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# Stone-built Heritage as a Proxy Archive for Long-term Historical Air Quality: A study of weathering crusts on three generations of Stone Sculptures on Broad Street, Oxford

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## Abstract

Black crusts on historic buildings are mainly known for their aesthetic and deteriorative impacts, yet they also can advance air pollution research. Past air pollutants accumulate in distinct layers of weathering crusts. Recent studies have used these crusts to reconstruct pollution to improve our understanding of its effects on stone-built heritage. However, the majority of the studies provide only coarse resolution reconstruction of pollution, able to distinguish between 'inner=old' and 'outer=modern' crust layers. In contrast, very few studies have linked distinct periods of exposure to pollution variations in the composition of these crusts. Here we address this research gap by developing a finer-scale resolution pollution record. Our study explored the unique configuration of limestone sculptures in central Oxford, which have been exposed over the last 350 years to three different periods of atmospheric pollution; the early Industrial Revolution, the Victorian period and the 20th century. When the first two generations of sculptures were moved to less polluted areas, their 'pollution clocks' were stopped. Here we discuss the potential of investigating the 'pollution clock' recorded in the geochemical makeup of each sculpture generation's weathering crust layers. We found the analysed crusts record clear changes related to the evolution of modes of transport and industrial and technological development in Oxford. Higher levels of Arsenic (As), Selenium (Se) are linked to pollution from coal burning during Victorian times and Lead (Pb) indicated leaded petrol use in modern times. Our work shows that stone-built heritage with a known history of air pollution exposure allows improving the pollution reconstruction resolution of these weathering crusts. The results provide the basis

for calibrating long-term geochemical archives. This approach may be used to reconstruct past air quality and has the potential to inform stone weathering research and conservation, in addition to improving the reconstruction of historical pollution.

Keywords: geochemical archives; coal burning; black crusts; palaeopollution; environmental pollution; heavy metals

## 1 Introduction

Despite improvements in European air quality over the last 50 years, atmospheric pollution and its legacy remain one of the major threats to urban stone-built heritage (e.g. Fassina, 1978; Zappia et al. 1998; Bonazza et al., 2007; García-Florentino et al., 2020). Limestone is particularly susceptible to the effects of air pollution, and easily dissolved or indurated (e.g. Searle and Mitchell, 2004; Brimblecombe and Grossi, 2009; Graue et al., 2013). These processes are irreversible, with past pollution effectively damaging stone-built heritage, and promoting the accelerated loss of unique sites and sculptures (e.g. Schiavon, 1996; Prieto-Taboada et al., 2013). Reconstructing past air pollution profiles may guide conservation interventions including cleaning and consolidation (Fassina, 1978, Sgobbi et al., 2010), and address new challenges posed through detrimental synergies between carbon-rich black crusts, microbiology, and climate change (McAlister et al., 2003; Moroni et al., 2004).

Common measures of pollution rely on frequent sampling or biological receptors (e.g. lichens, pine needles, mosses, cf. Monna et al., 2008; Parviainen et al., 2020). However, these approaches have limitations in terms of spatial and temporal coverage. Short-term studies are prone to high levels of variability, where concentrations and source apportionment are highly affected by short-term meteorological factors and seasonal human activities (e.g. Gauri and Holdren, 1981; El-Gohary 2008; Mijić et al., 2010; Etyemezian et al., 2013). Consequently, Salmon et al. (1978) stated that air pollution records should cover

decades to establish clear trends. Environmental records (e.g. peat bogs and lake sediments) have been used to fill this gap, allowing for the long-term reconstruction of changing levels of pollution on decadal and millennial scales (e.g. Longman et al., 2018; Shotyk et al., 1998; Le Roux et al., 2004). However, such studies are typically located in rural locations, and so reconstructions of urban pollution using these archives is challenging. A complementary and economical method to cover a larger spatial and temporal scale, and to provide urban pollution records, is the study of weathering crusts on stone substrates.

Weathering crusts, also known as gypsum or black crusts, damage or weathering layers, are surface and subsurface alterations of the exposed stone substrate, caused by interaction with acidic water (with pH of 5 or lower common for precipitation; Camuffo, 1983; Graue et al., 2013) and further promoted through the presence of atmospheric sulphur oxide (e.g. Calparsoro et al., 2017). Crusts occur more often and are more pronounced in polluted environments such as urban settings (e.g. Marszałek et al., 2014; García-Florentino et al., 2020). As a result, crusts contain varying mixtures of dust, airborne particles, Polyaromatic hydrocarbons (PAHs) and carbonaceous particulate matter (e.g. El-Gohary, 2008; Ruffolo et al., 2015; Pozo-Antonio et al., 2017; Valotto et al., 2018). Following technological developments in transportation and combustion the composition of pollutants in the air has changed over the past several centuries, which should be reflected within weathering crusts where pollutants accumulate (e.g. Fobe et al., 1995; Farkas et al., 2018). This accumulation has been investigated as long-term repositories for air pollutants over the last two decades (Ausset et al., 1998; Del Monte et al., 2001a; Schiavon et al., 2004; Slezakova et al., 2011; Prieto-Taboada et al., 2013; Ruffolo et al., 2015; Morillas et al., 2016 and 2019; Pozo-Antonio et al., 2017; La Russa et al., 2017 and 2018; Rampazzi, 2019; Comite et al., 2020; García-Florentino et al., 2020). However, the majority of recent studies provide only coarse resolution reconstruction of pollution, able to distinguish between ‘inner=ancient/old’ and ‘outer=modern’ crust layers. In contrast, very few studies have linked distinct exposure periods to observed variations in pollution based on composition of these crusts’

stratigraphies (e.g. Del Monte et al. 2001b; Bonazza et al., 2007; Török et al., 2011; La Russa et al., 2018; Barca et al., 2014; Ruffolo et al., 2015; Rampazzi, 2019; García-Florentino et al., 2020).

Here, we addressed this research gap and conducted a proof-of-concept study to develop a finer-scale resolution pollution record. Our study focusses on a unique set of stone sculptures located in succession over 350 years in the city centre of Oxford (Figure 1). The sculptures have been replaced over time, with each generation exposed to a set of different environmental conditions. The 1st generation dates back to 1669, where air pollution was dominated by burning wood. The 2nd generation being put in place in 1868 coincided with an increase in air pollution and increased use of coal (Viles, 1998). The current 3rd generation replaced the second set in 1972, was exposed to gradually cleaner air following the Clean Air Act in 1956.

Three common sources for anthropogenic air pollutants are relevant for this study i) domestic heating, ii) industrial combustion/activities and iii) vehicle exhausts (e.g. Marcazzan et al. 2003; Bonazza et al. 2005; Perrino et al. 2008). Our hypothesis for this study was that the 1st generation (1669–1869) had accumulated pollutants deriving from wood burning and coal after 1790 when the Oxford canal opened. In contrast, the 2nd generation (1868–1972) has been exposed mostly to coal burning (up until c. 1950 when oil-fired domestic heating and power generation took over from coal-fired) and then oil burning, with some lead from leaded petrol (introduced c. 1920). The 3rd generation should have primarily experienced inputs from the combustion of leaded petrol (up until the 1980s). We expected different pollution signals related to the different pollution sources dominating the respective periods to be apparent in the crust layers of the individual generations.

