

Research article

A case study in the wintertime Vaal Triangle Air-Shed Priority Area on the utility of the nitrogen stable isotopic composition of aerosol nitrate to identify NO_x sources

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Abstract

In South Africa, the Highveld region and the Johannesburg-Pretoria megacity are known as global NO_x ($\text{NO}_x = \text{NO} + \text{NO}_2$) “hotspots” identified by satellite-based instruments. The ultimate sink for atmospheric NO_x is conversion to aerosol nitrate. However, measurements of aerosol nitrate concentrations do not provide information on which NO_x sources served as nitrate precursors at that location. This complicates efforts to reduce concentrations of particulate matter (PM) in these air quality priority areas. Here, we measured the nitrogen stable isotope composition of nitrate from daily wintertime collections of coarse mode $\text{PM}_{2.5-10}$ ($\text{PM} \leq 10$ and $>2.5 \mu\text{m}$ in diameter) at three air quality monitoring stations located in the Vaal Triangle Air-Shed Priority Area (VTAPA). The overall aim of this case study was to evaluate the use of the distinct stable isotope signatures of various NO_x sources to identify their relative contribution to aerosol nitrate across the Highveld. The nitrogen isotope ratios of aerosol nitrate were similar across the three sites, with greater day-to-day variability than site to site variability. Air mass history was the main driver of the variability in the nitrogen isotope ratios of aerosol nitrate, with significantly higher isotopic ratios observed for air masses originating from the southwest. Using an isotope mixing model we determined that NO_x from coal-burning is the dominant contributor to aerosol nitrate (66%), followed by biomass burning (16%), vehicles (12%), and soil emissions (6%).

Keywords

Aerosol Nitrate, Stable Isotopes, NO_x Sources, Highveld, Vaal Triangle

Introduction

High concentrations of ambient aerosols are associated with increased mortality risks. There is a wide range of evidence documenting the large health costs associated with high levels of air pollution (Pervin et al. 2008; Zhao et al. 2016; Altieri and Keen 2019). In many regions of South Africa, particulate matter (PM) is considered the pollutant of greatest concern (City of Cape Town 2008; Thabethe et al. 2014). Anthropogenic aerosol sources include fugitive dust, fires, mining, transportation, electricity generation, industrial activities, domestic fuel burning, and traffic. The latter two sources are typically considered the largest contributors to the South African PM burden (Feig et al. 2016; Venter et al. 2012). Natural sources are dominated by dust and sea spray. PM can be emitted to the atmosphere or formed through gas-to-particle conversion and is composed of a complex mixture of inorganic species, organic carbon, and black

carbon with small amounts of trace metals (Seinfeld and Pandis 2012).

Globally, the emission of anthropogenic nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) to the atmosphere has increased tenfold since preindustrial times (Galloway et al. 2004). NO_x itself is a local air pollutant, and it impacts regional air pollution by serving as a precursor to ozone and secondary PM formation. In South Africa, the Highveld region and the Johannesburg-Pretoria megacity are known as global NO_x “hotspots” identified by satellite-based instruments (Lourens et al. 2012). This region, along with the neighbouring Vaal Triangle, is responsible for > 90% of South Africa’s anthropogenic NO_x emissions (Lourens et al. 2012). Similarly, there are large emissions of sulfur dioxide (SO_2) from industrial activities, coal mines, and power generation, particularly in winter (Feig et al. 2016; Lourens et al.

2011; Venter et al. 2012). NO_x and SO₂ emissions are the main precursors to secondary inorganic PM formation and highlight the coupling between gaseous emissions and the formation of secondary aerosols.

Air transported to the central plateau of South Africa originates primarily from the Atlantic and Indian Oceans, with a 25% contribution from the African continent (Freiman and Piketh, 2003). As oceanic NO_x sources are very low, the only external NO_x source to the Highveld/Vaal area would be seasonal biomass burning from neighbouring African countries. The fate of NO_x produced in the Highveld and Vaal regions includes dry and wet deposition and conversion to aerosol nitrate. The local recirculation time scale is 2 to 9 days (Freiman and Piketh 2003; Collett et al. 2010; Igbafe et al. 2015), allowing for complete NO_x conversion to nitrate, such that aerosol nitrate concentrations in the Highveld/Vaal area are primarily influenced by local NO_x emissions. Similarly, local industrial emissions of SO₂ make a considerable contribution to sulfate aerosols, the main component of the summer and winter haze layer in this region (Piketh et al. 1999).

