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New insights from zinc and copper isotopic compositions of atmospheric particulate matter from two major European cities

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Abstract

This study reports spatial and temporal variability of Zn and Cu isotopes in atmospheric particulate matter (PM) collected in two major European cities with contrasting atmospheric pollution, Barcelona and London. We demonstrate that non-traditional stable isotopes identify source contributions of Zn and Cu and can play a major role in future air quality studies.

In Barcelona, fine PM were collected at street level at sites with variable traffic density. The isotopic signatures ranged between −0.13±0.09 and −0.55±0.09‰ for $\delta^{66}Zn_{IRMM}$ and between +0.04±0.20 and +0.33±0.15‰ for $\delta^{65}Cu_{AE633}$. Copper isotope signatures similar to Cu sulphides and Cu/Sb ratios within the range typically found in brake wear suggest that non-exhaust emissions from vehicles are dominant. Negative Zn isotopic signatures characteristic for gaseous emissions from smelting and combustion and large enrichments of Zn and Cd suggest contribution from metallurgical industries.

In London, coarse PM collected on the top of a building over 18 months display isotope signatures ranging between +0.03±0.04 and +0.49±0.02‰ for $\delta^{66}Zn_{IRMM}$ and between +0.37±0.17 and +0.97±0.21‰ for $\delta^{65}Cu_{AE633}$. Heavy Cu isotope signatures (up to +0.97±0.21‰) and higher enrichments and Cu/Sb ratios during winter time suggest important contribution from fossil fuel combustion. The positive $\delta^{66}Zn_{IRMM}$ signatures are in good agreement with signatures characteristic for ore concentrates used for the production of tires and galvanised materials, suggesting non-exhaust emissions from vehicles as the main source of Zn.

1. Introduction

Source identification using trace metals in atmospheric particulate matter (PM) is key to air quality programmes in major cities around the world.[1] Different techniques such as principal component analysis and positive matrix factorization are typically applied,[1, 2] but they require in general the statistical analysis of multi-elemental datasets containing large number of samples collected over long periods. Therefore, the recently explored application of non-traditional stable isotopes for source identification of metal pollutants in the atmosphere is of great interest as it requires smaller sets of samples.[3]

Previous work found that the main sources of Zn in atmospheric PM are emissions from incineration, metal production, fossil fuel combustion and non-exhaust sources from road traffic.[4, 5] ZnO is the dominant species emitted from tire-treads[6] and has been identified in emissions from metal smelting along with ZnS.[7] Copper has likewise been linked to multiple sources, including smelting, oil combustion, wood smoke and brake wear.[4, 8, 9] Copper typically occurs as oxide, silicate and carbonate, and is often associated with the organic fraction in PM.[5, 10]

The Zn isotope composition relative to the widely used standard JMC 3-0749L Lyon (expressed generally as $\delta^{66}Zn_{Lyon}$) is mostly positive in igneous rocks, ranging between +0.2 and +0.5‰ in basalts and between +0.4 and +0.6‰ in more acidic rocks, e.g. in granodiorites and granites.[11] The $\delta^{66}Zn_{Lyon}$ of sphalerite, the major source of Zn concentrates used for industrial purposes, ranges typically between −0.04 and +0.30‰.[12-14] In contrast, combustion and smelting processes seem to produce lighter (up to −0.52 ‰) and heavier Zn (up to +1.49‰) in the flue gas and residues, respectively.[13, 15, 16] These values are outside the natural range of Zn isotope signatures and this is likely due to evaporation and condensation processes.[16] Ore tailings collected from a smelter and fly ash in different coal-fired power plants had $\delta^{66}Zn_{Lyon}$ values as heavy as +1.49‰.[13, 16, 17] Previous work on Zn isotopes in PM collected in industrial, urban and remote areas showed indeed significant isotopic variability with $\delta^{66}Zn_{Lyon}$ ranging from −1.13 to +0.33‰, suggesting that different sources and anthropogenic activities impart a distinctive isotopic composition to PM .[15, 18-20] Zinc in PM smaller than 10 μm (PM_{10}) emitted from a refinery in northern France imparted light isotope signatures with $\delta^{66}Zn_{Lyon}$ ranging between −0.52 and +0.02‰.[15] Light Zn was also identified in PM collected in São Paulo, with $\delta^{66}Zn_{Lyon}$ ranging between −1.05 and −0.46‰ in $PM_{2.5\text{-}10}$ and between −1.13 and –0.07‰ in $PM_{2.5}$.[19] The isotopic composition of PM_1 collected over the equatorial eastern North Atlantic region had $\delta^{66}Zn_{Lyon}$ signatures ranging between +0.03±0.04‰ and +0.17±0.10‰.[18] These values are not significantly different from the isotopic signatures of natural sphalerite but lighter than PM_4 separated from soil dust collected from the Sahel region, ranging between +0.23±0.05‰ and +0.28±0.08‰.[12, 13, 18] Atmospheric PM collected over the North Atlantic Ocean exhibited $\delta^{66}Zn_{Lyon}$ between +0.13±0.08 and +0.54±0.08‰ which falls within the range found for igneous rocks.[21] In summary, Zn in natural materials including igneous rocks and minerals used in the production of ore concentrates likely has an isotope fingerprint between +0.2 and +0.6‰, while residues and particles produced by smelting, refining and combustion processes have isotope signatures outside this range.

Copper isotopes were investigated for their potential to identify source contributions in surface and groundwater, and in soils near mines or smelters.[22-26] The average Cu isotope composition expressed as $\delta^{66}Cu_{NIST976}$ for chalcopyrite ($CuFeS_2$) is +0.32±0.04‰.[27] The $\delta^{65}Cu_{NIST976}$ values in other natural minerals vary between −16.96 and +9.98‰, but most signatures fall within the range of −1.5 and +2.5‰.[22, 27-30] Copper isotope signatures are variable within and between mineral groups, including native Cu or Cu sulphides and carbonates.[27] Studies assessing the potential of Cu isotopes for tracing source contributions in the atmosphere are scarce. The $\delta^{66}Cu_{NIST976}$ values in PM_1 collected over the North Atlantic Ocean (West Africa) ranged between −0.14±0.09 and −0.02±0.10‰.[18] These signatures were slightly more negative than the isotopic signatures in Sahel soil dust, which ranged between +0.03±0.12 and +0.20±0.16‰.[18] The Cu isotope signatures in PM collected over the North Atlantic Ocean ranged between −0.18±0.11 and +0.30±0.11‰.[21] Changes in mineralogy and mixing with industrial emissions from North Africa were suggested as possible mechanisms for the variability of Cu isotope signatures.[18,21]

Emissions from fossil fuel combustion are likely more important during winter in Europe and soil dust and non-exhaust vehicle emission sources (tires, brakes or brake discs) are likely to dominate during spring and summer.[31] Therefore, significant temporal variability in source contributions of trace metals is expected in urban PM. This should be reflected in the Zn and Cu isotope signatures in PM collected during different seasons. This hypothesis, however, has not been tested before and, indeed, there is a lack of knowledge on both the spatial and temporal variability of Zn and Cu isotopes in atmospheric PM.