## 2 Methods and materials

### 2.1 Location

Our study focussed on three generations of sculpted Heads located at the eastern end of Broad Street, Oxford, UK (51°45′15″N 1°15′18″W). Interspersed plinths support the Head sculptures as part of a boundary wall with railings separating the Sheldonian Theatre (SHE) and the History of Science Museum (HSM) from Broad Street (Figure 1). The sculptures face north towards Broad Street (traffic-calmed since 1999) and sit on the plinths at the height of ~5.20 m with each sculpture measuring between ~ 1.14 – 1.36 m in height. The sculptures resemble men with various beard designs which allow for differentiated water run-off with pronounced sheltered and non-sheltered areas resulting in uneven weathering crust cover (cf. Barca et al. 2010; Bisquert et al. 2017). Weathering features were the main reason for the removal with the 1st generation (dating back to 1669) being replaced after 200 years, and the 2nd generation (dating back to 1868) in 1972. The two removed sets were relocated in less polluted areas such as college and private gardens.

All three generations of sculptures were carved from Middle Jurassic limestone quarried in the UK. The 1st and 2nd generation derived from the Great, and the 3rd generation from the Inferior Oolite Group. For the first and second generation, different stone varieties were used for the Heads sculptures in front of the Sheldonian Theatre and the History of Science Museum with the stone originating from various local quarries in the Cotswolds (such as Burford, Taynton and Milton, i.e. the Taynton Limestone Formation). In contrast, for the last set of sculptures the same variety, Clipsham limestone (Lincolnshire Limestone Formation), was used for both the Head sculptures in front of the Theatre and the History of Science Museum. In general, all stone varieties show high porosity (~20.8 – 23.5%; cf. Siegesmund and Duerrast, 2011) and present inherent heterogeneity at the block scale affecting weathering responses (cf. Turkington et al., 2003; McCabe et al., 2015). Notably, the second generation in front of the Sheldonian showed severe levels of weathering after only 50 years.

This inherent lower resistance to weathering was expected to have been compounded by higher levels of air pollution accelerating their decay.

### 2.2 Sampling strategy

The formation of weathering crusts is complex and depends on several factors, including the macro scale location (i.e. coastal, inland, urban, rural with respective pollution levels), the stone substrate (i.e. inherent and/or external sources of calcite), exposure height and aspect (determines water and wind effects), surface orientation (vertical, inclined or horizontal), volume and geometry of the structure, water retention characteristics (e.g. porosity, time of wetness), the surface texture and hence receptibility to dry deposition, water regime and wet deposition activity (e.g. Warke et al., 2003; Bityukova, 2006, Smith and Viles, 2006; Ruffolo et al., 2015). For heritage structures, these factors result in discontinuous crust cover, also described as intra-facade variability (Monna et al., 2008) and are comparable to block-scale heterogeneity, as emphasised by McCabe et al. (2015). The morphology of crusts can vary with colours ranging from white, grey to black, and layers of laminar, framboidal, and cauliflower shape (e.g. Török, 2008; Fronteau et al., 2010; Morillas et al., 2016; Farkas et al., 2018). Although different crust morphologies show varying levels of air pollutants contamination (Fronteau et al., 2010; Graue et al. 2013), all of them function as non-selective quasi passive samplers for air pollutants (Rampazzi, 2019; García-Florentino et al., 2020).

The sampling for this study was designed to be as comparable as possible between the three different generations of sculptures despite their location changes, and thus potential aspect and height (from ~ 5.20 to 0 m) differences. The height variations are considered negligible (cf. Etymezian et al., 2013; Monna et al., 2008) and comparison to other studies shows that only a considerable height above ground will show a difference statistically (e.g. 35m cf. Barca et al., 2014 and Ozga et al., 2014). We focussed on vertical sections of the face, including the ears exposed towards Broad Street (North) and excluded the back and top of the sculptures (cf. Barca et al. 2010).

Table 1 shows six sampling locations, with 13 sampling areas and 18 weathering crust samples/subsamples in total. The size of the individual sampling areas was about 21 mm x 24 mm (Figure 2). Due to the required resistance to abrasion to not contaminate our samples, we used a stainless-steel blade (420HC, higher carbon) with a Rockwell hardness of 58 for the on-site sample removal. We only sampled the weathering crusts, to be minimally-invasive, as the majority of pollution-related trace metals would have been accumulated in the weathering crust, and to avoid interpretation of the underlying substrate. This approach is supported by numerous studies stating a sharp drop of pollutant concentration between the host rock and the crust (e.g. Fobe et al., 1995; Török, 2002; Farkas et al., 2018).

Similarly, to previous studies, we observed laminar and framboidal crusts (the latter is also called dendritic, globular or cauliflower, e.g. Török, 2002; Farkas et al., 2018) and a mixture of both (Table 1). The morphology of crusts is relevant as Farkas et al. (2018) state that due to the bigger surface and complex geometry of framboidal crusts a higher number of pollutants might get trapped (instead of washed off by run-off as would be the case for laminar crusts). For our three distinct groups, we sampled a mixture of different crust morphologies.

### 2.3 **Inorganic elemental geochemistry**

For each crust, samples were homogenised using an agate pestle and mortar prior to preparation. Subsamples of 20–30 mg were digested with reverse aqua regia (9 ml $HNO_3$ to 3 ml HCl) in a MARS microwave system, according to USEPA 3051A. Samples were then diluted and analysed on a Perkin Elmer 2000B ICP-MS coupled to an ESI prepFAST sample introduction system. Calibration was performed via sequential dilutions on the prepFAST of a single mixed-element standard. Reference material Sigma metals in soil (SRC 001) was prepared in the same manner and analysed periodically to ensure the reliability of the method, although as there is no certified reference material for gypsum crusts, we only used

these values indicatively. Repeat blank analyses were used to determine internal detection limits, and to determine no contamination was present. A suite of 14 trace elements was analysed.

To ensure we only interpret the anthropogenic fraction of the metal content in the crusts, we use two approaches. Firstly, we normalise our data to strontium (Sr), which is a major component in gypsum crusts and a conservative element. As such, it should vary according to the type of crust forming rather than the pollution regime acting on the location (c.f. Barca et al., 2010). In addition, and using Sr as our normalising element, we calculated enrichment factors (E.F.s) according to the following equation:

$$EF = \frac{\left(M/M_{REF}\right)_{sample}}{\left(M/M_{REF}\right)_{UCC}}$$

Where M is the element of interest, and $M_{REF}$ is the normalising element, in this case, Sr. We calculated E.F.s relative to the composition of the upper continental crust (UCC).

### 2.4 Statistical Analysis

Principal Component Analysis (PCA) was carried out on the normalised dataset, and on the anomaly-removed dataset to identify clustering of sculptures with similar geochemical makeup. All data were transformed into z-scores prior to analysis.