NO_x negatively impacts human health and, as NO₂, is controlled by both minimum emission standards (MES) and national ambient air quality standards (NAAQS) in South Africa (Government Gazette, 24 December 2009, No. 32816). NO_x and volatile organic compounds lead to ozone formation, which is controlled by NAAQS due to its adverse impacts on human health and visibility. The ultimate sink for atmospheric NO_x is the conversion to aerosol nitrate. Nitrate can be present in PM aerosols as ammonium nitrate, sodium nitrate, magnesium nitrate, and calcium nitrate. Due to the adverse impacts on human health and visibility, PM is also controlled by NAAQS. The Highveld Priority Area (HPA) and the Vaal Triangle Air-Shed Priority Area (VTAPA) occasionally record NO₂ values above the NAAQS. However, PM and ozone are regularly out of compliance at stations across the HPA and VTAPA (saaqis.environment.gov.za). Although NO_x emissions rarely exceed the MES, emissions reductions would positively influence air quality in these regions by reducing ozone and PM. However, measuring the nitrate concentration in PM does not provide information on which specific NO_x sources lead to aerosol nitrate formation at that location. This complicates efforts to reduce concentrations of PM in these air quality priority areas.

The atmospheric cycle of NO_x and the conversion of NO_x to aerosol nitrate is complex, with different processes taking place during the day and night (Altieri et al. 2013). In addition to NO_x being a precursor to ozone, ozone can be consumed in the conversion of NO_x to nitrate aerosols, further complicating the influence of NO_x on the chemistry of local and regional air pollution. Previous studies have used nitrogen and oxygen isotopes of nitrate as a tool for distinguishing NO_x sources, as well as the chemical pathway through which NO_x was converted to nitrate in polluted environments (Freyer 1978; Elliott et al. 2007). As NO_x is converted to nitrate, the nitrogen atom is conserved; therefore the δ¹⁵N of nitrate will reflect the δ¹⁵N of the NO_x source. Indeed,

studies of the isotopic composition of NO_x have shown that NO_x from vehicle emissions, power generation, industrial activities, lightning, soils, and biomass burning all have distinct isotopic compositions (Felix et al. 2012; Felix and Elliott 2014; Fibiger et al. 2014; Walters et al. 2015; Walters et al. 2015).

The fate of NO_x emissions are usually investigated using dispersion models, but these models lack ozone and secondary PM formation and cannot directly address the relationship between NO_x emissions and measured PM concentrations. Air mass back trajectory analysis is a useful approach for identifying which air masses are associated with higher/lower concentrations of a pollutant. However, the trajectory analysis does not account for loss processes, mixing, and secondary formation processes and only provides a qualitative connection between emission sources and ambient concentrations. The stable isotope approach is unique in that it enables us to quantitatively identify the NO_x sources contributing to aerosol nitrate. Despite the hotspot of NO_x emissions and the high levels of PM recorded at air quality monitoring stations in the HPA and VTAPA, to our knowledge, the nitrogen stable isotope approach has not been used in South Africa to attribute PM nitrate to local and regional NO_x sources.

