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SI: Notre-Dame de Paris

Historical monuments and lead pollution: Lessons from the case of Notre-Dame de Paris and Sainte-Chapelle

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ABSTRACT

To investigate the potential spreading of leaded dust over Paris and its inhabitants, following the fire of Notre-Dame de Paris cathedral in April 2019, we developed a dedicated protocol to identify the geochemical fingerprint of the emitted particles. This method could be transposed to a contemporary monument to Notre-Dame de Paris which had not burnt and which had to undergo a major restoration phase: Sainte-Chapelle de Paris. Thus, a new study was performed on the indoor dust collected in this monument, to which the protocol developed for the dusts of Notre-Dame was applied. The comparison of the geochemical fingerprint of both monuments highlights the complexity of establishing the chemical signatures of such buildings. The homogeneity of the isotopic and elemental results obtained on the samples from Notre-Dame de Paris compared to those from Sainte-Chapelle de Paris reveals the homogenizing role of the fire, which simplifies the geochemical signature determination. Moreover, this study does not show any significant impact of anthropogenic pollution (road traffic, industry, incinerators) on the indoor environment of monuments, which are nevertheless rich in construction lead. The notion of "polluter-polluted monument" could be problematic in the event of an accident during restoration phase. These new results obtained on dust samples from a building that has not experienced any recent major deterioration underlines the multiple sources of lead present in these monuments and the importance of identifying univocally their signature. However, the concentrations of metal and metalloid in the indoor dust do not show any major pollution inside Sainte-Chapelle de Paris that could be a threat to human health.

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1. Introduction

The fire of Notre-Dame de Paris (hereafter referred to as Notre-Dame) that occurred in 2019 devastated an important part of its lead roof and spire. It resulted in many controversies in the media on the potential lead pollution caused by such an incident and its impact on the health of local residents, especially children [1–5]. Citizen associations and two families accused authorities to not act adequately to prevent children exposure to the lead fallout. Lead poisoning is a major societal issue. Even if leaded gasoline phasing out in the 2000s in France drastically reduced concentrations in the environment [6,7], many sources of lead are reported in urban

environments such as ancient foundries, incinerators or road traffic but even more in Paris city where lead was greatly used for roofing, plumbing or painting and this, until the beginning of the 21st century [8]. Historical monuments are an important part of French cultural heritage and require special care during their maintenance and renovation phases to limit possible metal pollution in the urban environment. However, following the fire of Notre-Dame, many questions were raised about the impact of a historical monument (e.g. Eiffel Tower) [9] considered as a "potential emitter" of contaminants, in particular in metals / metalloids harmful to human health, towards its proximal environment. Indeed, does a historical monument containing lead and other toxic metals pollute its environment continuously or only during degradation events (e.g. natural disasters, fires, restoration phases, lead oxidation with ambient air and acid rain)?

To answer this question, a first study was performed on indoor dust samples collected in Notre-Dame after the fire to

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determine their geochemical signature [10]. This last was approximated from tracers commonly used in the literature to determine the sources of environmental pollution: lead isotopic ratios ($^{206}\text{Pb}/^{207}\text{Pb}$; $^{208}\text{Pb}/^{206}\text{Pb}$) [11–14] and elemental ones (Sn/Cu; Sb/Cu; Cd/Pb; Cu/Pb) [15,16]. Our study highlighted the heterogeneity of isotopic and elemental signatures depending on the matrix collected and the selected substrate (wood; fabric; metals; stained-glass). Therefore, a rigorous sampling strategy inside a building (non-contaminating substrate, fine and homogeneous matrix) is required to define the geochemical signature of a historical monument [10]. To understand the impact of a degradation event on a historical monument signature, we will propose a geochemical signature of Sainte-Chapelle de Paris (hereafter referred to as Sainte-Chapelle) indoor dusts, a contemporary monument to Notre-Dame (construction period between the 12th and 13th centuries) subjected to similar urban pollution pressures and also covered with a lead roof. This monument is located 400 m northwest from Notre-Dame in the centre of Paris, on the “Ile-de la Cité”. In addition, these two monuments underwent many restoration phases over the centuries. The Sainte-Chapelle built in the middle of the 13th century went through many modifications such as the installation of its rose window in the 15th century, the repairs following its fire in the 17th c. or another important restoration phase, especially for the roof, performed in the 19th century [17]. Since 2008, restoration of the masonry and stained-glass windows of the east, north and west (with the frontage rose window) was carried out by the architectural conservator, i.e. *Architecte en Chef des Monuments Historiques* (ACMH). Concerning Notre-Dame, construction started in the second half of the 12th century and lasted till the mid-13th century. The cathedral roof was entirely renovated in the 18th century. During the 19th century, Notre-Dame was extensively restored and its emblematic spire made of wood covered with lead sheets overhanging the once again renovated lead roof was erected. A few parts (roof top and spire ornaments) were also restored during the 20th century [18].

Thus, the present study focuses on indoor dust samples, collected in Sainte-Chapelle before the installation of the scaffolding necessary for its restoration planned in 2022. We applied the protocol and geochemical tracers, previously used for the study of Notre-Dame, in order to define Sainte-Chapelle geochemical fingerprint and compare it with Notre-Dame signature [10] to better understand the lead pollution originating from such environment.

2. Research aim

This study focuses on the contribution of historical monuments, in particular Notre-Dame and Sainte-Chapelle, to the lead contamination of urban environments, with a specific application to the city of Paris. The project aims more broadly to identify the multiple sources of lead pollution in this urban environment using lead isotopic and elemental tracing. Our previous work on the fire of Notre-Dame de Paris demonstrated the ability of elemental and lead isotope ratios to discriminate between these different lead sources in the Parisian environment [10]. The project's goal is to refine the tracing of Parisian lead by establishing the chemical fingerprint of a historical monument, having suffered no recent damage as Sainte-Chapelle, representative of the different times and uses, to tend towards a historical retrospective of the impacts of construction leads, relying on natural records of environmental contamination. Ultimately, these studies on historical monuments will help to clarify the real risks of lead propagation from these edifices and will allow the addition of quantified elements to the necessary discussion to adapt the standards for carrying out restoration work. Indeed, in the presence of lead in a monument under restoration works, the “lead protocol” for safety and health at work has to protect the health of the workers and of the inhab-

itants of the surrounding buildings, while avoid imposing disproportionate actions that threaten the welfare of the workers (such as wearing heavy personal protection equipment) and the success of the restoration project.

3. Materials and methods

3.1. Material study strategies

Defining the geochemical lead signature of a historical monument is not a straightforward question as many different lead uses coexist within each monument. Different kinds of construction leads (sealing, stained glass, roofing) were implemented during the edification or later restoration of the monument. Yet, both the isotopic and elemental signatures can differ significantly between materials depending on the type of lead construction used and its time of implementation. Indeed, the geochemical signature of pure lead varies according to the lead source (ores sources) but also depends on lead mixing which could be operated on the building site itself. This is particularly obvious during the upkeep or restoration phases of the roof, when lead is salvaged and recycled into new lead sheets. Lead supply sources are also much likely to evolve over time, throughout the Middle Ages and the modern period. Major differences in lead elemental signatures was for example highlighted in Beauvais, Bourges, Chartres and Metz cathedrals regarding lead sealing and roof sheets [19,20]. Thus, the construction of a given monument induces multiple lead signatures which correspond to different lead supplies. In addition, paintings, sculptures and organs are also potential lead sources in such monuments, each of them having its own signature.