## 3 Results and discussion

Table 2 shows the raw data of the trace elements from the ICP-MS analysis in this study. Figure 3 shows our data normalised (to Sr) to the composition of the upper continental crust (Rudnick and Gao, 2014). Lead (Pb), Selenium (Se), and Cadmium (Cd) are clearly elevated, and Arsenic (As), Antimony (Sb), and Zinc (Sn) partly elevated. To mark sets of

pollution sources typical for different periods, we focussed on three representative metals, Pb, Se and As, for their association to leaded petrol and coal burning respectively (e.g. Silk et al., 1986; Zou and Hooper, 1997; Farkas et al., 2018). Despite the gradual reduction since the 1980s and ultimate ban of leaded petrol by E.U. law in 2000, Pb can still be present in weathering crusts and potentially accelerate stone deterioration through catalysing sulphur oxidation and thus, promoting crust formation (e.g. Török et al., 2011; Ruffolo et al., 2015). Furthermore, high levels of Pb, As, and Se all pose a risk to the environment and human health (Zwolak & Zaporowska, 2012; Xie et al., 2006; García-Florentino et al., 2020).

Table 3 shows mean Lead (Pb) concentrations of previous studies in comparison to our study. Oxford ranges in the lower and midfield depending on the location within the city. Remarkably, sculptures which have resided in rural locations such as Nuneham Courtenay and Wytham since removal from Broad Street show higher levels of airborne pollutants compared to those which remained in Oxford. This clearly suggests the crusts have recorded pollution from the sculptures' initial exposure, rather than overprinting by subsequent crust growth. The qualitative comparison of normalised data reveals differences within the crust layers of our samples for the sculptures from the 1$^{st}$ generation (removed from Broad Street in 1868 now located in Worcester (WOR), and Malvern (MAL), and also within the 2$^{nd}$ generation (removed from Broad Street in 1972 now in Wytham (WYT), and Harcourt Arboretum (HAR); Table 2).

The samples from Malvern, MAL_A-2 and MAL_A-3, show low Pb contamination compared to MAL_A-1, which is the outermost and youngest of the crust layers. The low-level Pb contamination of MAL_A-2 and MAL_A-3 can be explained through little exposure to lead pollution from car fuels before the sculptures' removal from Broad Street in 1886. The level detected in MAL_A-1 is comparable to levels found for parts of the crust of the second generation (HAR_A-3, HAR_B-2, HAR_B-3) and even third-generation (HSM_4-2, SHE_4-2, SHE_4-3) which had been exposed to leaded petrol fumes. This suggests a clear

stratigraphy of changing pollution levels is recorded in this crust, with an aspect of overprinting in the outermost layer.

In contrast to the sculptures in Malvern, WOR_A-1 from Worcester College garden shows a lower Pb value compared to WOR_A-2 and WOR_A-3 despite very close vicinity of the sampling locations. In Figure 2B, it can be seen that the sample with the lower Pb value is right underneath the carved hair of the Head sculpture and thus, might have been loaded differently due to water run-off. Otherwise, WOR_A-2 and A-3 are comparable to MAL_A-2 and MAL_A-3 (i.e. low Pb contamination).

In comparison to the 1st generation, we found for both 2nd generation sculptures in Harcourt Arboretum that the outermost crust samples, HAR_A-1 and HAR_B-1, show lower values compared to the innermost crust. This indicates that after the sculptures had been removed in the 1970ies, they were exposed to lower Pb levels, comparable to the 3rd (current) generation's outermost samples in front of the Sheldonian Theatre and the History of Science Museum, SHE_4-1 and HSM_4-1. For the samples HAR_A-2, HAR_A-3 and HAR_B-2, HAR_B-3 (the innermost crust sections) we find the highest levels of Pb in our study. This is a good reflection of the level of pollution on Broad Street between 1868 and 1972 with leaded petrol having been introduced in 1922. Figure 4 shows the pollution signal variations schematically within the crust layers of the three generations of sculptures.

When comparing our findings to previous studies, it becomes clear that intra-city differences and variations within the crust stratigraphy need to be considered, as they can vary on a city scale but also, and more importantly for individual heritage objects in close spatial vicinity. Török et al. (2011) and our study (cf. sample sets WOR, HSM and SHE, Table 2) show significant differences within the same city, and even within the same location (e.g. WOR_A-1 and WOR_A-2). This is further supported by findings of Barca et al. (2010), who find apparent differences in crust stratigraphy within the same built structure.

Since there may be aspects of overprinting, we narrowed down our dataset to yield a better distinction between the different periods. Table 2 shows the respective section in italics and the following samples were removed from the further data processing, MAL A-1 (1st gen), WOR A-1 (1st gen), HAR A-1(1st gen), HAR B-1(1st gen), WYT 1 (2nd gen), HSM 4-1 (3rd gen), SHE 4-1 (3rd gen). We excluded samples where the chronology of the pollution signal was diffused, overprinted, or microclimatic conditions set the sample apart from the rest of the respective set. The latter applied to HSM 4-1, HSM 4-2 and WOR_A-1 where the micromorphology of the sculpture might have allowed for different deposition and water run-off conditions resulting in lower Pb accumulation in the crust. For MAL_A-1, the outer crust shows higher values than the layers below and is the second highest value in our complete set. Only SHE 4-3 is higher with 257.68 ppm. The sample from Wytham (WYT-1) is one individual sample and not part of a set. Given the variations displayed in other sets, we decided to exclude it from the whole dataset. Both outer crusts of the Harcourt sample set (HAR_A-1 and HAR_B-1) show lower Pb levels compared to the rest of the sample set, and thus we concluded that they were representative of a younger, less polluted air quality record.

The subsequent PCA of Sr-normalised data shows two groups, with a small number of outliers (Figure 5) with three principal components (PCs) comprising 80.7% of the variance (PC1: 46%; PC2: 21.3%; PC3: 13.4%; Table 4). PC1 is controlled by loading of the majority of the heavy metals analysed which are representative of prevalent ‘modern’ pollution (Table 4 and Figure 6), with clear positive loading of elements such as Lead (Pb), Cadmium (Cd) and Antimony (Sb) which are linked to the increased use of leaded gasoline (e.g. Krachler et al., 2005; Novak et al., 2008), or are by-products of combustion and industry (e.g. Auras et al., 2013; Ozga et al. 2014; Bisquert et al., 2017).

Zirconium (Zr), Nickel (Ni), and Arsenic (As) are all loaded preferentially on PC2 (Table 4 and Figure 6). Zr, in combination with Cu, has been associated with industrially produced alloys or ceramics (Conny and Norris, 2011). Ni is the most abundant metal in petroleum

(Lee and von Lehmden, 1973) and has been linked to gasoline diesel after the abolition of leaded fuel (La Russa et al. 2017). Ni can also be associated with brake pad wear (Harmens and Norris, 2008; Barca et al.,2014). As (in combination with Zr and Ni) has been associated with friction and wear of asphalt and other manufacturing industries (Harmens et al., 2007; Barca et al., 2014; Graue et al., 2013; Comite et al., 2017). Thus, PC2 is mainly driven by modern pollution, similar to PC1. PC3 is controlled by positive loadings for Silver (Ag), Arsenic (As), Selenium (Se) and Titanium (Ti) (Table 4 and Figure 6). Salmon et al. (1978) related a drop in Se and As to the introduction of the "Clean Air Act" and thus, a reduction in black smoke and coal burning. Further, Ti has been linked to coal burning (Ozga et al., 2014; Yang et al., 2017) as well as Se in combination with As (e.g. Lee and von Lehmden, 1973; Salmon et al., 1978; Mamane et al., 1986; Sabbioni and Zappia, 1992; Xie et al., 2006; Monna et al., 2008). The simultaneous loading of Ag, As, Se and Ti in PC3 suggests that their behaviour is controlled by the same process which leads to As fluctuations, and so we assume PC3 is coal-related.

