmospheric pollution of the northern hemisphere by heavy metals as documented in central
465 Greenland snow. *J. Geophys. Res.* 100,107-128.

466 Cauet, S.W.D., Herbosh, A., 1982. Genetic study of Belgian lead zinc mineralizations in carbonate
467 environments through lead isotope geochemistry. *Bulletin du BRGM* 3, 29-41.

468 Chang, S.J., Jeong, G.Y., Kim, S.J. 2008. The origin of black carbon on speleothems in tourist caves in
469 South Korea: chemical characterization and source discrimination by radiocarbon measurement.
470 *Atmos. Environ.* 42, 1790-1800.

471 Cheng, H., Edwards, R.L., Hoff, J., Gallup, C.D., Richards, D.A., Asmerom, Y., 2000. The half-lives of
472 uranium-234 and thorium-230. *Chem. Geol.* 169, 17-33.

473 Cheng, H., Edwards, R.L., Broecker, W.S., Denton, G.H., Kong, X., Wang, Y., Zhang, R., Wang, X.,
474 2009a. Ice Age terminations. *Science* 326, 248-252.

475 Cheng, H., Fleitmann, D., Edwards, R.L., Wang, X.F., Cruz, F.W., Auler, A.S., Mangini, A., Wang,
476 Y.J., Kong, X.G., Burns, S.J., Matter, A., 2009b. Timing and structure of the 8.2 kyr BP event inferred
477 from delta O-18 records of stalagmites from China, Oman, and Brazil. *Geology* 37, 1007-1010.

478 Chester, R., Stoner, J.H., 1973. Pb in particulates from the lower atmosphere of the eastern Atlantic.
479 *Nature* 245, 27–8.

480 Citeau, L., Lamy, I., van Oort, F., Elsass, F., 2003. Colloidal facilitated transfer of metals in soils under
481 different land use. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 217, 11-19.

482 Cloquet, C., Carignan, J., Libourel, G., 2006. Atmospheric pollutant dispersion around an urban area using
483 trace metal concentrations and Pb isotopic compositions in epiphytic lichens. *Atmos. Environ.* 40 (3),
484 574-587.

485 Deflandre, G., Bastin, B., Quinif, Y., Gewalt, M., 1987. La grotte du Père Noël. *Colloque International*
486 *de Sédimentologie karstique, Livret Guide des Excursions:* 37-44.

487 Dejonghe, L., 1998. Zinc-lead deposits of Belgium. *Ore Geol. Rev.* 12, 329-354.

488 Delvaux de Fenffe, D., 1985. Géologie et Tectonique du parc de Lesse et Lomme au bord sud du
489 Bassin de Dinant (Rocheftort, Belgique). Bull. de la Soc. Belge de Géologie, 94 (1), 81-95.

490 Dredge, J., Fairchild, I.J., Harrison, R.M., Fernandez-Cortes, A., Sanchez-Moral, S., Jurado, V., Gunn, J.,
491 Smith, A., Spoetl, C., Matthey, D., Wynn, P.M., Nathalie G., 2013. Cave aerosols: distribution and
492 contribution to speleothem geochemistry. Quaternary Sci. Rev. 63, 23-41.

493 Drysdale, R. N., Hellstrom, J. C., Zanchetta, G., Fallick, A. E., Sanchez Go ´ ni, M. F., Couchoud, I.,
494 McDonald, J., Maas, R., Lohmann, G., and Isola, I., 2009. Evidence for obliquity forcing of Glacial
495 termination II. Science 325, 1527–1531.

496 Durali-mueller, S., Grey, G.P., Wigg-Wolf, D., Lahaye, Y., 2007. Roman lead mining in Germany: its
497 origin and development through time deduced from lead isotope provenance studies. J. Archeol. Sci. 34,
498 1555-1567.

499 Edwards, R.L., Chen, J.H., Wasserburg, G.J., 1987. ^{238}U - ^{234}U - ^{230}Th - ^{232}Th systematic and the precise
500 measurement of time over the past 500 000 years. Earth Planet. Sci. Lett. 81, 175-192.

