



# EA-IRMS: Using isotope fingerprints to track sources of PM<sub>2.5</sub> in air pollution

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## Goal

Trace the origin of PM<sub>2.5</sub> particles in air pollution using carbon, nitrogen and sulfur isotope fingerprints.

## Introduction

Air pollution, also known as haze events, is a growing global issue that results from a high concentration of sub-micron particles (PM<sub>2.5</sub>) in air in the form of sulfate aerosols and nitrous oxides derived from fossil fuel burning, ozone and volatile organic compounds<sup>1,2,3</sup>. PM<sub>2.5</sub> particles have a high scattering coefficient on solar radiation and combined with high humidity, reduce visibility significantly. These factors impact the surface temperature of the earth, thereby affecting weather and climate, and carry serious implications for human cardiovascular and respiratory health<sup>1,4</sup>. In order to improve air quality, it is important to identify the source of air pollutants (referred to as source apportionment) and application of isotope fingerprint analysis using isotope ratio mass spectrometry (IRMS) is an informative and rapid technique for achieving this<sup>1,2,3</sup>.

## Analytical configuration

PM<sub>2.5</sub> particles were collected on quartz microfiber filters (254 mm x 203 mm x 2.2 μm) in Seoul, South Korea from November 2016 through January 2017, using a high volume PM<sub>2.5</sub> impactor sampler. Sampling times reflected changes in air pollution levels. For simultaneous nitrogen, carbon and sulfur stable isotope analysis, 5-6 mg of quartz filter was weighed into tin capsules. The tin capsules were then introduced to the combustion reactor of the Thermo Scientific™ EA IsoLink™ IRMS System from the Thermo Scientific™ MAS Plus Autosampler and combusted in the presence of oxygen. The gases were then passed over hot copper where nitrous oxides were reduced to N<sub>2</sub> and excess oxygen was removed from the gas stream, producing N<sub>2</sub>, CO<sub>2</sub> and SO<sub>2</sub> gas for isotope analysis. Analysis time was 10 minutes, using 1.4 liters of helium per sample. Each filter sample was analyzed in triplicate. Carbon and Nitrogen isotope values were referenced by single point calibration against USGS 40 and IAEA N1, respectively and sulfur isotope ratios were referenced by 3-point calibration against IAEA S1, IAEA S2 and USGS 42.

## Isotope fingerprints in air pollution

For air pollution studies, carbon isotope fingerprints principally indicate a fossil fuel source, such as coal or diesel emissions from road vehicles and/or maritime vessels. The global carbon isotope fingerprint range spans -19‰ to -35‰, indicating that fossil fuel origin can be identified<sup>3,5</sup>, where vehicle emissions are reported in the range of -25‰ to -28‰<sup>3,6</sup>. However, marine biota and biomass burning can also contribute to the source of carbon in air particles<sup>6</sup>.

Besides the large nitrogen atmospheric reservoir, nitrogen in air particles/aerosols is present as NO<sub>x</sub>, deriving from coal-fired plants, vehicle and maritime emissions and in China, winter heating via coal burning<sup>1,6</sup>. The nitrogen isotope fingerprints of coal-fired power plants range between 6‰ and 20‰<sup>2</sup> with the nitrogen isotope composition of coal from China documented in the range of -6‰ to +4‰, similar to that reported from Europe and North America where the range is -2.5‰ to +3.5‰<sup>7</sup>. NO<sub>x</sub> contributions from vehicle and maritime emissions have been reported to have nitrogen isotope fingerprints of -13‰ to +8‰<sup>2</sup>, with a recent study in Seoul reporting values of ca. 8.6‰<sup>6</sup>. Contributions from soils, particularly fertilized soils, are reported in the range of -49‰ to -20‰<sup>2</sup>.

The sulfur isotope fingerprint in air particles and aerosols can differentiate between man-made and natural sources. Maritime sulfate aerosols, deriving from sea salt sulfate and dimethyl sulfide (DMS) as a primary productivity by-product, tend to have a sulfur isotope fingerprint of 19‰ to 21‰<sup>1</sup>. Man-made sources of sulfate have a sulfur isotope fingerprint of +1 to +11‰<sup>8</sup>. Biogenic sulfur released from terrestrial sources, such as soils and wetlands, ranges from -10‰ to -2‰<sup>1</sup>. The sulfur isotope fingerprint in coal from north China has been reported to be 6.6‰<sup>1</sup>, however the range of sulfur in coals can vary from -15‰ to +50‰<sup>6</sup>, depending on the source of organic material at the time of sedimentation<sup>7</sup>.

## Haze events in Seoul, South Korea

The nitrogen, carbon and sulfur isotope fingerprints from the samples collected on the quartz filters are presented in Table 1 and illustrated in Figure 1. For the analyzed haze events covering November 2016 through January 2017, the carbon isotope fingerprint (δ<sup>13</sup>C) ranged from -26.33‰ to -27.59‰ (seasonal average: -26.8±0.5‰); the nitrogen isotope fingerprint (δ<sup>15</sup>N) ranged from 4.19‰ to 8.58‰ (seasonal average: 6.7±1.5‰); and the sulfur isotope fingerprint (δ<sup>34</sup>S) ranged from 4.01‰ to 7.35‰ (seasonal average: 5.8±1.2‰).