Indoor dusts present monument can be analysed to define the historical lead signature knowing that this material is currently used to determine the Pb signature of potential exposure [21–24]. Surprisingly, there is no such study dedicated to historical monuments, although lead pollution is a concern in many restoration yards. This might be partly explained by the short time spent by most of the population in such indoor environments. Nevertheless, indoor dusts host multiple lead sources present inside the building (e.g. construction lead, paints, stained glass) but they can also be mixed with the surrounding lead signature, especially in urban areas. Multiple lead sources and other metals are indeed recorded in large cities, and historical monuments are more affected by lead pollution in such environments than in rural areas where the environmental lead contamination is significantly lower [25]. Thus, the dust collected inside a monument, combining the different sources of lead of the monument as well as the possible influence of the building's environment, is more representative of the monument average lead signature than every single construction lead composing the monument.

3.2. Substrate selection and dust collection methods

The substrate choice to collect the indoor dust is an essential step to avoid the contamination of the samples by the substrate. Sampling dusts on metal, stained glass (that contains lead) or fabrics (which may also contain metals found in pesticides for cotton production and in dyes) must be avoided [26,27]. In this study, we favoured inert substrate such as wood, plastic and rubber in which metals and metalloids concentrations are considered negligible.

Several dust sampling techniques can be used, such as wet sampling on tissue. The “wipe protocol” of the AFNOR NF X46–032 standard is commonly used by French public health organizations to determine the surface lead concentrations in house, schools and nurseries [28,29]. This protocol is also used in many countries like UK or USA [30,31]. However, this technique of cleaning a known surface, usually $33 \times 33 \text{ cm}^2$, with a wipe is only certified for

Table 1
Elemental and lead isotope ratios of Sainte-Chapelle dust samples and Notre-Dame dust samples [10].

Historical monuments	Dust samples ID	Inert substrate	Cu g kg ⁻¹	Ag mg kg ⁻¹	Cd mg kg ⁻¹	Sn g kg ⁻¹	Sb mg kg ⁻¹	Pb g kg ⁻¹	Bi mg kg ⁻¹	²⁰⁶ Pb/ ²⁰⁷ Pb	2SE	²⁰⁸ Pb/ ²⁰⁶ Pb	2SE
Sainte-Chapelle (This study)	SC_070721-PN	Plastic	0.28	3.9	5.1	0.04	23.5	4.5	8.0	1.1730	0.0056	2.0951	0.0144
	SC_070721-PA	Rubber	0.67	4.4	3.4	0.06	20.5	2.3	6.5	1.1726	0.0070	2.0914	0.0088
	SC_070721-EF	Wood	0.61	2.2	5.4	0.12	22.5	12.5	2.1	1.1713	0.0063	2.0893	0.0123
	SC_070721-MF	Plastic	0.05	26.0	0.5	0.01	2.5	10.4	0.3	1.1793	0.0065	2.0862	0.0086
Notre-Dame [10]	ND_110,220-02_PO	Wood	1.08	7.3	28.2	1.49	78.9	127.8	17.8	1.1664	0.0034	2.1013	0.0065
	ND_110,220-01_PO	Wood	0.95	6.9	33.1	1.77	96.5	122.1	16.5	1.1655	0.0035	2.0991	0.0042
	ND_311,019-02	Wood	1.16	10.3	64.7	3.51	137.1	192.3	25.5	1.1662	0.0037	2.0983	0.0070
	ND_140,619-05	Wood	1.26	8.6	55.8	2.99	115.0	160.0	20.4	1.1666	0.0034	2.1004	0.0054
	ND_311,019-01	Wood	1.38	11.4	71.6	3.99	150.5	181.3	26.0	1.1672	0.0033	2.1000	0.0045
	ND_311,019-04	Wood	1.09	10.9	60.1	3.21	131.3	189.2	25.4	1.1684	0.0026	2.0961	0.0051
	ND_140,619-06	Wood	1.85	21.0	65.2	3.51	152.5	281.6	41.0	1.1666	0.0033	2.0983	0.0049
	ND_060220-01_B	Wood	1.08	8.5	49.1	2.66	123.3	203.9	22.4	1.1655	0.0025	2.1014	0.0048
	ND_110,220-03_B	Wood	1.58	13.5	59.9	3.21	149.7	238.4	32.2	1.1661	0.0043	2.1052	0.0113

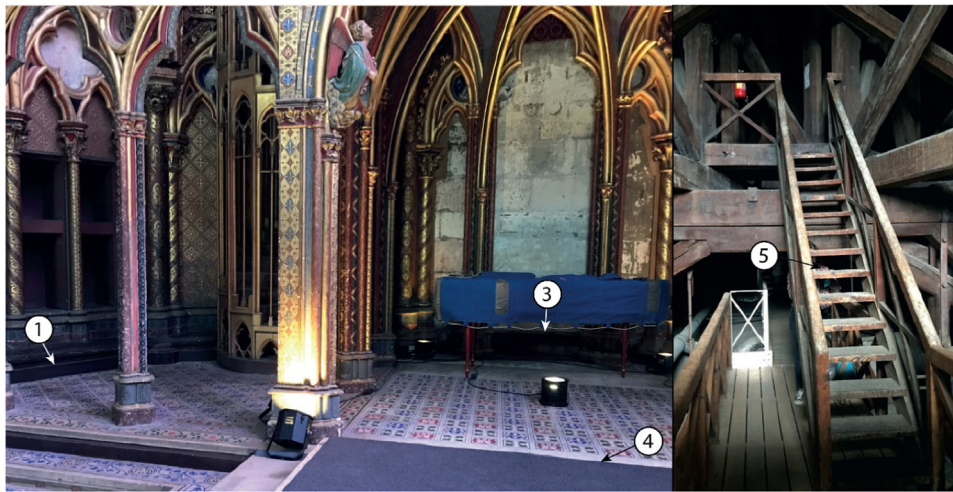


Fig. 1. Location of the samplings. Left, the tribune of the upper chapel. Right, the staircase in the main attic. 1: SC_070721_PN, 2: SC_070721_PA, 3: SC_070721_MF, 5: SC_070721_EF.

lead concentrations, and not for other metals / metalloids concentrations or lead isotopes yet. Moreover, the wipe protocol provides a surface concentration (i.e. mass of metal per m²) while geochemical studies use mass concentrations (i.e. mass of metal per kg of dust). Finally, the wipe protocol was developed for smooth surfaces, and is not adapted to rough surfaces often encountered in monuments. Thus, within this study, dry dust sampling (total dry matter) was favoured to obtain a sufficient representativeness of the metals / metalloids proportions composing them. All dust samples from Sainte-Chapelle (n = 4) were collected with a polypropylene spatula on inert (i.e. metal-free) substrates such as wood, plastic and rubber (Table 1). Three samples (SC_070721_PN, SC_070721_PA, SC_070721_MF) were collected on the floor of the upper chapel in the vicinity of the tribune located in the apse, at the eastern end “tribune”, a space of the chapel which is not accessible to visitors. The last sample (SC_070721_EF) was collected in the attic above the main vaults, on a wooden staircase leading to the base of the 19th century spire (Fig. 1). The collected material (between 3.0 to 24.6 mg) was then stored in hermetically sealed polyethylene boxes.