The aim of this study was to assess spatial, and short and long temporal variations of Zn and Cu isotope signatures in PM collected in Barcelona and London and to test associations with pollution sources. London and Barcelona have been selected in this study due to their contrasting sources of metals in PM following the findings of previous studies.[32-34] In London, studies based on particle size distributions and traffic tracers (Cu, Fe, Sb and Ba) indicate that the sources of PM are dominated by non-exhaust traffic emissions from vehicles; in Barcelona, metallurgical emissions, characterised mainly by high Pb and Zn concentrations, contribute significantly to the metal burden of the city.[32-34] To this end, we first determined the spatial and short-term temporal variability of Zn and Cu isotope signatures in PM_{10} collected at sites with low and high traffic density at street level over two sampling campaigns during autumn of 2012 and spring of 2013 in Barcelona. Long-term seasonal variability, and hence possible influence of fuel burning, at elevated heights was evaluated using continuous sampling of $PM_{2.5\text{-}80}$ during 18 months in London. Enrichment factors (EF) of elemental tracers for non-exhaust traffic emissions (Fe for brake discs and Sb for brakes) and for metallurgical emissions (Cd),[7] were determined to assist possible source attribution. Finally, the results were compared with previously reported Zn and Cu isotope signatures in atmospheric and anthropogenic PM to critically assess if it is possible to pinpoint anthropogenic sources.

2. Materials and Methods

Sample collection and digestion

In Barcelona, PM_{10} were sampled at street level at sites located in areas with high and low traffic using high volume samplers (MCV PM1025 and DIGITEL DH80) for 24 or 48 h on quartz fiber filters (Ø15 cm, Pallflex or Munktell). Filters were collected at a height of 3 m over a period of three weeks during two sampling campaigns in 2012 and 2013. Twelve samples were collected at Torre Girona (B1-B6) and Corsega Avenue (T1-T6) during February and March 2012, and eight samples at Palau Reial (B7-B10) and Valencia Avenue (T7-T10) during June 2013. Valencia Avenue and Corsega Avenue are the high traffic sites (14,000 and 11,000 veh day^{-1}, respectively). Torre Girona and Palau Reial represent sites with low traffic and are situated 20 km away from a metallurgical industry. A map showing the monitoring locations and further information about the studied area is given in the Supporting Information (Figure S1). Half of each filter was digested using 2.5 ml of 16 M HNO_3 and 5 ml of 28 M HF in PFA vials (Savillex, MN, USA) at 140 °C on a hotplate for 24 h. Then, 2 ml of $HClO_4$ (65-71 % w/w) were added to oxidise the organic matter and the residual samples were digested until complete dissolution. 10 mg of Standard Reference

Material (SRM) NIST-1648a (urban particulate matter) and 50 mg of certified reference material (CRM) BHVO-2 (basalt) from USGS were processed following the same protocol. The solutions were dried down at 230 °C and then re-fluxed and evaporated twice in 0.3 ml of ca. 16 M HNO_3 to remove the excess of fluorides. The digested solutions were re-fluxed in 300 µl of 7 M HCl and then re-dissolved in 4 ml of 7 M HCl for analysis. HNO_3, HF and HCl purified by sub-boiling distillation in quartz stills and high purity $HClO_4$ (SpA grade, Romil Ltd) were used.

To assess the long-term variability of Zn and Cu isotope signatures in coarse PM at building height, the passive sampler Sigma-2 (Deutscher Wetterdienst) was set up approx. 20 m above the street level on the top roof of the Royal School of Mines, Imperial College London. This location is close to roads with high traffic densities (Cromwell Road, Exhibition Road, and Kensington Road). Twelve samples were taken at intervals of approx. five weeks over a period of 18 months between February 2014 and August 2015. The Sigma-2 passive sampler is widely used to monitor continuously atmospheric particles with a size range from 2.5 to 80 µm ($PM_{2.5\text{-}80}$) that are deposited via sedimentation into a small receptor dish that has a diameter of 5.5 cm.[35] The dish was acid-cleaned with 4 M HNO_3, 3 M HCl and 2 M distilled HNO_3. The concentrations are given as mass of the elements deposited in the receptor dish per day (ng day^{-1}). The samples were transferred from the receptor dish into PFA vials (Savillex, USA) with 15 ml of 0.1 M HNO_3 and then dried down for subsequent acid digestion. The samples and aliquots of NIST-1648a and BHVO-2 were digested by refluxing in closed vials using a mixture of 3 ml of HNO_3, 1 ml of HF and 0.5 ml of $HClO_4$ over four days on a hot plate at 140 °C. Solutions were evaporated to dryness at 230 °C, re-fluxed in ca. 16 M HNO_3 and 7 M HCl, evaporated again and re-dissolved in 2 ml of 7 M HCl for subsequent analysis.

Two samples of Zn ore concentrates from mines in Kazakhstan were purchased from Alex Stewart International to constrain the isotope signature of Zn used for the manufacturing of non-combustion vehicle sources like tires and galvanized steel parts. The samples were ground in an agate pestle and mortar, and digested along with BHVO-2 in duplicate in Teflon vessels in a microwave (Milestone Ethos). Aliquots of 30 mg were digested using a mixture of 6 ml and 2 ml of HNO_3 and HF, respectively, and dried down and re-dissolved in 7 M HCl for subsequent analysis.

Determination of element concentrations, enrichment factors and isotope ratios

Samples were prepared in Class 10 laminar flow hoods hosted in metal-free Class 1000 clean laboratories. Dilute acid solutions were prepared using 18.2 MΩ grade water (Millipore system, USA).

An aliquot of the digested PM was used for elemental analysis by quadrupole inductively couple plasma mass spectrometry (Q-ICP-MS) using an Agilent 7700x, while the concentrations in the ore concentrates were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Thermo iCap 6500 Duo. The accuracy of the methods was evaluated by using NIST-1648a and BHVO-2 for all elements used in this study (Cu, Zn, Fe, Al, Sb, Cd) and was within the precision of the certified values.

