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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 $-0.13 \pm 0.09$ and $-0.55 \pm 0.09\%$ for $\delta^{66}\text{Zn}_{\text{IRMM}}$ and between $+0.04 \pm 0.20$ and $+0.33 \pm 0.15\%$ for $\delta^{65}\text{Cu}_{\text{AE633}}$. 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 $+0.03 \pm 0.04$ and $+0.49 \pm 0.02\%$ for $\delta^{66}\text{Zn}_{\text{IRMM}}$ and between $+0.37 \pm 0.17$ and $+0.97 \pm 0.21\%$ for $\delta^{65}\text{Cu}_{\text{AE633}}$. Heavy Cu isotope signatures (up to $+0.97 \pm 0.21\%$) and higher enrichments and Cu/Sb ratios during winter time suggest important contribution from fossil fuel combustion. The positive $\delta^{66}\text{Zn}_{\text{IRMM}}$ 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. Different techniques such as principal component analysis and positive matrix factorization are typically applied, 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.

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. ZnO is the dominant species emitted from tire-treads and has been identified in emissions from metal smelting along with ZnS. Copper has likewise been linked to multiple sources, including smelting, oil combustion, wood smoke and brake wear. Copper typically occurs as oxide, silicate and carbonate, and is often associated with the organic fraction in PM.
The Zn isotope composition relative to the widely used standard JMC 3-0749L Lyon (expressed generally as $\delta^{66}\text{Zn}_{\text{Lyon}}$) 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. The $\delta^{66}\text{Zn}_{\text{Lyon}}$ of sphalerite, the major source of Zn concentrates used for industrial purposes, ranges typically between −0.04 and +0.30‰. 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. These values are outside the natural range of Zn isotope signatures and this is likely due to evaporation and condensation processes. Ore tailings collected from a smelter and fly ash in different coal-fired power plants had $\delta^{66}\text{Zn}_{\text{Lyon}}$ values as heavy as +1.49‰. Previous work on Zn isotopes in PM collected in industrial, urban and remote areas showed indeed significant isotopic variability with $\delta^{66}\text{Zn}_{\text{Lyon}}$ ranging from −1.13 to +0.33‰, suggesting that different sources and anthropogenic activities impart a distinctive isotopic composition to PM. Zinc in PM smaller than 10 μm (PM$_{10}$) emitted from a refinery in northern France imparted light isotope signatures with $\delta^{66}\text{Zn}_{\text{Lyon}}$ ranging between −0.52 and +0.02‰. Light Zn was also identified in PM collected in São Paulo, with $\delta^{66}\text{Zn}_{\text{Lyon}}$ ranging between −1.05 and −0.46‰ in PM$_{2.5-10}$ and between −1.13 and −0.07‰ in PM$_{2.5}$. The isotopic composition of PM$_{1}$ collected over the equatorial eastern North Atlantic region had $\delta^{66}\text{Zn}_{\text{Lyon}}$ signatures ranging between +0.03±0.04‰ and +0.17±0.10‰. These values are not significantly different from the isotopic signatures of natural sphalerite but lighter than PM$_{a}$ separated from soil dust collected from the Sahel region, ranging between +0.23±0.05‰ and +0.28±0.08‰. Atmospheric PM collected over the North Atlantic Ocean exhibited $\delta^{66}\text{Zn}_{\text{Lyon}}$ between +0.13±0.08 and +0.54±0.08‰ which falls within the range found for igneous rocks. 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. The average Cu isotope composition expressed as $\delta^{66}\text{Cu}_{\text{NIST976}}$ for chalcopyrite (CuFeS$_2$) is +0.32±0.04‰. The $\delta^{65}\text{Cu}_{\text{NIST976}}$ 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‰. Copper isotope signatures are variable within and between mineral groups, including native Cu or Cu sulphides and carbonates. Studies assessing the potential of Cu isotopes for tracing source contributions in the atmosphere are scarce. The $\delta^{66}\text{Cu}_{\text{NIST976}}$ values in PM$_{1}$ collected over the North Atlantic Ocean (West Africa) ranged between −0.14±0.09 and −0.02±0.10‰. 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‰. The Cu isotope signatures in PM$_{1}$ collected over the North Atlantic Ocean ranged between −0.18±0.11 and +0.30±0.11‰. Changes in mineralogy and mixing with industrial emissions from North Africa were suggested as possible mechanisms for the variability of Cu isotope signatures.
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. 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. 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. To this end, we first determined the spatial and short-term temporal variability of Zn and Cu isotope signatures in PM 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 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), 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 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 HNO₃ 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 HClO₄ (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 HNO₃ 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. HNO₃, HF and HCl purified by sub-boiling distillation in quartz stills and high purity HClO₄ (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 (PM₂.₅-₈₀) 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 HNO₃, 3 M HCl and 2 M distilled HNO₃. 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 HNO₃ 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 HNO₃, 1 ml of HF and 0.5 ml of HClO₄ over four days on a hot plate at 140 °C. Solutions were evaporated to dryness at 230 °C, re-fluxed in ca. 16 M HNO₃ 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 HNO₃ 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 \(\mu\)l of resin reservoir containing 150 \(\mu\)l 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 \(\mu\)l 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\(_{\text{IRMM}}\) and \(\delta^{66}\)Cu\(_{\text{AE633}}\) according to Eq. 2 and Eq. 3:

