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Strong evidence for the continued contribution of lead deposited during the 20th century to the atmospheric environment in London of today

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Abstract

Although leaded gasoline was banned at the end of the last century, lead (Pb) remains significantly enriched in airborne particles in large cities. The remobilization of historical Pb deposited in soils from atmospheric removal has been suggested as an important source providing evidence for the hypothetical long-term persistency of lead and possibly other pollutants in the urban environment. Here, we present novel data on Pb isotopic composition in airborne particles collected in London (2015–2018) which provide strong support that lead deposited via gasoline combustion still contributes significantly to the lead burden in present-day London. Lead concentration and isotopic signature of airborne particles collected at a heavily trafficked site did not vary significantly over the last decade, suggesting that sources remained unchanged. Lead isotopic composition of airborne particles matches that of road dust and topsoils and can only be explained with a significant contribution (estimate of 32 ± 10 to 43 ± 9% based on a binary mixing model) of Pb from leaded gasoline. The lead isotopes furthermore suggest significant contributions from non-exhaust traffic emissions even though isotopic signatures of anthropogenic sources are increasingly overlapping. Lead isotopic composition of airborne particles collected at building height shows a similar signature to that collected at street level, suggesting effective mixing of lead within the urban street canyon. Our results have important implications on the persistence of Pb in urban environments and suggest that atmospheric Pb reached a baseline in London which is difficult to decrease further with present policy measures.

Keywords: lead isotopes, urban air pollution, aerosols, source tracing, contaminant persistence, re-suspension.

Significance Statement

Lead is a highly toxic element and low-level environmental lead exposure remains a prime concern due the effects on neurodevelopment in children. It provides a well-researched example of the impact of human activities on environmental quality and the effectiveness of mitigation policies. Using recent and historical data on lead isotopic composition in London airborne particles, we show strong evidence that sources have not changed substantially since the ban in 1999 of leaded gasoline, the main source of environmental lead during the 20th century, suggesting that historical gasoline-derived lead remains an important source of lead in the urban environment due to its persistence and effective remobilization. Novel abatement policies need to be considered if this cycle is to be interrupted.

Introduction

Risk assessments of environmental lead (Pb) exposure have drawn the conclusion that it is not possible to identify a blood Pb level below which no adverse impact is detectable (1, 2). Even very low blood Pb levels in children are associated with a loss of full-scale IQ, and the curve steepens at lower blood Pb levels, with a greater loss of IQ per unit of blood Pb in the lowest exposure groups (1, 2). Although currently available research has included subjects with very low blood Pb, it is not possible for such studies to go to zero lead, but it is prudent to treat Pb as a non-threshold toxin (3). Bellinger (2012) estimated full-scale IQ point losses in the early 2000's in the USA child population associated with six medical conditions, four neurodevelopmental disorders, two socioeconomic, nutritional and psychosocial factors and three environmental chemical exposures (methylmercury, organophosphate pesticides and Pb) (1). Lead exposure ranked second amongst all fifteen risk factors, behind only pre-term birth, and first among the environmental chemical exposures. Much of the summed IQ loss occurred amongst the lowest exposed groups due to their larger numbers, and even if population blood lead levels have declined since the Bellinger study, and more children have hence moved into the lower exposure groups (4), the total IQ loss across the population may remain substantial.

A major policy achievement in our efforts to reduce Pb in the environment has been the global phase-out of Pb from gasoline at the end of the last century which resulted in a drastic decrease of atmospheric Pb concentration, especially in urban and remote areas of Europe and North America. While exposure to Pb from paints, Pb pipes, and Pb-containing toys are now recognized as the main cause of elevated blood lead levels in children in non-industrial environments, Pb remains an environmental pollutant of great concern (5) as its ongoing existence in the environment affects environmental quality in cities and is raising particular concerns regarding the long-term exposure (6). A significant association between Pb concentration in PM_{10} and USA population's blood was recently demonstrated (7), suggesting that inhalation and/or ingestion of coarse particle might be an important pathway for human exposure to Pb. Viewed in this context, Pb in the environment remains a significant threat to public health and it is absolutely essential to accurately identify and monitor the sources and pathways of Pb in the urban environment.

While it has been suggested that lead sources in urban environments today include local and/or distant emissions from industries, coal burning and traffic (exhaust and non-exhaust emissions) (8–11), recent works studying Pb contamination of airborne particles in (peri-)urban environments (10, 12), have suggested that ongoing contributions of lead, released into the environment by leaded gasoline combustion during the last century, remain an important but underestimated source. If confirmed more widely, then abatement strategies aimed at eliminating Pb fully from the urban environment need to be adjusted. It is very important to note that these recent findings are in line with an early study of Pb in sediments and water of the San Francisco bay suggesting already in the early 2000's that recycling of legacy lead from leaded gasoline may be a continuing threat to environmental health (13, 14). Furthermore, a shift in Pb concentrations within size distribution, from the fine range ($PM_{2.5}$) to the coarse range (PM_{10}), has been highlighted after the ban of leaded gasoline in the USA and Europe and ascribed to a change in dominant Pb sources consisting of industrial emissions and road dust resuspension instead of direct vehicle exhausts (15).

Alkyl lead motor fuel additives were used in the United Kingdom from the 1930s until phase-out was completed at the end of 1999. Although added in an organometallic form, Pb emissions from the vehicle were predominantly in the form of a fine aerosol of inorganic lead salts (16). The maximum permitted level of Pb in UK motor fuel was 0.84 $g.L^{-1}$. The limit fell successively to 0.40 $g.L^{-1}$ in 1981 and 0.15 $g.L^{-1}$ in 1986. At its peak in the early 1980s, of the order of 7,000 tons per year of Pb were emitted from road traffic exhaust in the UK which had fallen to just three tons by the year 2000 (17). Until its final ban, leaded gasoline combustion remained the most important source of Pb emissions in the UK atmosphere (17). In the early 1980s, annual average airborne Pb concentrations at background sites in

central London were around 500-600 ng.m^{-3} which fell to around 300 ng.m^{-3} in the second half of the 1980s, and then dropped progressively to around 20 ng.m^{-3} in 2000. Airborne concentrations now are generally less than 10 ng.m^{-3} and have remained steady over the last decade (18).

Using lead isotope composition of atmospheric particles has been a crucial tool in tracing the origin of Pb in the environment and identifying leaded gasoline as a dominant source during the 20th century (19). Following the removal of Pb additives from gasoline in Europe, Pb isotope ratios of atmospheric particles generally changed towards more radiogenic values due to the increase in the relative contribution of other Pb sources (19). Such an evolution was recorded in London airborne particles between 1998 and 2001 during the final phasing out of leaded gasoline in the UK (20). However, this trend was no longer observed a decade later leading to the suggestion that leaded gasoline remained an important source of atmospheric Pb (9).

The aim of this study was to test if remobilization of historical gasoline-derived Pb remains today an important and persistent source of Pb in London and the urban environment. To this end, we studied the Pb isotope composition of airborne particles collected in central London between 1995 and 2018, using new and historical data and quantified the possible contribution of historical gasoline lead. London is representative of many large cities in developed countries where particle emissions from industries and coal combustion are now relatively low and where traffic emissions and dust resuspension represent dominant sources of airborne particles. Therefore, it constitutes an ideal site to study the persistence of Pb in urban environments almost twenty years after the complete phase out of leaded gasoline. The variability of Pb concentration and isotopic composition was determined in PM_{10} and total suspended particles (TSP) during one month at a heavily trafficked site in central London (Marylebone Road site, MR) where particle emissions are dominated by traffic. The data were compared with previously published isotopic composition of potential Pb sources and PM_{10} from this historically monitored site. In addition, the variability of Pb isotopic composition in $TSP_{passive}$ collected between 2014 and 2018 at building height in central London (Imperial College London site, IC) is reported to determine mixing and source contributions within the urban canyon.