501 Edwards, R.L., Gallup, C.D., Cheng, H., 2003. Uranium-series dating of marine and lacustrine carbonates,
502 In: Bourdon, B., Henderson, G.M., Lundstrom, C.C., Turner, S.P., Uranium-series Geochemistry.
503 Washington, DC (Mineralogical Society of America), pp. 363-405

504 Elless, M.P., Lee, S.Y., 1998. Uranium solubility of carbonate-rich uranium-contaminated soils. Water Air
505 Soil Pollut. 107, 147–162.

506 Fairchild, I. J., Baker, A., Borsato, A., Frisia, S., Hinton, R. W., McDermott, F., & Tooth, A. F., 2001.
507 Annual to sub-annual resolution of multiple trace-element trends in speleothems. J. Geol. Soc. 158(5),
508 831–841.

509 Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Matthey, D., McDermott, F., E.I.M.F.,
510 2006. Modification and preservation of environmental signals in speleothems. Earth Sci.Rev. 75 (1–4),
511 105–153.

512 Fairchild, I.J., Treble, P.C., 2009. Trace elements in speleothems as recorders of environmental change
513 Quaternary Sci. Rev. 28 (5-6), 449-468.

514 Fairchild IJ., Spötl, C., Frisia, C., Borsato, A., Susini, J., Wynn P.M., Causid, J., and EIMF 2010.
515 Petrology and geochemistry of annually laminated stalagmites from an Alpine cave (Obir, Austria):
516 seasonal cave physiology. Geological Society of London Special Publication, 336, 295-321.

517 Fleitmann, D., Burns, S.J., Neff, U., Mudelsee, M., Mangini, A., Matter, A., 2004. Palaeoclimatic
518 interpretation of high-resolution oxygen isotope profiles derived from annually laminated speleothems
519 from Southern Oman. Quaternary Sci. Rev. 23, 935-945.

520 Fleitmann, D., Borsato, A., Frisia S., Badertscher, S., Cheng, H., REwards, L., Tüysüz, O., 2012.
521 Speleothems as sensitive recorders of volcanic eruptions – the Bronze Age Minoan eruption recorded

522 in a stalagmite from Turkey. EGU General Assembly 2012, held 22-27 April, 2012 in Vienna, Austria.,
523 p.9293.

524 Finch, A., Shaw, P., Holmgren, K. and Lee-Thorp, J., 2003. Corroborated rainfall records from aragonitic
525 stalagmites. *Earth Planet. Sci. Lett.* 215, 265–273.

526 Frisia, S., Borsato, A., Fairchild, I.J., Susini, J., 2005. Variations in atmospheric sulphate recorded in
527 stalagmites by synchrotron micro-XRF and XANES analyses. *Earth Planet. Sci. Lett.* 235, 729–740.

528 Gangloff, S., Stille, P., Pierette, M.C., Weber, T., Chabaux, F., 2014. Characterization and evolution of
529 dissolved organic matter in acidic forest soil and its impact on the mobility of major and trace elements
530 (case of the Strengbach watershed). *Geochim. Cosmochim. Acta.* 130, 21–41.

531 Geagea, M.L., Stille, P., Millet, M., Perrone, T., 2007. REE characteristics and Pb, Sr and Nd isotopic
532 compositions of steel plant emissions. *Sci. Total Environ.* 373, 404–419.

533 Geagea, M.L., Stille, P., Gauthier-Lafaye, F., Millet, M., 2008. Tracing of Industrial Aerosol Sources in an
534 Urban Environment Using Pb, Sr, and Nd Isotopes. *Environ. Sci. Technol.* 42, 692–698.

535 Genty, D., and Massault, M., 1999. Carbon transfer dynamics from bomb-14C and d13C time series of a
536 laminated stalagmite from SW-France—Modelling and comparison with other stalagmite. *Geochim.*
537 *Cosmochim. Acta.* 63, 1537–1548.

538 Genty, D., Blamart, D., Ghaleb, B., Plagnes, V., Causse, C.h., Bakalowicz, M., Zouari, K., Chkir, N.,
539 Hellstrom, J., Wainer, K., Bourges, F., 2006. Timing and dynamics of the last deglaciation from
540 European and North African d 13 C stalagmite profiles—comparison with Chinese and South
541 Hemisphere stalagmites. *Quaternary Sci. Rev.* 25, 2118–2142.

