Identifying NO\textsubscript{x} Sources in Arequipa, Peru Using Nitrogen Isotopes in Particulate Nitrate

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We reported on the first time series of $\delta^{15}$N in aerosol nitrate from South America. Particulate matter less than 2.5 microns in diameter (PM\textsubscript{2.5}) was collected at four sites located in Arequipa, a major city in southern Peru. The $\delta^{15}$N values for nitrate in PM\textsubscript{2.5} ranged from -1.7 to 15.9‰ and averaged 5.3 ± 3.0‰, with no significant difference between the four study sites and no discernable seasonal trend. These values are significantly higher than those in aerosol nitrate from southern hemisphere marine environments and those from the northern hemisphere. We explain the elevated values using an isotope mass balance mixing model that estimates a source NO\textsubscript{x} $\delta^{15}$N of -8 ± 3‰, derived mainly from anthropogenic sources (vehicles, industry). An isotope enabled 0-D photochemical box model was used to estimate the isotope enrichment of nitrate relative to NO\textsubscript{x} due to kinetic, equilibrium, and photolysis isotope effects occurring during NO\textsubscript{x} oxidation. This “source plus photochemistry” approach resulted in general agreement with the observations. This suggests that if the photochemistry effect can be accounted for, nitrate $\delta^{15}$N can be used to assess the relative importance of NO\textsubscript{x} sources and could be a new tool to validate NO\textsubscript{x} emission inventories.

Keywords: isotope N 15, aerosol, Peru, NO\textsubscript{x}—oxides of nitrogen, air quality (AirQ)

INTRODUCTION

Air quality is important because it impacts human quality of life and health, yet relative to northern hemisphere countries, there are relatively few studies that have investigated air quality in developing countries in South America, particularly Peru (Pearce et al., 2009; De La Cruz et al., 2019; Alvarez-Tolentino & Suarez-Salas, 2020; Romero, et al., 2020). According to the World Health Organization (WHO) air pollution is a leading cause of global mortality, accounting for an estimated seven million premature deaths (Lelieveld et al., 2015). Roughly 3.7 million of these deaths are partially attributed to outdoor air pollution within cities and these disproportionately impact disadvantaged populations (Hajat et al., 2015). Aerosols and some trace gases, such as nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}), SO\textsubscript{2}, and O\textsubscript{3} are the main vectors for the adverse effects of poor air quality. Of the few studies that have been published on Peruvian air quality, most have focused on Lima, Peru’s capital city (Silva et al., 2017; Romero, et al., 2020; Romero, et al., 2020). Like many large cities in developing countries, Lima suffers from poor air quality that is associated with vehicle traffic, industry, and commerce (Romero, et al., 2020; Romero, et al., 2020). There are only a couple of published air quality studies in Peru outside of Lima (Pearce et al., 2009; De La Cruz et al., 2019; Alvarez-Tolentino & Suarez-Salas, 2020) and only recently has one been published on air quality in Arequipa, Peru’s second largest city.
Despite their importance, ground based air quality studies of aerosols, trace gases, and other air pollutants in Arequipa are noticeably absent.