Results and discussion

Lead sources at a heavily-trafficked site in central London

The PM_{10} concentration measured at the Marylebone Road (MR) site ranged between 16 and 25 µg.m^{-3} (Table 1) and matched the daily means reported by the London Air Quality Network during the same period (23 ± 5 µg.m^{-3} (21)). Southerly to westerly winds prevailed over the sampling period and only a few short rain showers occurred (Supplementary Information, Figure S1). Under such wind conditions, the air flow is coming from the nearby road junction or from adjacent traffic to the monitoring station, promoting high PM_{10} and air pollutant concentrations related to traffic emissions (22).

Table 1 shows Pb concentrations (PM_{10}), deposition rates (TSP), enrichment factors (EF_{Pb}) and isotope ratios in PM_{10} and $TSP_{passive}$ collected at the MR site during the summer 2018. Lead deposition rates and enrichment factors were determined using Equations 1 and 2, respectively (Material and Methods). Lead concentration in PM_{10} ranged between 3.9 and 19.4 ng.m^{-3} and were slightly higher than those measured at the MR site in July 2010 (1.1-8.8 ng.m^{-3}, (9)). Lead deposition rates for the $TSP_{passive}$ were between 11700 and 45800 ng.m^{-2}.d^{-1} which represent 10-40 times and 2-9 times the Pb deposition rates recorded using the same sampling device at a busy boulevard in Strasbourg, France, and a German highway, respectively (23). This is due to the high traffic-related particle load characteristic of the MR site. The enrichment factor for lead, EF_{Pb} ranged between 100 and 559 in PM_{10} and 66 to 91 in $TSP_{passive}$ (Table 1), indicating the high contribution of anthropogenic Pb in airborne particles at the MR site and showing an influence of the particle size on the enrichment of Pb. Elements commonly associated with traffic emissions from vehicle wear such as Ba, Cr, Cu, Fe, Ni and Sb (24, 25) were highly enriched in PM_{10} (EF > 10) and to a lesser extent in $TSP_{passive}$ (Figure 1 and SI, Table S1). This observation is in line with

the known effect of the size contribution on the enrichment of these elements. In contrast, Zn presented similar high EF in both PM_{10} ($181 \leq EF_{Zn} \leq 318$) and $TSP_{passive}$ ($179 \leq EF_{Zn} \leq 749$), reflecting the important contribution of tire abrasion to the coarse fraction (PM_{10}) and the super-coarse fraction (> 10 µm) as well (25, 26). Elements released by brake abrasion (Ba, Cu, Cr, Fe) show strong correlations in PM_{10} ($r > 0.7$, SI Table S2), and in $TSP_{passive}$ despite the lower enrichment values observed (Figure 1). Surprisingly, EF_{Sb} in PM_{10} are 5-time lower in 2018 than in 2010 and do no longer correlate well with other metals ($0.4 < r < 0.7$, SI Table S2). This is likely the consequence of the progressive removal of Sb from brake pads by constructors because of its suspected carcinogenic effect (27) and our observation is consistent with the higher than usual Cu/Sb ratio reported for new brake pads in London in 2010 (9). Enrichment factors of Pb are not correlated with EF of any other metal as already observed in a previous study at the site (9). This is suggesting that its emission is not controlled by a dominant source such as brake (Ba, Cu, Fe, Cr) or tire wear (Zn) but rather results from another dominant source or more likely from a mixture of different sources. The lower EF observed in $TSP_{passive}$ can be explained by the collection of super-coarse particles less enriched with Pb and other metals (except Zn), which probably consist of road surface material besides tire particles. This is further supported by TLM (transmitted-light microscope) images of $TSP_{passive}$ samples showing opaque elongated and round/irregular shaped super-coarse particles which are typical for tire-road wear (SI, Figure S2, samples MR1b-MR3b). Recent high time resolution measurements of Pb and Si in PM_{10} at the MR site showed that Pb and Si, a marker for soil-derived mineral dust, exhibited the same diurnal trend suggesting that resuspension with high traffic is associated with higher airborne Pb (SI, Figure S3).

Average Pb isotope ratios in PM_{10} and $TSP_{passive}$ measured over the same time period at the MR site were not significantly different (t-test, $p>0.31$) ($^{206}Pb/^{207}Pb = 1.137 \pm 0.003$, $^{208}Pb/^{206}Pb = 2.125 \pm 0.003$ and $^{206}Pb/^{204}Pb = 17.70 \pm 0.05$ for PM_{10} (n=8) and $^{206}Pb/^{207}Pb = 1.133 \pm 0.005$, $^{208}Pb/^{206}Pb = 2.127 \pm 0.005$, $^{206}Pb/^{204}Pb = 17.64 \pm 0.08$ for $TSP_{passive}$ (n=5)). Differences of Pb isotopic composition observed between PM_{10} and $TSP_{passive}$ at each sampling date were smaller than the variability observed within PM_{10} and $TSP_{passive}$ over the sampling period (Figure 2). The results suggest that most of the Pb mass is associated with the PM_{10} fraction which is supported by the lower EF_{Pb} observed in $TSP_{passive}$ indicating a 'dilution' by less contaminated super-coarse particles. Therefore, in this context, the continuous monitoring of Pb isotopic composition of $TSP_{passive}$ collected using the passive sampler Sigma-2 appears as a suitable low-cost technique to monitor long-term changes of Pb sources in coarse airborne particles. However, it should be noted that passive sampling does not allow investigation of Pb deposition changes with a high time resolution. For example, the sample MR6a showed the highest Pb concentration together with a relatively low $^{206}Pb/^{207}Pb$ ratio compared to the average value. This was likely due to a short-term event (e.g. construction works in the street, building demolition…) and was not visible with passive sampling because the corresponding sample (MR5b) integrated a longer period of time.

Lead isotope ratios of PM_{10} and $TSP_{passive}$ collected during the summer 2018 were not statistically different to that of PM_{10} measured by Dong et al. (9) in 2010 at the same site (t-test, $p>0.30$) showing that the Pb isotope composition displayed a stable signature over the last decade and that Pb sources remained unchanged (Figure 3). A source apportionment study of aerosols collected at the MR site based on a statistical factor analysis of the chemical composition suggested that coarse particles (2.5-10 µm) are composed of construction dust (6%), vehicle wear (13%), resuspended road dust (31%) and sea-salt (49%) while fine particles (< 2.5 µm) are composed mainly of construction dust (9%), sea-salt (10%), exhaust and non-exhaust traffic emissions (33%) and secondary inorganic aerosols (49%) (24). Lead was not included in the source apportionment of coarse particles due to concentrations being close to the relatively high detection limit of the analytical technique used (PIXE). Lead was not included in the source apportionment of coarse particles due to concentrations being close to the relatively high detection limit of the analytical technique used (PIXE). In the fine particles ($PM_{2.5}$), Pb was largely associated with a long-range transported "secondary inorganic aerosols" factor containing also crustal elements. In a separate sampling campaign during the same 2012 research program, Visser et al. (28) found using a different analytical technique (SR-XRF) an appreciable fraction of Pb (41% on average)