The anthropogenic contribution of Zn, Cu, Fe, Sb and Cd in the PM was assessed calculating EF using Al as reference element and the upper continental crust as reference reservoir:[36]

$$EF = \frac{C_{x,s}/C_{Al,s}}{C_{x,c}/C_{Al,c}} \quad \text{[Eq. 1]}$$

where $C_{x,s}$ and $C_{Al,s}$ represent the concentrations of the element x and Al in the sample, respectively, and $C_{x,c}$ and $C_{Al,c}$ represent their concentrations in the upper continental crust. Enrichment factors higher than 5.0 are considered as significant.[37]

Separation of Zn and Cu from the sample matrix prior to isotope analysis was achieved using anion-exchange chromatography.[18,38] To this end, 0.7 ml of Bio-Rad AG MP-1 resin (100–200 mesh) was added to Bio-Rad polypropylene columns with 2 ml of resin reservoir. The Zn fraction was collected in PFA vials, dried down on a hot plate at 120 °C and treated with 0.3 ml of ca. 16 M HNO_3 to digest any organic column residue. The solution was dried again and re-dissolved in 2 ml of 0.1 M HNO_3 for isotopic analysis. The Cu fraction was dried down, refluxed, re-dissolved in 0.3 ml of 7 M HCl, and further purified using an in-house made Teflon column of 200 µl of resin reservoir containing 150 µl of the same resin. Possible effect of isotope fractionation during the ion exchange procedure was addressed by achieving complete recovery of Cu (96–108%).

Isotope ratios of Zn and Cu were determined using a Nu Plasma multi collector ICP-MS (Nu Instruments Limited, UK) equipped with a Nu DSN-100 Desolvation Nebulizer System and a glass nebulizer (100 µl min^{-1}). The isotopes ^{62}Ni, ^{63}Cu, ^{64}Zn, ^{65}Cu, ^{66}Zn, ^{67}Zn and ^{68}Zn were measured simultaneously and the calculated isotope ratios are referenced to IRMM-3702 and ERM-AE633 for Zn and Cu, respectively. Isobaric interferences of ^{64}Ni were monitored measuring the intensity of ^{62}Ni but were negligible for all the analysis performed in this study. All samples were scanned for elements such as Na, Mg, Ca, Ba, etc, that would cause polyatomic interferences on the plasma.[39] The concentrations of the interfering elements in the fractions were below the detection limit, except for Ca and Fe that were below 0.36% and 0.25% of the total amount in the sample loaded onto the columns, respectively, and were not affecting the accuracy of the isotope ratio analysis. Instrumental mass bias effects were corrected using an in-house ^{64}Zn–^{67}Zn double-spike for Zn and standard sample bracketing for Cu.[40, 41] Further analytical details of the anion-exchange procedure, spike calibration and mass bias corrections are given in the Supporting Information. The Zn and Cu isotope ratios are reported as $\delta^{66}Zn_{IRMM}$ and $\delta^{66}Cu_{AE633}$ according to Eq. 2 and Eq. 3:

$$\delta\,^{66}Zn_{IRMM} = \left[\frac{(^{66}Zn/^{64}Zn)_{sample}}{(^{66}Zn/^{64}Zn)_{IRMM}} - 1\right] \times 1000 \quad \text{[Eq. 2]}$$

$$\delta\,^{65}Cu_{AE633} = \left[\frac{(^{65}Cu/^{63}Cu)_{sample}}{(^{65}Cu/^{63}Cu)_{AE633}} - 1\right] \times 1000 \quad \text{[Eq. 3]}$$

Previously published Zn and Cu isotope ratios referring to JMC 3-0749L Lyon and NIST 976 standards were recalculated to IRMM-3702 and SRM AE633 using an isotopic offset of +0.32‰ for Zn and no isotopic offset for Cu.[11, 42] The analytical precision of the isotope

analysis of individual samples (2SD) has been assessed using one passage of the digested sample and at least three individual sample measurements. Accuracy and reproducibility were assessed for each analytical session by repeated measurements of BHVO-2 and commercial single element solutions (denoted as Romil Zn and Romil Cu). The isotopic composition for BHVO-2 ($\delta^{66}Zn_{IRMM}$ = +0.11 ± 0.25‰, n=5), Romil Zn (−9.10±0.10‰, n=4) and Romil Cu ($\delta^{65}Cu_{AE633}$ = +0.18 ± 0.05‰, n=4) are in good agreement with previous published data.[42] Average isotopic compositions of NIST-1648a determined from individual analytical sessions over six months were $\delta^{66}Zn_{IRMM}$ = −0.19±0.15‰ (n=6) and $\delta^{65}Cu_{AE633}$ = +0.11±0.20‰ (n=6).

3. Results and Discussion

3.1. Spatial and temporal variability of concentrations, enrichment factors and isotope ratios in PM_{10} in Barcelona

Table 1 shows concentrations (Zn, Cu, Fe, Sb and Cd), EF (EF_{Zn}, EF_{Cu}, EF_{Fe}, EF_{Sb} and EF_{Cd}), and isotope signatures ($\delta^{66}Zn_{IRMM}$ and $\delta^{65}Cu_{AE633}$) determined in PM_{10} collected in Barcelona at sites with low (Torre Girona and Palau Reial) and high (Corsega Avenue and Valencia Avenue) traffic occurrence during 2012 and 2013.

The concentrations of Cu, Fe and Sb are higher at the sites with high traffic (T1−T10) than at the sites with low traffic (B1−B10). During February and March 2012, the concentrations of Cu (76±31 ng m^{-3}), Fe (1543±631 ng m^{-3}) and Sb (8±4 ng m^{-3}) in the PM_{10} collected at Corsega Avenue are significantly higher than those measured at the low traffic site in Torre Girona (Table 1). The concentrations of Zn and Cd, in contrast, are similar at both sites. The sampling campaign during June 2013 shows higher concentrations of Cu (53±15 ng m^{-3}), Fe (1140±317 ng m^{-3}) and Sb (6±3 ng m^{-3}) at Valencia Avenue compared to Palau Reial (low traffic site). The concentrations of all the elements are higher in autumn 2012 than in spring 2013, possibly reflecting drier weather conditions leading to decreased deposition.[43]

We find large enrichments of Cu, Fe and Sb, which reflect significant anthropogenic contribution (Figure S4). The EF are higher at Valencia Avenue (EF_{Fe} = 5.7±0.6, EF_{Cu} = 268±26 and EF_{Sb} = 8678±596) and Corsega Avenue (EF_{Fe} = 3.1±0.9, EF_{Cu} = 155±47 and EF_{Sb} = 4282±1239) than at Palau Reial and Torre Girona (Table 1), respectively. The EF_{Zn} and EF_{Cd}, in contrast, are similar at the low and high traffic sites. The EF_{Zn} ranges between 77 and 180 and between 172 and 347 during 2012 and 2013, respectively. The EF_{Cd} ranges between 67 and 381, except in sample T6, and between 132 and 312 during 2012 and 2013, respectively (Table 1). The EF_{Zn}, EF_{Cu} and EF_{Sb} in Valencia Avenue are significantly higher than those in Corsega Avenue which averages 3000 vehicles day^{-1} less.