All 1st generation sculptures show negative values for PC1, near-zero scores for PC2 and mixed scores for PC3. Negative loading of PC1 appears to confirm the more modern nature of the pollution signal recorded in this component (Figure 5 and Table 5). Concurrent low loadings of PC2 suggest little of that type of pollution is observed in these samples, possibly due to their age and PC3 suggests a small-scale effect of coal burning; they were installed prior to the opening of the Oxford canal, and before large-scale industrialisation reached the city (Viles, 1996). Any pollution recorded, therefore, is likely to be wood-burning related.

The 2nd generation sculptures show positive loadings for PC1, PC2 and PC3, suggesting increased pollution from the sources controlling all three components (Figure 5 and 6, Table 5). Such positive loadings indicate an overall increase in pollution from the 1st generation to the 2nd generation and a shift away from wood-burning. In this case, it appears the primary pollution mechanism has shifted toward coal (PC3), but with input from a second, more modern source (PC 2). We argue this is likely the signal of leaded gasoline, which was

introduced to the UK in the 1930s (Farmer et al., 1999), before the removal of this generation of sculptures.

The 3rd generation shows high scores for PC1 and negative loading of PC2, suggesting the source of pollution controlling PC2 is not present in the modern crusts, but that PC1 continues to pollute. However, the signature of leaded petrol is still clear, with some of the highest values for Pb and Cd present in third generation crusts, clearly indicating the ongoing legacy of tetraethyl Pb addition, even long after its phase-out in the UK (Vane et al., 2011). For PC3, we observe mainly negative scores with the exception of SHE_4-3, which scores below 1. This clearly indicates that coal phase-out has improved air quality in Oxford, with low PC3 loadings corresponding to drops in As and Se content.

## 4 Conclusions

This study utilises weathering crusts on stone built heritage as economical, long-term geochemical archives for urban trace element contamination covering past centuries. We developed a pollution record of Oxford city centre by linking distinct time intervals of exposure to observed variations in pollution present in the composition of crusts on a unique set of stone sculptures. The stone sculptures had been exposed successively over 350 years at the same location to three different periods of atmospheric pollution in Oxford; the early Industrial Revolution, the Victorian period and the 20th century. When the first two generations of sculptures 'retired' to less polluted areas (e.g. private and college gardens), their 'pollution clocks' stopped, meaning the pollution recorded in their weathering crusts is representative of historical periods. Our study focussed on three 'marker' trace metals, Arsenic (As), Selen (Se) and Lead (Pb) and Principal Component Analysis of Sr-normalised geochemical data, as representatives for two different sets of pollution sources. As and Se with the Principal Component 3 (PC3) signifies coal burning mainly from 1790 (when the canal opened up) to the 1950s when it was superseded by oil-fired domestic heating and power generation. Thus, this pollution occurred during the installation of the first set of sculptures and peaked during the installation of the second set of sculptures. Pb and PC1

and PC2, on the other hand, indicate a set of modern pollution including but not limited to leaded petrol, which was introduced in the 1930s and banned by E.U. law in 2000. The signature of this pollution started with the second set of sculptures (>1868) and continues until today. Therefore, the 3rd set of sculptures, though not affected by the Victorian coal burning-related pollution, continues to respond to modern pollution.

While we investigated movable stone-built heritage, the results are transferable to immovable stone-heritage. Our sample sets with the unique feature of the stopped 'pollution clock' provide the basis for potentially 'calibrating' crusts which have been exposed to Oxford's environment over the whole period of 350 years; thus, allowing to advance the understanding and finer-scale resolution of the stratigraphy of air pollution within the stone-built archive. Future research should be aimed at increasing the resolution of the pollution reconstruction, and of dating within the crust stratigraphy to improve apportionment to the various pollution sources active over centuries. As we have made clear here, advancing the utilisation of weathering crusts as economical long-term quasi passive samplers for air pollutants has wide-ranging potential applications in stone weathering research and conservation.

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**CRediT authorship contribution statement**

**Katrin Wilhelm**: Conceptualisation, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - Original Draft, Writing - Review & Editing, Visualisation, Supervision, Project administration, Funding acquisition. **Jack Longman**: Conceptualisation, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - Review & Editing, Visualisation, Funding acquisition. **Scott Allan Orr**: Conceptualisation, Writing - Review & Editing, Funding acquisition. **Heather Viles**: Conceptualisation, Validation, Investigation, Writing - Review & Editing.

All authors have read and agreed to the published version of the manuscript.

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Table 1 Overview of samples from this study with respective locations, current aspect, stone type, generation, date of installation and number of total physical samples. SHE=Sheldonian Theatre, HSM=History of Science Museum, S.W.=South West, E=East, S.E.=South East, N.E.=North East, N=North, F=Framboidal crust morphology, L=Laminar crust morphology.

| Current location | Type of current location | Sample aspect | Generation | Date of installation on Broad St | Former (likely) location | Stone type | Crust morphology | Number of samples |
|---|---|---|---|---|---|---|---|---|
| 1. Malvern (MAL) | Rural | S.W. | 1st | 1669 | SHE | 1 | F/L | 3 |
| 2. Worcester College (WOR) | | E | 1st | 1679-83 | HSM | 2 | F/L | 3 |
| 3. Wytham test site (WYT) | Rural | S.W. | 2nd | 1867-69 | SHE | 3 | F/L | 1 |
| 4. Harcourt Arboretum (HAR) | Rural | S.E. & N.E. | 2nd | 1875 | HSM | 4 | F | 6 |
| 5. History of Science Museum (HSM) | Urban | N & E | 3rd | 1972 | HSM | 3 | F/L | 2 |
| 6. Sheldonian Theatre (SHE) | Urban | N & E | 3rd | 1972 | SHE | 5 | L | 3 |
| | | | | | | | *Total* | 18 |

Table 2 Trace elements, raw data [ppm]. Crust section samples indicating a change in pollution signal in the crust layers are in italics. Elements of central interest to this study are in bold. Samples where concentration was below instrument detection limit are marked BDL.