associated with the coarse fraction showing a fairly balanced distribution of Pb between fine and coarse particles. During the sampling period, air masses generally travelled across the North Atlantic Ocean and crossed the southern UK before reaching the sampling site (SI, Figure S4). Air trajectories coming from Northern France, Belgium and Netherland were recorded only during the sampling of MR1. Under these conditions, the contribution of Pb transported from European mainland must be minimal (29). The emissions inventory reported by the UK National Atmospheric Emission Inventory estimates that brake and tire abrasion could be the major current source of atmospheric Pb in London, representing about 60% of Pb primary emissions (17). However, this inventory is associated with high uncertainties and has been shown by Dore et al. (2014) to seriously underestimate Pb emissions as compared to Pb deposition measurements (30). Tire and brake material, as well as road surface material have more radiogenic isotope ratios than $TSP_{passive}$ and PM_{10} (Figure 3, (9)). However, the isotopic composition of road dust ($^{206}Pb/^{207}Pb$ = 1.133 ± 0.011, $^{208}Pb/^{206}Pb$ = 2.129 ± 0.011, $^{206}Pb/^{204}Pb$ = 17.66 ± 0.21, n=6, (9)) and urban topsoils of London ($^{206}Pb/^{207}Pb$ = 1.139 ± 0.017, $^{208}Pb/^{206}Pb$ = 2.125 ± 0.017, n=50) (31) overlaps with that of airborne particles (Figure 3). As shown on Figure 3, they fall on a mixing line between the signature of leaded gasoline formerly used in the UK (32) and of natural geogenic Pb in the UK (32), UK Pb ore (33) and non-exhaust emissions (9). A compilation of $^{206}Pb/^{207}Pb$ ratio of potential Pb sources in London is presented in Table S3 (SI). They all have a more radiogenic composition than airborne particles, except for lead paint. Data for lead paint remain scarce, isotope composition published for paint in Scotland showed a $^{206}Pb/^{207}Pb$ ratio of 1.117 ± 0.003 (34), overlapping with present-day signature of airborne particles. It is reasonable to assume that lead paint contributes to "Pb hotspot" in urban private and public gardens where old lead paint is deteriorating, but it is an unlikely major source in atmospheric particles in urban canyons. For example, a study in Tokyo, Japan, showed that while gasoline and paint chips were found to contribute to increased Pb in surface soils of playgrounds, the contribution of paint chips was significantly smaller than gasoline Pb (35). In New Orleans, USA, it was estimated that at least ten times more Pb dust was released from vehicle exhaust than from lead paint (36). Therefore, the isotope signatures strongly suggest that only a contribution of historical Pb originating from leaded gasoline can explain the less radiogenic composition observed in soils, road dust and airborne particles. This is also in line with previous results from a study that assessed that up to 43% of Pb in UK road dusts derived from leaded gasoline in 2010 (37). Indeed, Dore et al. (2014) showed that national primary emissions of Pb estimated by the UK NAEI could only account for 7% of the measured Pb atmospheric concentration and suggested that wind-driven re-suspension of surface dust could partly explain the gap between modeled and measured values (30). Amato et al. (38) in a study of dust resuspension on a Mediterranean freeway calculated an emission factor of 16-22 µg $Pb/veh.km^{-1}$. Using this value and road traffic statistics in London, we calculated that 450-650 kg of Pb would be emitted in London every year by dust resuspension. Alternatively, Denier van der Gon et al. (39) provided emissions factors of PM_{10} for light and heavy-duty vehicles (48 and 432 mg $PM_{10}/veh.km^{-1}$, respectively). Based on a Pb concentration in road dust in London of 22-410 $\mu g.g^{-1}$ (9), we calculated that 45-800 kg of Pb would be emitted yearly through resuspension. The latter upper-bounding estimate is in line with the former. Despite the uncertainty associated with this estimate, it shows that remobilization of Pb from road dust resuspension is likely of the same order than current estimation of primary Pb emissions. This is consistent with our conclusions based on isotopic ratios.

Lead isotopic compositions in 2010 and 2018 were slightly different than those between 1998-1999 characterized by a less thorogenic composition (i.e. lower $^{208}Pb/^{204}Pb$) and those between 2000-2001 characterized by a more radiogenic composition (i.e. higher $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$) (Figure 3). During this period (1998-2001), a progressive shift of Pb isotope ratios is observed indicating a declining contribution of leaded gasoline interpreted as the result of the final ban of leaded petrol in the UK in 2000 (20). The isotopic shift was accompanied by a rapid decline of Pb concentrations in airborne particles. The disparity observed between 1998-2001 and 2010-2018 data is likely explained by the contribution of a different traffic-related Pb source at the end of 20th century. We propose that this additional source is related to either unleaded gasoline combustion (20) and/or to increased contribution

from vehicle wear (e.g. Pb wheel weights) before the introduction of a regulation in 2003 prohibiting the use of Pb in materials and components in vehicles sold in the EU market (European Directive 2000/53/EC). Indeed, in the early 2000's unleaded gasoline still contained low levels of Pb in Europe and data available for an unleaded French gasoline could explain the observed trend (40). However, Pb isotope composition of unleaded gasoline and vehicle component may have varied in the past depending on the provenance of the original crude oil or Pb ore. The lack of isotope data for the materials used during this period undermines our ability to definitely identify the additional source(s) responsible for the observed off-set. Recent European diesel (n=26) and gasoline (n=64) contained less than 1.5 $\mu g.kg^{-1}$ of Pb (41). This was confirmed by measuring lead concentration in gasoline (n=2) and diesel (n=2) collected in June 2018 from two different petrol stations in London. Lead content in gasoline and diesel was lower than 2 and 0.6 $\mu g.kg^{-1}$, respectively. Calculations accounting for fuel consumption in London (~1.5 Mt of diesel and 0.9 Mt of gasoline per year) and the Pb content in fuel measured in this study and others (41) demonstrate unequivocally that fuel combustion is no longer a relevant source of Pb (less than a few kg per year).

Lead isotopic composition variation between 2013 and 2018 at building height in central London

Lead deposition rates, enrichment factors (EF_{Pb}) and Pb isotope ratios in $TSP_{passive}$ collected between 2014 and 2018 at the Imperial College London (IC) site are presented in Table 1. Lead deposition rates varied from ~ 3100 to 9800 $ng.m^{-2}.d^{-1}$ which represent on average 26% of the Pb deposition rates recorded at the MR site. EF_{Pb} varied from 71 to 475 with an average of 209 ± 95 (n=19). Lead deposition rates were lower in autumn and winter than in spring and summer certainly due to suppression of resuspension in the wetter months of the year (SI, Figure S5). Seasonality in coarse particles has been observed at both traffic (Marylebone Road) and urban background sites in London and attributed to a more effective resuspension process during the drier seasons (42). However, EF_{Pb} do not exhibit such seasonal variations (Figure 4 and SI, Figure S5) showing that Pb level in $TSP_{passive}$ was not sensitive to seasonal emission sources like domestic fuel combustion, different to what has been found for Cu in 2014 in London (43). EF_{Pb} does not display a declining long-term trend indicating that Pb reached a steady level in the atmosphere of central London. Similar EF_{Pb} values in $TSP_{passive}$ were recorded at the IC site and at Marylebone Road over the same period. EF_{Pb} does not correlate with enrichment factors of other metals as already observed at the MR site. Other elements studied (Ba, Cu, Cr, Fe, Ni, Sb, Zn) show slightly lower enrichment factor values at the IC site compare to the MR site but still denote anthropogenic inputs (Figure 1). Elements typical of brake wear emissions fall on the same regression line as MR samples demonstrating a common origin (Figure 1).

