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## Carbon in Black Crusts from the Tower of London

ALESSANDRA BONAZZA,<sup>†</sup> PETER BRIMBLECOMBE,<sup>\*,‡</sup> CARLOTA M. GROSSI,<sup>‡</sup> AND CRISTINA SABBIONI<sup>†</sup>

*Institute ISAC-CNR, Bologna 40129, Italy, and School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK*

This paper investigates the origin, fluxes, and transformation of carbon compounds within black crusts on the stone walls of the Tower of London. The crusts were analyzed for elemental and organic carbon, including the water soluble fraction. Elemental carbon and low solubility compounds such as oxalates appeared to be conserved because of long residence times. Conversely, more soluble ions, like chloride and formate would be removed from the layers relatively quickly by rainfall. At higher organic carbon concentrations acetic acid may be produced within the crusts from biological transformations. Currently, traffic sources contribute to increasingly organic rich crusts. The deposition of elemental carbon to buildings darkens surfaces and has important aesthetic implications. The increased organic content may have further aesthetic consequence by changing the color of buildings to warmer tones, particularly browns and yellows. Management of historic buildings requires us to recognize the shift away from simple gypsum crusts to those richer in organic materials.

### Introduction

Urban air pollution is a major source of damage to architectural heritage. Whereas in the early twentieth century building surfaces were blackened and sulfated by coal use, now they appear to be darkened by diesel soot (1) and possibly more affected by nitrogen deposition than previously (2). In the foreseeable future it is likely that damage from atmospheric pollutants will derive more from organic deposits than traditional sulfation of the past (3). Thus gypsum rich crusts may be replaced by more organic rich layers on carbonate stone surfaces along with an increased potential for greater biological activity (4). Typically damage layers are composed of transformation products, deposited aerosol, and fragments of the original substrate. These black crusts contain embedded organic and elemental carbon. The high optical absorption of elemental, or black, carbon is the main agent of darkening, and therefore responsible for much contemporary aesthetic impact.

The present work investigates the formation and origin of elemental carbon and some simple organic compounds (i.e., oxalate, formate, and acetate) in black crusts. The composition of the layers provides an insight into their formation, but we often have to work with limited numbers

of samples from heterogeneous substrates. In the case of older buildings the history of restoration is usually not well documented. Nevertheless, we have tried to examine samples of crust from the Tower of London to gain an understanding of the deposition, transformation, and accumulation of disfiguring black layers on urban stone surfaces.

### Experimental Section

**Tower of London.** The Tower of London incorporates many buildings in addition to the central *White Tower* and is divided into three fortified wards: the *Inmost Ward*, comprising the central and Norman parts of the building (5). To the north, east, and west, this is surrounded by the *Inner Ward*, and beyond lies the *Outer Ward*, a fortified corridor created at the end of the 13th century. The wharf and moat revetment are outside these wards. More than twenty different stones were employed during the centuries of construction. One widely used material was a hard limestone (Kentish Ragstone), which is most frequently encountered in uncoursed walling (6), and is the substrate for most of the sampling undertaken during this project.

**Environment.** Since the late 13th century London has been a polluted city. The last 100 years have seen a transition from coal smoke to emissions from petrol and later diesel fuels (7). In the Victorian period, English cities were badly polluted, and building stones rapidly became blackened and damaged by sulfation (8). Although there have been many improvements in overall air quality in the last 50 years, emissions in central London remain high. Before the 1950s air pollution came from coal burning (3), and contained elemental carbon (with adsorbed organic compounds) and sulfur dioxide. Today the chemical composition of aerosols is more varied, but includes elemental carbon (EC) and organic carbon (OC) arising mainly from vehicle emissions, especially diesel, and sulfur is less dominant.

Measurements of aerosol composition in central London at background sites since the late 1990s (3, 9) show particulate EC and total OC to be  $2.6 \mu\text{g}\cdot\text{m}^{-3}$  and  $5.2\text{--}7.6 \mu\text{g}\cdot\text{m}^{-3}$ , respectively (i.e., OC/EC from 2.0 to 2.9). The reported concentration of EC and OC at London and Birmingham roadsides was higher ( $9.2$  and  $8.3 \mu\text{g}\cdot\text{m}^{-3}$ ) and suggests lower OC/EC ratios, i.e.,  $\sim 0.9$ . Elemental carbon in London is believed to derive mainly from on-road vehicle emissions, whereas OC originates primarily from inputs outside the street canyon (10). There are high OC emissions from gasoline and smaller emissions from diesel (11), with typical OC/EC ratios of 2.2 and 0.8 for light-duty gasoline and heavy duty diesel vehicles, respectively (12). London currently has a large diesel fleet. The OC contributions from wood (12), biomass, and coal burning are higher than those of EC (13, 14).