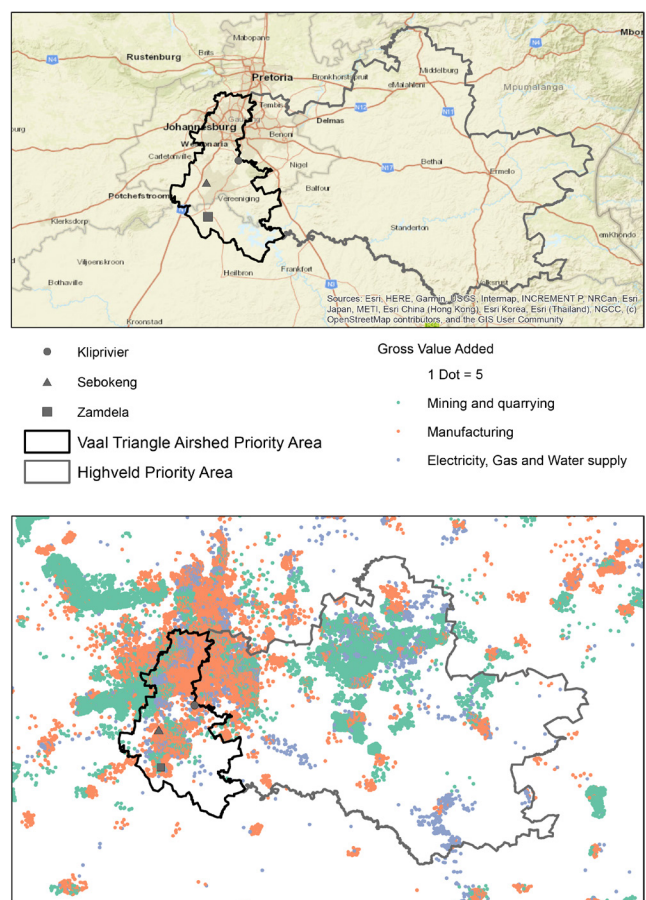


Figure 1: Map showing the VTAPA and Highveld Priority Area and the three sampling sites in relation to a) the metropolitan area of Pretoria and Johannesburg with major roads indicated and b) the dot density of the gross value add (2009 Rands) of mining and quarrying, manufacturing, and electricity, gas and water supply (Naude et al. 2007).

Methods

The VTAPA is a well-studied air pollution priority area in South Africa located near the Johannesburg-Pretoria megacity (Figure 1). Aerosol samples analysed for nitrogen stable isotope in this study were collected for a PM source apportionment study (Muyemeki et al. 2021). Briefly, continuous samples were collected at multiple sites using dichotomous low volume samplers with a flow rate of 15 L min⁻¹ for the coarse size fraction (PM_{2.5-10}) on 47 mm quartz fiber filter membranes. Two consecutive continuous 12-hour samples were collected daily (10:00 – 22:00 and 22:00 to 10:00).

For the nitrogen isotope case study presented here, sixteen coarse mode samples (8 days and 8 nights) collected from 21 June 2018 to 5 July 2018 at three sites were analysed (n = 48). Two of the sites are in densely populated low-income settlements (i.e., Sebokeng (26.5879°S, 27.8410°E) and Zamdela (26.8449°S, 27.8551°E)) and the third is in a low-density area (i.e., Kliprivier (26.4203°S, 28.0849°E); Figure 1). The wintertime samples were the focus of this study as the highest median values for PM_{2.5-10} occurred during winter (Muyemeki et al. 2021). The sampling and methodological approach used here results in a focus on the thermodynamically stable aerosol nitrate. Given the sampling was limited to coarse mode aerosols in the winter, there is little concern that fine mode ammonium nitrate volatilization is impacting the sampling of aerosol nitrate (Schaap et al. 2004). Furthermore, the isotopic approach is specific to inorganic nitrate such that organic nitrate molecules are excluded from analysis (Sigman et al. 2001).

Daytime and nighttime aerosol filters were combined to ensure sufficient sample nitrate for isotope analysis such that each combined sample represents 24-hours (e.g., Filter A = 21 June 2018 10:00 to 22:00 and Filter B = 21 June 2018 22:00 to 22 June 2018 10:00 were combined to generate extract 1 which is representative of 21 June 2018 10:00 to 22 June 2018 10:00).

Aerosol filters were extracted in 10 mL of ultrapure Milli-Q water, sonicated for one hour, stored at 4°C for 12-hours to maximize extraction efficiency, and then frozen for nitrate concentration and isotopic analysis (Gobel et al. 2013). The ¹⁵N/¹⁴N isotopic ratio of NO₃⁻ (δ¹⁵N) was determined using the denitrifier method following (Sigman et al. 2001) at Brown University. Briefly, natural strains of denitrifying bacteria (*Pseudomonas aureofaciens*) that lack the nitrous oxide (N₂O) reductase enzyme needed to convert N₂O to N₂ were used to convert 20 nmol of NO₃⁻ to N₂O. The N₂O was then analysed by Gas-Chromatograph Isotope Ratio Mass Spectrometry (Thermo-Scientific Delta V Plus) for isotopic determination of ¹⁵N/¹⁴N (Sigman et al. 2001). International reference materials IAEA-N-3 and USGS-34 were used to normalize isotopic values to N₂ in air. The pooled standard deviations of references IAEA-N3 and USGS-34 for δ¹⁵N were 0.09‰ (n=7) and 0.12‰ (n=7), respectively. The pooled standard deviation of sample replicates and duplicates for δ¹⁵N was 0.25‰.