542 Genty, D., Blamart, D., Ouahdi, R., Gilmour, M., Baker, A., Jouzel, J., Van- Exter, S., 2003. Precise
543 dating of Dansgaard–Oeschger climate oscillations in western Europe from stalagmite data. *Nature*
544 421, 833–837.

545 Goede, A., McCulloch, M., McDermott, F., Hawkesworth, Ch., 1998. Aeolian contribution to strontium and
546 strontium isotope variations in a Tasmanian speleothem. *Chem. Geol.* 149, 37–50.

547 Gobeil, C., Macdonald, R.W., Smith, J.N., 1999. Mercury profiles in sediments of the Arctic Ocean
548 basins. *Environ. Sci. Technol.* 33, 4194–4198.

549 Hartland, A., Fairchild, I.J., Lead, J.R., Zhang, H., Baalousha, M., 2011. Size, speciation and lability of
550 NOM-metal complexes in hyper alkaline cave dripwater. *Geochim. Cosmochim. Acta.* 75, 7533–7551.

551 Hartland, A., Fairchild, I.J., Lead, J.R., Borsato, A., Baker, A., Frisia, S., Baalousha, M., 2012. From soil
552 to cave: Transport of trace metals by natural organic matter in dripwaters. *Chemical Geol.* 304, 68 – 82.

553 Hellstrom, J., McCulloch, M., Stone, J., 1998. A detailed 31,000 year record of climate and vegetation
554 change, from the isotope geochemistry of two New Zealand speleothems. *Quatern. Sci.* 50, 167–178.

555 Hong, S.M., Candelone, J.P., Patterson, C.C., Boutron, C.F., 1994. Greenland ice evidence of hemispheric
556 lead pollution two millennia ago by Greek and Roman civilizations. *Science* 265, 1841-1843.

557 Hopper, J.F., Ross, H.B., Sturges, W.T., Barrie, L.A., 1991. Regional source discrimination of
558 atmospheric aerosols in Europe using the isotopic composition of lead. *Tellus* 43B, 45–60.

559 Jo, K.N., Woo, K.S., Hong, G.H., Kim, S.H., Suk, B.C., 2010. Rainfall and hydrological controls on
560 speleothem geochemistry during climatic events (droughts and typhoons): an example from Seopdong
561 Cave, Republic of Korea. *Earth Planet. Sci. Lett.* 295 (3–4), 441–450.

562 Kaste, J. M., Friedland, A. J., Stürup S., 2003. Using stable and radioactive isotopes to trace
563 atmospherically deposited Pb in montane forest soils. *Environ. Sci. Technol.* 37, 2560-2567.

564 Kaufman, A., Wasserburg, G.J., Porcelli, D., Bar-Matthews, M., Ayalon, A., Halicz, L., 1998. U-Thisotope
565 systematics from the Soreq Cave, Israel, and climatic correlations. *Earth Planet. Sci. Lett.* 156, 141–
566 155.

567 Lazareth, C. E., Willenz, P., Navez, J., Keppens, E., Dehairs, F., André, L., 2000. Sclerosponges as a new
568 potential recorder of environmental changes: Lead in *Ceratoporell anicholsoni*. *Geology* 28(6), 515-
569 518.

570 Li, W. X., Lundberg, J., Dickin, A. P., Ford, D. C., Schwarcz, H. P., McNutt, R. H. and Williams, D.
571 1989. High-precision mass-spectrometric uranium-series dating of cave deposits and implications for
572 palaeoclimate studies. *Nature* 339- 534.

573 Lundberg, J., Ford, D.C., Hill, C.A., 2000. A preliminary U-Pb date on cave spar, Big Canyon, Guadalupe
574 Mountains, New Mexico, USA. *J. Cave Karst Stud.* 62, 144-148.

575 Mangini, A., Spötl, C. and Verdes, P., 2005. Reconstruction of temperature in the Central Alps during the
576 past 2000 yr from a delta O18 stalagmite record. *Earth Planet. Sci. Lett.* 235, 741-751.