One of the main compounds found in aerosols produced in large cities such as Arequipa is atmospheric nitrate (NO$_{15s}$), a secondary pollutant that plays a key role in atmospheric chemistry. NO$_{15s}$ is the sum of nitrate ions dissolved in rain, fog, or clouds (NO$_{2g}$, in gas phase nitric acid produced photochemically (HNO$_3$), and particulate nitrate (pNO$_3$) produced by N$_2$O$_5$ heterogeneous reactions or by uptake of HNO$_3$ on existing aerosols surfaces (Monks, 2005; Monks et al., 2009). NO$_{15s}$ is the reaction product of NO$_3$, which is mainly emitted by combustion, that is then oxidized via O$_3$ and organic radical chemistry (Seinfeld & Pandis, 1998; Pye et al., 2010) into higher nitrogen oxides (NO$_x$ = NOx + NO$_{15s}$ + all other N oxides). NO$_3$ and NO$_{15s}$ are key components of atmospheric chemistry (Monks et al., 2009), controlling the oxidation state of the troposphere (Prinn, 2003), influencing particulate matter (PM) formation (Feng & Penner, 2007), altering the pH of rainwater (Lynch et al., 2000), and facilitating the movement of nitrogen through the N cycle (Galloway et al., 2003). NO$_3$ also produces ozone (O$_3$) either directly through NO$_2$ photolysis, or indirectly as a catalyst when volatile organic compounds (VOCs) are present (Monks, 2005). O$_3$ photolysis, in turn, generates OH radicals that initiates a radical chain reaction involving HO$_2$ and organic peroxy radicals that results in the oxidation of chemically reduced compounds and the formation of secondary PM (Seinfeld & Pandis, 1998; Finlayson-Pitts & Pitts, 2000) including nitrate and sulfate aerosols (Pusede et al., 2016; Cao et al., 2017; Pan et al., 2018). Thus, understanding NO$_3$ sources and the photochemistry that converts it into NO$_{15s}$ is critical for understanding the origin poor air quality.

Despite this importance, there are numerous knowledge gaps in understanding the cycling of NO$_3$ in the atmosphere, particularly in South America. The NO$_3$ emission budget is still poorly constrained. Most emission inventories rely on fixed emission factors for some sources that may, in fact, be spatially or temporally variable. For example, power plant NO$_x$ emissions are based on assumed efficiency of catalytic converters that may not be accurate in all operating conditions (Srivastava et al., 2005; Felix et al., 2012). Soil NO emissions are highly dependent on soil moisture, redox conditions, fertilizer application rates, type, and timing making them challenging to constrain (Galloway et al., 2004; Pilegaard, 2013). There are also several unresolved issues regarding the chemistry that transforms NO$_3$ into NO$_{15s}$. These include uncertainties in heterogeneous uptake coefficients of N$_2$O$_5$ (Brown et al., 2001; Brown et al., 2006; Chang et al., 2011), the formation of organic nitrates in urban forests (Kastler & Ballschmitter, 1998; Romer et al., 2016), the relative importance and mechanism of HONO formation versus HONO emissions, and reactions of NO$_3$ in the aqueous phase and mixed aerosols (Zhang et al., 2019; Guo et al., 2020; Peng et al., 2020). Further, chemical transport models (CTMs) do not accurately predict aerosol nitrate concentrations or other NO$_x$ mixing ratios (Spak & Holloway, 2009; Y.; Zhang et al., 2009) making predicting NO$_{15s}$ formation a significant challenge.

Therefore, it is important that these uncertainties in NO$_3$ cycling be resolved if we aim to have accurate air quality forecasts used to try an develop quality mitigation strategies aimed at improving poor air.

It has been suggested that stable N isotopes can provide clues to the origin of NO$_3$ (Elliott et al., 2009; Felix & Elliott, 2014; Walters, Tharp, et al., 2015) and the oxidation pathways that transform into nitrate (Walters & Michalski, 2015, 2016). $\delta^{15}$N is defined by the relative difference between the $^{15}$N/$^{14}$N ratio in a N compound and the ratio in air N$_2$ (the arbitrary reference compound) and is typically reported in delta notation (in permil, %):

$$\delta^{15}\text{N (‰)} = \left( \frac{^{15}\text{N} / ^{14}\text{N}}{^{15}\text{N}_\text{air} / ^{14}\text{N}_\text{air}} \right) \times 1000 \ (1)$$