3.3. Construction lead collection at Sainte-Chapelle

Sampling was performed on the lead joints located between the mullions of the upper bays of Sainte-Chapelle during their restoration in 2013. Eight lead samples of centimetre size were cut off from bays 107 & 109 (corresponding to the middle bays on the northern side).

Notre-dame construction leads were collected by Glorennec et al. [29] mainly on lead elements from the roof and spire.

3.4. Analytical methods

3.4.1. Elemental composition analysis

Some metals or metalloids are commonly associated with lead (in varying proportions depending on the source and the recycling degree) in construction lead [19,20,32]. This is particularly the case for Cu, Ag, Cd, Sn, Sb and Bi. However, these metals are also present in urban environments linked to road traffic [16] (Cu ; Sn ; Sb) and incinerators [15] (Cd ; Cu ; Pb). To determine the pollution source of these metals and metalloids, the correlation degree between the metals can be proposed to know whether they come from an only one source or from multiple sources and to determine the signature from the elemental ratio as Metal/Pb. These ratios highlight the pollution source origin. Elemental concentration analyses were also performed in the LSCE Laboratory (Gif-Sur-Yvette, France) with a Thermo Scientific™ iCAP™ TQ ICP-MS following the same analytical protocol as the Notre-Dame dusts [10] where certified reference materials were used to evaluate the quality of the determined concentrations [10].

3.4.2. Lead isotope composition analysis

Lead owns four isotopes. Three of them i.e. ²⁰⁸Pb, ²⁰⁷Pb, ²⁰⁶Pb are coming from the radioactive decay of ²³²Th, ²³⁵U and ²³⁸U respectively and one i.e. ²⁰⁴Pb is stable (its abundance has remained the same since the Earth formation). Lead isotopes allow

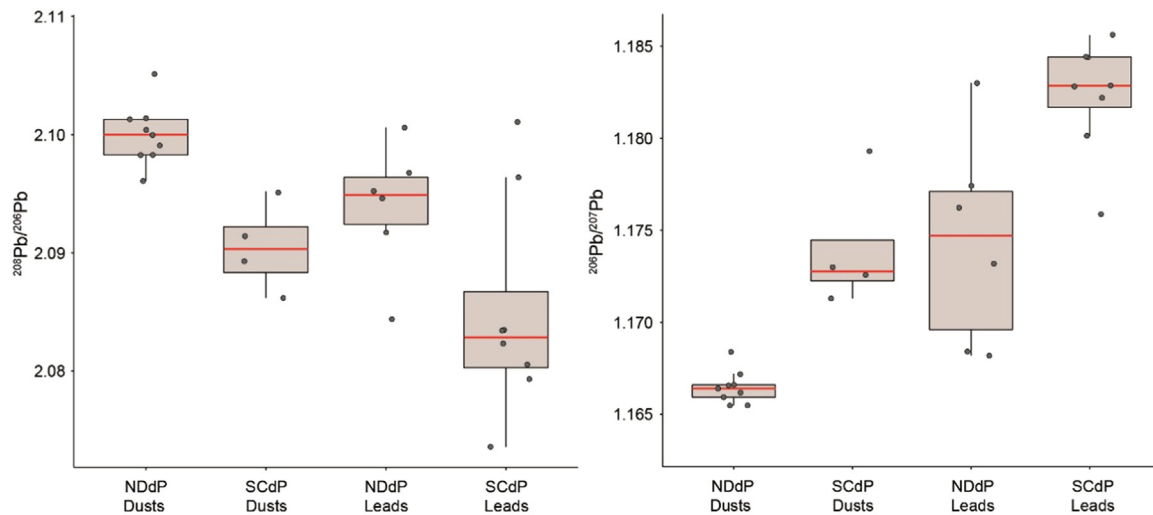


Fig. 2. Boxplot of indoor dusts and lead construction lead isotopic ratios of Sainte-Chapelle (SCdP) and Notre-Dame (NDdP) [10,29]. The top of the box represents the 75th percentile, the bottom of the box represents the 25th percentile, and the red line in the boxes represents the 50th percentile (or median). The whiskers represent the highest and lowest values which are not outliers or extreme values. Data are represented with grey circle. Mean values are statistically different (U Man Whitney test at $\alpha = 0.05$), except for the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of NDdP and SCdP leads. The ratio values variability (Kolmogorov-Smirnov test, $\alpha=0.05$) is lower for NDdP than SCdP, except for the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of NDdP and SCdP leads.

the sources tracing in many different contexts (e.g. historical, geological, environmental...). They can also trace the different lead sources hosted by historical monuments [10,33,34]. For nearly fifty years, Pb isotopic ratios have been used to determine the pollution signatures and trace them in the environment [11,29,35,36]. In this study, we focused on the three most abundant lead isotopes in the environment: ^{208}Pb , ^{207}Pb , and ^{206}Pb . From 3.0 to 24.6 mg of Sainte-Chapelle dust samples were dissolved with 2 mL HClO_4 (65–71%) and 4 mL HF (47–51%) in Teflon vessels on hot-plates for 360 min at 150 °C (Digiprep, SCP Science protocol). After cooling, solutions were evaporated to dryness. Samples were then digested at 120 °C for 180 min (Digiprep SCP Science protocol) using aqua regia: 3.75 mL HCl (34–37%) and 1.25 mL HNO_3 (67%). Solutions were then evaporated to dryness. Finally, samples were dissolved and evaporated successively three times in 1 mL of HNO_3 (67%) and diluted in 50 mL of ultrapure water (Milli-Q). Analyses were performed with a Thermo Scientific™ iCAP™ TQ ICP-MS in the Laboratory LSCE (Gif-Sur-Yvette, France) where mass bias and drift of the isotope ratios were corrected based on repeated measurements of the Pb reference material NIST SRM-981 [10,12,37].

4. Results and discussions

4.1. Isotopic signature of historical monuments

4.1.1. Lead isotopic signature variability

The isotopic results of Sainte-Chapelle dusts vary between 1.1713 ± 0.0056 and 1.1793 ± 0.0070 (median = 1.1728) and between 2.0862 ± 0.0086 and 2.0951 ± 0.0144 (median = 2.0904) for the ratios $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ respectively (Table 1; Fig. 2). Indeed, signatures of Sainte-Chapelle appear to be lower in $^{206}\text{Pb}/^{207}\text{Pb}$ and higher in $^{208}\text{Pb}/^{206}\text{Pb}$ and with a greater values dispersion compared to the dust samples of Notre-Dame (Fig. 2). Similar observations are made for construction leads.