Results and discussion

The coarse mode (PM_{2.5-10}) aerosol δ¹⁵N-NO₃⁻ ranged from 1.1‰ to 16.6‰ (n=24) (Table 1). The aerosol δ¹⁵N-NO₃⁻ values observed here in the Highveld are comparable to winter observations in other regions where coal is the dominant energy source. For example, δ¹⁵N-NO₃⁻ in PM_{2.5} in Beijing had a winter average of 11.9‰ ± 4.4 whereas in summer the average was 2.2‰ ± 2.5 (Song et al. 2019). A similar study in Beijing focused on winter pollution and found daily PM_{2.5} δ¹⁵N-NO₃⁻ to range from 1.0‰ to 19.6‰ (Zhang et al. 2020). Similar patterns have been observed in the coal-burning Midwest region of the United States, where winter aerosol δ¹⁵N-NO₃⁻ was 7.6‰ higher than in summer (Elliott et al. 2009, 2019). For most locations where seasonal nitrate isotope data are available, winter is the season of highest δ¹⁵N-NO₃⁻ (Song et al. 2019; Zhang et al. 2020, 2021; Zong et al. 2017, 2020). This is typically attributed to the use of fossil fuel sources for heating and residential combustion. A complete seasonal analysis of aerosol δ¹⁵N-NO₃⁻ will reveal if similar patterns are evident in the Highveld region.

Table 1: The range, average, and standard deviation (SD) of 24-hour coarse mode (PM_{2.5-10}) aerosol nitrate δ¹⁵N samples collected at Zamdela (n=8), Sebokeng (n=8), and Kliprivier (n=8) from 21 June 2018 – 6 July 2018.

Site	δ ¹⁵ N-NO ₃ ⁻ (‰) Range	δ ¹⁵ N-NO ₃ ⁻ (‰) Average (±SD)
Zamdela	3.6-13.0	6.2 (3.0)
Sebokeng	3.4-16.6	7.0 (4.3)
Kliprivier	1.1-14.1	7.1 (4.4)

The δ¹⁵N was very similar across all three sites (Table 1; p >> 0.05), and the day-to-day variability was generally higher than the between site variability (Figure 2). In particular, the 4 July 2018 sample is higher in δ¹⁵N at all sites than any of the other sample days (Figure 2). This suggests that the aerosol nitrate resulted from a different combination of NO_x sources, or that there was a change in atmospheric or chemical conditions such that isotopic fractionation occurred. The average NO₃⁻ concentration varied little across the last three sampling days, from 2.5 μg m⁻³ on the 2 July, 3.6 μg m⁻³ on the 4 July, and 3.1 μg m⁻³ on the 6 July. However, the across site average δ¹⁵N-NO₃⁻ increased dramatically from the 2 to 4 July, i.e., from 3.5‰ to 14.6‰, and then decreased back to 3.8‰ on the 6 July (Figure 2). The air mass back trajectories for each of these days shows that there was indeed a change in the source region from the 2 to 4 July (Figure 3). This highlights the sensitivity of the δ¹⁵N to changes in NO_x sources, as compared to the insensitivity of concentration changes with respect to changes in NO_x sources.