\[
\delta^{66}\text{Zn}_{\text{IRMM}} = \left[\frac{\left({^{62}\text{Zn}}/{^{64}\text{Zn}}\right)_{\text{sample}}}{\left({^{62}\text{Zn}}/{^{64}\text{Zn}}\right)_{\text{IRMM}}} - 1\right] \times 1000 \quad [\text{Eq. 2}]
\]

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

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 ($\delta^{66}$ZnIRMM = +0.11 ± 0.25‰, n=5), Romil Zn (−9.10±0.10‰, n=4) and Romil Cu ($\delta^{65}$CuAE633 = +0.18 ± 0.05‰, n=4) are in good agreement with previous published data. Average isotopic compositions of NIST-1648a determined from individual analytical sessions over six months were $\delta^{66}$ZnIRMM = −0.19±0.15‰ (n=6) and $\delta^{65}$CuAE633 = +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 ($\delta^{66}$ZnIRMM and $\delta^{65}$CuAE633) determined in PM$_{10}$ collected in Barcelona at sites with low (Torre Girona and Palau Real) 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 Real (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.

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 Real 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 $\delta^{66}$ZnIRMM 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 are in line with our results suggesting important contribution from metallurgical processes in PM in Barcelona. 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. 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 $+1%_{oo}$, and Cu sulphides being the dominant chemical species in brake lining materials. 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.

### 3.2. Spatial and temporal variability of concentrations, enrichment factors and isotope ratios in PM$_{2.5-80}$ 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. 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, and with ore concentrates (mainly sphalerite) analysed in our study (δ66ZnIRMM = +0.03±0.10‰, two samples). Particles from tire wear are in general larger than 10 μm, and therefore have possibly been preferentially accumulated in the passive sampler, supporting further contribution from tire wear.

The δ65CuAE633 values vary between +0.37±0.17 to +0.97±0.21‰ (Table 1). These values are significantly heavier than in PM10 collected in Barcelona. We find significant isotope variability over the entire time period assessed, but most notable are the heavier δ65CuAE633 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 δ65CuAE633 during November and December 2014 (S7). The Cu/Sb ratio of brake wear is typically 4.6±2.3. 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 PM10, respectively. The influence of emissions from metallurgy for Zn is supported by (i) the lack of correlation between δ66ZnIRMM and the EF Sb (Figure 2b), and between the EF Zn, EF Sb and EF Fe (Figure 3); (ii) the high variability in the δ66ZnIRMM 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. Significant contribution from brake wear to Cu enrichment in PM10 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 PM10 (Table 1) which are close to the Cu/Sb ratios previously reported for brake wear particles.