The isotope ratios of Zn and Cu are shown in Figure 1. Zinc is isotopically light with $\delta^{66}Zn_{IRMM}$ ranging between –0.13±0.09 and –0.51±0.05‰ (Table 1). The temporal (between sampling campaigns) and spatial (between sites) variability are significant relative to the

typical average internal precision of 0.07‰ for each isotope ratio measurement. Isotopic light Zn found in PM_{10} and emissions from high temperature industrial activities[15, 16] are in line with our results suggesting important contribution from metallurgical processes in PM in Barcelona.[32, 33] The insignificant correlations between $\delta^{66}Zn_{IRMM}$ and EF_{Zn} and EF_{Sb} (Figure 2a and 2b), and the weak correlation between EF_{Zn} and Sb and Fe which are well established tracers for brake wear particles (Figure 3a) support this hypothesis. Furthermore, samples with negative isotope signatures at Torre Girona and Palau Reial, i.e., the sites located close to the metallurgical industry in Barcelona, are also enriched in Zn and Cd (Figure S4).

The spatial and temporal variations of $\delta^{65}Cu_{AE633}$ range between +0.04±0.20 and +0.33±0.15‰ (Table 1), with one negative value measured in sample B3 ($\delta^{65}Cu_{AE633}$ = –0.43±0.10‰). Significant correlations between $\delta^{65}Cu_{AE633}$ and EF_{Cu} and EF_{Sb} (Figures 2d and 2e) suggest that the observed Cu isotope signature is controlled by non-exhaust vehicle emissions, i.e., brake wear.[44] This is indeed supported by the strong positive correlation between the EF_{Cu} and EF_{Fe} (R^2 = 0.9722) and the EF_{Cu} and EF_{Sb} (R^2 = 0.9305) (Figure 3b). Consequently, an estimated Cu isotope signature for brake-derived particles of $\delta^{65}Cu_{AE633}$ = +0.18±0.14‰ (n=19, except B3) can be proposed using the average isotopic composition of the PM_{10}. This in line with the $\delta^{65}Cu_{AE633}$ determined for primary Cu sulphides ranging between –1 and +1‰,[22] and Cu sulphides being the dominant chemical species in brake lining materials.[44, 45] Sample B3 has a very light Cu isotope signature along with a low EF_{Cu} (EF_{Cu} = 43) and EF_{Sb} (EF_{Sb} = 1327) (Figures 2d and 2e). This light signature may be explained by the temporal contribution from flue gas emissions from the metallurgical industry, which in fact has been previously proposed to explain the enrichment of Cu in PM in Barcelona.[32, 33]

3.2. Spatial and temporal variability of concentrations, enrichment factors and isotope ratios in $PM_{2.5\text{-}80}$ in London

Table 1 shows concentrations (Zn, Cu, Fe, Sb and Cd), EF (EF_{Zn}, EF_{Cu}, EF_{Fe}, EF_{Sb} and EF_{Cd}), and isotope signatures ($\delta^{66}Zn_{IRMM}$ and $\delta^{65}Cu_{AE633}$) determined in PM collected using a passive sampler in London.

Elemental concentrations and EF were low during February 2014 (sample S1) and between November 2014 and February 2015 (samples S7, S8 and S9). This is likely because of high wet depositional flux of particles during periods of rain associated with the winter season in London.[46]

The $\delta^{66}Zn_{IRMM}$ values vary between +0.03±0.04 and +0.49±0.02‰ (Table 1) and correlate positively with the EF_{Zn}, except sample S5 which was collected between September and October 2014 (Figure 2a). The different $\delta^{66}Zn_{IRMM}$ and significantly high EF_{Zn} and EF_{Cd} for sample S5 (Table 1) indicate additional sources. The $\delta^{66}Zn_{IRMM}$ values are weakly correlated with EF_{Sb} (Figure 2c), suggesting some contribution from brake wear. The samples S6, S7, S9 and S12 have the highest EF_{Zn} and $\delta^{66}Zn_{IRMM}$ values close to 0.00‰. The $\delta^{66}Zn_{IRMM}$ in the PM enriched in Zn agree well with those found for ZnO which is added to

tire-tread rubber to facilitate the vulcanization process,[14] and with ore concentrates (mainly sphalerite) analysed in our study ($\delta^{66}Zn_{IRMM}$ = +0.03±0.10‰, two samples). Particles from tire wear are in general larger than 10 μm,[44, 45] and therefore have possibly been preferentially accumulated in the passive sampler, supporting further contribution from tire wear.

The $\delta^{65}Cu_{AE633}$ values vary between +0.37±0.17 to +0.97±0.21‰ (Table 1). These values are significantly heavier than in PM_{10} collected in Barcelona. We find significant isotope variability over the entire time period assessed, but most notable are the heavier $\delta^{65}Cu_{AE633}$ signatures found in samples S6, S7, S8 and S9 collected during winter and end of autumn (Figure 1b). This could suggest that emissions from fossil fuel combustion control significantly the isotope signatures, with a maximum peak on $\delta^{65}Cu_{AE633}$ during November and December 2014 (S7). The Cu/Sb ratio of brake wear is typically 4.6±2.3.[47,54] The Cu/Sb ratios in PM collected during winter in London (Table 1) are well above this value which supports an important contribution from fuel or oil combustion.

3.3. Conceptual models for the controls of Zn and Cu isotope fingerprints in particulate matter in Barcelona and London

Figure 4 shows preliminary conceptual models summarizing the possible controls of Zn and Cu isotope signatures in fine and large PM collected in Barcelona and London, respectively. These models warrant further work; however, they form an important starting point for the possible inclusion of these isotope systems in air quality studies.