Although day-to-day variability is greater, there is still between site variability, particularly on the 26 June and 2 July. It is possible that the sites have different air mass histories on those days, but the coarse resolution of the meteorology input data (GDAS 1°) and back trajectory modeling limits our ability to run specific back trajectories for each site. Given how close the three

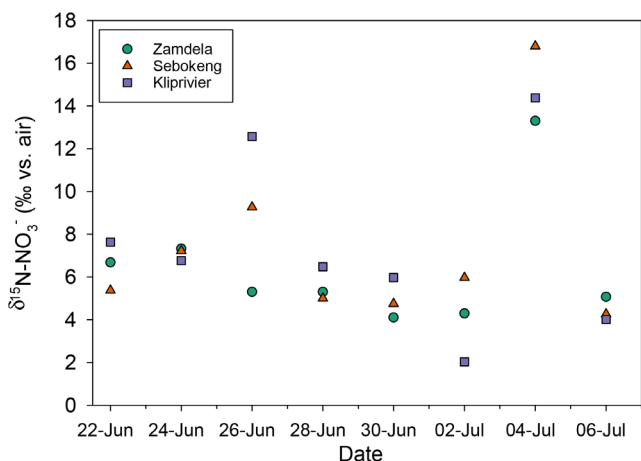


Figure 2: Coarse mode ($PM_{2.5-10}$) aerosol nitrate $\delta^{15}N$ collected over 24-hours from 22 June 2018 to 6 July 2018 at Zamdela (green circles), Sebokeng (orange triangles), and Kliprivier (purple squares).

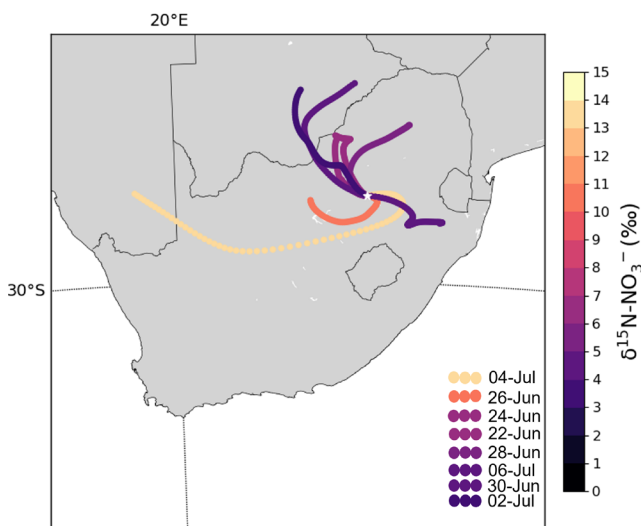


Figure 3: 72-hour air mass back trajectories clustered for each 24-hour aerosol sample and coloured by mass-weighted average $\delta^{15}N-NO_3$ (‰ vs. air). The legend indicates the sample date and corresponding mass-weighted average $\delta^{15}N-NO_3$ (in order of descending $\delta^{15}N$) to facilitate comparison with Figure 1.

sites are, very high-resolution meteorological data are needed to distinguish site-specific air mass back trajectories. Another possibility is that local emissions are influencing the sites on those days. Although they are all located in the Vaal Triangle and influenced by domestic fuel burning, the sites have different proximities to local industry. Zamdela is just south of the Sasol Chemical Industries Complex, Sebokeng is north of both metallurgical industries and mining activities, and Kliprivier is near steel and metal alloy industries (Figure 1). Therefore, the between-site variability could be due to differing regional sources that are not evident with low-resolution back trajectory modeling, or site-specific local sources.

Source apportionment using a Bayesian isotope mixing model

Bayesian isotope mixing models are a commonly used approach for mathematically determining the contribution from multiple

sources to a measured isotope value, in this case, the contribution of multiple NO_x sources to a measured aerosol nitrate sample. *simmr* is a stable isotope mixing model designed to solve mixing equations for stable isotope data within a Bayesian framework (Parnell et al. 2010, 2013). In this model, Markov chain Monte Carlo works by considering all possible solutions within the given space of uncertainty (i.e., 95% confidence interval). *simmr* requires a minimum of 3 input objects; the measured isotopic composition of the samples, the mean $\delta^{15}N$ of the possible sources, and the associated standard deviations of the source $\delta^{15}N$ (Figure 4).

simmr model inputs

The expected dominant NO_x sources in the Highveld include coal combustion, vehicles, biomass burning, and biogenic soil emissions (Collett et al. 2010). The utility of the nitrogen stable isotope composition is dependent on these NO_x sources having differing isotopic signatures. Below we present the most recent and community accepted $\delta^{15}N-NO_x$ values and discuss their relevance to the South African context.