Isotopic measurements of NO$_{15s}$ show a wide range of $\delta^{15}$N values, which has been suggested to indicate variability in NO$_3$ emission sources, chemical processing, and/or a combination of these effects. A number of studies have measured the $\delta^{15}$N values of NO$_3$ collected from NO$_x$ sources such as power plants (Felix et al., 2012), automobiles (Walters, Goodwin, et al., 2015), biomass burning (Fibiger & Hastings, 2016), and non-road sources (Felix & Elliott, 2014). Many studies have measured the $\delta^{15}$N values of NO$_{15s}$ collected from the troposphere. Most of the NO$_{15s}$ $\delta^{15}$N data is for nitrate that has been collected on filters (PM$_{2.5}$, PM$_{10}$, TSP (total suspended particles)) (Moore, 1977; Savard et al., 2017), as the dissolved NO$_3^-$ anion in rain (Heaton, 1987; Hastings et al., 2003; Elliott et al., 2007; Felix et al., 2015), or as gas phase HNO$_3$ (Elliott et al., 2009; Savard et al., 2017). The range of NO$_{15s}$ $\delta^{15}$N values span from -50 to +15‰ but the average is ~0‰ (Song et al., 2021).

Two hypotheses have been offered to explain these variations: source and photochemistry. The source hypothesis (Elliot et al., 2007; Hastings et al., 2013) suggests that the NO$_{15s}$ $\delta^{15}$N range reflects the spatial and temporal mixing of NO$_3$ sources with different $\delta^{15}$N values that is then converted into NO$_{15s}$. The photochemistry hypothesis (Freyer, 1978; Freyer et al., 1993; Walters et al., 2018) suggests that the observed NO$_{15s}$ $\delta^{15}$N variations arise via isotope effects occurring when photochemical cycling partitions N into the myriad of NO$_x$ compounds. Recent modeling work (Fang et al., 2021), has shown that only a handful of reactions in the NO$_3$ cycle impact the $\delta^{15}$N of nitrate. These include NO$_2$ photolysis (photo induced isotope effect; Miller and Yung, 2000), the kinetic isotope effect occurring during the NO + O$_3$ reaction (Walters and Michalski, 2016), equilibrium isotope effect during the NO$_2$ + OH (Fang et al., 2021) and NO$_2$ + NO$_3$ $\leftrightarrow$ N$_2$O$_5$ (Walters and Michalski, 2015) reactions, and isotope exchange reaction $^{15}$NO + NO$_2$ $\leftrightarrow$ NO + $^{17}$NO$_2$ (Walters and Michalski, 2015; Walters, Simonini, and Michalski (2016). A full description of the relative importance of these effects can be found in Fang et al. (2021). These two hypotheses are not mutually exclusive. Indeed, it is likely to be a combination of both source and chemistry, but their relative importance likely shifts depending on environmental conditions such as a region’s NO$_x$ source diversity, plume versus dispersed chemistry, photolysis intensity, and oxidant load. In turn, the $\delta^{15}$N data might be a new key to reconciling some of the current
Arequipa is at the northern edge of the hyper-arid Atacama Desert, sometimes called the Sechura Desert in Peru, and the landscape is characterized by wide sandy plains and dunes and sparse vegetation except in a few river valleys (quebradas) and the Andean highlands. Arequipa’s climate is dry throughout the year with annual precipitation averaging ~100 mm that almost exclusively occurs during a rainy season extending from January to March. The weather is mild with daily temperature averages of 15 ± 1.6°C and relative humidity averages of 42 ± 21.5% during the 2019 study year (Weatheronline.co.uk. accessed 2019). The region contributes about 5.6% of the nation’s GDP, with mining (23.9%), manufacturing (18.2%), services (17%), commerce (14.6%) and agriculture (12.6%) as the main economic activities (DIGESA, 2005). Agriculture is largely limited to a few river valleys that drain from the Andes, including one that passes through the city, and several large-scale desert irrigation projects (Figure 1).

**Arequipa PM Collection Sites and Methodology**

Sample collection was performed at four sites throughout Arequipa that were located in urban, industrial, suburban, and agricultural sections of the city (Figure 1). The urban site Avenida Independencia (AI), is located near the city center where vehicle congestion is very heavy during the week. The industrial site Rio Seco (RS) is located near borate-processed manufacture plants, tanneries, brick kilns, and chicken processing plants. This district is also located near the main highway by which trucks and buses exit the city and many of the roads in this district are unpaved. Tingo Grande (TG), is a suburban development located in the western edge of the city (2,600 masl) and 6 km due north of a large open pit copper mining operation. Yarabamba (YB), is a small town located 15 km outside of the city center surrounded by rural farmland.