In Barcelona, we propose that the isotope signatures identify significant contributions from emissions from metallurgical and non-exhaust vehicle emissions for Zn and Cu in PM_{10}, respectively. The influence of emissions from metallurgy for Zn is supported by (i) the lack of correlation between $\delta^{66}Zn_{IRMM}$ and the EF_{Sb} (Figure 2b), and between the EF_{Zn}, EF_{Sb} and EF_{Fe} (Figure 3); (ii) the high variability in the $\delta^{66}Zn_{IRMM}$ at the low and high traffic sites, and the similarity in the EF_{Cd} and EF_{Zn} in both sites (Figure 1a and Table 1); and (iii) the known light isotope signature of Zn in PM emitted from metallurgical and coal combustion processes.[15-17] Significant contribution from brake wear to Cu enrichment in PM_{10} is supported by (i) the correlation between the EF_{Cu}, EF_{Fe} and EF_{Sb}, which are typical tracers of brake wear (Figure 3), and (ii) the Cu/Sb ratios in the PM_{10} (Table 1) which are close to the Cu/Sb ratios previously reported for brake wear particles.[47,54]

In London, we propose that Zn and Cu in $PM_{2.5\text{-}80}$ are dominated by non-exhaust emissions from road vehicles. The correlation between $\delta^{66}Zn_{IRMM}$ and EF_{Sb} (Figure 2c), and the similarity between $\delta^{66}Zn_{IRMM}$ of the $PM_{2.5\text{-}80}$ samples enriched in Zn (Table 1) and of ore minerals typically used in the production of tires and galvanized steel[12-14] support this idea. The $\delta^{65}Cu_{AE633}$ in the $PM_{2.5\text{-}80}$ collected during winter and late autumn is heavier than during the other seasons, and we propose that this is due to the dominant contribution of isotopically heavy Cu in residual particles from fossil fuel combustion, as previously found for Zn in PM from smelting and coal combustion.[13, 16, 17] The Cu/Sb ratios of $PM_{2.5\text{-}80}$ (Cu/Sb = 19±7) are significantly higher than those typically found in brakes (Cu/Sb = 4.6±2.3)[47,54] and those of

PM_{10} collected in Barcelona (Cu/Sb=9±2) (Table 1). The $\delta^{65}Cu_{AE633}$ and the Cu/Sb ratios of $PM_{2.5\text{-}80}$ collected during spring and summer in London are closer to those of PM_{10} in Barcelona (Table 1 and Figure 4). These conclusions are in line with the strong correlation between the $\delta^{65}Cu_{AE633}$ and the Cu/Sb ratios (R^2 = 0.820) in the PM (Figure 2f), the significantly isotopic heavier Cu found in London compared to Barcelona, and the contribution of brake wear particles in Barcelona which are typically smaller than 10 μm.[48, 49]

3.4. Zinc and Cu isotope signatures in atmospheric particulate matter: a global perspective

Figure 5 shows Zn and Cu isotope signatures determined in atmospheric PM collected from cities in Europe and South America (Barcelona, London, Metz and São Paolo)[19, 20] and over the North Atlantic Ocean.[18, 21] In an attempt to characterise potential isotope signatures of natural and anthropogenic sources, we also plot the measured isotope ratios of various different source materials.

With respect to Zn, we constrain the isotope signature of natural sources (wind-blown mineral dust and soil) using values determined for igneous rocks.[11] The anthropogenic signatures include (i) ore concentrates and sphalerite[12-14] representing non-exhaust traffic sources (i.e., tire wear, galvanised steel), and (ii) PM collected around smelters and from coal-fired power plants representing PM from high temperature processes.[15, 17, 20] As shown in Figure 5, we find that the isotopic compositions of Zn in PM collected over the North Atlantic region overlap mostly with those in ore concentrates and minerals.[11-14, 18, 21] This suggests that either natural sources from wind-blown mineral dust or anthropogenic sources derived from non-exhaust traffic emissions are dominant. Isotopically light Zn is dominant in most PM collected in São Paulo and Barcelona,[20] and we propose that this reflects a possible control of Zn from high temperature processes. This is supported by previous work that shows that trace element concentrations in PM in Barcelona and São Paulo are affected by metallurgical emissions and biomass burning, respectively.[22, 32, 33] The isotope signatures in PM collected in Metz and in time series in London are in good agreement with the isotopic composition of sphalerite, i.e., non-exhaust traffic emissions.

With respect to Cu, the isotope signatures in PM collected in Barcelona and over the North Atlantic region overlap with the signature for primary Cu sulphides ($\delta^{65}Cu_{AE633}$ = −1 to +1‰).[18, 21, 22] The Cu signatures in $PM_{2.5\text{-}80}$ collected in London are significantly different from the $\delta^{65}Cu_{AE633}$ in natural dust, most probably due to the influence of combustion emissions during the winter season.[13, 16, 17]

Figure 5 suggests that the cities investigated so far have their own ‘isotope signature’ and we propose that the isotope fingerprints reflect the importance of emissions from high temperature processes and non-exhaust traffic emissions such as brake and tire wear. These observations are among the first to place constraints on the use of Zn and Cu isotopes as tracers of anthropogenic sources in atmospheric PM and support previous hypothesis suggesting that smelting and combustion induce a significant isotope fractionation.

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Supporting Information

Further details regarding the sampling locations in Barcelona, ion exchange procedure, mass bias correction for Zn isotope analysis and analytical data are detailed in the Supporting information. This information is available free of charge via the Internet at http://pubs.acs.org/.

Table 1. Concentrations, EF and isotope signatures in PM collected in Barcelona (PM_{10}) and London ($PM_{2.5-80}$).*: sample S5 has not been considered to calculate the average EF_{Cd}.