The NO_x emitted from coal-burning power stations is formed from either the reaction of air N_2 with O_2 during combustion and/or the reaction of nitrogen in the coal with O_2 . The $\delta^{15}N$ of NO_x emitted from coal-fired power plants is therefore dependent on the $\delta^{15}N$ of the nitrogen in the coal, and on the technologies used to reduce NO_x emissions (or lack thereof) (Felix et al. 2012). The $\delta^{15}N$ of coal does not vary considerably, with reported values ranging from 1.0‰ to 4.0‰ for coal from a diversity of sources (Felix et al. 2012). Furthermore, a local study of South African coal- $\delta^{15}N$ found values of 1.0‰ to 1.2‰ (Heaton 1990). A study in the USA of multiple power stations burning the same coal with different technologies found that the dominant control on the NO_x $\delta^{15}N$ was the presence (or absence) of NO_x reduction technologies (Felix et al. 2012). Coal-fired power stations in South Africa are not currently operated with NO_x or sulfur-reducing technologies such as over fire air, selective catalytic (or noncatalytic) reduction, low NO_x burners, or flue gas desulfurization. As such, the closest analogue from measured power station $\delta^{15}N-NO_x$ includes power stations in the USA measured with the selective catalytic reduction turned off ($\delta^{15}N-NO_x = 10.5‰ \pm 2$) (Felix et al. 2012; Walters et al. 2015), and a study of power plants in China with a range of emissions reductions ($\delta^{15}N-NO_x = 14.5‰ \pm 4.4$) (Song et al. 2019). Interestingly, the $\delta^{15}N$ of NO_x emitted from four South African power stations was measured in the 1980's and was found to range from 6‰ to 13‰ (Heaton 1990). However, these values should be treated with caution given recent studies on methodological challenges associated with capturing NO_x in these environments and the rigorous procedures that are now considered standard for capturing NO_x for isotopic analyses (Walters et al. 2015; Walters et al. 2015; Felix et al. 2012; Fibiger et al. 2014). In order to capture the variability in measured values, the $\delta^{15}N-NO_x$ for coal-fired power stations was set at $13.7‰ \pm 4.6$ (Figure 4), in line with other recent studies on air pollution in Chinese cities (e.g., Chang et al. 2018, 2019).

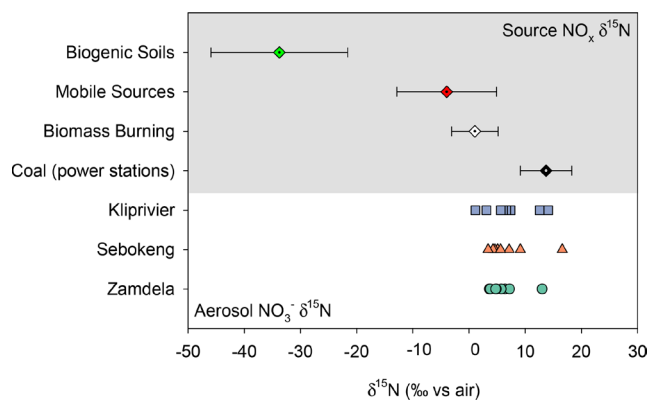


Figure 4: Inputs to the *simmr* package include average and standard deviations of source NO_x $\delta^{15}\text{N}$ (grey shaded area) and the measured coarse mode aerosol $\delta^{15}\text{N}$ for Zamdela (green circles), Sebokeng (orange triangles), and Kliprivier (purple squares). Literature references used for the source NO_x $\delta^{15}\text{N}$ ranges are in the text.

The $\delta^{15}\text{N}$ of vehicle emitted NO_x is well constrained with respect to the emissions from specific vehicles across driving conditions (Walters et al. 2015). The thermal production of NO_x in the combustion chamber of vehicles results from N_2 in air, which has a $\delta^{15}\text{N}$ of 0‰. In a study of 26 different petrol and diesel vehicles representing 12 manufacturers and varying in model year from 1995 to 2015, the $\delta^{15}\text{N}\text{-NO}_x$ ranged from -19.1‰ to 9.8‰. Diesel vehicles had distinctly lower $\delta^{15}\text{N}\text{-NO}_x$ values than petrol vehicles (-23.9‰ to -15.9‰ vs. -15.1‰ to 10.5‰, respectively) due to the different combustion conditions. The same South African study that measured power station NO_x in the 1980's also measured vehicle exhaust, and the $\delta^{15}\text{N}\text{-NO}_x$ ranged from -2‰ to -13‰ (Heaton 1990), which is comparable to the more modern values. The vast majority of NO_x emissions result in the first few minutes when a cold engine is started, and as a result, vehicle run time is highly correlated with the $\delta^{15}\text{N}\text{-NO}_x$ emitted.