**Sampling Sites.** Early restoration at the Tower is poorly documented and until recently projects were managed on a day-to-day basis. In the past the Tower was not cleaned, but repairs were undertaken after 1850 when cement began to replace lime as a binder for the repair mortars. Surface soiling is linked to local sources of pollution and derives from a balance of EC accumulation and its redistribution by wind-driven rain. Boat traffic from the River Thames on the southern side and heavy road traffic on the northern one are the two main local sources of pollution that affect the Tower. The distance from the main buildings to the roads and the river is about 30–50 m. However, the number of particles decreases rapidly with distance from traffic so we can consider the Tower of London to resemble a London urban background site.

\* Corresponding author phone: 44(1603)593003; fax: 44(1603)-507719; e-mail: p.brimblecombe@uea.ac.uk.

<sup>†</sup> Institute ISAC-CNR.

<sup>‡</sup> University of East Anglia.

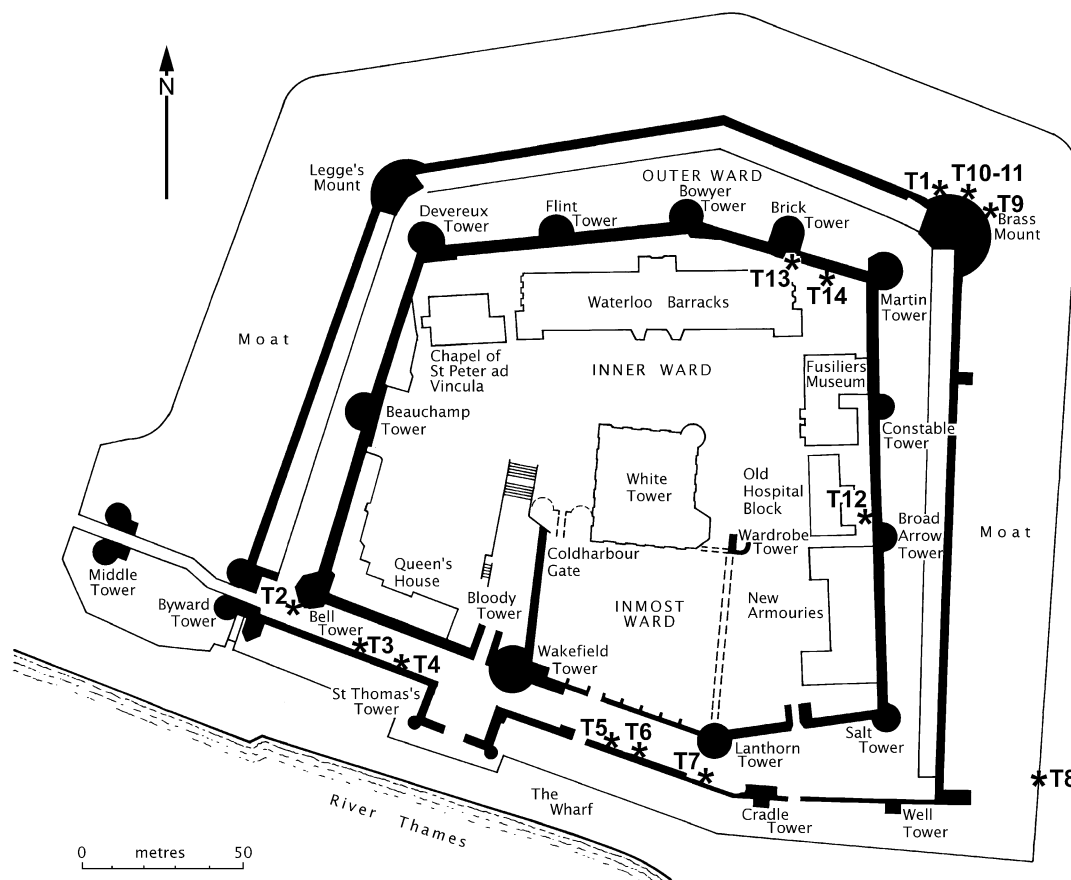


FIGURE 1. General plan of the Tower of London showing the sampling points (from English Heritage).