			Concentrations ng m^{-3} (Barcelona) and ng day^{-1} (London)							EF_{Zn}	EF_{Cu}	EF_{Fe}	EF_{Sb}	EF_{Cd}	$\delta^{66}Zn_{IRMM}$ (‰)	±2SD	$\delta^{65}Cu_{AE633}$ (‰)	±2SD
	Sample label	Date of collection	Al	Zn	Cu	Fe	Sb	Cd	Cu/Sb									
Barcelona	B1	02/2012	1549	102	93	2114	10.6	0.31	8.8	77	90	2.0	2824	81	–0.29	0.05	+0.20	0.02
(PM_{10})	B2	02/2012	874	102	38	866	5.0	0.21	7.7	137	66	1.5	2347	101	–0.40	0.05	+0.15	0.06
Torre Girona	B3	03/2012	694	62	20	575	2.2	0.17	9.0	105	43	1.2	1327	100	–0.16	0.05	–0.43	0.10
	B4	03/2012	774	101	51	1208	6.5	0.38	7.8	153	98	2.3	3460	204	–0.44	0.05	+0.20	0.05
	B5	03/2012	534	36	13	384	1.9	0.09	6.9	78	38	1.1	1498	67	–0.28	0.05	+0.04	0.05
	B6	03/2012	574	87	36	763	3.7	0.53	9.7	179	93	1.9	2642	381	–0.24	0.07	+0.15	0.03
	Average±SD		833±373	82±28	42±29	985±620	5±4	0.3±0.2		122±42	71±27	1.7±0.5	2350±815	156±121				
	T1	02/2012	992	125	128	2658	12.9	0.33	9.9	148	192	3.9	5358	139	–0.30	0.06	+0.23	0.02
	T2	02/2012	601	92	77	1481	7.8	0.22	10.0	180	193	3.6	5315	152	–0.22	0.11	+0.20	0.05
Corsega Avenue	T3	03/2012	809	73	51	1186	6.0	0.18	8.4	106	93	2.1	3041	94	–0.24	0.15	+0.33	0.15
	T4	03/2012	556	51	40	773	3.4	0.18	11.6	108	107	2.0	2533	130	–0.37	0.09	+0.25	0.05
	T5	03/2012	807	115	80	1668	8.3	0.41	9.7	167	149	3.0	4242	210	–0.25	0.05	+0.22	0.04
	T6	03/2012	594	78	78	1490	7.5	0.96	10.4	155	196	3.7	5200	663	–0.44	0.09	+0.22	0.03
	Average±SD		727±171	89±28	76±31	1543±631	8±4	0.4±0.3		144±31	155±47	3.1±0.9	4282±1239	231±215				
	B7	06/2013	278	56	26	597	3.3	0.21	7.8	238	138	3.1	4856	312	–0.16	0.05	+0.26	0.11
Palau Reial	B8	06/2013	184	48	16	406	1.9	0.12	8.1	304	129	3.2	4351	262	–0.13	0.09	+0.04	0.05
	B9	06/2013	282	83	33	754	3.9	0.15	8.3	347	174	3.9	5751	216	–0.28	0.04	+0.04	0.21
	B10	06/2013	302	44	26	674	3.9	0.10	6.7	172	130	3.3	5324	132	–0.51	0.05	+0.13	0.17
	Average±SD		262±53	58±18	25±7	608±149	3±1	0.15±0.05		265±77	143±22	3.4±0.4	5071±603	231±77				
	T7	06/2013	386	91	62	1313	8.2	0.26	7.6	278	242	5.0	8753	273	–0.36	0.06	+0.11	0.09
Valencia Avenue	T8	06/2013	344	80	63	1358	7.8	0.17	8.0	274	274	5.8	9375	199	–0.39	0.07	+0.09	0.08
	T9	06/2013	321	76	54	1217	6.2	0.14	8.8	280	254	5.6	7922	178	–0.23	0.06	+0.24	0.06
	T10	06/2013	154	40	31	673	3.3	0.05	9.5	307	300	6.4	8661	132	–0.27	0.05	+0.24	0.04
	Average±SD		301±102	72±23	53±15	1140±317	6±3	0.16±0.09		285±15	268±26	5.7±0.6	8678±596	196±59				
London	S1	02/2014−03/2014	406	43	14	323	0.7	0.02	20	123	51	1.2	704	25	+0.32	0.12	+0.58	0.15
($PM_{2.5-80}$)	S2	03/2014−05/2014	746	66	21	827	1.3	0.06	16	104	43	1.6	723	34	+0.37	0.10	+0.37	0.17
	S3	07/2014−08/2014	496	61	13	504	1.1	0.04	12	147	39	1.5	891	32	+0.34	0.04	+0.55	0.15
	S4	08/2014−09/2014	580	59	18	557	1.3	0.06	14	120	47	1.5	886	40	+0.49	0.02	+0.46	0.12
	S5	09/2014−10/2014	314	61	18	283	0.6	0.21	32	239	87	1.3	729	271	+0.37	0.20	+0.51	0.20
	S6	10/2014−11/2014	352	56	22	493	0.7	0.05	31	188	91	2.1	810	58	+0.16	0.16	+0.88	0.22
	S7	11/2014−12/2014	207	35	11	265	0.5	0.02	24	197	78	1.9	896	33	+0.08	0.05	+0.97	0.21
	S8	12/2014−01/2015	281	32	14	300	0.6	0.02	22	132	72	1.6	902	30	+0.19	0.17	+0.84	0.21
	S9	01/2015−02/2015	282	43	14	382	0.7	0.03	19	180	74	2.0	1077	37	+0.14	0.04	+0.66	0.17
	S10	03/2015−04/2015	660	67	18	822	1.5	0.04	13	119	42	1.8	906	23	+0.12	0.09	+0.52	0.14
	S11	05/2015−06/2015	670	81	20	787	1.8	0.05	12	143	45	1.7	1077	31	+0.14	0.13	+0.52	0.22
	S12	07/2015−08/2015	478	65	18	520	1.2	0.04	14	160	55	1.6	1053	34	+0.03	0.04	+0.53	0.11
	Average±SD		456±178	56±15	17±4	505±210	1.0±0.5	0.05±0.05		154±40	60±19	1.7±0.3	888±132	34±10*				