577 Matthey, D. et al., 2008. A 53 year seasonally resolved oxygen and carbon isotope record from a modern
578 Gibraltar speleothem: Reconstructed drip water and relationship to local precipitation. *Earth Planet. Sci.*
579 *Lett.* 269, 80-95.

580 McConnell, J. R., Kipfstuhl, S. and Fischer, H., 2006. The NGT and PARCA shallow ice core arrays in
581 Greenland: A brief overview, *PAGES news*, 14 (1), 13-14.

582 McDermott, F., 2004. Palaeo-climate reconstruction from stable isotope variations in speleothems: a
583 review. *Quaternary Sci. Rev.* 23, 901–918.

584 McDermott, F., Atkinson, T.C., Fairchild, I.J., Baldini, L.M., Matthey, D.P., 2011. A first evaluation of the
585 spatial gradients in $\delta^{18}\text{O}$ recorded by European Holocene speleothems. *Global Planet Chang.* 79, 275-
586 287.

587 McFarlane, D.A., Lundberg, J., Neff, H., 2013. A Speleothem Record of Early British and Roman Mining
588 at Charterhouse, Mendip, England. *Archaeometry*. 2013. DOI: 10.1111/arc.12025.

589 McMillan, E.A., Fairchild, I.J., Frisia, S., Borsato, A., McDermott, F., 2005. Annual trace element cycles
590 in calcite-aragonite speleothems: evidence of drought in the western Mediterranean 1200-1100 yr BP.
591 J.Quater. Sci. 20,423-433.

592 Millot, R., Allègre, C.J., Gaillardet, J., Roy, S., 2004. Lead isotopic systematics of major river sediments:
593 a new estimate of the Pb isotopic composition of the Upper Continental Crust. Chem. Geol. 203, 75-
594 90.

595 Nriagu, J .O., 1989. A global assessment of natural sources of atmospheric trace metals. Nature 338, 47-
596 49.

597 Nriagu, J .O., 1996.A history of global metal pollution. *Science* 272 (5259), 223-224.

598 Outridge, P.M., Rausch, N., Percival, J.B., Shotyk, W., a McNeely, R., 2011. Comparison of mercury and
599 zinc profiles in peat and lake sediment archives with historical changes in emissions from the FlinFlon
600 metal smelter, Manitoba, Canada. Sci. Total Environ. 409, 548-563.

601 Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the
602 atmosphere from anthropogenic sources worldwide. Environ. Rev. 9, 269-298.

603 Pacyna, E.G., Pacyna, J.M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., Panasiuk, D.,
604 Nitter, S., Pregger, T., Pfeiffer, H., Friedrich, R., 2007. Current and future emissions of selected heavy
605 metals to the atmosphere from anthropogenic sources in Europe. Atmos. Environ. 41, 8557-8566.

606 Perrette, Y., 2000. Etude de la structure interne des stalagmites : contribution à la connaissance
607 géographique des évolutions environnementales du Vercors (France). Unpublished PhD thesis, Univ.
608 De Savoie, Géographie, France. 277pp.

609 Quinif, Y., Bastin, B., 1986. Le système karstique de Han-sur-Lesse (Belgique). Actes 9 ièmeCong. Int.
610 Espeleol., Barcelona 1, 147-161.

611 Richard, D.A., Dorale, J.A., 2003. Uranium-series chronology and environmental applications of
612 speleothem, In: Bourdon, B., Henderson, G.M., Lundstrom, C.C., Turner, S.P. (Eds.), Uranium-series
613 Geochemistry. Reviews Mineralogy and Geochemistry 52, pp. 407–460.

614 Roberts, M., Smart, P., Hawkesworth, C., Perkins, W. and Pearce, N., 1999. Trace element variations in
615 coeval Holocene speleothems from GB Cave, southwest England. Holocene 9, 707–713.

616 Rosman, K.J.R., Chisholm, W., Hong, S.M., Candelone, J.P., Boutron, C.F., 1997. Lead from
617 Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 BC to
618 300 AD. Environ. Sci. Technol. 31, 3413–3416.