The fact that these general features are not seen for the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of Notre-Dame and Sainte-Chapelle leads is attributed to outlier values in the measurement of the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of Notre-Dame dusts and leads [29] as underlined in Briard et al. [10] and Le Roux et al. [38].

Regarding construction lead signatures, they reflect the isotopic compositions of the different types of materials located

Table 2

Lead isotope ratios of Sainte-Chapelle lead samples (this work) and Notre-Dame lead samples [29].

Historical monuments	$^{206}\text{Pb}/^{207}\text{Pb}$	2SD	$^{208}\text{Pb}/^{206}\text{Pb}$	2SD
Sainte-Chapelle (This study)	1,1759	0,0089	2,1011	0,0259
	1,1844	0,0087	2,0835	0,0207
	1,1822	0,0077	2,0964	0,0185
	1,1828	0,0138	2,0736	0,0086
	1,1856	0,0138	2,0793	0,0116
	1,1844	0,0093	2,0834	0,0257
	1,1829	0,0118	2,0806	0,0102
	1,1801	0,0098	2,0823	0,0132
	2,1540	0,0155	1,1693	0,0027
	2,1242	0,0076	1,1416	0,0028
Notre-Dame [29]	2,0844	0,0171	1,1830	0,0071
	2,0968	0,009	1,1732	0,0034
	2,0952	0,0127	1,1762	0,0044
	2,1006	0,0132	1,1682	0,0026
	2,0917	0,0111	1,1774	0,0031
	2,0946	0,0171	1,1684	0,0025

in the monument. Indeed, in this study (Table 2), construction lead of Notre-Dame originated from remaining pieces of the roof and spire [29] and those of Sainte-Chapelle were sampled from lead joints of the upper bays [10]. It is worth noticing that the Pb signature of the construction lead collected at Sainte-Chapelle are more scattered than those from NDdP. They are in range of lead construction signatures of both NDdP and Chartres cathedral.

Regarding dust samples, given the geographical proximity of the two monuments, they experience the same anthropogenic pressure and their different isotopic signatures cannot be produced by particular urban pollutions. Thus, it must be due to the variability in lead materials used for construction and renovation phases. Indeed, the fire in Notre-Dame which led to a greater influence of the 19th century roof and spire in the chemical composition of the dusts collected inside the monument [10]. On the other hand, the dust signature of Sainte-Chapelle is significantly different and could be influenced by its numerous wall paintings (compared to Notre-Dame), which may contain lead and impact the isotopic signature of the monument [39,40].

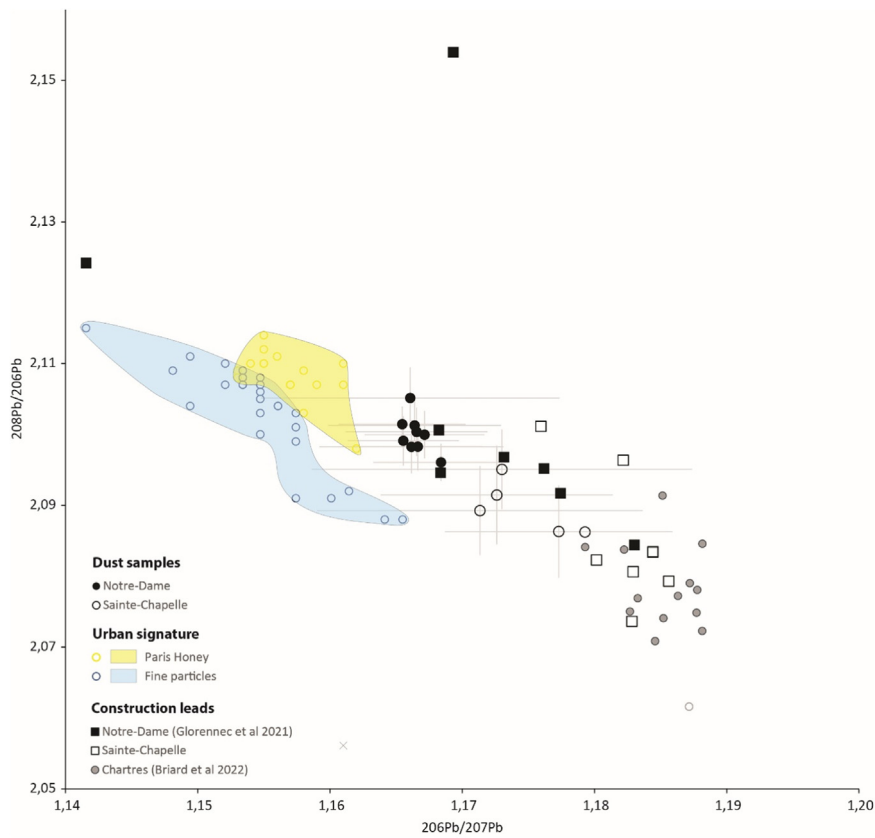


Fig. 3. Comparison between the lead isotopic signature of Sainte-Chapelle and Notre-Dame indoor dusts and the construction lead of these two historic monuments [10]. The urban signatures correspond to data acquired on Parisian honeys (yellow envelope) [14] and on atmospheric particles (brown envelope) [11]. The construction lead signatures correspond to the data acquired on the lead from Chartres cathedral and Versailles Palace (grey envelope) [10,41]. Uncertainties are shown in grey lines.

4.1.2. Urban lead impact on lead isotopic signature of historical monuments

For both Sainte-Chapelle and Notre-Dame, an enrichment in $^{206}\text{Pb}/^{207}\text{Pb}$ (from 1.1748 to 1.1829 for Sainte-Chapelle and from 1.1664 to 1.1747 for Notre-Dame, calculated from medians) and an impoverishment in $^{208}\text{Pb}/^{206}\text{Pb}$ (from 2.0904 to 2.0828 for Sainte-Chapelle and from 2.1000 to 2.0949 for Notre-Dame calculated from medians) are observed in dust samples compared to construction lead samples (Fig. 2). The U-Mann Whitney test ($\alpha=0.05$) confirms a significant difference between dusts and metallic construction leads in $^{206}\text{Pb}/^{207}\text{Pb}$ with a p-value of 0.029 and 0.007, for Notre-Dame and Sainte-Chapelle, respectively. Regarding $^{208}\text{Pb}/^{206}\text{Pb}$, the test is significant and insignificant with p-values calculated at 0.029 and 0.081 for Sainte-Chapelle and Notre-Dame, respectively. Overall, the isotopic signatures of both monuments are closer than their construction leads to the urban signature (Fig. 3), characterized by low $^{206}\text{Pb}/^{207}\text{Pb}$ values and high $^{208}\text{Pb}/^{206}\text{Pb}$ values and illustrated by isotopic ratios from Parisian honey [14] and fine atmospheric particles [11] (Fig. 3).

Thus, we can assume that the indoor dust signature of a historical monument, that did not burn, is a mixture between its construction lead isotopic signature and the urban lead isotopic signature.

