**FINAL PUBLISHABLE SUMMARY REPORT**

**STABLE ISOTOPES OF METALS AS POLLUTANT TRACERS IN THE ATMOSPHERIC ENVIRONMENT (ISOTRACE)**

**Relevance of ISOTRACE**

***Emissions of Zn and Cu into the atmosphere* –** The release of metals into the atmospheric environment from anthropogenic activities poses major risks to ecosystems and human health. The airborne particulate material causes serious lung diseases, basically through the inhalation of small particles with diameters of 10 μm or less which can be absorbed in the alveolar region producing tissue damage. The US EPA has listed elements such as copper (Cu) and zinc (Zn) as priority pollutants under the Clean Water Act. This is of particular concern in large cities such as London and other major European cities. Stable metal isotopes have been suggested as a novel and exciting tool to identify the various possible sources, but this is yet to be established unequivocally.

***Stable isotope techniques in environmental samples* –** The development of plasma source multi-collector mass spectrometers (MC-ICP-MS) has enabled us to use stable isotope variations to study the environmental chemistry of pollutant metals such as Zn and Cu. This technique has a great potential to identify the sources and help unravelling transport processes in the atmosphere. Isotopic fractionation during high temperature processes such as refining or combustion was proposed to impart light isotope signatures while non-combustion sources such as tires, galvanised road furniture, etc., preserve the isotope signature of original concentrates derived from the ore Zn.

***Objectives of ISOTRACE* –** ISOTRACE aimed to deliver a comprehensive assessment of the potential of stable isotope ratios to trace pollutant metal sources affecting urban air quality and to aid therefore the development of targeted control emissions. This included (i) deconvolving the mechanism that lead to isotopic fractionation in source materials and by-products derived from combustion, (ii) assessing temporal and spatial isotope variations in urban atmospheric particulate matter in major European cities and identifying changes in source contributions, and (iii) critically assess analytical methods for high precision and accurate isotope ratio measurements.

**Achievements**

***Objective 1: Mechanisms that lead to isotopic variations in source materials***

We developed the first predictive model to determine Zn Isotopic fractionation during combustion. The zinc (Zn) isotope compositions of feed materials and combustion by-products were investigated in three different coal-fired power plants, and we developed a generalized model that accounts for the observed isotope fractionations. The bottom ashes collected were isotopically depleted in the heavy isotopes relative to the coals, suggesting that the heavy isotopes are preferentially released into the vapour phase. In contrast, the fly ash in all of these power plants was enriched in the heavy isotopes relative to coal, likely due to condensation onto the particles. Our findings demonstrate that the isotopic composition of the coal controls the isotope signature of the particles emitted to the atmosphere and depends on the speciation of the metal in the fuels. Our results confirm that the Zn derived from high temperature combustion processes is isotopically different than that derived from the use of concentrates (see below). Our results demonstrate that the elemental speciation in the coal, evaporation, and condensation are the processes governing the isotopic variations within coal power plants.

***Objective 2: Potential application of Zn and Cu isotopes for source tracing in airborne particles in European cities***

We demonstrated significant temporal and spatial isotopic variations of Zn and Cu in airborne particulate matter collected in two major European cities, i.e. Barcelona and London, over weeks and years. The isotope variability demonstrates that there are several major sources contributing to the metal burden and there is not a single dominant point source. We furthermore constrained the isotope signatures of the different suggested sources in particulate matter for Zn including road dust, coal, tires, soil dust, etc. Comparing the isotope signatures and other tracers such as enrichment factors, element associations and elemental ratios, we demonstrate that non-combustion traffic sources (i.e brake pads) are indeed a major source as suggested before but we also clearly demonstrate that combustion sources are important during different times of the year. We finally found that the source contributions to the Cu and Zn burden in the atmosphere in Barcelona and London are different.

***Objective 3: Critical assessment of analytical methodology for high precision and accurate isotope ratio measurements in aerosols***

We critically compared the use of internal and external mass bias correction methods on the precision and accuracy of the isotope ratio measurements of Zn by comparing the double-spike with the standard sample bracketing method measuring several aerosols. We demonstrate that both methods yield precise isotope ratios and mostly identical results. However, we find in selected samples significant differences, emphasising the need of an international standard for particulate matter.

**Conclusions**

The project ISOTRACE delivers a comprehensive and detailed assessment of the potential of Zn and Cu isotopes for source tracing in atmospheric particles.

First, we demonstrated that Zn is fractionated during combustion process, leaving the residual bottom ash and the flue gas enriched in the lighter isotopes and the fly ash enriched in the heavier isotopes relative to the feed material. We also demonstrate that this pattern is reproducible across different plants, enabling us to develop a conceptual model that predicts Zn isotopic fractionation in the different by-products and the flue gas emissions produced in coal combustions plants, and therefore constraining the isotopic signature of Zn released by coal combustions utilities. Our work clearly shows that Zn derived from combustion is isotopically distinct from natural and ore Zn.

Second, we observed that significant isotopically variations exist between particulate matter collected in two major European cities over different time periods and at different heights. This shows for the first time that the dominant Zn sources do vary from city to city in Europe and also during the year in the same city, making abatement strategies challenging and complex. The comparison with the isotope signature of different sources and other source tracing techniques (enrichment factors and metal ratios) strongly suggests that non-exhaust emissions from traffic, i.e. tires, are important, but emissions form high temperature processes such as oil, waste or coal burning are equally significant at various times of the year.

Finally, we demonstrated that different analytical approaches yield accurate and precise isotope data but also critically highlight the need of international certified isotope standard for aerosols and the limitation of the present mass bias correction methods.

**Impact in the society**

We identify several significant impacts.

First, the model accounting for the isotope fractionation occurring in coal combustion can be used to estimate the Zn isotope signatures in atmospheric particulates leaving the combustion plants based on the analysis of the feed coal only. This enables the integration of isotopes as a quantitative tool for the source apportionment of this metal from coal combustion in the atmosphere.

Second, we show that sources of Zn and Cu do vary at time intervals of months and are likely controlled by the non-combustion traffic sources and by combustion processes. We show that the source contributions differ from city to city in Europe. This suggests that each city needs its own careful source assessment and abatement strategies taking into account the specific time period.

Third, we clearly demonstrate the need for an international reference material for isotope ratio measurements in aerosols.

Forth, during the project, two young researchers at undergraduate and postgraduate level (Tamara Markovic and Pavan Juttla) were taught in analytical techniques and methods as part of their PhD and MSc work.

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