In London, we propose that Zn and Cu in PM2.5-80 are dominated by non-exhaust emissions from road vehicles. The correlation between δ66ZnIRMM and EF Sb (Figure 2c), and the similarity between δ66ZnIRMM of the PM2.5-80 samples enriched in Zn (Table 1) and of ore minerals typically used in the production of tires and galvanized steel support this idea. The δ65CuAE633 in the PM2.5-80 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. The Cu/Sb ratios of PM2.5-80 (Cu/Sb = 19±7) are significantly higher than those typically found in brakes (Cu/Sb = 4.6±2.3) 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$_{2.5-80}$ 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$_{2.5-80}$ 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.
Acknowledgements

R.O.G. thanks The European Commission (FP7-PEOPLE-2012-IEF) for funding the project ISOTRACE (proposal 329878). The authors wish to thank the MAGIC group and in particular Katharina Kreissig at Imperial College for their assistance in the laboratories, Emma Humphreys-Williams (Natural History Museum) for conducting the ICP-OES analysis, and the important feedback provided by three reviewers. Fraser Wigley is thanked for his help during the collection of samples in London.

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$_{Cu}$.

<table>
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<tr>
<th>Sample label</th>
<th>Date of collection</th>
<th>Concentrations ng m$^{-3}$ (Barcelona) and ng day$^{-1}$ (London)</th>
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<th>EF$_{Cu}$</th>
<th>EF$_{Fe}$</th>
<th>EF$_{Sb}$</th>
<th>$\delta^{64}$Zn$_{PM10}$ (‰)</th>
<th>±2SD</th>
<th>$\delta^{64}$Cu$_{PM10}$ (‰)</th>
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* Sample S5 has not been considered to calculate the average EF$_{Cu}$. 
Figure 1. a) Variability in the Zn (diamonds) and Cu (squares) isotope signatures (expressed as $\delta^{66}$ZnIRMM and $\delta^{65}$CuAE633, 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 $\delta^{65}$CuAE633. 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 R² 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 $\delta^{66}$ZnIRMM determined for sphalerite and ore concentrates (literature and this study) is shown using the shaded area.$^{12-14}$ The $\delta^{66}$ZnIRMM in rocks ranges between +0.52 and +0.92‰ (panel a), and the $\delta^{65}$CuAE633 in Cu sulphides ranges between −1 and +1‰. $^{11,22}$ The $\delta^{66}$ZnLyon and $\delta^{65}$CuNIST976 taken from the literature were normalised to $\delta^{66}$ZnIRMM and $\delta^{65}$CuAE633, respectively, assuming an isotope offset of $\Delta^{66}$ZnIRMM-Lyon = +0.32‰ and no isotope offset for Cu ($\Delta^{65}$CuNIST976-AE633 $\approx$ −0.01±0.04‰). $^{11,42}$ 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.
References


depositions within a 5 km radius of a Pb–Zn refinery. *Atmospheric Environment* 2009, 43, (6), 1265-1272.


43. Querol, X.; Alastuey, A.; Rodriguez, S.; Plana, F.; Ruiz, C. R.; Cots, N.; Massagué, G.; Puig, O., PM10 and PM2.5 source apportionment in the Barcelona


TOC

London
Cu from combustion-emissions

Barcelona
Zn from traffic-emissions

Traffic

PM2.5
(sampling height: 2 m)

PM10
(sampling height: 2.5 m)

Low and high traffic sites
Short temporal variability

Seasonal variability over 18 months

\[ \text{PM}_{2.5} \text{mean} = 4.35 \pm 1.29 \mu \text{g/m}^3 \]

Traffic

\[ \text{PM}_{10} \text{mean} = 10.05 \pm 1.97 \mu \text{g/m}^3 \]

\[ \text{Cu(s)} \text{mean} = 12 - 30 \text{ (part of autumn, winter)} \]

\[ \text{Cu(s)} \text{mean} = 15 - 30 \text{ (spring, summer, early autumn)} \]