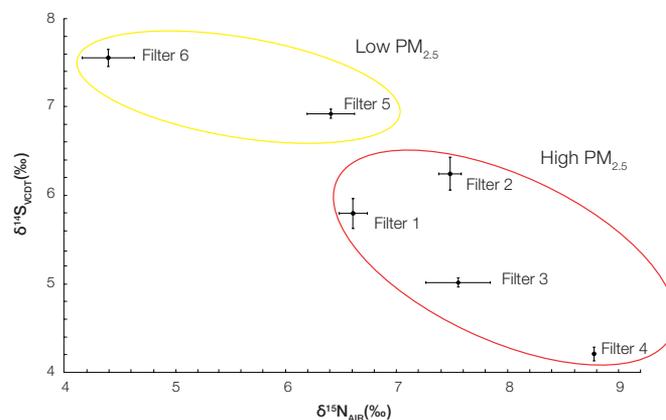


Figure 1. Nitrogen and sulfur isotope fingerprints from filtered air from Seoul, South Korea.

Table 1. δ<sup>15</sup>N, δ<sup>13</sup>C and δ<sup>34</sup>S from air filter samples as mean ± 1σ (n = 3).

Sample	δ <sup>15</sup> N <sub>AIR</sub> (‰)	μg N	δ <sup>13</sup> C <sub>VPDB</sub> (‰)	μg C	δ <sup>34</sup> S <sub>VCDT</sub> (‰)	μg S
Filter 1	6.40 ± 0.25	2.6	-26.75 ± 0.38	36.9	5.59 ± 0.33	1.1
Filter 2	7.28 ± 0.20	1.9	-27.59 ± 0.15	35.8	6.05 ± 0.37	0.5
Filter 3	7.35 ± 0.68	3.5	-27.15 ± 0.48	51.0	4.82 ± 0.09	1.1
Filter 4	8.58 ± 0.04	10.4	-26.88 ± 0.31	67.6	4.01 ± 0.15	2.3
Filter 5	6.20 ± 0.60	1.8	-26.25 ± 0.17	38.0	6.73 ± 0.10	0.9
Filter 6	4.19 ± 0.47	1.6	-26.33 ± 0.23	44.5	7.35 ± 0.18	1.1

The  $\delta^{13}\text{C}$  value showed little variation and is indicative of vehicle emissions, aligning with recently reported data from Seoul<sup>6</sup>. The  $\delta^{34}\text{S}$  values decreased from 7.35‰ to 4.01‰ and the  $\delta^{15}\text{N}$  values increased from 4.2‰ to 8.6‰ as air pollution increased. The increase in  $\delta^{15}\text{N}$  values and total nitrogen is principally related to coal combustion and secondarily to vehicle emissions<sup>6</sup>. The  $\delta^{34}\text{S}$  values are indicative of a fossil fuel source and not maritime aerosols or biogenic sulfur sources, correlating with coal-burning during winter heating in northern and north-eastern China<sup>1,6</sup>.

## A rapid way to detect PM<sub>2.5</sub> sources in air pollution

The analytical approach here represents a direct measurement of PM<sub>2.5</sub> particles on quartz filters, utilizing the combined high sensitivity of the EA IsoLink IRMS System and fast analysis times. The analysis was complete in 10 minutes, with additional time taken to sub-sample, weigh and load samples into the autosampler for analysis. This represents a significantly shorter time from sample to data compared with longer sample chemical preparation techniques, such as, precipitating the sulfur as barium sulfate<sup>1</sup>, which has been employed to obtain sufficient elemental sulfur concentrations for analysis. Our approach is faster, less labor intensive and lower cost without compromising data quality. In addition, whilst nitrogen analysis using the denitrification method<sup>6</sup> provides a detailed source insight, direct measurement as shown here is sufficient for source identification when combined with carbon and sulfur isotope fingerprints.

## Summary

The measurement of carbon, nitrogen and sulfur isotope fingerprints of PM<sub>2.5</sub> particles on quartz filter papers allows source identification. Of the samples analyzed here, PM<sub>2.5</sub> particles are generated from fossil fuel sources derived from coal combustion due to winter heating and from vehicle and maritime emissions. Combining these direct measurements from quartz filters with isotope fingerprints reported in the literature, source identification of PM<sub>2.5</sub> particles is possible.

Using the EA IsoLink IRMS System for source identification of PM<sub>2.5</sub> particles in air pollution, laboratories provides:

- A rapid analytical technique for source identification using isotope fingerprints
- An efficient, automated technique for source identification that *does not require* sample chemical clean up, with its associated high labour and consumable costs
- A reliable analytical technique that produces high quality data comparable with published literature<sup>1,2,3,6</sup>

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