TABLE 1. Sample Characteristics

sample	location	description	past restoration work <sup>a</sup>
T4	outer curtain wall; facing N, 1.50 high	typical dendritic black crust; scarce stone substrate	restored during the 19th century by the architect Salvin; there does not appear to be any later interventions or repairs
T5–6	outer curtain wall; facing N, 1.50 high	typical black crust	restored during the 19th century by the architect Salvin; there does not appear to be any later interventions or repairs
T11	brass mount, outer curtain wall; facing NE, 1.50 high	thin gray–brown crust + abundant underlying material	the area of sampling appears to have been repaired with hard lime mortar around the 1930s with some later cement repairs
T12	opposite old hospital; east side, facing W, 1.50 high	thin “globular” black crust + very deteriorated and abundant underlying material	most of the surface has been repointed during the 1960s/70s; building activity around this area during the post war years would have been intense as part of the building suffered damage and was rebuilt repairs using pointing cement mortars date from the late 19th century
T14	inner curtain wall, between the brick tower and the Martin Tower; north side facing S, 2.50 high	very thick dendritic black crust	

<sup>a</sup> Richard Roberts, personal communication.

The facades of the Tower complex that face south are oriented to the prevailing winds and as a consequence are more frequently washed by rain. Thus they benefit from a self-cleaning effect, especially during the present period of decreased smoke emissions. This process was also observed in America and other European countries (4, 15).

In this research, the crusts were sampled using a thin metal blade and brushes (labeled T1–T14) in the form of incoherent material and fragments from the south, east, and

northeast side of the *Outer Curtain Wall* and the *Inner Curtain Wall* (Figure 1). The results presented here relate to samples from small areas of wall (<1 m<sup>2</sup>) T4, T5–6, T11, T12, and T14 (Table 1), chosen as representative of the whole sampling program, in terms of morphological features, location, and not directly exposed to intense wind-driven rain. Furthermore, the amount of material collected at these sampling points was sufficient to permit a complete set of analytical procedures on each sample.

**TABLE 2. Concentration and Cumulative Flux in Black Crust Samples<sup>a</sup>**

sample	T4	T5-6	T11	T12	T14
% of transformation layer	87	70	34	43	93
density ( $10^3 \text{ kg}\cdot\text{m}^{-3}$ )	2.21	2.60	2.62	2.49	2.28
thickness ( $10^{-3} \text{ m}$ )	1.32	1.24	0.05	0.24	2.13
calcite <sup>b</sup>	main mineral present	main mineral present	main mineral present	main mineral present	abundant
quartz <sup>b</sup>	present	abundant	very abundant	present	abundant
gypsum <sup>b</sup>	very abundant	abundant	very abundant	abundant	main mineral present
sulfate ( $\text{mol}\cdot\text{kg}^{-1}$ ) <sup>c</sup>	4.02	3.52	1.62	3.42	3.80
chloride ( $\text{mol}\cdot\text{kg}^{-1}$ ) <sup>c</sup>	0.043	0.016	0.037	0.063	0.101
nitrate ( $\text{mol}\cdot\text{kg}^{-1}$ ) <sup>c</sup>	0.011	0.034	0.010	0.141	0.008
formate ( $\text{mol}\cdot\text{kg}^{-1}$ ) <sup>c</sup>	0.164	0.070	0.128	0.135	0.323
acetate ( $\text{mol}\cdot\text{kg}^{-1}$ ) <sup>c</sup>	0.009	0.012	0.003	0.030	0.011
oxalate ( $\text{mol}\cdot\text{kg}^{-1}$ ) <sup>c</sup>	0.135	0.134	0.031	0.086	0.149
NCC ( $\text{mol}\cdot\text{kg}^{-1}$ ) <sup>d</sup>	3.15	2.83	1.86	3.50	2.73
CC ( $\text{mol(C)}\cdot\text{kg}^{-1}$ ) <sup>e</sup>	1.132	2.57	1.75	4.87	0.591
EC ( $\text{mol(C)}\cdot\text{kg}^{-1}$ ) <sup>d</sup>	1.07	0.820	0.198	0.404	0.849
OC ( $\text{mol(C)}\cdot\text{kg}^{-1}$ ) <sup>d</sup>	2.08	2.01	1.66	3.10	1.89
OC/EC	1.95	2.44	8.73	7.68	2.21
formate/EC	0.15	0.08	0.65	0.34	0.38
acetate/EC	0.01	0.01	0.02	0.07	0.01
oxalate/EC	0.13	0.16	0.15	0.21	0.17
EC <sub>A</sub> ( $\text{mol}\cdot\text{m}^{-2}$ ) <sup>f</sup>	2.69	4.04	0.323	0.618	3.85
OC <sub>A</sub> ( $\text{mol}\cdot\text{m}^{-2}$ ) <sup>f</sup>	5.27	9.91	2.71	4.74	8.51
SO <sub>4</sub> <sup>2-</sup> ( $\text{mol}\cdot\text{m}^{-2}$ ) <sup>f</sup>	10.2	17.4	2.65	5.23	17.2
lightness (L*) <sup>g</sup>	36	36	52	37	31