4.2. Elemental signature of historical monuments

4.2.1. Monument fire impact on metals / metalloids concentrations in indoor dusts

There is a significant variability in metal content amongst Sainte-Chapelle dust samples (Table 1). Indeed, the concentrations range between 0.05 and 0.67 g kg⁻¹ (average: 4.0 g kg⁻¹) for Cu, between 2.2 and 26.0 mg kg⁻¹ (average: 9.1 mg kg⁻¹) for Ag, be-

tween 0.5 and 5.4 mg kg⁻¹ (average: 3.6 mg kg⁻¹) for Cd, between 0.01 and 0.12 g kg⁻¹ (average: 0.06 g kg⁻¹) for Sn, between 2.5 and 23.5 mg kg⁻¹ (average: 17.26 mg kg⁻¹) for Sb, between 2.3 and 12.5 g kg⁻¹ (average: 7.4 g kg⁻¹) for Pb, and between 0.3 and 8.0 mg kg⁻¹ (average: 4.2 mg kg⁻¹) for Bi (Table 1). Only Ag shows an important variability within samples notably with dust sample SC_070721-PN collected from plastic substrate which is much richer in Ag (Fig. 4).

To determine if a monument blaze has an impact on the elemental concentrations of metals and metalloids found in indoor dust, we compare the elemental concentrations of the dusts of Sainte-Chapelle and Notre-Dame [10] (Table 1; Fig. 4). For most elements, the concentrations are much higher in Notre-Dame than in Sainte-Chapelle. They range from 3 times higher for Sn to 200 times higher for Pb (Fig. 4). This seems to correlate with the amount of lead that was scattered during the fire, with an estimated 150 to 1000 kg [42,43]. The fire therefore seems to have had a major impact on the metal / metalloid composition of the dusts.

We also note that the Pb concentrations between 2.3 and 12.5 mg kg⁻¹ measured in Sainte-Chapelle dust samples are significantly lower than the indoor dust Pb concentration measured worldwide (mean \approx 120 mg kg⁻¹; range: 14.2 – 7800 mg kg⁻¹) [44,45]. The Pb concentrations recorded in the Sainte-Chapelle dusts are also well below French health recommendations for Pb content in soil which limit the concentration to 100 mg kg⁻¹ for agricultural soils and 300 mg kg⁻¹ for recreative areas such as playgrounds [46]. Thus, the lead pollution generated by the construction and decorative lead in the Sainte-Chapelle remains very limited inside the building. However, it would be interesting to estimate the lead roof impact on the outdoor dust that could be collected in the gutter, at the gutter exit and on the sidewalk.

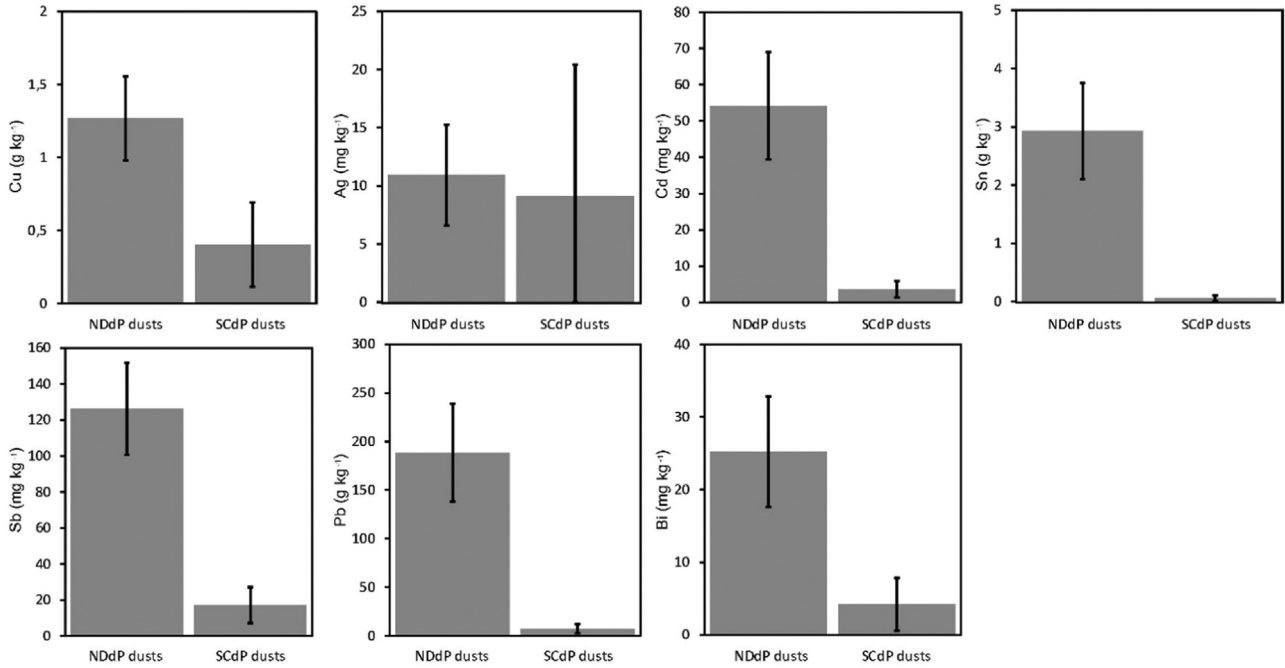


Fig. 4. Comparison between elemental concentrations in indoor dust of Sainte-Chapelle (SCdP) and Notre-Dame (NDdP) collected on inert substrates [10]. Grey rectangle corresponds to the concentrations average in g kg^{-1} for Cu, Sn, and Pb and in mg kg^{-1} for Ag, Cd, Sb and Bi. The black bar is the standard deviation (SD) of the mean value.