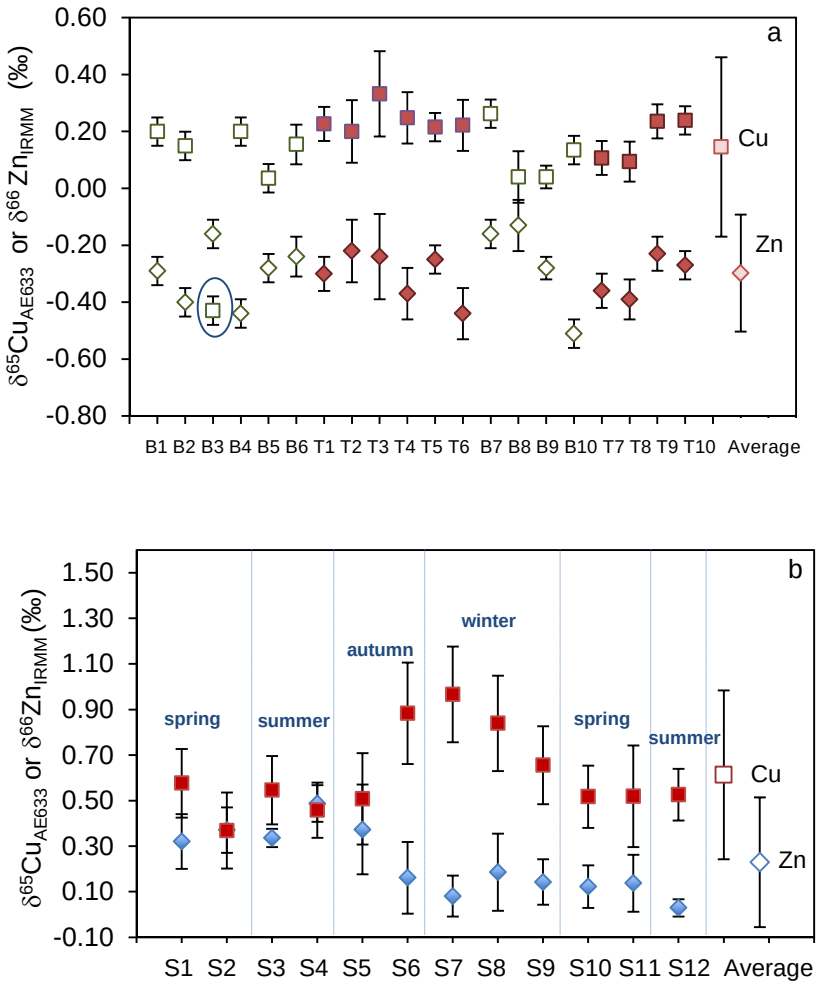

Figure 1. a) Variability in the Zn (diamonds) and Cu (squares) isotope signatures (expressed as $\delta^{66}Zn_{IRMM}$ and $\delta^{65}Cu_{AE633}$, respectively) in PM collected in Barcelona at Torre Girona (B1–B6) and Corsega (T1–T6) during autumn 2012, and at Palau Reial (B7–B10) and Valencia (T7–T10) during spring 2013. Open and closed symbols represent low traffic and high traffic sites, respectively. The sample B3 is circled as it shows an anomalous value for $\delta^{65}Cu_{AE633}$. b) Zinc and Cu isotope variability in PM collected between February 2014 and August 2015 in London. Average Zn and Cu isotopic compositions are also shown in the figures. Error bars represent the 2σ standard deviation of repeated sample measurements ($n \geq 3$).

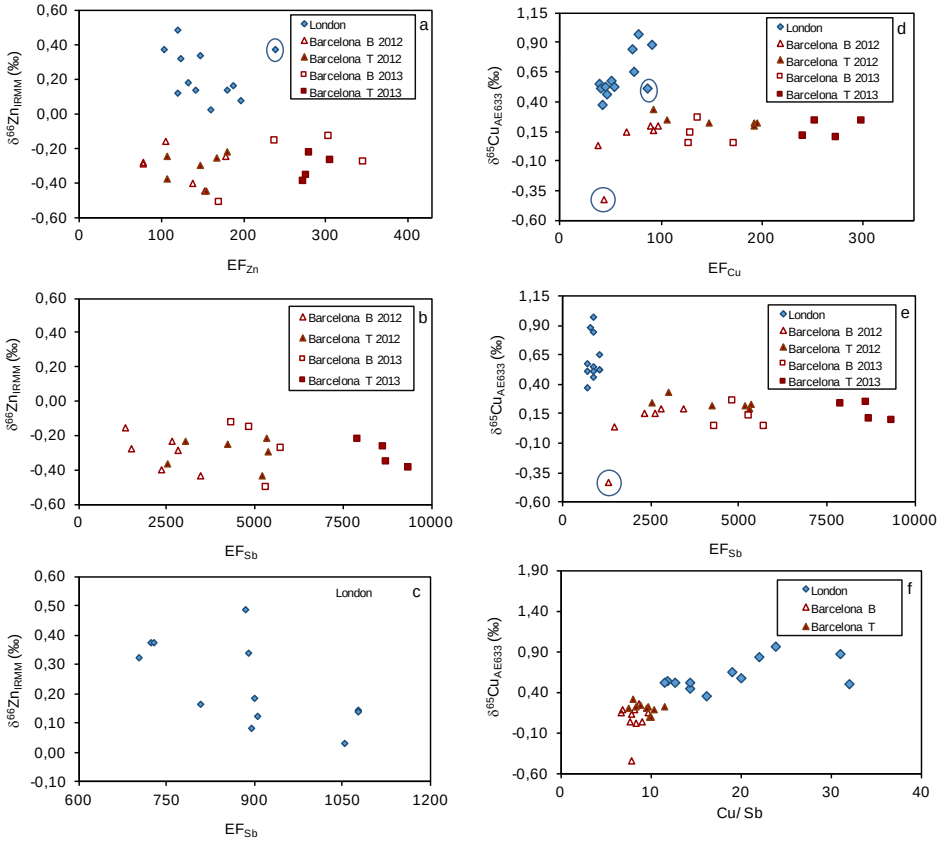

Figure 2. a) Zinc isotope composition vs. the EF of Zn (EF_{Zn}). The anomalous value for S5 in London (circled) is discussed in the text. b) and c) Zinc isotope compositions for PM collected in Barcelona and London, respectively, plotted vs. EF_{Sb}. d) Copper isotope compositions vs. EF_{Cu} in PM analysed during this study. Samples S5 and B3 are circled, as they do not follow the general trends. e) Copper isotope compositions plotted against EF_{Sb}. Sample B3 is circled and discussed in the text. f) Copper isotope compositions vs. Cu/Sb ratios. Open and closed symbols represent low traffic (B) and high traffic (T) sites, respectively.

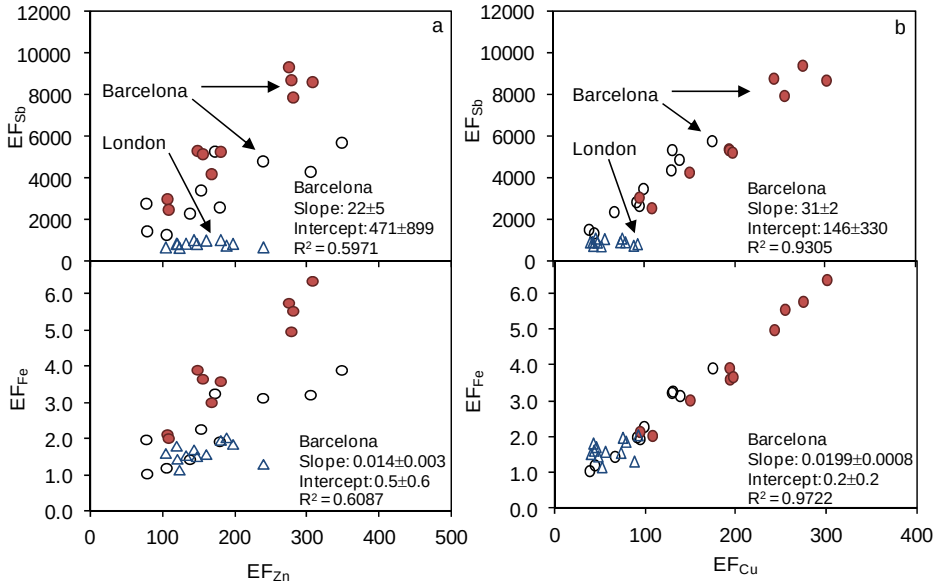

Figure 3. Relationship between the EF of Zn, Sb and Fe (panel a) and the EF of Cu, Sb and Fe (panel b) in PM collected in Barcelona (circles) and London (triangles). Open and closed circles represent low traffic and high traffic sites in Barcelona, respectively. The slopes (±1SD), intercepts (±1SD) and R^2 of the regression lines for PM collected in Barcelona are given in the panels.