<sup>a</sup> Analytical errors for the measurement of carbon had a coefficient of variation between 3 and 6%; that for the ions lay between 1 and 2%. However, variation due to difference between crusts on separate parts of the wall at the same site are much greater, typically 25% (see text). <sup>b</sup> XRD data. <sup>c</sup> IC data expressed as  $\text{mol}\cdot\text{kg}^{-1}$  of transformation layer. <sup>d</sup> Carbon data (NCC, EC, and OC) expressed as  $\text{mol(C)}\cdot\text{kg}^{-1}$  of transformation layer. <sup>e</sup> Contribution of carbonate original material (both within the damage layer or as underlying material): mol of carbon measured not adjusted. <sup>f</sup> Surface area concentrations or cumulative flux. <sup>g</sup> L\*: from 0 (black) to 100 (white).

Samples T4, T5-6, and T14 are old black crusts of different thickness and structure, with samples T4 and T14 being thicker and dendritic. The areas where these samples were collected were last restored during the 19th century, so they represent about one and a half century of accumulation. Sample T12 is a thin, well-defined crust in an area re-pointed during the 1960s/1970s. Sample T11, collected from the moat side of the *Outer Curtain Wall*, is a thin brownish crust, difficult to separate from the substrate, representing a damage layer that probably accumulated after the 1930s restorations. The available information on past restoration, sample description, and location is summarized in Table 1.

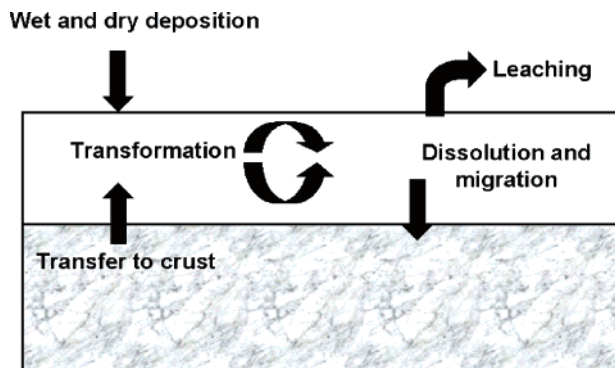
**Physical and Chemical Analysis Methods.** Microscopic examination (Olympus BX51 microscope) established the petrographic, mineralogical, and morphological features of the black crust and substrate material. Mineralogical composition was also determined by X-ray diffraction analysis using a Philips PW1730 diffractometer. A series of analyses by ion chromatography using a Dionex 4500i allowed determination of the concentration of soluble anions in the crust (16). The analyses included measurements of sulfate ( $\text{SO}_4^{2-}$ ), chloride ( $\text{Cl}^-$ ), formate ( $\text{HCO}_2^-$ ), acetate ( $\text{CH}_3\text{CO}_2^-$ ), and oxalate ( $\text{C}_2\text{O}_4^{2-}$ ).