| Gen | Sample | **As** | Ag | Cd | Cr | Cu | Fe | Ni | **Pb** | Sr | Sb | **Se** | Sn | Ti | V |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *1* | *MAL A-1* | **10.12** | 4.96 | BDL | 5.38 | 17.44 | 4916.84 | 9.97 | **255.39** | 249.60 | 2.36 | **8.32** | 5.72 | 195.10 | 20.52 |
| 1 | MAL A-2 | **3.15** | 4.13 | BDL | 2.82 | 13.69 | 4193.56 | BDL | **133.07** | 286.52 | 0.29 | **5.02** | BDL | 71.89 | 13.98 |
| 1 | MAL A-3 | **5.24** | 4.01 | BDL | 3.13 | 10.43 | 3781.31 | BDL | **132.25** | 244.20 | 0.17 | **10.88** | BDL | 63.73 | 9.88 |
| *1* | *WOR A-1* | ***1.21*** | *4.58* | BDL | *5.13* | *11.29* | *6474.27* | BDL | ***70.38*** | *427.00* | *0.25* | ***2.57*** | *0.93* | *37.13* | *16.73* |
| 1 | WOR A-2 | **4.59** | 5.53 | BDL | 6.12 | 20.36 | 6110.98 | 13.36 | **148.68** | 376.[illegible] | 2.69 | **4.60** | 3.82 | 120.06 | 24.20 |
| 1 | WOR A-3 | **3.23** | 3.48 | BDL | 2.42 | 7.59 | 2260.96 | BDL | **102.67** | [illegible]36.[illegible]5 | 0.62 | **3.19** | BDL | 39.30 | 8.67 |
| *2* | *HAR A-1* | ***3.89*** | *4.05* | BDL | *4.70* | *10.97* | *3797.50* | BDL | ***87.04*** | *419.14* | *0.75* | ***3.29*** | BDL | *29.63* | *18.10* |
| 2 | HAR A-2 | **7.38** | 4.27 | 0.19 | 6.03 | 14.40 | 4650.07 | BDL | **297.[illegible]3** | 168.54 | 3.12 | **6.36** | 4.48 | 122.15 | 16.34 |
| 2 | HAR A-3 | **15.91** | 4.73 | 0.17 | 10.49 | 26.61 | 8101.43 | 15.77 | **[illegible]57.00** | 321.18 | 4.64 | **6.60** | 6.31 | 256.40 | 34.11 |
| *2* | *HAR B-1* | ***9.91*** | *3.78* | *0.17* | *8.69* | *20.57* | *5429.49* | *10.[illegible]1* | ***166.47*** | *279.44* | *1.37* | ***6.31*** | *1.36* | *264.47* | *25.49* |
| 2 | HAR B-2 | **9.13** | 3.43 | 0.26 | 7.03 | 17.08 | 5[illegible]59.[illegible]7 | 8.81 | **326.45** | 288.23 | 2.93 | **1.20** | 3.61 | 113.41 | 24.79 |
| 2 | HAR B-3 | **11.56** | 4.37 | 0.20 | 8.92 | 17.[illegible]2 | 55[illegible]6.65 | 9.89 | **332.81** | 258.08 | 3.55 | **BDL** | 3.98 | 137.83 | 21.44 |
| *2* | *WYT 1* | ***0.90*** | *2.85* | *0.13* | *2.43* | *5.8[illegible]* | *[illegible]2660.56* | BDL | ***49.16*** | *245.33* | *0.33* | ***4.41*** | *0.90* | *36.06* | *8.91* |
| *3* | *HSM 4-1* | BDL | *3.16* | BDL | *7.41* | *8.[illegible]* | *4658.77* | BDL | ***87.51*** | *303.51* | *3.87* | ***4.70*** | *3.24* | *19.16* | *15.03* |
| 3 | HSM 4-2 | BDL | 4.58 | 1.00 | 9.[illegible]2 | [illegible]1.84 | 3829.84 | BDL | **239.22** | 209.75 | 6.63 | **4.00** | 5.14 | 83.72 | 16.19 |
| *3* | *SHE 4-1* | BDL | *8.52* | BDL | *10.[illegible]7* | *7.21* | *5555.67* | BDL | ***71.83*** | *331.93* | *2.11* | **BDL** | BDL | *48.05* | *28.54* |
| 3 | SHE 4-2 | **1.34** | 3.06 | 0.20 | 12.26 | 19.98 | 6091.69 | 6.82 | **221.97** | 240.10 | 6.50 | **3.28** | 5.82 | 62.28 | 18.56 |
| 3 | SHE 4-3 | BDL | 10.[illegible]85 | BDL | 9.56 | 26.85 | 4660.07 | BDL | **257.68** | 331.63 | 7.61 | **4.45** | BDL | 164.62 | 31.09 |

Table 3 Mean concentrations [ppm] of lead (Pb) in weathering crusts from previous studies with a focus on calcitic stones (modified after Sabbioni and Zappia (1992) and Farkas et al. (2018)). Small settlement < 50,000, medium settlement 100,000 – 350,000, large settlement >350,000 inhabitants. [1] Sabbioni and Zappia (1992); [2] Torfs and van Grieken (1997); [3] Török et al. (2011); [4] Farkas et al. (2018); [5] this study (shaded cells).

| City (Country) | Environment | Lead (Pb) [ppm] | Stone substrate |
|---|---|---|---|
| Göttingen (GER)[4] | Medium urban | 9 | Limestone |
| Bari (ITA)[4] | Medium urban | 40 | Marble |
| Bari (ITA)[2] | Maritime | 40 | Marble, limestone |
| Reims (FRA)[4] | Medium urban | 48 | Oolitic limestone |
| Wytham (ENG)[5] | Woodland | 49 | Oolitic limestone |
| Oxford (ENG)[5] | Medium urban | 107 | Oolitic limestone |
| Katowice (POL)[4] | Medium urban | 110 | Travertine |
| Halberstadt (GER)[4] | Small urban | 120 | Limestone |
| Venice (ITA)[1] | Maritime | 123 | Marble, limestone |
| La Spezia (ITA)[1] | Maritime | 149 | Limestone |
| Budapest (HUN)[4] | Large urban | 159 | Bioclastic Limestone |
| Malvern (ENG)[5] | Rural | 174 | Oolitic limestone |
| Oxford (ENG)[5] | Medium urban | 176 | Oolitic limestone |
| Braunschweig (GER)[4] | Medium urban | 196 | Oolitic limestone |
| Trento (ITA)[1] | Small urban | 214 | Marble, limestone |
| Nuneham Courtenay (ENG)[5] | Woodland | 261 | Oolitic limestone |
| Eleusis (GRC)[2] | Maritime, industrialised | 360 | Marble and limestone |
| Liege (BEL)[4] | Medium urban | 408 | Limestone |
| Bologna (ITA)[1] | Medium urban | 427 | Marble, limestone |
| Ravenna (ITA)[1] | Maritime, industrialised | 530 | Marble, limestone |
| Rome (ITA)[1] | Large urban | 532 | Marble, limestone |
| Verona (ITA)[1] | Small urban | 615 | Marble, limestone |
| Milan (ITA)[1] | Large, industrialised urban | 883 | Marble, limestone |
| Budapest (HUN)[3] | Large urban | 1,000 | Limestone |
| Halle (GER)[3] | Large urban | 2,000 | Limestone |