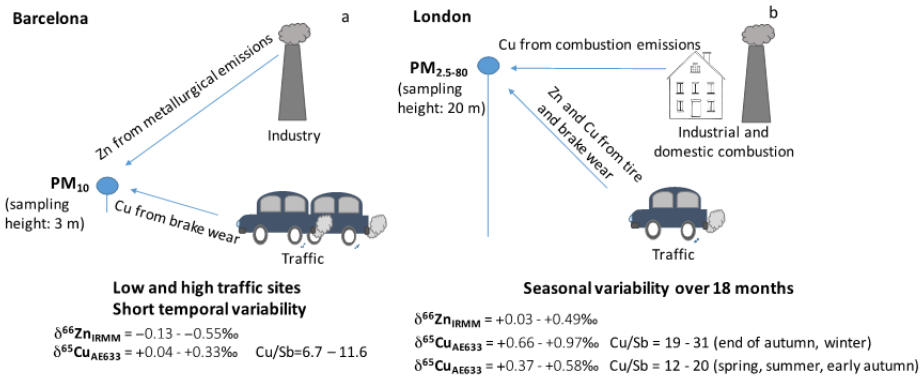

Figure 4. Proposed conceptual model of possible controls of Zn and Cu isotope signatures in fine PM in Barcelona (panel a) and coarse PM in London (panel b) derived from this study. In Barcelona, Zn and Cu are dominated by emissions from metallurgical industries and from non-exhaust vehicle emissions (brake wear), respectively. In London, Zn and Cu are both largely dominated by emissions from non-exhaust vehicle sources, unless during winter, where the heavy $\delta^{65}Cu_{AE633}$ suggests an increased contribution from fossil fuel combustion.

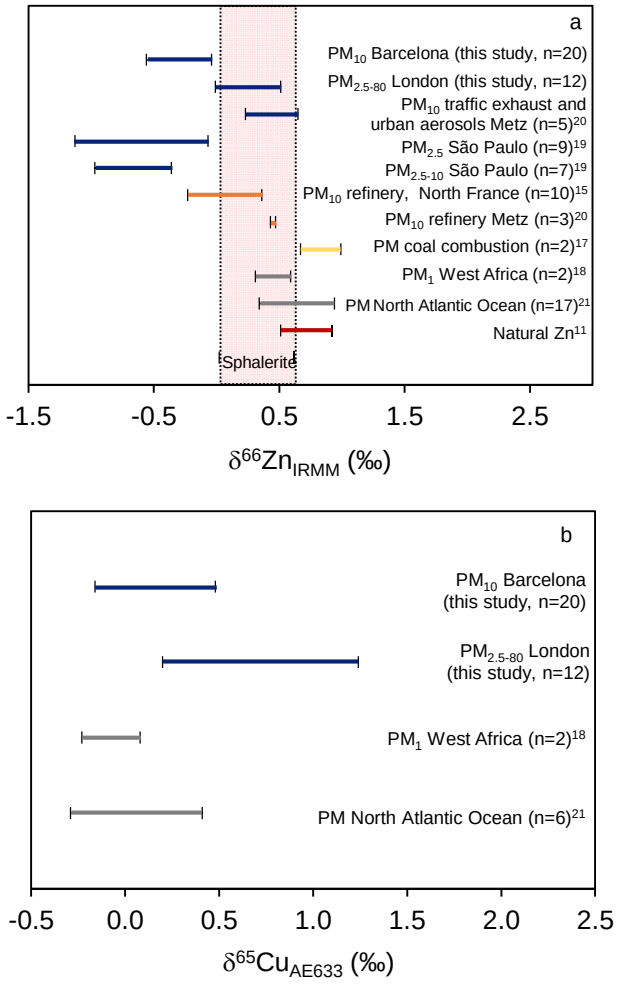

Figure 5. Zinc (panel a) and Cu (panel b) isotope compositions in PM collected at different locations around the world. The range of $\delta^{66}Zn_{IRMM}$ determined for sphalerite and ore concentrates (literature and this study) is shown using the shaded area.[12-14] The $\delta^{66}Zn_{IRMM}$ in rocks ranges between +0.52 and +0.92‰ (panel a), and the $\delta^{65}Cu_{AE633}$ in Cu sulphides ranges between –1 and +1‰.[11,22] The $\delta^{66}Zn_{Lyon}$ and $\delta^{65}Cu_{NIST976}$ taken from the literature were normalised to $\delta^{66}Zn_{IRMM}$ and $\delta^{65}Cu_{AE633}$, respectively, assuming an isotope offset of $\Delta^{66}Zn_{IRMM\text{-}Lyon}$=+0.32‰ and no isotope offset for Cu ($\Delta^{65}Cu_{NIST976\text{-}AE633} \approx -0.01\pm0.04$‰).[11, 42] Data obtained during this study and other cities in Europe and South America are presented in blue color whereas data from literature for PM from smelters and coal-fired power plants is shown in orange and yellow, respectively. Additional data for natural PM and natural sources of Zn are presented in grey and red, respectively.

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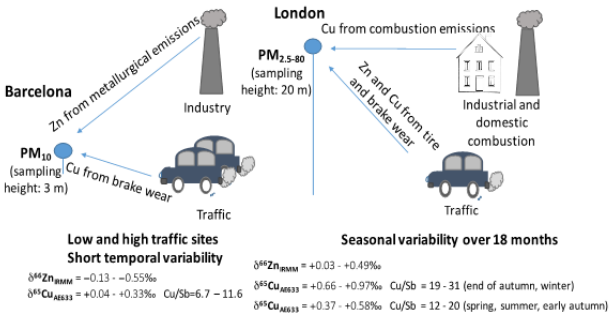
TOC


Barcelona
Zn from metallurgical emissions
Industry
PM10
(sampling height: 3 m)
Cu from brake wear
Traffic
Low and high traffic sites
Short temporal variability
δ66ZnIRMM = −0.13 - −0.55‰
δ65CuAE633 = +0.04 - +0.33‰ Cu/Sb=6.7 – 11.6
London
Cu from combustion emissions
PM2.5-80
(sampling height: 20 m)
Zn and Cu from tire and brake wear
Industrial and domestic combustion
Traffic
Seasonal variability over 18 months
δ66ZnIRMM = +0.03 - +0.49‰
δ65CuAE633 = +0.66 - +0.97‰ Cu/Sb = 19 - 31 (end of autumn, winter)
δ65CuAE633 = +0.37 - +0.58‰ Cu/Sb = 12 - 20 (spring, summer, early autumn)