The carbon fractions in the crusts were quantified using a novel analytical procedure (17). The analytical methodology consists of three steps and requires about 1 g of powdered material for a complete analysis. In the first step total carbon (TC) is determined by burning the bulk sample. In the second step the non-carbonate carbon (NCC) is measured by burning a bulk sample where carbonate carbon (CC) was removed by treatment with HCl vapor. Carbonate carbon is then calculated according to the relation  $\text{CC} = \text{TC} - \text{NCC}$ . A third step allows the determination of the elemental carbon (EC) content by CHNSO thermal analysis, after the elimination of the organic and inorganic carbon through a series of alternating acid and basic treatments. Organic carbon is calculated according to the relation  $\text{OC} = \text{NCC} - \text{EC}$ . The

methodology was tested using four simulated black crusts of known composition (17) with an error that had a coefficient of variation between 3 and 6%. Ion analysis was more accurate (1–2%), but sampling error was very much greater. Multiple sampling of the same part of the wall suggested a coefficient of variation of 25%.

The measurements of carbon, organic matter, and other deposited or transformed products are underestimated because the samples include fragments of underlying material as crusts are not easily separated from the substrate and carbonates can be introduced from dissolution of the stone substrate. The data in Table 2 correct the concentrations of the crust components by assuming that the carbonate carbon came from the underlying material as calcite (Kentish Ragstone is 86% calcite). Such adjustments allowed us to estimate the proportion of transformed or deposited material (first row of Table 2) and the substrate, which are very important in the case of thin layers where substrate is invariably incorporated in samples. The corrected values allow an assessment of the accumulation of components over long periods of time and also result in area concentrations which are useful in assessing the flux of material to the crust. The conversion to area concentration required the density ( $\text{kg}\cdot\text{m}^{-3}$ ) and thickness (m). The density of fragments was determined using a gas displacement pycnometer (Multivolume Pycnometer 1305) and suggested a total porosity of about 6.5% (low). The average thickness of fragments was determined by optical scanning and image analysis of multiple cross sections.

Finally, the blackening was characterized by the value of lightness (L\*) using spectrophotocolorimetry (Minolta CM-2600d), which scales from 0 (black) to 100 (white). The lightness was compared to the area concentration of EC which is the main component responsible for surface blackening.



**FIGURE 2.** Conceptual model showing the fluxes within the crust. It illustrates a dynamic system that involves atmospheric deposition, transfer to and from the stone substrate, chemical transformation, dissolution, migration, and loss of soluble compounds.

## Results and Discussion

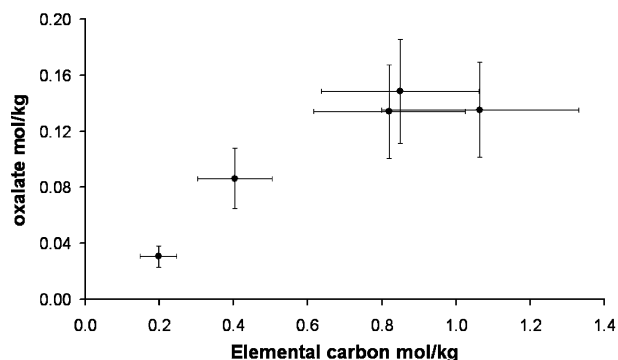
The observations under microscope revealed the typical morphology and composition of black crusts in urban and industrial areas. The stratigraphy of the old, thicker crusts highlighted the presence of prismatic particles, spherical aluminosilicates and metals, and carbonaceous particles. These are indicative of wood, coal, and oil combustion processes. Table 2 summarizes the analytical results, expressed in terms of corrected concentrations, along with the fraction of the transformed layer and the estimated cumulative flux ( $\text{mol}\cdot\text{m}^{-2}$ ). We will use the cumulative fluxes to reinforce arguments about deposition of material into the crust.

As expected, the main mineralogical phases are calcite, gypsum, and quartz. Calcite and quartz (the latter especially abundant in T11) derive mostly from the substrate, whereas the remaining materials, including all non-carbonate carbon (NCC), are the result of deposition or transformation. Gypsum is the best known reaction product from the interaction between limestone and atmospheric  $\text{SO}_2$ .