619 Rutledge, D., 2011. Estimating long-term world coal production with logit and probit transforms. Int. J.
620 Coal Geol.85, 23–31.

621 Sánchez-Moral, S., Soler V., Cañaveras, J.C., Sanz-Rubio, E., Van Grieken, R., Gysels, K., 1999.
622 Inorganic deterioration affecting the Altamira Cave, N Spain: quantitative approach to wall-corrosion
623 (solutional etching) processes induced by visitors. *Sci. Total Environ.* 243/244, 67-84.

624 Schmitz, C., 1979. *World Non-Ferrous Metal Production and Prices.1700-1976.* Routledge Chapman and
625 Hall.

626 Schwab, A.P.,Yinghong, H., Banks, M.K., 2005. The influence of organic ligands on the retention of lead
627 in soil. *Chemosphere*61, 856-866.

628 Shirahata, H., Elias, R.W., Patterson, C.C., 1980. Chronological variations in concentrations and isotopic
629 compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond.*Geochim.*
630 *Cosmochim. Acta* 44, 149–162.

631 Shotyky, W., Blaser, P., Grünig, A., Cheburkin, A.K., 2000. A new approach for quantifying cumulative,
632 anthropogenic, atmospheric lead deposition using peat cores from bogs: Pb in eight Swiss peat
633 bog profiles. *Sci.Total Environ.* 249 (1-3), 281-295.

634 Shotyky, W., Goodsite, M.E., Roos-Barraclough, F., Givélet, N., Le Roux, G., Weiss, D., Chemburkin,
635 A.K., Knudsen, K., Heinemeier, J., Van Der Knaap, W.O., Norton, S.A., Lohse, C., 2005.
636 Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on
637 the Faroe Islands.*Geochim.Cosmochim.Ac.* 69(1), 1-17.

638 Siklosy, Z., Kern, Z., Demeny, A., Pilet, S., Leel-Ossy, S., Lin, K., Shen, C.C., Szeles, E., Breitner, D.,
639 2011. Speleothems and pine trees as sensitive indicators of environmental pollution—A case study of
640 the effect of uranium-ore mining in Hungary. *Appl. Geochem.* 26, 666–678.

641 Sonke, J.E., Hoogewerf, J.A., van der Laan, S.R., Vangronsveld, J.A., 2002. Chemical and mineralogical
642 reconstruction of Zn-smelter emissions in the Kempen region (Belgium), based on organic pool
643 sediment cores. *Sci. Total Environ.* 292, 101–19.

644 Sonke, J.E., Sivry Y., Viers, J., Freydier, R., Dejonghe, L., Andre, L., Aggarwal, J.K., Fontan, F., Dupre,
645 B., 2008. Historical variations in the isotopic composition of atmospheric zinc deposition from a zinc
646 smelter. *Chem. Geol.* 252,145–157.

647 Strobel, B.W., Hansen, H.C.B., Borggaard, O.K., Andersen,M.K., Raulund-Rasmussen, K., 2001.
648 Composition and reactivity of DOC in forest floor soil solutions in relation totree species and soil type.
649 *Biogeochemistry* 56, 1–26.

650 Temminghoff, E.J.M., Van der Zee, S.E.A.T.M., De Haan,F.A.M., 1998. Effects of dissolved organic
651 matter on themobility of copper in a contaminated sandy soil. *Eur. J. Soil Sci.* 49, 617–628.

652 Treble, P., Shelley, J.M.G., Chappell, J., 2003. Comparison of high resolution sub-annual records of trace
653 elements in a modern (1911-1992) speleothem with instrumental climate data from southwest
654 Australia.*Earth Planet. Sci. Lett.*, 216, 141-153.

655 Treble, P.C., Chappell, J. and Shelley, J.M.G., 2005. Complex speleothem growth processes revealed by
656 trace element mapping and scanning electron microscopy of annual layers. *Geochim. Cosmochim. Ac.*
657 69, 4855-4863.

658 Timperman, M., 1989. *La Grotte de Han au fil des Siècles*. Ed. Duculot, Gembloux, Belgium, 66 pp.
659 USGS (United States Geological Survey).<http://minerals.usgs.gov/minerals/pubs>.