PM$_{2.5}$ samples were collected using a high-volume air sampler (ECOTECH ECO-HVS3000). Sample collection took place periodically throughout the year 2018 by moving the sampler from one sampling site to another. After each relocation, 24 h PM$_{2.5}$ aerosol samples were collected for three consecutive days before the sampler was moved to the next location. There were sampling gaps during the months of April, June, and July due to limited resources such as power outages and labor shortages. The flow rate was ~1 m$^3$/min and total volume as determined as a function of flow rate and time and corrected to standard temperature (273K) and pressure (101.3 kPa). The filter media was either pre-combusted quartz fiber filters (8 in × 10 in, Whatman, United States) or Teflon filters. Since filter sampling often collects both pNO$_3$ and HNO$_3$(g) we refer to the samples as NO$_3$$_{a}$m. Filters were equilibrated to room temperature and relative humidity and the PM mass was determined gravimetrically. The filters were then sectioned into 10 equal width strips used for various chemical, isotopic, and optical analysis. One of the filter sections was soaked in 15 ml of Milli-Q water for 20 min to extract water soluble anions and then filtered (0.45 um Fisher Scientific, USA) and analyzed for anions, cations and nitrate isotopes.

**METHODS**

**Study Area**

The city of Arequipa (Figure 1) is the second most populated city in Peru with a population of ~1 million people located 2,350 m above sea level at 71°32′05″ W, 16°23′56″ S. Arequipa is an isolated city with the closest major urban centers being Tacna, Peru (Pop. ~280,000) and Arica, Chile (Pop. ~230,000) roughly 250 km to the SE, La Paz, Bolivia (~770,000) 380 km to the east, and Lima located ~800 km to the NW. Therefore, Arequipa’s air quality is not significantly impacted by regional anthropogenic N pollution from urban centers outside of the city. It sits at the base on the Andean forearc and at the foot of the active volcano Misti and extinct volcanos Chachani and Pichu. Arequipa is at the northern edge of the hyper-arid Atacama Desert, sometimes called the Sechura Desert in Peru, and the landscape is characterized by wide sandy plains and dunes and sparse vegetation except in a few
Geochemical and Isotopic Analysis of Arequipa PM Collection

Nitrate concentrations and nitrogen isotopes were measured using standard techniques. Anion and cation concentrations were determined via standard methods using suppressed ion chromatography (Metrohm 940 Vario Professional). Anion eluent was a carbonate buffer (3.2 mM Na₂CO₃ and 1.0 mM NaHCO₃) and cation eluent was an oxalic acid solution (3.5 mM). The detection limit was 0.01 ppm and the accuracy and precision of the analysis was less than 0.3% and 0.3 ppm, respectively, based on replicate analysis of standard solutions. Nitrogen isotopes of nitrate were measured by converting NO₃⁻ into N₂O using TiCl₃ reduction in 12-ml vials (Altabet et al., 2019). The N₂O was extracted from the vials using a custom-made headspace cryogenic concentrator unit, purified using gas chromatography fitted with a PoraplotQ column. The gas stream is introduced into a Thermo DeltaV isotope ratio mass spectrometer through a custom-made helium flow open split and isotope ratios are determined by measured at Faraday cups tuned to detect ions with masses of 44, 45, and 46 amu. Based on standard replicates and bracketed calibrations curves the accuracy was 0.4% and a precision of 0.4‰. Three internal nitrate standards were used that were previously calibrated relative to international standards USGS 32, 34, and 35 (Michalski et al., 2002; Bohlke et al., 2003). Nitrate δ¹⁵N values are reported with respect to air N₂ and are reported in parts per thousand (‰) with a standard error that was 0.3‰ for δ¹⁵N.