Table 4 PCA loadings with three principal components (PCs) comprising 80.7% of the variance (PC1: 46%; PC2: 21.3%; PC3: 13.4%. PC1 is dominated by the majority of the heavy metals analysed except for Zirconium (Zr) and Nickel (Ni) showing even higher loadings in PC2, and Arsenic (As) loaded preferentially on PC2 and PC3. Finally, Selenium (Se) shows the highest load in PC3.

| Loadings | PC1 | PC2 | PC3 |
|---|---|---|---|
| Ag/Sr | 0.020159 | -0.36328 | 0.44535 |
| As/Sr | 0.15129 | 0.44428 | 0.31936 |
| Cd/Sr | 0.21497 | -0.30276 | -0.19335 |
| Cr/Sr | 0.33837 | -0.18952 | -0.18229 |
| Cu/Sr | 0.33301 | -0.28957 | -0.02534 |
| Fe/Sr | 0.32617 | 0.16138 | 0.093341 |
| Ni/Sr | 0.14793 | 0.40296 | -0.33605 |
| Pb/Sr | 0.34249 | 0.039696 | 0.23847 |
| Sb/Sr | 0.29965 | -0.33517 | -0.16793 |
| Se/Sr | -0.07176 | -0.117 | 0.5043 |
| Sn/Sr | 0.35636 | -0.00716 | -0.12544 |
| Ti/Sr | 0.28762 | 0.15498 | 0.36193 |
| V/Sr | 0.33853 | 0.064629 | 0.11074 |
| Zr/Sr | 0.20069 | 0.33902 | -0.09164 |

Table 5 PCA scores for data normalised to Sr and anomalies removed. The 1st generation scores are negative for PC1, near-zero for PC2, and middling for PC3. In comparison the 2nd generation scores mainly positive loadings for PC1, PC2, and PC3. In contrast, the 3rd generation scores high only for PC1, mainly negative for PC2 and PC3.

| Gen | Scores | PC1 | PC2 | PC3 |
|---|---|---|---|---|
| 1 | WOR A-2 | -1.9812 | 0.80412 | -1.2804 |
| 1 | WOR A-3 | -2.3635 | -0.43647 | 1.1287 |
| 1 | MAL A-2 | -3.532 | 0.18223 | -0.3391 |
| 1 | MAL A-3 | -3.6281 | 0.11639 | 1.1037 |
| 2 | HAR A-2 | 3.2726 | -0.05878 | 2.8193 |
| 2 | HAR A-3 | 2.7993 | 2.2038 | 0.60819 |
| 2 | HAR B-2 | 0.64613 | 2.1868 | -1.1931 |
| 2 | HAR B-3 | 1.3853 | 1.453 | -0.48474 |
| 3 | HSM 4-2 | 2.2866 | -3.3593 | -1.1423 |
| 3 | SHE 4-2 | 1.674 | -0.81596 | -2.0686 |
| 3 | SHE 4-3 | -0.55904 | -2.2759 | 0.84826 |

Highlights: Stone-built Heritage as a Proxy Archive for Long-term Historical Air Quality: A study of weathering crusts on three generations of Stone Sculptures on Broad Street, Oxford

- Novel concept of ‘pollution clock’ in layers of black crusts
- Finer-scale resolution pollution reconstruction of the ‘pollution clock’
- First time pollution signals in crusts linked to changing sources of air pollution
- Distinct pollutants represent modern pollution, leaded petrol use and coal burning
- Potential for calibrating black crusts with continuous pollution record