660 Van Rampelbergh, M., Verheyden, S., Allan, M., Quinif, Y., Keppens, E., and Claeys, P., 2014. Seasonal
661 variations recorded in cave monitoring results and a 10 year monthly resolved speleothem $\delta^{18}\text{O}$ and
662 $\delta^{13}\text{C}$ record from the Han-sur-Lesse cave, Belgium, *Clim. Past Discuss.*, 10, 1821-1856,
663 doi:10.5194/cpd-10-1821-2014, 2014.

664 Verheyden, S., Keppens, E., Fairchild, I.J., McDermott, F., Weis, D., 2000. Mg, Sr and Sr isotope
665 geochemistry of a Belgian Holocene speleothem: implications for paleoclimate reconstructions. *Chem.*
666 *Geol.* 169, 131-144.

667 Verheyden, S., Baele, J.M., Keppens, E., Genty, D., Cattani, O., Cheng, H., Lawrence, E., Zhang, H.,
668 Van Strijdonck, M., Quinif, Y., 2006. The Proserpine stalagmite (Han-sur-Lesse Cave, Belgium):
669 preliminary environ- mental interpretation of the last 1000 years as recorded in a layered
670 speleothem. *Geologica Belgica* 9 (3-4), 245–256.

671 Verheyden, S., Nader, F.H., Cheng, H.J., Edwards, L.R., Swennen R., 2008. Paleoclimate reconstruction in
672 the Levant region from the geochemistry of a Holocene stalagmite from the Jeita Cave, Lebanon
673 *Quaternary Res.* 70, 368-381.

674 Von Storch, H., Costa-Cabral, M., Hagner, C., Feser, F., Pacyna, J., Pacyna, E., Kolb, S., 2003.
675 Four decades of gasoline lead emissions and control policies in Europe: a retrospective assessment.
676 *Sci. Total Environ.* 311 (1-3), 151-176.

677 Wang, Y.J., Cheng, H., Edwards, L., Kong, X., Shao, X., Chen, S., Wu, J., Jiang, X., wang, X., An, Z.,
678 2008. Millennial- and orbital-scale changes in the East Asian monsoon over the past 224,000 years.
679 *Nature*, 451, 1090-1093.

680 Weis, D., Kieffer, B., Maerschalk, C., Pretorius, W., Barling, J., 2005. High precision Pb–Sr–Nd–Hf
681 isotopic characterization of USGS BHVO-1 and BHVO-2 reference materials: comparison of first
682 and second generation samples. *Geochem. Geophys. Geosyst.* 6, Q02002,
683 doi:10.1029/2004GC000852.

684 Wynn, P.M., Fairchild, I.J., Baker, A., Frisia, S., Borsato, A., Baldini, J., McDermott, F., 2008. Isotopic
685 archives of sulphur in speleothems. *Geochim. Cosmochim. Ac.* 72, 2465–2477.

686 Wynn, P.M., Fairchild, I.J., Frisia, S., Spotl, C., Baker, A. and Borsato. 2010. High-resolution sulphur
687 isotope analysis of speleothem carbonate by secondary ionisation mass spectrometry. *Chemical*
688 *Geology*, 271, 101 – 107

689 Wynn, P.M., Fairchild, I.J., Spötl, C., Hartland, A., Matthey, D., Fayard, B., Cotte, M., 2014. Synchrotron X-
690 ray distinction of seasonal hydrological and temperature patterns in speleothem carbonate. *Environ.*
691 *Chem.* 11(1) 28-36.

692 Zhao, L. Y. L., Schulin, R., Nowack, B., 2009. Cu and Zn mobilization in soil columns percolates by
693 different irrigation solutions. *Environ. Pollut.* 157, 823-833.

694 Zhou, H., Feng, Zhao, J.-X., Shen, C.-C., You, C.-F., Lin, Y., 2009. Deglacial variations of Sr and $^{87}\text{Sr}/^{86}$
695 Sr ratio recorded by a stalagmite from Central China and their association with past climate and
696 environment. *Chem. Geol.* 268, 233-247/
697
698

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 10-30 $\mu\text{m s}^{-1}$ with 22 μm 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