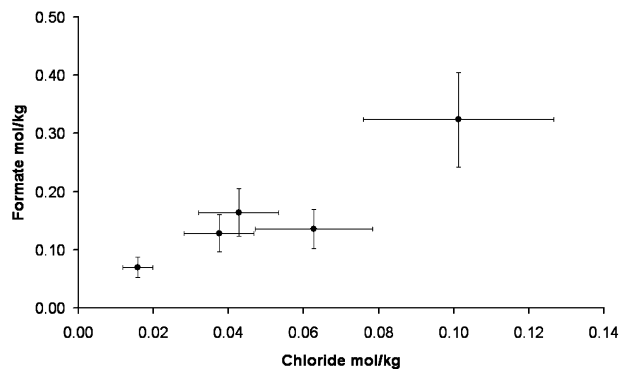
Figure 2 illustrates the types of fluxes and transformations of atmospheric materials on the stone surfaces. This conceptual model involves deposition and accumulation, and the formation of damage products due to material-atmosphere interaction. Once formed, water soluble components can undergo dissolution and leaching, or migrate to the underlying substrate. Gavino et al. (18) found both aliphatic and aromatic carboxylic acids and phenols in black crusts. Their solubility allows them to migrate and form a yellow layer at the crust/stone interface. Transfer from the substrate to the crust is an important part of crust formation. One would imagine that, once deposited, elemental carbon is unlikely to be rapidly removed, and undergo transformation relatively slowly. Thus it would be largely conserved. A similar case might be made for oxalates which accumulate over time, but are rather insoluble so tend to be retained. Hence these two components are expected to be related in way that is shown in Figure 3. The data in this figure, as with that in Figures 4 and 5 is the corrected data from Table 2, but the graphs show very similar trends if plotted using the raw analytical data.

Soluble ions would also be expected to show a good correlation. Thus chloride concentrations in the crust should be related to ions such as formate as they are both soluble and removed from the crust in similar ways by rainfall. The correlation between these two ions is shown in Figure 4.

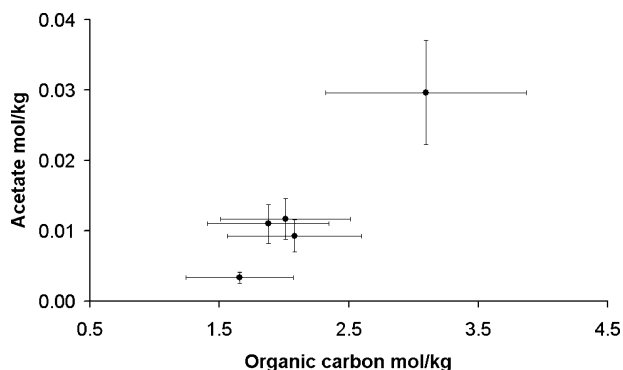
Acetic acid is also soluble so it should be lost from the crust, but it is also potentially a product of continuous biological transformation of organic carbon within the crust. This is particular evident in the case of T12, which has noticeably high concentrations of acetate and organic carbon.



**FIGURE 3.** Oxalate versus elemental carbon concentrations in the crusts.



**FIGURE 4.** Formate versus chloride concentrations in the crusts.

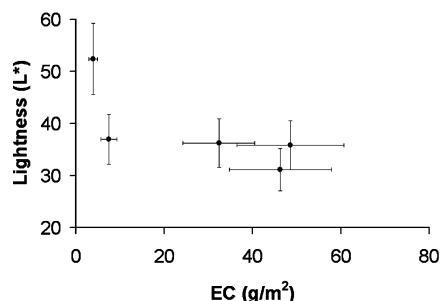


**FIGURE 5.** Acetate versus organic carbon concentrations in the crusts.

Although there is a clear relationship between acetate and organic carbon (Figure 5), we should also note that there appears to be a minimum concentration of organic carbon (e.g., about  $1.4 \text{ mol}\cdot\text{kg}^{-1}$ ) before any acetate production. It might be that more easily metabolized organic carbon is consumed leaving more refractory materials that are less easily converted to acetate. If acetate concentrations in crusts were set by a balance between production and loss, at low concentrations our observations would suggest low production rates where there is little metabolizable organic carbon.