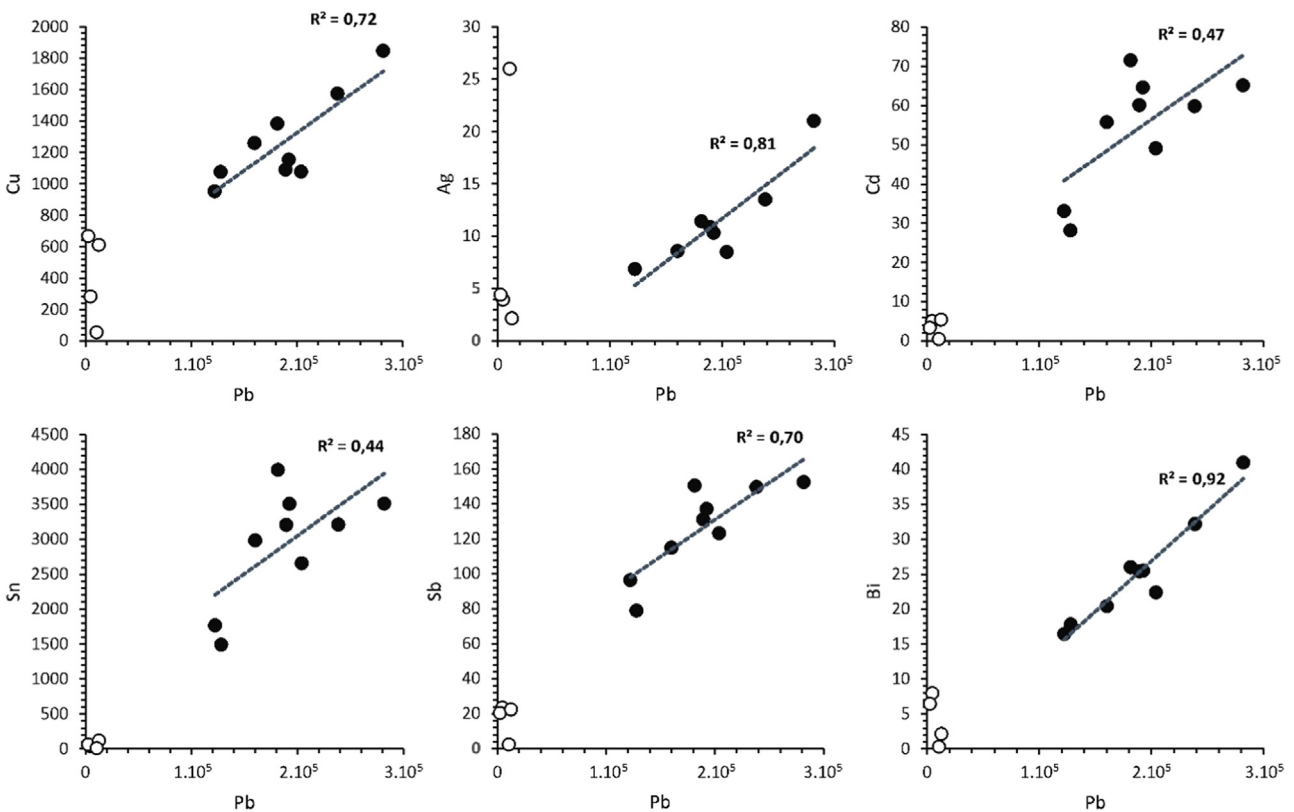


Fig. 5. Bivariate concentration plots of selected trace element concentrations versus Pb concentration for Sainte-Chapelle dust samples and Notre-Dame dust samples [10] (unit : mg kg^{-1}). Each colour corresponds to localities where the dust samples were collected (white = Sainte-Chapelle; black = Notre-Dame). The coefficients of determination (R^2) are obtained from the elemental concentrations calculated in the Notre-Dame indoor dusts. R^2 values in bold means that the Pearson correlation p values is lower than 0.05, proving the correlation between element X and Pb concentration values.

Concerning Ag, the averages seem similar between both historical monuments, yet noting a greater variability of Ag concentrations in the dust samples of Sainte-Chapelle (Fig. 4). This similarity excludes the lead roof fire as a source of Ag in these buildings. A local source of Ag can therefore be considered. As the most concentrated sample (SC_070721_MF) was collected next to the tribune where the great silver Chasse which held the relics used to be, this local increase in Ag concentration could be the result of its melting during the French Revolution in 1791.

4.2.2. Historical monuments: multiple sources of metals and metalloids

The lack of correlation (Pearson test at $\alpha = 0.05$) of Cu, Ag, Cd, Sn, Sb and Bi with Pb concentrations for Sainte-Chapelle indoor dusts (Fig. 5) and their variable Pb isotopic signatures highlight the presence of multiple lead sources emitting metals (e.g. stained glasses, paintings, roof) [20]. Conversely, Cu, Ag, Cd, Sb and Bi concentrations are correlated with lead concentrations observed in Notre-Dame indoor dusts, with R^2 between 0.62 and 0.90 for Sb and Bi, respectively (Fig. 5). It indicates a common source with variable degree of dilution by metal-free material, or similar mechanisms of mobility [13,47].

However, Notre-Dame contains lead from as many different sources as Sainte-Chapelle, but the Pb content of the Notre-Dame fire dust originated mainly from the roof and the spire. Indeed, the fire and the associated air motions could have homogenized the dusts inside the cathedral. This hypothesis also seems to be supported by the more homogeneous isotopic data for Notre-Dame dusts than the Sainte-Chapelle ones. In view of the correlation between metals and metalloids, elemental ratios can be proposed to trace the signature of Notre-Dame fire [10]. Conversely, it is impossible to compare these ratios with those of Sainte-Chapelle where the variability is more important. Definitely, intensive sampling of indoor and outdoor dusts at Sainte-Chapelle is needed to infer the full picture of the Pb sources in this emblematic monument of the 13th century.

5. Conclusions

This new study performed on the indoor dust of Sainte-Chapelle to determine its geochemical fingerprint highlights a significant disparity of lead isotopic and elemental signatures. As the sampling strategy excludes dust contamination by the substrate, these disparities reflect the multiple sources of lead in the building. Unlike Sainte-Chapelle, dusts collected in Notre-Dame are homogeneous for lead isotopes and elemental ratios despite the presence of different sources in the construction and roof lead. This homogeneity is most likely caused by a signature homogenization by air motions during the fire of 2019.

Comparison of indoor dusts and construction leads for Sainte-Chapelle and Notre-Dame highlights a shift between the two lead isotopic signatures. Indoor dusts always have lower values in $^{206}\text{Pb}/^{207}\text{Pb}$ and higher in $^{208}\text{Pb}/^{206}\text{Pb}$ compared to construction leads. It could suggest a potential impact of urban lead pollution on indoor dust under typical monument operating situations. To conclude, a potentially polluting monument may itself be polluted by its surrounding environment.

The metals and metalloids concentrations in Sainte-Chapelle dusts are very low (except for Ag) compared to Notre-Dame, which indicates that without the fire triggering the lead roof destruction and the lead dust release, the lead level is low, with no risk for the population. This result also suggests that the Pb background level in Notre-Dame before the fire was much lower and also had a different signature compared to the Pb released by the fire. However, it would be interesting to continue the study of Sainte-Chapelle dust during and after the work phase planned for 2022–2023 to

determine whether a renovation phase can change the geochemical signature of a historical monument by remobilizing urban lead from facades or internal lead sources coming from the monument. It would also be interesting to complete this new study with the collection of outdoor dust to determine the impact of roof lead runoff on Sainte-Chapelle close environment and to highlight if their signatures are significantly different from indoor dust and closer to urban lead.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2023.04.010.