Given these controls on the $\delta^{15}\text{N}\text{-NO}_x$ from vehicle emissions, vehicle run time is commonly used to predict the $\delta^{15}\text{N}$ of vehicle emissions for petrol and diesel vehicles (Walters et al. 2015). Walters et al. (2015) apply this numerical approach to estimate $\delta^{15}\text{N}\text{-NO}_x$ from vehicle emissions for the USA using commute times and assuming all vehicles are petrol (the diesel share is ~ 2% in the USA). Following their approach, we calculate an estimate of the range of $\delta^{15}\text{N}\text{-NO}_x$ values for the South African vehicle fleet using local commute times and the market share of petrol and diesel vehicles. South African commute times are significantly longer than the OECD country average according to a comprehensive analysis of four surveys across a 20 year period (Kerr 2015). The total calculated commute times reported were 68 to 94 minutes per day, with driving times reported to range from 29 to 42 minutes and minibus times from 38 to 53 minutes. Vehicle fleet data suggest diesel vehicles are ~ 17% of the South African fleet (Posada 2018). Using commute times of 23 to 59 minutes, we calculate that the $\delta^{15}\text{N}\text{-NO}_x$ for petrol vehicles ranges from -2.2‰ to -0.6‰ and for diesel vehicles ranges from -17.6‰ to -15.7‰. The mass-weighted average and standard deviation for South African vehicle emissions $\delta^{15}\text{N}\text{-NO}_x$, assuming diesel vehicles account for 17% of the total fleet, is calculated as

-3.96‰ ± 8.9 (Figure 4). This is remarkably similar to the globally recommended value for mobile emissions of -3.71‰ ± 10.4 (Chang et al. 2018). Here, we used the South African estimate, although it is important to note that what is presented here is overly simplistic. It is recommended that an in-depth analysis of commute times as a function of transport mode, vehicle type, age, and fuel usage be conducted to constrain this end member input for future isotope studies.

The $\delta^{15}\text{N}$ of the NO_x released during biomass burning is primarily driven by the $\delta^{15}\text{N}$ of the biomass being burned. A comprehensive assessment of multiple biomass types burned in controlled conditions resulted in an average $\delta^{15}\text{N}\text{-NO}_x$ of 1.04‰ ± 4.1 (Fibiger and Hastings 2016). The biomass species burned in Fibiger and Hastings (2016) were all North American, and there is evidence that climatic drivers influence plant and soil $\delta^{15}\text{N}$ with higher values observed in the mid-latitude southern hemisphere than in the mid-latitude northern hemisphere (Amundson et al. 2003). Indeed, a study of plant- $\delta^{15}\text{N}$ from a variety of species collected over three years from multiple habitats in Kruger National Park had values ranging from 2.3‰ to 6.7‰ (trees), 1.7‰ to 6.4‰ (grasses), and 2.3‰ to 8.4‰ (forb) (Codron et al. 2013). However, lower values were observed during the dry season than the wet season, e.g., dry season grasses had a $\delta^{15}\text{N}$ of 2.7‰ ± 2.0. There is significantly less rainfall in winter in the study region, which suggests the lower end of the isotopic range is most appropriate for this study. Until a more comprehensive assessment of the $\delta^{15}\text{N}$ of local biomass can be determined, the Fibiger and Hastings (2016) estimate for biomass burning $\delta^{15}\text{N}\text{-NO}_x$ (i.e., 1.04‰ ± 4.1; Figure 4) is used in this study as it overlaps the values measured in at least one region of South Africa.