The Pb isotopic composition of $TSP_{passive}$ at the IC site shows a larger range of isotopic ratios than at the MR site with $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ ratios varying from 1.0977 to 1.1482, 2.1153 to 2.1636 and 17.049 to 17.900, respectively (Table 1). The sample S18 (09/2017) displays unusually low $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios and has the highest EF_{Pb} and Pb deposition rate. A three-day pollution episode (high $PM_{2.5}$ and PM_{10}) occurred during S18 sampling interval. Polluted air arriving from the continent to the area of London might explain the unusual Pb signature (21). Alternatively, the anomaly could be related to local emissions and possibly to demolition works carried out next to the sampling site at that time. Apart from this event, as observed for EF_{Pb}, Pb isotope ratios do not exhibit a seasonal or long-term trend (Figure 3) confirming that Pb sources remained the same throughout the year – that suggest that coal and fossil fuel burning does not add significantly to the lead burden. Lead isotope ratios at the IC site are not significantly different (t-test, $p>0.77$) to that measured in PM_{10} and $TSP_{passive}$ at the MR site (Figure 5). Samples S20 and S21 collected during the summer 2018 show similar EF_{Pb} and Pb isotope ratios as $TSP_{passive}$ collected during the same period at the MR site indicating that Pb sources are the same. These results suggest that Pb has a homogeneous origin in airborne particles of different sizes in urban canyons in central London and that there is no apparent additional source at the IC site compared to the MR site. This is consistent with TLM optical analysis of $TSP_{passive}$ samples of the IC site showing that tire wear particles emitted from traffic are, in small numbers, also present even at

building height (SI, Figure S2, sample S20). Changes in the $^{206}Pb/^{207}Pb$ ratio with possible varying contribution of coal has been modelled using a mixing equation between a) the average composition of air particles at Marylebone Road measured during the summer 2018 (representative of Pb emissions from traffic and dust resuspension) and b) the average composition of coal used in the UK which has a $^{206}Pb/^{207}Pb$ ratio between 1.18 and 1.22 (SI, Table S3). An increase in Pb emissions due to coal combustion would be responsible of an increase of $^{206}Pb/^{207}Pb$ values in airborne particles toward a more radiogenic isotope composition (SI, Figure S6). All samples (except S1) indicate a coal contribution to Pb signature lower than 10%, ruling out a significant contribution of coal combustion to Pb burden (SI, Figure S6). Indeed, coal consumption has drastically declined in the UK during the last decade. Combustion of fuel (oil and coal) in relation with domestic, industrial and commercial sectors has been estimated at ~300 kg of Pb per year in the Greater London Area representing a maximum of 8% of total emissions (17) in accordance with our results.

Quantification of leaded gasoline contribution to Pb contamination of airborne particles

We made an attempt to estimate the historical contribution of Pb originating from leaded gasoline (X in %) using a binary mixing model (Equation 1) considering two end-members, i.e. (1) "gasoline Pb" using the signature of leaded gasoline used in the past in the UK (32) and (2) "non-gasoline Pb" representative of other possible sources (present-day non-exhaust emissions and historical UK coal and ore). Natural crustal source can reasonably be neglected considering the high enrichment factor values ($54 < EF_{Pb} < 559$) observed in airborne particles both at the traffic MR site and the IC site (Table 1).

$$X = \frac{\left(^{206}Pb/^{207}Pb\right)_{sample} - \left(^{206}Pb/^{207}Pb\right)_{non-gasoline\ Pb}}{\left(^{206}Pb/^{207}Pb\right)_{gasoline\ Pb} - \left(^{206}Pb/^{207}Pb\right)_{non-gasoline\ Pb}} \times 100 \qquad \text{(Equation 1)}$$

To test the validity of this approach, a sensitivity analysis was performed to assess the contribution of leaded gasoline using different isotopic compositions for the "non-gasoline Pb" end-member calculated using different proportions of Pb from non-exhaust emissions, UK ore and UK coal. To this end, the Pb isotopic composition of the "vehicle wear" end-member was calculated using recent Pb emission factors associated with tire and brake abrasion (SI, Table S4) indicating a contribution of 17% from tire wear and 83% from brake wear and the isotopic composition of tire and brake used in London as reported by Dong et al. (9). Results do not significantly change if the average isotope composition of all non-exhaust emissions or vehicle wear alone (SI, Figure S7). The results obtained using the two extreme "non-gasoline Pb" sources (i.e. 100% vehicle wear and 100% UK coal and ore) are presented in Table 1 and Figure S7 (SI). Other ratios ($^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$) gave similar results with a maximum bias of 8%.

At the heavily trafficked MR site, leaded gasoline could contribute to 32 ± 5% of Pb in PM_{10} which is similar to the contribution of 37 ± 8% determined using 2010 data from Dong et al. (9) when using vehicle wear as the "non-gasoline Pb" source end-member. An equivalent average gasoline contribution was found in $TSP_{passive}$ at the MR site (29 ± 3%) and at the IC site (32 ± 10%). Estimated contribution of leaded gasoline to airborne Pb reaches 42 ± 4% (PM_{10}, MR site), 40 ± 3% ($TSP_{passive}$, MR site) and 43 ± 9% ($TSP_{passive}$, IC site) when using UK coal and ore as the "non-gasoline Pb" source end-member. These results highlight a continuous and significant contribution of historical Pb from gasoline in central London airborne particles over the last decade.

It should be noted that this approach does not allow estimation of the relative contribution of other historical sources (UK coal and ore) and present-day non-exhaust emissions due to the similarity of their isotopic signatures, nor the contribution of lead paint because its signature is not well constrained and is probably overlapping that of airborne particles. However, vast amounts of Pb have been emitted from leaded gasoline combustion in the London atmosphere during the 20th century. It is estimated that ~140,000 tons of gasoline-derived Pb were released in the UK atmosphere between 1970 and 2000 (17). Consequently, Pb has been deposited in urban soils in which it can have a long residence time (44–46)

as reflected by the high median Pb concentration (175 µg.g^{-1}) reported for topsoils in the Greater London Area (31, 47–49). Soil isotope composition has been explained by the long-term accumulation of anthropogenic emissions from several sources including leaded gasoline combustion but also from coal burning and demolition of buildings during the Second World War (paint, pipes) (31, 48). However, higher median Pb concentrations are measured in topsoils located near to roads (< 100m) probably due to accumulation of greater amount of Pb from leaded gasoline (48). A recent study of a sediment core sampled in the Thames in London showed that sediments were already enriched with Pb in the 1940's (^{206}Pb/^{207}Pb ratio ≈ 1.16) but the isotope composition shifted later with the lowest ^{206}Pb/^{207}Pb values recorded between 1950's- 1980's when leaded gasoline consumption was at its highest level (50). Lead isotope composition in the most recent sediments did not return to the <1940's value (^{206}Pb/^{207}Pb ratio ≈ 1.14) providing further evidence of the long-term contribution of leaded gasoline. This is consistent with the results of Ayrault et al. (51) who found that only 1.4% of Pb emitted annually in the Seine River basin during the use of leaded gasoline was exported in the river implying that most of the gasoline Pb accumulated in soils of the basin (51). The conclusion is supported by several studies showing that urban and roadside soils preserved the gasoline signature (37, 52). Old buildings in cities kept the signature of past Pb atmospheric emissions as well (53, 54) demonstrating the general 'impregnation' of the urban environments with historical gasoline-derived Pb.

Environmental significance

Lead concentrations measured in PM_{10} in London over a decade were stable and low compared to the concentration recorded during the last century (annual average of 8.8 ± 0.9 ng. m-^{3} for the period 2010-2017 at London Westminster (18)). Nevertheless, this study shows that historical Pb stored in the urban environment represents a persisting source of Pb in airborne particles in London via the remobilization of contaminated dust. Non-combustion traffic-related emissions represent a major source of atmospheric Pb through direct emissions from road and vehicle wear and indirect emissions consisting of the resuspension of road dust which is a mixture of abrasion particles (vehicle and road wear) and of mineral dust deriving from historically contaminated soils and urban surfaces. Lead isotopic composition of airborne particles collected at building height showed a similar signature to that collected at street level, suggesting that Pb is well mixed within the urban environment in central London and reached a steady baseline. Even though health policy needs to solve the problem of high-level exposure of children as a matter of priority, our study clearly shows the persistence of lead historically emitted from leaded gasoline combustion in urban environments and may be important from an environmental health perspective. Positive correlation has been found between soil resuspension, airborne lead and children's blood lead level in several large cities in the USA (10, 36, 55). Our data strongly suggest that soils act as a persistent source for airborne Pb in London implying that lead remobilization might be an overlooked exposure pathway in London. Future research is now needed to investigate the seasonal variations of airborne Pb in relation to soil resuspension and to assess its possible relationship with children's blood lead levels. If such a link exists, historical lead remobilization could only be interrupted by new abatement strategies. Possible remediation strategies to reduce mobilization of soil lead include covering contaminated urban soils with low Pb soil driven by a high resolution Pb soil mapping, which has been effective in reducing children's blood lead levels in New Orleans (6).