Figure 1

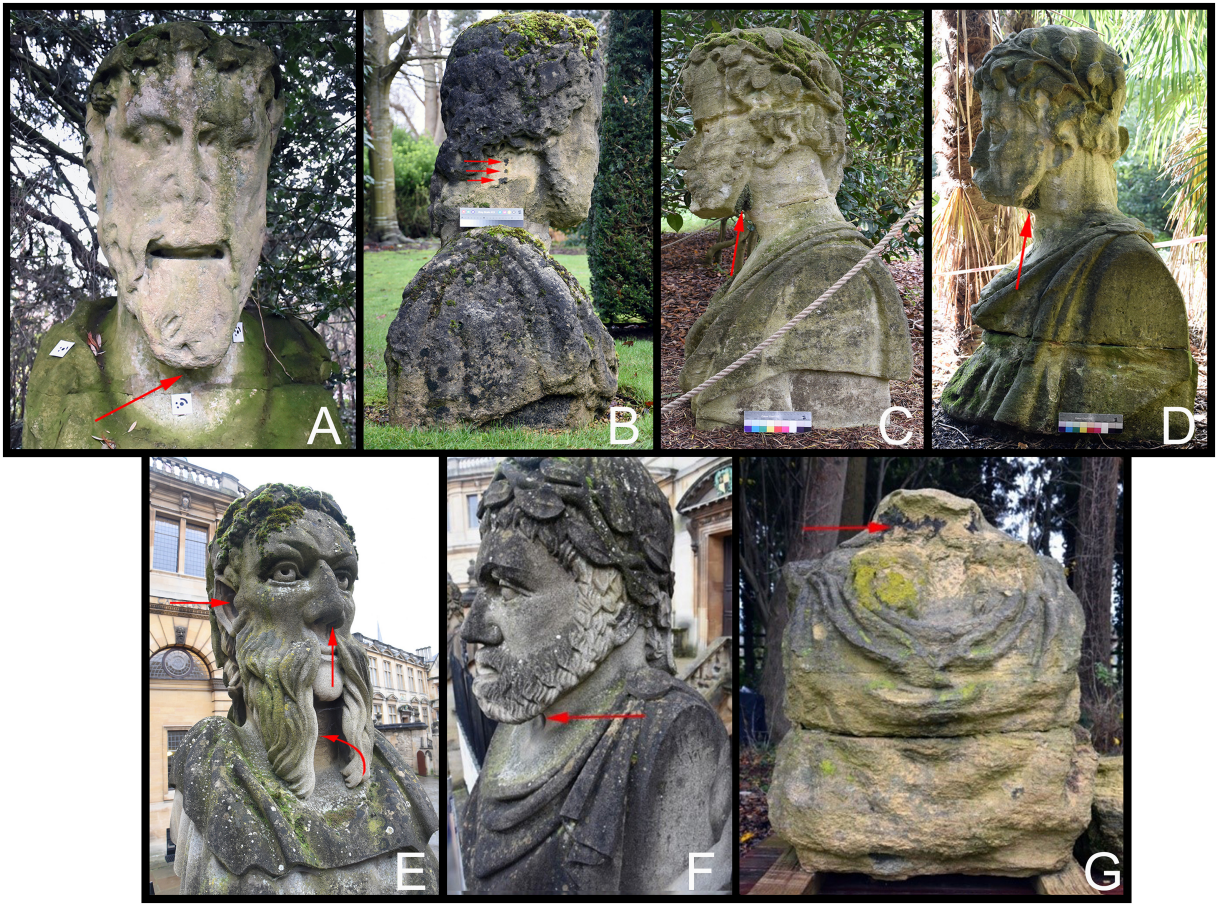


Figure 2

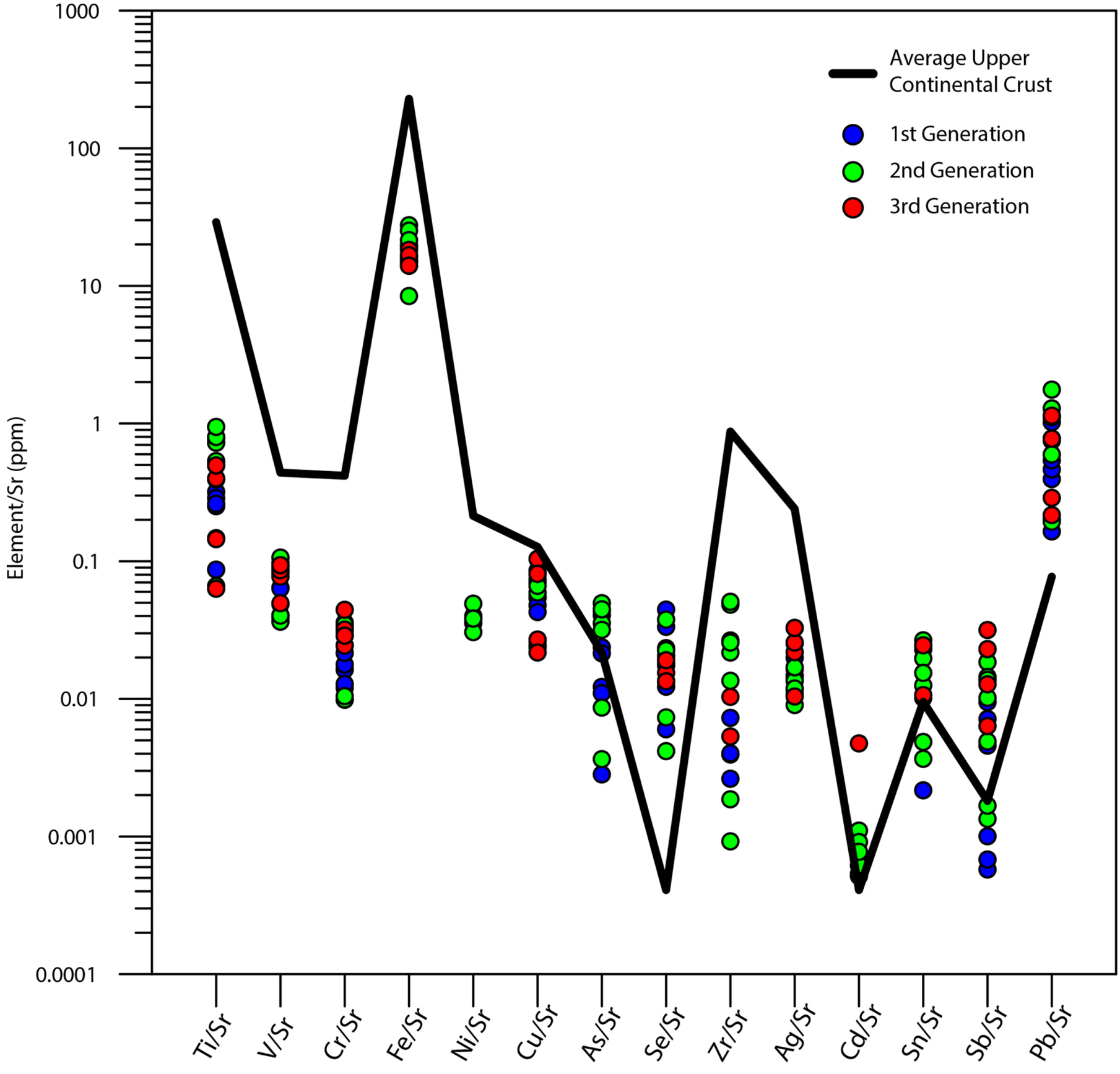
1000
100
10
1
0.1
0.01
0.001
0.0001
Element/Sr (ppm)
Average Upper Continental Crust
1st Generation
2nd Generation
3rd Generation
Ti/Sr
V/Sr
Cr/Sr
Fe/Sr
Ni/Sr
Cu/Sr
As/Sr
Se/Sr
Zr/Sr
Ag/Sr
Cd/Sr
Sn/Sr
Sb/Sr
Pb/Sr

Figure 3

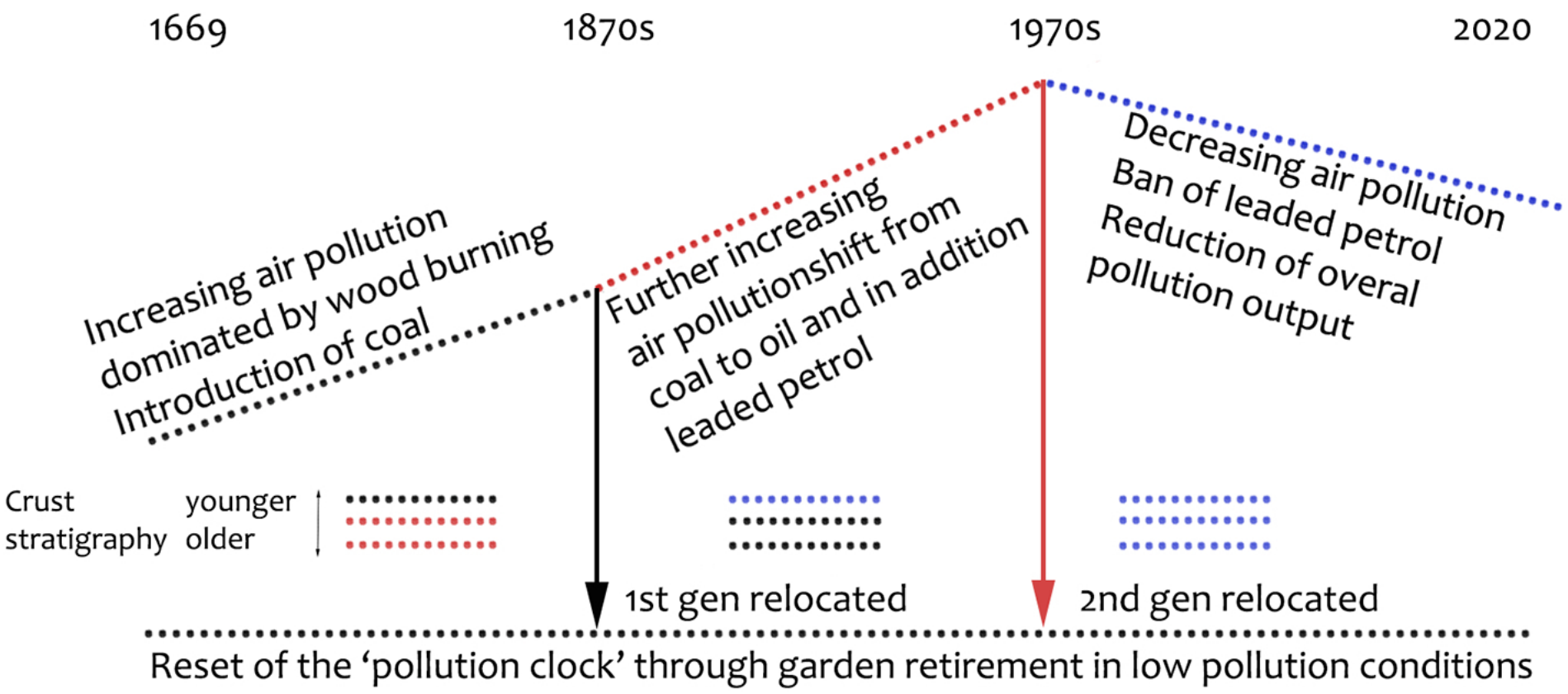
1669
1870s
1970s
2020
Increasing air pollution
dominated by wood burning
Introduction of coal
Further increasing
air pollutionshift from
coal to oil and in addition
leaded petrol
Decreasing air pollution
Ban of leaded petrol
Reduction of overal
pollution output
Crust
stratigraphy
younger
older
1st gen relocated
2nd gen relocated
Reset of the 'pollution clock' through garden retirement in low pollution conditions