The $\delta^{15}\text{N}$ of biogenic NO emissions from soils is not dependent on the soil $\delta^{15}\text{N}$ or the $\delta^{15}\text{N}$ of fertilizer (i.e., if the soils are fertilized), but rather the biological processes that lead to NO release (Li and Wang 2008). The NO that is released is an intermediate that forms from nitrification of ammonium to nitrate and denitrification from nitrate to nitrogen gas. Both processes result in a strong kinetic preference for ^{14}N such that the products (in this case NO) are heavily depleted in $\delta^{15}\text{N}$ (Ludwig et al. 2001). As a result, NO from soils is very isotopically depleted (-50‰ to -30‰) and is isotopically distinct from all other NO_x emission sources. As the biological processes would be the same in South African soils, we use the commonly accepted $\delta^{15}\text{N}\text{-NO}_x$ for biogenic soil emissions of -33.8‰ ± 12.2 (Li and Wang 2008) (Figure 4).

simmr model results

The *simmr* mixing model results were identical for the three sites when each dataset was input separately. Therefore, the results from the *simmr* model presented below are based on using the mass-weighted average for each sample day across the three sites. To summarize the above discussion, the source NO_x $\delta^{15}\text{N}$ values used were 13.7‰ ± 4.6 for coal-fired power stations, -3.96‰ ± 8.88 for mobile sources (i.e., vehicles), 1.04‰ ± 4.13 for biomass burning, and -33.77‰ ± 12.16 for biogenic soil emissions (Figure 4).

According to the *simmr* model output, coal combustion NO_x is the dominant source and accounts for 66% ($\pm 8.1\%$) of the aerosol nitrate. This is in addition to the large direct contribution coal combustion makes to the fine (>60%) and coarse (up to 20%) PM fraction (Muyemeki et al. 2021). NO_x from biomass burning contributes 15.6% ($\pm 10.3\%$) to aerosol nitrate. This is consistent with the seasonal patterns in biomass burning in South Africa with an expected peak in late winter and early spring (Hersey et al. 2015). The third largest NO_x source to aerosol nitrate was vehicles, which contributed 12.0% (± 7.5). Vehicles were also a large contributor to coarse PM concentrations (14%) (Muyemeki et al. 2021). The smallest NO_x source was soils, which contributed 6.4% ($\pm 3.1\%$). Given that it was winter, it is expected that soil biological activity should be at a minimum.

The Monte Carlo analysis incorporates the uncertainty in the NO_x source signature $\delta^{15}\text{N}$. These estimates could be refined by directly measuring the source $\delta^{15}\text{N}\text{-NO}_x$ in South Africa. In particular, the emissions from coal fired power plants need to be measured directly due to the unique technology used in South African power stations as well as the lack of pollution control technologies. In addition, a more nuanced understanding of vehicle fleet composition and commute times would allow for a narrower estimate of vehicle emission $\delta^{15}\text{N}\text{-NO}_x$, and perhaps even site-specific source estimates. The results of this study suggest that future work on site-specific fleet modeling would be useful for understanding the impact of vehicle emissions on NO_x and aerosol nitrate.

Conclusions

Coarse mode ($\text{PM}_{2.5-10}$) aerosol samples were collected at three sites during winter in the VTAPA and the nitrogen isotope composition of the aerosol nitrate was determined. The range and variability in the $\delta^{15}\text{N}\text{-NO}_3^-$ was similar across all three sites. The sample days with elevated $\delta^{15}\text{N}\text{-NO}_3^-$ have different air mass back trajectories compared to the rest of the sample set, suggesting that those regions have a different combination of NO_x sources. A Bayesian isotope mixing model was used along with source NO_x $\delta^{15}\text{N}$ data from the literature to determine the NO_x source contributions to the observed aerosol $\delta^{15}\text{N}\text{-NO}_3^-$. Over two-thirds of the aerosol nitrate was formed from power station coal-burning NO_x emissions, while biomass burning and vehicle NO_x emissions contributed the remainder. Soil emissions made a minor contribution. This study highlights the utility of the nitrogen stable isotopes in constraining the relative importance of different NO_x sources to secondary PM, and in determining the NO_x sources that impact the nitrate component of PM at a given site. Ultimately this information can be used to design NO_x reduction strategies in a way that maximizes the impact on the PM burden.

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