Material and methods

Sample collection

Eight samples of PM_{10} and five samples of total suspended particles ($TSP_{passive}$) were collected during the summer 2018 at street level (height of 3.5 m) at a heavily trafficked site in central London (Marylebone Road, MR). This site belongs to the London Air Quality Network and has been used extensively for air quality studies including for Pb isotopic composition monitoring during the period 1998-2001 and in 2010 (9, 20). The station is located on the curbside of a street canyon characterized

by high traffic (>80 000 vehicles per day) and frequent congestion. PM_{10} (MR1a - MR8a) were collected over 96 h on acid-cleaned PVDF filters (Ø 47mm, 1 µm) during 32 days in July and August 2018 using a Partisol-Plus Model 2025 Sequential Air Sampler. In parallel, two passive samplers (Sigma-2 device, Deutscher Wetterdienst DWD) were installed next to the active sampler inlet (distance of ~1 m and height of ± 25 cm) to collect $TSP_{passive}$ (defined as particulate matter with a diameter up to 50 µm deposited via sedimentation in the passive sampler device (26, 56)). One passive sampler collected TSP in an acid-cleaned receptor dish (Ø 65 mm) and was dedicated to geochemical analyses (Pb and metal concentrations and Pb isotope ratios). Standard DWD transparent sticky foil was placed in the second passive sampler and used for transmitted-light microscope analysis (TLM). The receptors of both passive samplers were exposed for 96 h and exchanged at the same time as PM_{10} filters (MR1b –MR4b) except the last sample (MR5b) which integrated a longer sampling period (4x 96 h). The passive sampling method was used in addition to the conventional active sampling of PM_{10} to determine the influence of the size of particles (coarse 2.5-10 µm and "super-coarse" 10-50 µm) on Pb isotopic composition due to the possible contribution of different Pb sources to the different size fractions.

In addition, the variability of Pb isotopic composition in $TSP_{passive}$ at building height in central London was assessed by analyzing a series of samples collected using a passive sampler Sigma-2 installed on the roof top (24 m above the street level) of the Royal School of Mines at Imperial College London (IC site). Twenty samples (S1-S21) were taken at intervals of 4-8 weeks between February 2014 and August 2018. $TSP_{passive}$ were collected in a receptor dish as described above. Metal deposition rates and enrichment factors (Al, Zn, Cu, Fe, Sb and Cd) and Cu and Zn isotopic signature of the samples S1-S12 have been presented in Ochoa Gonzalez et al. (43).

Sample digestion

All the experimental work was carried out in a Class 1000 clean lab and under Class 10 laminar flow hoods in the MAGIC laboratories at Imperial College London. All material was acid-cleaned before use. Acids were of Suprapur quality or purified by distillation. For each set of digestion, a blank and two certified reference materials (20 mg of granite USGS G-2 and road dust BCR 723) were processed in the same way as for samples.

PM_{10} filters were weighed before and after the collection to determine the PM_{10} concentration. The filters were placed in PFA vials and particles were recovered by refluxing the filter with 4 mL of 15 M HNO_3 and 2 mL of 70% v/v $HClO_4$ at 100 °C during 24 h, using an ultrasonic bath for 1 h every 12 h. Then, filters were removed using clamps and rinsed with 5 mL of 0.5 M HNO_3. Solutions were evaporated to dryness at 230 °C, refluxed with 1.5 mL of 15 M HNO_3 and 1 mL of 40% v/v HF, evaporated again, and re-dissolved in 2 mL of 0.5 M HNO_3.

Samples of $TSP_{passive}$ collected with the passive sampler were prepared following the protocol described in Ochoa Gonzalez et al. (43). The samples were transferred from the receptor dish into PFA vials with 15 mL of 0.1 M HNO_3 and then dried down. The samples and reference standard materials were digested using a mixture of 3 mL of 15 M HNO_3, 1 mL of 40% v/v HF, and 0.5 mL of 70% v/v $HClO_4$ during four days on a hot plate at 150 °C. Solutions were evaporated to dryness at 230 °C, refluxed in a 1:3 mixture of 15 M HNO_3 and 6 M HCl, evaporated again, and re-dissolved in 2 mL of 0.5 M HNO_3.

Aliquots of 0.5 ml were used for concentration measurement using ICP-MS and the remaining volume of each solution was prepared for Pb isotope ratios measurement by MC-ICP-MS.

In addition, samples of unleaded gasoline and diesel were collected in two different petrol stations in London to determine the present-day concentration of Pb in fuel. Sample digestion procedure is described in Supplementary Information.

Determination of Pb concentrations, deposition rates and enrichment factors

Small amounts of digest solutions were available for samples S1-S12 already analyzed for metal concentrations and Cu and Zn isotopes during a previous study (43). Lead concentration of samples S3-S8 was not available and they were analyzed during this study using isotope dilution technique and MC-ICP-MS analysis (protocol in Supplementary Information). All other PM_{10} and $TSP_{passive}$ samples and fuel samples were analyzed for Pb and metal concentrations after an adequate dilution in 1% HNO_3 by ICP-MS either at Imperial College London or at the AETE-ISO platform (OSU-OREME/Université de Montpellier). Concentrations were determined with external calibration using In and Bi as internal standards to correct potential sensitivity drifts. Digestion blanks represented less than 1% of Pb analyzed in the samples and less than 5% for other elements (Al, Ba, Cd, Cu, Cr, Fe, Ni, V, Zn, Sb). The concentrations determined for the reference material BCR 723 were within 10% of the indicative values for all studied elements.

The weight of $TSP_{passive}$ collected in the receptor dish using the Sigma-2 passive sampler device was too small (< 5 mg) for precise weighing. Therefore, Pb concentration is expressed as a deposition rate (DR) corresponding to the elemental mass deposited on a specific surface per day ($ng.m^{-2}.d^{-1}$) and calculated using Equation 2 (23).

$$DR = W_{Pb}/(S \times t) \qquad \text{(Equation 2)}$$

with W_{Pb} is the total mass of lead recovered in the receptor dish (ng), S is the surface of the receptor dish (m^2) and t is the collection time (in days).

Metal enrichment factors (EF) in airborne particles (PM_{10} and $TSP_{passive}$) were calculated (Equation 3) using Al-normalized metal concentration and the upper continental crust (UCC) value as reference (57).

$$EF = (Me/Al)_{sample}/(Me/Al)_{UCC} \qquad \text{(Equation 3)}$$

with Me and Al representing the metal and aluminum concentrations (in µg/g).

Aluminum and silicon concentrations are highly correlated in airborne particles at the Marylebone Road site and the Si/Al ratio is very close to the ratio in average crustal material (22, 24). In addition, Si and Al concentrations at the MR site are similar to that observed at a background site in London (22, 24). This shows that aluminum has no significant traffic-related sources and is thus a good proxy of resuspended particles made of soil and other crustal material. Aluminum is preferred as geological proxy due to its more uniform distribution in geological material (aluminum silicates) than Ti or Sc. The UCC value was used as reference to facilitate comparison with results from previous studies (9, 43) although it is important to note that it is not representative of the local geochemical background. An EF_{Pb} value of 3 was calculated using median concentrations of topsoils (n=1599) sampled in rural areas in the London region showing a slightly higher regional background than UCC composition (49) but it is widely recognized that EF<5 are not reliable to be interpreted as an anthropogenic enrichment.