References

- [1] M.A.S. Laidlaw, M.P. Taylor, Potential for childhood lead poisoning in the inner cities of Australia due to exposure to lead in soil dust, *Environ. Pollut.* 159 (2011) 1–9, doi:10.1016/j.envpol.2010.08.020.
- [2] P. Glorennec, J. Lucas, A. Etchevers, Y. Oulhote, C. Mandin, J. Poupon, Y. Le Strat, P. Bretin, F. Douay, B. Le Bot, A. Le Tertre, Exposition au plomb des enfants dans leur logement. Projet Plomb-Habitat (2008–2014): principaux résultats, retombées et perspectives, *Env. Risque Sante* 14 (2015) 28–37, doi:10.1684/ers.2014.0751.
- [3] P.J. Landrigan, R. Fuller, N.J.R. Acosta, O. Adeyi, R. Arnold, N. (Nil) Basu, A.B. Baldé, R. Bertollini, S. Bose-O'Reilly, J.I. Boufford, P.N. Breyse, T. Chiles, C. Mahidol, A.M. Coll-Seck, M.L. Cropper, J. Fobil, V. Fuster, M. Greenstone, A. Haines, D. Hanrahan, D. Hunter, M. Khare, A. Krupnick, B. Lanphear, B. Lohani, K. Martin, K.V. Mathiasen, M.A. McTeer, C.J.L. Murray, J.D. Ndahimananjara, F. Perera, J. Potočnik, A.S. Preker, J. Ramesh, J. Rockström, C. Salinas, L.D. Samson, K. Sandilya, P.D. Sly, K.R. Smith, A. Steiner, R.B. Stewart, W.A. Suk, O.C.P. van Schayck, G.N. Yadama, K. Yumkella, M. Zhong, The Lancet Commission on pollution and health, *Lancet* 391 (2018) 462–512, doi:10.1016/S0140-6736(17)32345-0.
- [4] A. Vallée, E. Sorbets, H. Lelong, J. Langrand, J. Blacher, The lead story of the fire at the Notre-Dame cathedral of Paris, *Environ. Pollut.* 269 (2021) 116140, doi:10.1016/j.envpol.2020.116140.
- [5] P. Glorennec, J.-P. Lucas, C. Mandin, B. Le Bot, French children's exposure to metals via ingestion of indoor dust, outdoor playground dust and soil: contamination data, *Environ. Int.* 45 (2012) 129–134, doi:10.1016/j.envint.2012.04.010.
- [6] A. Véron, P. Flament, M.L. Bertho, L. Alleman, R. Flegat, B. Hamelin, Isotopic evidence of pollutant lead sources in Northwestern France, *Atmos. Environ.* 33 (1999) 3377–3388, doi:10.1016/S1352-2310(98)00376-8.
- [7] F. Monna, J. Lancelot, I.W. Croudace, A.B. Cundy, J.T. Lewis, Pb isotopic composition of airborne particulate material from France and the Southern United Kingdom: implications for Pb pollution sources in Urban Areas, *Environ. Sci. Technol.* 31 (1997) 2277–2286, doi:10.1021/es960870-.
- [8] L. Lestel, Non-ferrous metals (Pb, Cu, Zn) needs and city development: the Paris example (1815–2009), *Reg. Environ. Change* 12 (2012) 311–323, doi:10.1007/s10113-011-0255-4.
- [9] S.M. Nageotte, J. Phillip Day, Lead concentrations and isotope ratios in street dust determined by electrothermal atomic absorption spectrometry and inductively coupled plasma mass spectrometry, *Analyst* 123 (1998) 59–62, doi:10.1039/a704940d.
- [10] J. Briard, S. Ayrault, M. Roy-Barman, L. Bordier, M. L'Héritier, A. Azéma, D. Syvilay, S. Baron, Determining the geochemical fingerprint of the lead fallout from the Notre-Dame de Paris fire: lessons for a better discrimination of chemical signatures, *Sci. Total Environ.* 864 (2023) 160676, doi:10.1016/j.scitotenv.2022.160676.
- [11] D. Widory, S. Roy, Y. Le Moullec, G. Goupil, A. Cocherie, C. Guerrot, The origin of atmospheric particles in Paris: a view through carbon and lead isotopes, *Atmos. Environ.* 38 (2004) 953–961, doi:10.1016/j.atmosenv.2003.11.001.
- [12] S. Ayrault, M. Roy-Barman, M.-F. Le Cloarec, C.R. Priadi, P. Bonté, C. Göpel, Lead contamination of the Seine River, France: geochemical implications of a historical perspective, *Chemosphere* 87 (2012) 902–910, doi:10.1016/j.chemosphere.2012.01.043.