Arequipa Meteorology, Trace Gas Data, Chemistry Modeling, and Stable Isotope Approaches

Additional atmospheric data was obtained from the few available datasets in the Arequipa region. Meteorological data (temperature, relative humidity) for the sampling period was acquired from Arequipa’s Rodríguez Ballón International Airport (purchased through Weather Online Data Center, https://www.woeurope.eu/). Additional wind and air humidity data were obtained from the United States National Oceanic and Atmospheric Administration’s (NOAA) Global Data Assimilation System 0.5-degree model. There was very little ancillary trace gas data available for the study period, which highlights the limited air quality research in the region. The local Arequipa Health Ministry monitored PM, CO, SO₂, NOₓ, and O₃ during 2010–2011 (Arequipa, G.R. 2020) but these measurements were discontinued thereafter. During the study period there were 8 months of SO₂ monitoring and a few months of PM measurements.

We used iNRACM (Fang et al., 2021), an isotope enabled version of the Regional Atmospheric Chemical Model (RACM), a 0-D photochemical box model (Stockwell et al., 1997) to simulate atmospheric nitrate production. Briefly, the iNRACM traces 17 stable inorganic compounds, four inorganic intermediates, 32 stable organic compounds, including four biogenic organics, and 24 organic intermediates as they are transformed by 237 chemical reactions, including 23 photolysis reactions (Atkinson, 1990; Atkinson et al., 1992). The iNRACM added ¹⁵N isotopologues for the two primary (NO, NO₂) and the 11 secondary N pollutants found in the original RACM mechanism and rate constants that accounted for relevant isotope effects. iNRACM was also modified to account for heterogenous N₂O₅ reactions on aerosols that are known to be important for atmospheric nitrate formation. This was done by reducing N₂O₅ heterogeneous hydrolysis to a first order reaction with a rate constant that is a function of N₂O₅ molecular speed, the N₂O₅ uptake coefficient and the aerosol surface area density (Riemer et al., 2003).

iNRACM initial conditions and emissions were based on the limited available data. Temperature, relative humidity (RH), pressure data, and [SO₂] were taken from observations during the study year. Initial CO, O₃, and NOₓ were taken from the monthly averages of the 2010–2011 Arequipa Health Ministry data set, under the assumption that the average of these trace gases did not significantly change between 2011 and 2018. This seems justified since the population changed by less than 10% during this time frame. VOC initial concentrations were based on average urban values taken from Stockwell et al. (1997). NOₓ and VOC emissions rates were based the equipartition of annual VOC and NOₓ emissions from the 2005 DIGESA emission inventory (DIGESA, 2005), the only inventory compiled in the region, and scaled up by 20% based on the population increase between 2005 and 2018. An aerosol mass–surface area ratio of 1.40 μg/cm² (Guelle et al., 2001) and the observed PM₁₀ mass (Valdivia et al., 2020) was used to determine the aerosol surface area density used in calculating the N₂O₅ uptake coefficient.
RESULTS AND DISCUSSION

Results for PM Nitrate Concentrations and \( \delta^{15}\text{N} \) Values

Aerosol nitrate \( \delta^{15}\text{N} \) values varied throughout the year and were positive except for two of the samples. The aerosol nitrate \( \delta^{15}\text{N} \) values ranged from a minimum of -1.8‰ to a maximum of 16‰ (outlier) and averaged 5.3 ± 3.0‰. There is no obvious seasonal or location dependence of the aerosol nitrate \( \delta^{15}\text{N} \) values, but the lower values tended to cluster in the southern hemisphere summer months (Jan.—March) when sparse rains occur (Figure 2). The \( \delta^{15}\text{N} \) values for the 3 days at any given sampling site tended to be ± 2–3‰. Nitrate and other water-soluble ions varied over the course of the year and between sites. PM nitrate concentrations ranged from a minimum of 0.17 mg/m\(^3\) to a maximum of 2.87 mg/m\(^3\) and averaged 0.90 mg/m\(^3\) and accounted for 9–12% of the ion mass. The most abundant anion was SO\(_4^{2-}\) (average = 3.1 ± 1.3 mg/m\(^3\)) accounting for ~35% of the total ion mass and CI\(^-\) was less than NO\(_3^-\) and made up less than 8% of total ion mass. Na\(^+\) and Ca\(^{2+}\) were the main cations (SI Supplementary Figures S1, S2), averaging 0.96 ± 0.38 mg/m\(^3\) and 0.87 ± 0.62 mg/m\(^3\) followed by NH\(_4^+\) (0.57 ± 0.28 mg/m\(^3\)).