Determination of Pb isotope ratios

Lead was separated from the sample matrix by ion exchange chromatography (Sr-Spec resin) following a procedure adapted from Weiss et al. (58) described in the supplementary information (SI, Table S5). The isotope ratios were determined using a Nu Plasma multi-collector ICP-MS (Nu Instruments) equipped with an Aridus II Desolvating Nebulizer System (CETAC Technologies). The instrumental mass bias was corrected using an exponential law with Tl doping (58).

The total procedural blank was < 75 pg of Pb. To assess the precision and accuracy of Pb isotope ratios measurements, analyses of the NIST SRM 981 and USGS G-2 reference materials were performed. Average values of $^{208}Pb/^{206}Pb$ = 2.16761 ± 52 (2σ), $^{206}Pb/^{207}Pb$ = 1.09301 ± 14 (2σ), $^{206}Pb/^{204}Pb$ = 16.9335 ± 53 (2σ), $^{207}Pb/^{204}Pb$ = 15.4925 ± 58 (2σ), $^{208}Pb/^{204}Pb$ = 36.7052 ± 181 (2σ) were obtained for NIST SRM 981 standards treated as samples (n=51) corresponding to an accuracy < 45 ppm for $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$ ratios and <450 ppm for $^{20X}Pb/^{204}Pb$ ratios relative to reference values (59). Ratios measured for USGS G-2 reference material were $^{208}Pb/^{206}Pb$ = 2.11422 ± 49 (2σ, n=7), $^{206}Pb/^{207}Pb$ = 1.17639 ± 26 (2σ), $^{206}Pb/^{204}Pb$ = 18.3949 ± 34 (2σ), $^{207}Pb/^{204}Pb$ = 15.6369 ± 44 (2σ), $^{208}Pb/^{204}Pb$ = 38.8911 ± 144 (2σ) which are in good agreement with published data ($^{206}Pb/^{204}Pb$ = 18.3992 ± 219 (2σ), $^{207}Pb/^{204}Pb$ = 15.6357 ± 38 (2σ), $^{208}Pb/^{204}Pb$ = 38.9006 ± 154 (2σ), (60)).

Long-term dataset of Pb isotopic composition in London airborne particles

New data determined in this study were interpreted in the context of the long-term evolution of Pb isotopic composition in London airborne particles using data published in the literature. Hamilton and Clifton (61) provided the first measurement of Pb isotopes in London airborne particles in 1968. Later, Monna et al. (32) and Véron et al. (62) measured Pb isotopes in PM_{10} collected in London in 1995 and 1996 when leaded gasoline was still on the market. Noble et al. (20) and Dong et al. (9) reported Pb isotopic composition for PM_{10} sampled at the Marylebone Road station (MR site) between 1998 and 2001 and in 2010, respectively. Literature also provided reference values for Pb isotopic composition of natural geogenic Pb in the UK (61), UK leaded gasoline (32, 63), UK ore (33), UK coal and imported coal (64, 65), UK lead paint (34), topsoils in London (31) and modern non-exhaust emissions from vehicle and road wear in London (9). All data are summarized in Supplementary Information (Table S3).

Data Availability

All data produce in this study are included in the article and supporting information. Reference to original database and papers are given for data already published used in this study.

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Table and figure legends

Table 1: Lead concentrations and enrichment factors, and Pb isotope ratios in airborne particles collected at Marylebone Road (MR) site (PM_{10} and $TSP_{passive}$) and at Imperial College London site ($TSP_{passive}$). The percentage contribution of leaded gasoline estimated using the binary mixing model (Equation 1) is indicated for the two extreme "non-gasoline Pb" end-members considered (100% vehicle wear and 100% UK coal and ore; sensitivity analysis shown in Figure S7).

Figure 1 : Relationship between the enrichment factor of Fe (EF_{Fe}) Ba (EF_{Ba}), Cr (EF_{Cr}), Cu (EF_{Cu}) and Sb (EF_{Sb}) in PM_{10} and $TPS_{passive}$ at Marylebone Road (open circles) and in $TSP_{passive}$ at building height Imperial College London (filled diamonds).

Figure 2: $^{206}Pb/^{207}Pb$ ratio measured in PM_{10} and $TSP_{passive}$ collected over a 96 h period at the Marylebone Road site (except the last sample MR5b which integrates $TSP_{passive}$ deposition over 16 days).

Figure 3: $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram of historic and current PM_{10} and $TSP_{passive}$ at the Marylebone Road site and potential traffic-related and natural Pb sources. Grey dashed line represents mixing lines between the leaded gasoline end-member and a natural/non-exhaust end-member. References: [1]Monna et al. (32), [2]Widory et al. (40) , [3]Dong et al. (9), [4]Noble et al. (20), [5]calculated in this study using data from (9).

Figure 4: Temporal variations of $^{206}Pb/^{207}Pb$ ratio of $TSP_{passive}$ collected at the Imperial College London site. EF_{Pb} are represented by black diamonds and $^{206}Pb/^{207}Pb$ ratio by colored circles indicating the season (green: spring, yellow: summer, orange: autumn and blue: winter).

Figure 5: $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram of historic and current PM_{10} and $TSP_{passive}$ collected at various urban sites in London (Teddington[2], North Kensington[4], Imperial College London IC site[5], Marylebone Road MR site[4,5]). The variation range observed in road dust[3] (dashed line) and in airborne particles at the MR site (2010-2018) (blue area) are represented. The isotopic composition of natural lead[2] (+), leaded gasoline[2] (△), vehicle wear[4] (✳),UK ore[6] (◇) end-members are indicated. References: [1]Hamilton and Clifton (61), [2]Monna et al. (32), [3]Véron et al. (62), [4]Dong et al. (9), [5]this study, [6]Rhol (33).

Table 1: Lead concentrations and enrichment factors, and Pb isotope ratios in airborne particles collected at Marylebone Road (MR) site (PM_{10} and $TSP_{passive}$) and at Imperial College London site ($TSP_{passive}$). The percentage contribution of leaded gasoline estimated using the binary mixing model (Equation 1) is indicated for the two extreme "non-gasoline Pb" end-members considered (100% vehicle wear and 100% UK coal and ore; sensitivity analysis shown in Figure S7).