Figure 4

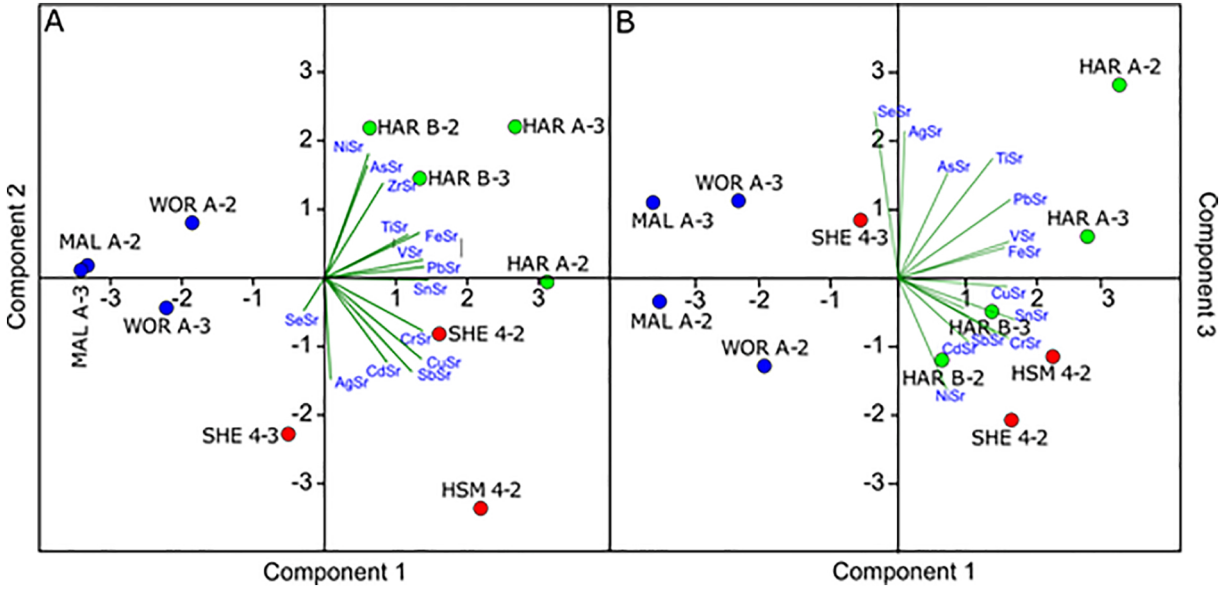
A
B
Component 1
Component 2
Component 3
HAR B-2
HAR A-3
HAR B-3
HAR A-2
WOR A-2
MAL A-2
MAL A-3
WOR A-3
SHE 4-2
SHE 4-3
HSM 4-2
NiSr
AsSr
ZrSr
TiSr
FeSr
VSr
PbSr
SnSr
SeSr
CrSr
AgSr
CdSr
CuSr
SbSr

Figure 5

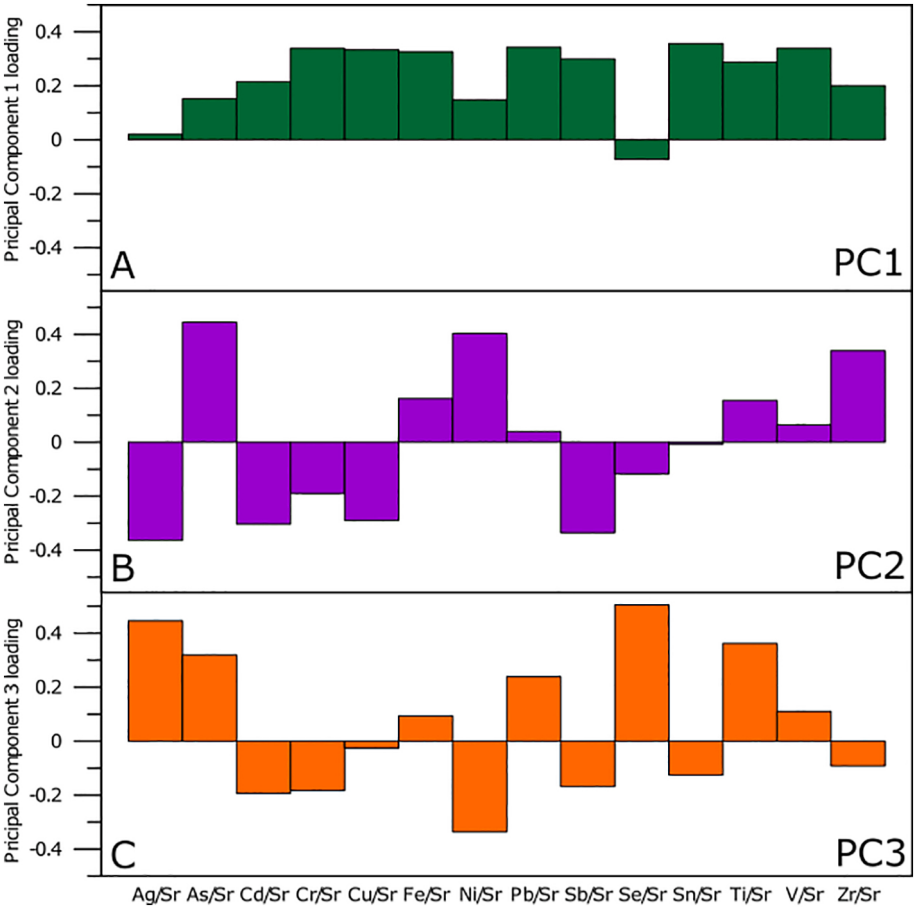
Pricipal Component 1 loading
0.4
0.2
0
-0.2
-0.4
A
PC1
Pricipal Component 2 loading
0.4
0.2
0
-0.2
-0.4
B
PC2
Pricipal Component 3 loading
0.4
0.2
0
-0.2
-0.4
C
PC3
Ag/Sr As/Sr Cd/Sr Cr/Sr Cu/Sr Fe/Sr Ni/Sr Pb/Sr Sb/Sr Se/Sr Sn/Sr Ti/Sr V/Sr Zr/Sr

Figure 6