- [13] K.E. Smith, D. Weis, M. Amini, A.E. Shiel, V.W.-M. Lai, K. Gordon, Honey as a biomonitor for a changing world, *Nat. Sustain.* 2 (2019) 223–232, doi:10.1038/s41893-019-0243-0.
- [14] K.E. Smith, D. Weis, C. Chauvel, S. Moulin, Honey Maps the Pb fallout from the 2019 fire at Notre-Dame cathedral, Paris: a geochemical perspective, *Environ. Sci. Technol. Lett.* 7 (2020) 753–759, doi:10.1021/acs.estlett.0c00485.
- [15] A. Font, K. de Hoogh, M. Leal-Sanchez, D.C. Ashworth, R.J.C. Brown, A.L. Hansell, G.W. Fuller, Using metal ratios to detect emissions from municipal waste incinerators in ambient air pollution data, *Atmos. Environ.* 113 (2015) 177–186, doi:10.1016/j.atmosenv.2015.05.002.
- [16] Y.-C. Lin, C.-J. Tsai, Y.-C. Wu, R. Zhang, K.-H. Chi, Y.-T. Huang, S.-H. Lin, S.-C. Hsu, Characteristics of trace metals in traffic-derived particles in Hsuehshan Tunnel, Taiwan: size distribution, potential source, and fingerprinting metal ratio, *Atmospheric Chem. Phys.* 15 (2015) 4117–4130, doi:10.5194/acp-15-4117-2015.
- [17] A. Granboulan, Jean-Michel Leniaud, Françoise Perrot, La Sainte-Chapelle, Paris, Nathan-C.N.M.H., 1991, 245 p., *Bull. Monum.* Tome 150 N°2 Année 1992. (1992). https://www.persee.fr/doc/bulmo_0007-473x_1992_num_150_2_4442_t1_0188_0000_4.
- [18] P. Villeneuve, Cathédrale Notre-Dame Paris IV, Restauration des couvertures en plomb du grand comble, (2015).
- [19] D. Syvilay, A. Texier, A. Arles, B. Gratuze, N. Wilkie-Chancellier, L. Martinez, S. Serfaty, V. Detalle, Trace element quantification of lead based roof sheets of historical monuments by Laser Induced Breakdown Spectroscopy, *Spectrochim. Acta Part B At. Spectrosc.* 103–104 (2015) 34–42, doi:10.1016/j.sab.2014.10.013.
- [20] M. L'Héritier, A. Arles, A. Dissier, B. Gratuze, Lead it be! Identifying the construction phases of gothic cathedrals using lead analysis by LA-ICP-MS, *J. Archaeol. Sci. Rep.* 6 (2016) 252–265, doi:10.1016/j.jasrep.2016.02.017.
- [21] Y. Oulhote, B. Le Bot, J. Poupon, J.-P. Lucas, C. Mandin, A. Etchevers, D. Zmirou-Navier, P. Glorennec, Identification of sources of lead exposure in French children by lead isotope analysis: a cross-sectional study, *Environ. Health.* 10 (2011) 75, doi:10.1186/1476-069X-10-75.
- [22] R.H. Gwiazda, D.R. Smith, Lead isotopes as a supplementary tool in the routine evaluation of household lead hazards, *Environ. Health Perspect.* 108 (2000) 1091–1097, doi:10.1289/ehp.001081091.
- [23] M.A.S. Laidlaw, S. Zahran, N. Pingitore, J. Clague, G. Devlin, M.P. Taylor, Identification of lead sources in residential environments: sydney Australia, *Environ. Pollut.* 184 (2014) 238–246, doi:10.1016/j.envpol.2013.09.003.
- [24] B. Gulson, Stable lead isotopes in environmental health with emphasis on human investigations, *Sci. Total Environ.* 400 (2008) 75–92, doi:10.1016/j.scitotenv.2008.06.059.
- [25] S.S. Jørgensen, M. Willems, The fate of lead in soils: lead originating from roofs of ancient churches, *Ambio* 16 (1987) 16–19.
- [26] S.R. Tariq, M. Shaffiq, G.A. Chotana, Distribution of heavy metals in the soils associated with the commonly used pesticides in cotton fields, *Scientifica (Cairo)* 2016 (2016) 1–11, doi:10.1155/2016/7575239.
- [27] Swarnkumar Reddy, W.J. Osborne, Heavy metal determination and aquatic toxicity evaluation of textile dyes and effluents using Artemia salina, *Biocatal. Agric. Biotechnol.* 25 (2020) 101574, doi:10.1016/j.bcab.2020.101574.
- [28] AFNOR (Association française de normalisation), Norme NFX-46-032. Méthodologie de mesure du plomb dans les poussières de sol., (2008).
- [29] P. Glorennec, A. Azema, S. Durand, S. Ayrault, B. Le Bot, The isotopic signature of lead emanations during the fire at notre dame cathedral in Paris, France, *Int. J. Environ. Res. Public Health.* 18 (2021) 5420, doi:10.3390/ijerph18105420.
- [30] M. Millson, P.M. Eller, K. Ashley, Evaluation of wipe sampling materials for lead in surface dust, *Am. Ind. Hyg. Assoc. J.* 55 (1994) 339–342, doi:10.1080/15428119491018989.
- [31] J.E. Gallacher, P.C. Elwood, K.M. Phillips, B.E. Davies, D.T. Jones, Relation between pica and blood lead in areas of differing lead exposure, *Arch. Dis. Child.* 59 (1984) 40–44, doi:10.1136/adc.59.1.40.
- [32] V. Comite, J.S. Pozo-Antonio, C. Cardell, T. Rivas, L. Randazzo, M.F. La Russa, P. Fermo, Metals distributions within black crusts sampled on the facade of an historical monument: the case study of the Cathedral of Monza (Milan, Italy), in: *IMEKO TC4 Int. Conf. Metrol. Archaeol. Cult. Herit. International Measurement Federation Secretariat (IMEKO)*, 2019, pp. 73–78.
- [33] P. Budd, A.M. Pollard, B. Scaife, R.G. Thomas, The possible fractionation of lead isotopes in ancient metallurgical processes, *Archaeometry* 37 (1995) 143–150, doi:10.1111/j.1475-4754.1995.tb00732.x.
- [34] S. Baron, J. Carignan, S. Laurent, A. Ploquin, Medieval lead making on Mont-Lozère Massif (Cévennes-France): tracing ore sources using Pb isotopes, *Appl. Geochem* 21 (2006) 241–252, doi:10.1016/j.apgeochem.2005.09.005.
- [35] E. Resongles, V. Dietze, D.C. Green, R.M. Harrison, R. Ochoa-Gonzalez, A.H. Tremper, D.J. Weiss, Strong evidence for the continued contribution of lead deposited during the 20th century to the atmospheric environment in London of today, *Proc. Natl. Acad. Sci.* 118 (2021) e2102791118, doi:10.1073/pnas.2102791118.
- [36] K.W. Bruland, K. Bertine, M. Koide, E.D. Goldberg, History of metal pollution in southern California coastal zone, *Environ. Sci. Technol.* 8 (1974) 425–432, doi:10.1021/es60090a010.
- [37] M. Le Gall, S. Ayrault, O. Evrard, J.P. Lacey, D. Gateuille, I. Lefèvre, J.-M. Mouchel, M. Meybeck, Investigating the metal contamination of sediment transported by the 2016 Seine River flood (Paris, France), *Environ. Pollut.* 240 (2018) 125–139, doi:10.1016/j.envpol.2018.04.082.
- [38] G. Le Roux, O. Masson, C. Cloquet, M.-J. Tavella, M. Beguin-Leprieux, O. Saunier, D. Baqué, T. Cambouvie, J. Berger, T. Aigouy, F. Maube, S. Baron, S. Ayrault, M. L'Héritier, Lead from Notre-Dame fire plume caught 15km from Paris, *ACS Earth Space Chem.* (2023), doi:10.1021/acsearthspacechem.2c00321.
- [39] A.G. Nord, K. Billström, K. Tronner, K.B. Olausson, Lead isotope data for provenancing mediaeval pigments in Swedish mural paintings, *J. Cult. Herit.* 16 (2015) 856–861, doi:10.1016/j.culher.2015.02.009.
- [40] L. Hendriks, I. Hajdas, E.S.B. Ferreira, N.C. Scherrer, S. Zumbühl, M. Küffner, L. Carlyle, H.-A. Synal, D. Günther, Selective dating of paint components: radiocarbon dating of lead white pigment, *Radiocarbon* 61 (2019) 473–493, doi:10.1017/RDC.2018.101.
- [41] E. Pons-Branchu, S. Ayrault, M. Roy-Barman, L. Bordier, W. Borst, P. Branchu, E. Douville, E. Dumont, Three centuries of heavy metal pollution in Paris (France) recorded by urban speleothems, *Sci. Total Environ.* 518–519 (2015) 86–96, doi:10.1016/j.scitotenv.2015.02.071.
- [42] F. Tognet, B. Truchot, Modélisation de la Dispersion des Particules de Plomb du Panache de L'incendie de Notre Dame., *Ineris-200480-879062-V20.* (2019).
- [43] A. Geen, Y. Yao, T. Ellis, A. Gelman, Fallout of lead over paris from the 2019 Notre-Dame cathedral fire, *GeoHealth* 4 (2020), doi:10.1029/2020GH000279.
- [44] P.E. Rasmussen, C. Levesque, M. Chénier, H.D. Gardner, H. Jones-Otazo, S. Petrovic, Canadian House Dust Study: population-based concentrations, loads and loading rates of arsenic, cadmium, chromium, copper, nickel, lead, and zinc inside urban homes, *Sci. Total Environ.* 443 (2013) 520–529, doi:10.1016/j.scitotenv.2012.11.003.
- [45] T. Shi, Y. Wang, Heavy metals in indoor dust: spatial distribution, influencing factors, and potential health risks, *Sci. Total Environ.* 755 (2021) 142367, doi:10.1016/j.scitotenv.2020.142367.
- [46] HCSP, Expositions au plomb : détermination de nouveaux objectifs de gestion., Paris HCSP. (2014) 201.
- [47] C. Gunawardana, P. Egodawatta, A. Goonetilleke, Adsorption and mobility of metals in build-up on road surfaces, *Chemosphere* 119 (2015) 1391–1398, doi:10.1016/j.chemosphere.2014.02.048.