Sample label	Date of collection	PM_{10} concentration ($\mu g.m^{-3}$)	Pb concentration ($ng.m^{-3}$)	EF_{Pb}	Pb isotope ratios						Leaded gasoline contribution (%)	
					$^{206}Pb/^{207}Pb$	2SD	$^{208}Pb/^{206}Pb$	2SD	$^{206}Pb/^{204}Pb$	2SD	"Non-gasoline Pb": 100% Vehicle wear	"Non-gasoline Pb": 100% UK coal and ore
Marylebone Road site (PM_{10})												
MR1a	25/07/18 - 29/07/18	19	8.8	100	1.1407	0.0001	2.1195	0.0001	17.774	0.002	24	36
MR2a	29/07/18 - 02/08/18	21	3.9	118	1.1331	0.0001	2.1279	0.0001	17.636	0.003	32	43
MR3a	02/08/18 - 06/08/18	16	6.1	154	1.1333	0.0001	2.1255	0.0001	17.644	0.004	32	42
MR4a	06/08/18 - 10/08/18	25	7.6	155	1.1364	0.0001	2.1235	0.0002	17.694	0.003	29	40
MR5a	10/08/18 - 14/08/18	21	4.1	141	1.1322	0.0001	2.1282	0.0001	17.619	0.003	33	43
MR6a	14/08/18 - 18/08/18	21	19.4	559	1.1281	0.0001	2.1331	0.0002	17.541	0.003	37	47
MR7a	18/08/18 - 22/08/18	18	5.4	159	1.1370	0.0001	2.1220	0.0001	17.699	0.004	28	39
MR8a	22/08/18 - 26/08/18	16	5.1	197	1.1268	0.0001	2.1330	0.0001	17.523	0.003	39	48
	Average ± sd	20 ± 3	7.6 ± 5.1	198 ± 149	1.134 ± 0.005		2.127 ± 0.005		17.64 ± 0.08		32 ± 5	42 ± 4
Marylebone Road site ($TSP_{passive}$)			Pb deposition rate ($ng.m^{-2}.d^{-1}$)									
MR1b	25/07/18 - 29/07/18	n.a.	45813	84	1.1383	0.0001	2.1232	0.0001	17.724	0.002	27	38
MR2b	29/07/18 - 02/08/18	n.a.	18154	90	1.1355	0.0001	2.1257	0.0002	17.675	0.001	30	41
MR3b	02/08/18 - 06/08/18	n.a.	11698	66	1.1319	0.0001	2.1289	0.0001	17.621	0.002	33	44
MR4b	06/08/18 - 10/08/18	n.a.	18661	54	1.1399	0.0001	2.1212	0.0001	17.754	0.001	25	37
MR5b	10/08/18 - 26/08/18	n.a.	24069	91	1.1375	0.0001	2.1241	0.0001	17.711	0.006	28	39
	Average ± sd		23679 ± 13127	77 ± 16	1.137 ± 0.003		2.125 ± 0.003		17.70 ± 0.05		29 ± 3	40 ± 3
Imperial College site ($TSP_{passive}$)												
S1	14/02/14 - 14/03/14	n.a.	n.d.	n.d.	1.1482	0.0001	2.1153	0.0002	17.900	0.003	17	30
S3	11/07/14 - 20/08/14	n.a.	8685	296	1.1354	0.0001	2.1281	0.0002	17.681	0.001	30	41
S4	20/08/14 - 26/09/14	n.a.	7240	204	1.1392	0.0001	2.1244	0.0001	17.748	0.002	26	37
S5	26/09/14 - 27/10/14	n.a.	7757	256	1.1403	0.0001	2.1217	0.0001	17.765	0.002	25	36
S6	27/10/14 - 27/11/14	n.a.	3691	179	1.1419	0.0001	2.1203	0.0001	17.792	0.003	23	35
S7	27/11/14 - 27/12/14	n.a.	5840	271	1.1358	0.0001	2.1263	0.0001	17.687	0.002	29	40
S8	27/12/14 - 22/01/15	n.a.	4665	251	1.1331	0.0001	2.1290	0.0001	17.639	0.002	32	43
S9	22/01/15 - 25/02/15	n.a.	3094	175	1.1240	0.0001	2.1380	0.0001	17.477	0.001	42	51
S10	25/02/15 - 22/04/15	n.a.	5474	132	1.1357	0.0001	2.1267	0.0001	17.685	0.002	30	40
S11	22/04/15 - 03/07/15	n.a.	8194	195	1.1403	0.0002	2.1223	0.0001	17.761	0.006	25	36
S12	03/07/15 - 26/08/15	n.a.	9000	300	1.1334	0.0001	2.1293	0.0001	17.645	0.005	32	42
S13	27/03/17 - 02/05/17	n.a.	6371	90	1.1343	0.0001	2.1281	0.0002	17.664	0.002	31	42
S14	02/05/17 - 02/06/17	n.a.	9411	181	1.1303	0.0001	2.1317	0.0001	17.598	0.003	35	45
S15	02/06/17 - 06/07/17	n.a.	9785	221	1.1304	0.0001	2.1327	0.0001	17.595	0.003	35	45

S16	06/07/17 - 03/08/17	n.a.	3903	146	1.1351	0.0001	2.1269	0.0001	17.677	0.003	30	41
S17	03/08/17 - 04/09/17	n.a.	4933	276	1.1219	0.0001	2.1412	0.0002	17.448	0.002	44	52
S18	04/09/17 - 06/10/17	n.a.	9748	475	1.0977	0.0001	2.1636	0.0001	17.049	0.003	69	74
S19	06/10/17 - 10/11/17	n.a.	3957	176	1.1355	0.0001	2.1276	0.0001	17.684	0.004	30	41
S20	31/07/18 - 07/08/18	n.a.	2862	71	1.1373	0.0001	2.1253	0.0001	17.710	0.003	28	39
S21	07/08/18 - 30/08/18	n.a.	2465	84	1.1327	0.0001	2.1285	0.0001	17.627	0.002	33	43
	Average ± sd		6162 ± 2508	209 ± 95	1.13 ± 0.01		2.13 ± 0.01		17.64 ± 0.17		32 ± 10	43 ± 9

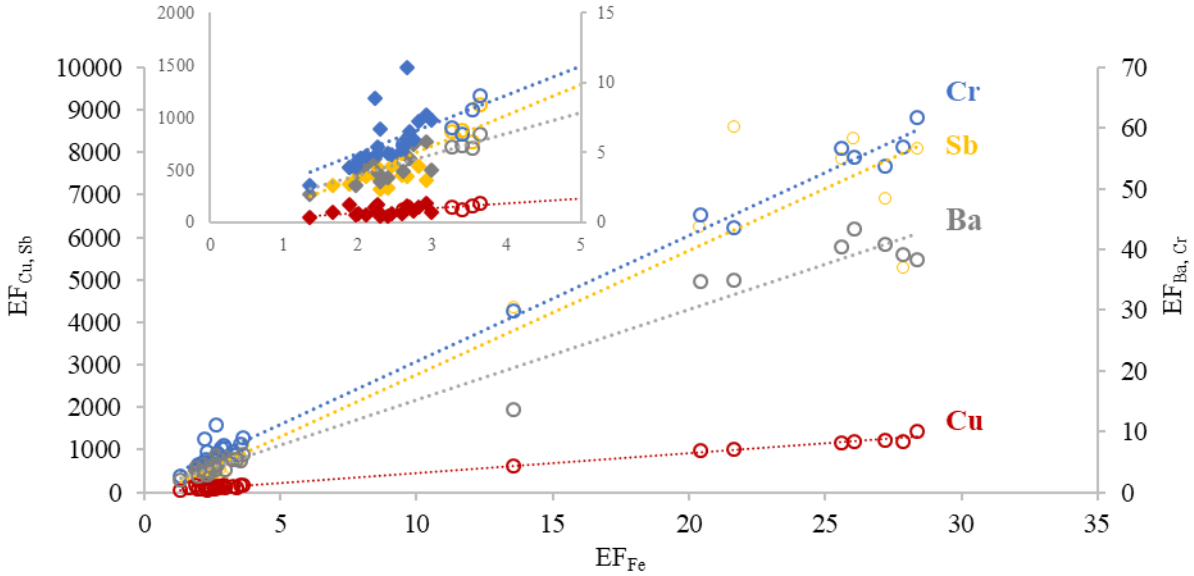

Figure 1 : Relationship between the enrichment factor of Fe (EF_{Fe}) Ba (EF_{Ba}), Cr (EF_{Cr}), Cu (EF_{Cu}) and Sb (EF_{Sb}) in PM_{10} and $TPS_{passive}$ at Marylebone Road (open circles) and in $TSP_{passive}$ at building height Imperial College London (filled diamonds).