The relationships illustrated in Figures 3–5 aid our consideration of the net flux of these materials in the crusts (see bottom of Table 2). Even in the current atmosphere low in sulfur dioxide, substantial proportions of sulfate accumulate in the crust. However, in the thinner and possibly more modern crusts (T11 and T12) we find a higher  $\text{OC}/\text{SO}_4$ , reminding us that these are more organic rich. It should also be noted that EC is more stable than OC, so as OC degrades over time it would produce lower  $\text{OC}/\text{EC}$  ratios in older crusts, so even the semivolatile organic compounds from coal burning might be slowly lost over time. The  $\text{OC}/\text{EC}$  ratio





**FIGURE 6. Measured lightness ( $L^*$ ) versus elemental carbon area concentrations in the crusts.**

measured in modern crusts at the Tower of London is about 8, i.e., much higher than the 2.9 OC/EC found in city centers (10, 19). This suggests that other process such as biological productivity produce this excess of organic material. In recent decades lower sulfur dioxide (a phytotoxin) concentrations and increasing deposition of nitrogen compounds and organic compounds in the late 20th century have encouraged biological activity on buildings (4).

Data for the carboxylic acids in the crust yield further information about the changes underway. Acetate and formate could be produced by biological activity, and this is reflected in high formate/EC and acetate/EC ratios in modern crusts. The ratios in the modern crusts are thus expected to be higher than those in the contemporary atmosphere. There are no simultaneous measurements of formate, acetate, oxalate, and EC for London's atmosphere. However, some values for formate (7.3 ppb) and acetate (3.9 ppb) are found from Yokohama–Japan (20), a city with high petroleum consumption, much like London. There are also no measurements for oxalate in London aerosols, so we have adopted the value  $6 \text{ nmol} \cdot \text{m}^{-3}$  (21). These along with values of EC ( $2.08 \cdot 10^{-7} \text{ mol} \cdot \text{kg}^{-1}$ ), formate ( $2.98 \cdot 10^{-7} \text{ mol} \cdot \text{kg}^{-1}$ ), and acetate ( $1.55 \cdot 10^{-7} \text{ mol} \cdot \text{kg}^{-1}$ ) suggest the following mole ratios: formate/EC = 1.43, acetate/EC = 0.74, and oxalate/EC = 0.02. Oxalate is clearly more abundant in crusts than in the modern urban atmosphere (relative to EC), suggesting that biological activity on the building surfaces is a dominant source in accordance with previous work (22).

Blackening of historic buildings by diesel soot is of contemporary concern and in the case of the Tower of London, the keep is known as the *White Tower*, which raises visitor expectations (23). The lightness ( $L^*$ ) of the samples, measured colorimetrically, related to the area concentrations of EC (Figure 6), falls rapidly with EC at low concentrations, and reaches a limiting value at high concentrations. Such exponential relationships are typical of the blackening process (24).

The figure also suggests a minimum value of lightness  $L^*$  around 35 where EC area concentration in the crust is around  $10 \text{ g} \cdot \text{m}^{-2}$  and above. Public perception of the lightness of historic buildings has been used to propose aesthetic thresholds for acceptable darkening (25). These thresholds provide a method for setting limit values of EC in the air, so that historic buildings do not become unacceptably blackened. Initial studies suggest that EC concentrations of around  $2\text{--}3 \text{ mg} \cdot \text{m}^{-3}$  might be acceptable. In the past, it is likely that the Tower of London was exposed to much higher concentrations of EC. In the foreseeable future, a continued lowering of EC concentrations is expected as a result of the effort to minimize airborne particulate matter because of health concerns. While it is true that heritage has benefited from regulations that have addressed the effects of urban air on public health, it is somewhat coincidental given the very different cause/effect relationships involved. Health effects derive primarily from particle size and concentration in the air, but for the blackening of buildings the effects derive

mainly from color (i.e., EC content) and cumulative flux. In particular one should note that modern deposits have taken on a slightly different color and now appear more brownish (26). These changes may arise from oxidation processes in the organic rich materials. The color change is particular evident here at the Tower of London, where yellowing may become of greater concern than the habitual blackening in the near future.

Conservation science is motivated by a desire to protect our heritage. The results here suggest substantial changes in the nature of building crusts over the past century. Approaches to caring for buildings can no longer assume a simple gypsum layer with embedded carbonaceous particles. We now find deposits with a potential for a greater amount of organic chemistry and biological activity. The changing nature of the crust will have aesthetic implications through changes in color, and economic impacts in terms of the approaches for cleaning and maintaining the buildings. It is also a reminder that the management of air pollution for the purpose of protecting human health should be seen as being distinct from measures taken for the preservation of the built heritage.

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