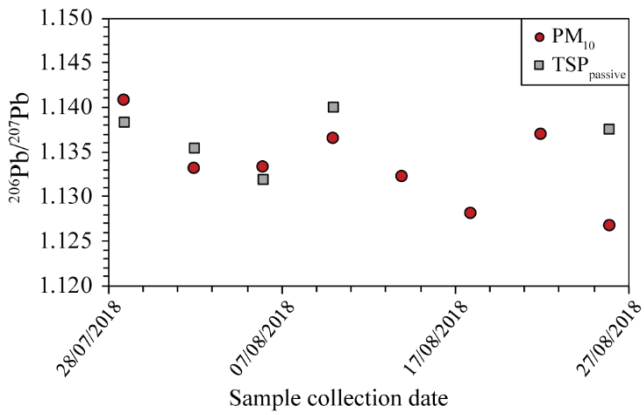

Figure 2: $^{206}Pb/^{207}Pb$ ratio measured in PM_{10} and $TSP_{passive}$ collected over a 96 h period at the Marylebone Road site (except the last sample MR5b which integrates $TSP_{passive}$ deposition over 16 days).

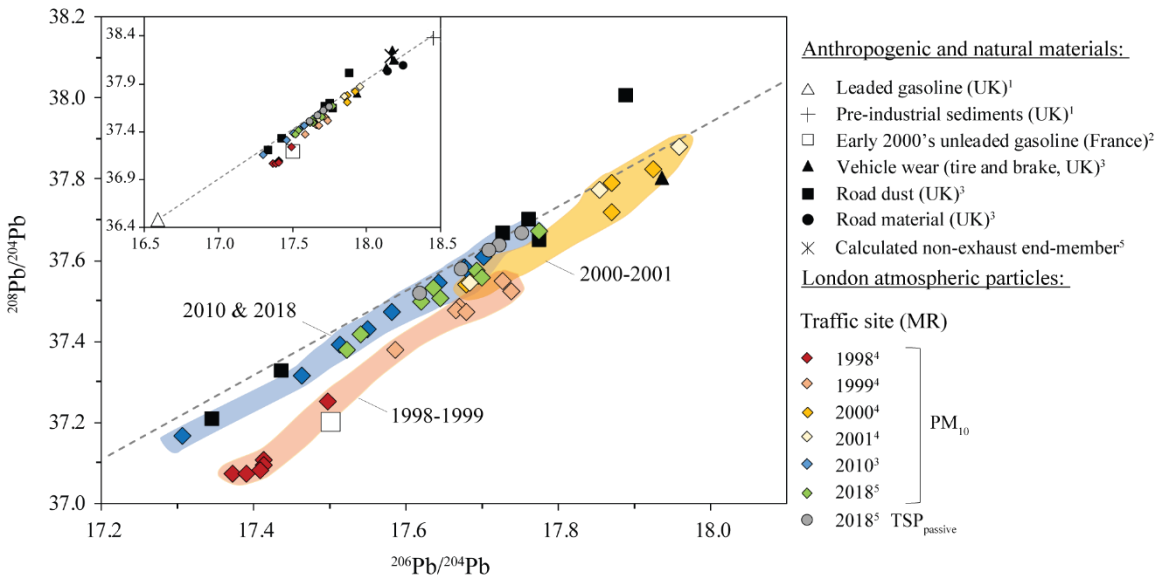

Figure 3: $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram of historic and current PM_{10} and $TSP_{passive}$ at the Marylebone Road site and potential traffic-related and natural Pb sources. Grey dashed line represents mixing lines between the leaded gasoline end-member and a natural/non-exhaust end-member. Inset panel displays a 'zoomed-out' view showing the signature of leaded gasoline, traffic-related and natural sources. References: [1]Monna et al. (32), [2]Widory et al. (40) , [3]Dong et al. (9), [4]Noble et al. (20), [5] calculated in this study using data from (9).

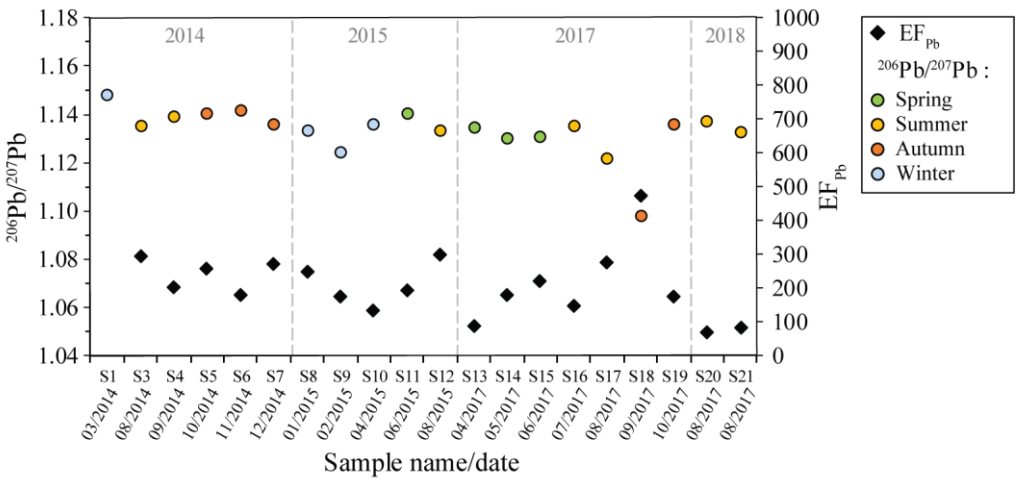

Figure 4: Temporal variations of $^{206}Pb/^{207}Pb$ ratio of $TSP_{passive}$ collected at the Imperial College London site. EF_{Pb} are represented by black diamonds and $^{206}Pb/^{207}Pb$ ratio by colored circles indicating the season (green: spring, yellow: summer, orange: autumn and blue: winter).

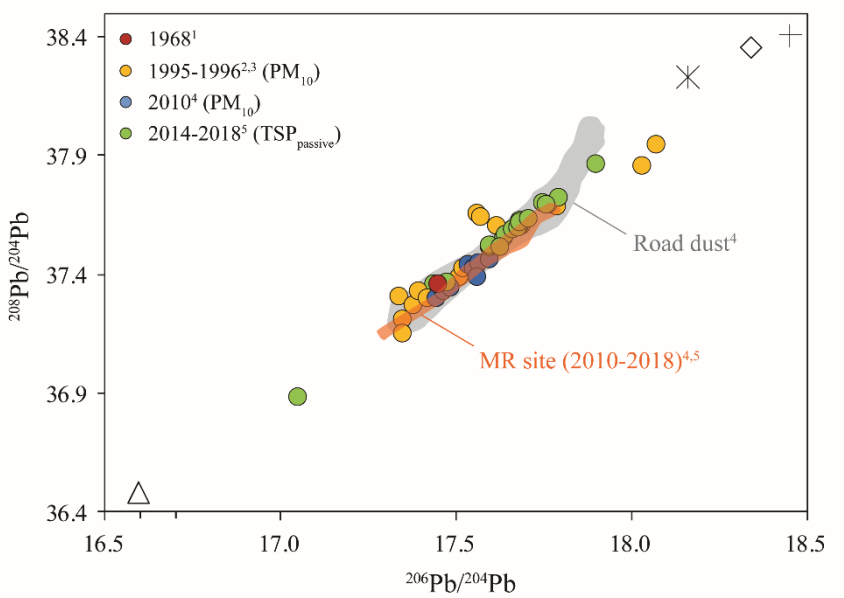

Figure 5: $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram of historic and current PM_{10} and $TSP_{passive}$ collected at various urban sites in London (Teddington[2], North Kensington[4], Imperial College London IC site[5], Marylebone Road MR site[4,5]). The variation range observed in road dust[3] (dashed line) and in airborne particles at the MR site (2010-2018) (blue area) are represented. The isotopic composition of natural lead[2] (+), leaded gasoline[2] (△), vehicle wear[4] (✳), UK ore[6] (◇) end-members are indicated. References: [1]Hamilton and Clifton (61), [2]Monna et al. (32), [3]Véron et al. (62), [4]Dong et al. (9), [5]this study, [6]Rhol (33).