Comparison of Arequipa PM Nitrate \( \delta^{15}\text{N} \) Values With Other Studies

There are only a handful of studies investigating the \( \delta^{15}\text{N} \) of NO\(_3^-\) atm collected from the midlatitudes in the southern hemisphere that we can draw on to compare with our data (Song et al., 2021). Most southern hemisphere NO\(_3^-\) atm isotope data have been focused on polar samples from Antarctica (Jarvis et al., 2009; Berhanu et al., 2015; Savarino et al., 2016; Walters et al., 2019) that has unique NO\(_3^-\) atm isotope dynamics due to volatilization and photolysis of HNO\(_3)/NO_x\) occurring in the snowpack (Jarvis et al., 2009; Berhanu et al., 2015) that makes for a poor comparison for our data. Thus, we focus our comparison on the non-polar, southern hemisphere data. NO\(_3^-\) atm isotopes were determined on aerosols collected along S-N transect across the Atlantic Ocean between Cape Town, South Africa, and northern France during April/May (Morin et al., 2009). Open ocean NO\(_3^-\) atm between 30°S and 10°N had \( \delta^{15}\text{N} \) values were mostly negative (with respect to air N\(_2\)), ranging from -7.1 to -1.6‰, averaging -4 ± 2‰ and only became positive when influenced by urban/industrial plumes (Morin et al., 2009). In contrast, the Arequipa NO\(_3^-\) atm \( \delta^{15}\text{N} \) were almost all positive during the year and in April/May they ranged narrowly between +2 and +10‰ (exceeding the +16‰ outlier). Measurements of \( \delta^{15}\text{N} \) values of NO\(_3^-\) collected at a coastal site in New Zealand (Li et al., 2021) were similar to the mid-Atlantic, ranging from -12‰ to +6‰. But most values were negative averaging at -4‰, and the lowest was April \( \delta^{15}\text{N} \) was around -8‰, significantly lower than those in Arequipa. In addition, in New Zealand, there was a significant seasonal variation, with higher \( \delta^{15}\text{N} \) values in the winter (range: -5‰ to +6‰; mean: 0‰) relative to summer (-12‰ to -4‰; -8‰). In contrast, the Arequipa the seasonal effect is less obvious relative to New Zealand, with the summer months (Jan.-March) encompassing all of the lowest \( \delta^{15}\text{N} \) values. The \( \delta^{15}\text{N} \) of NO\(_3^-\) atm collected in dry deposition along a E-W transect in northern Chile were similar to our Arequipa results (Wang et al., 2014). Long-term (2 years) collection of NO\(_3^-\) atm in the Atacama Desert, 800 km south of Arequipa, had \( \delta^{15}\text{N} \) values ranging from +1.5 to +10.6‰, that generally decreased from \( \delta^{15}\text{N} \) highs along the coast (~+8.5‰) and Andes (+10.5‰) to central valley values of +4.0 ± 2‰ (Wang et al., 2014). This average is similar to the annual mean in Arequipa of +5.3‰, suggesting similar NO\(_x\) sources and/or photochemical oxidation pathways in both these regions. Along the inland portion of the Chile transect, the +4.0 ± 2‰ \( \delta^{15}\text{N} \) value was attributed to mobile NO\(_x\) sources associated with the city of Calama, regional mining vehicles, and the Chilean central highway. Any seasonal variation associated with the transect deposition was masked by the 2-years collection period. These comparisons suggest that southern hemisphere ocean/coastal NO\(_3^-\) atm is either derived from unique NO\(_x\) sources relative to southern hemisphere urban environments, like Arequipa, or that possibly the oxidation pathways converting NO\(_x\) into NO\(_3^-\) atm is different in cleaner environments relative to urban systems.

Northern hemisphere NO\(_3^-\) atm \( \delta^{15}\text{N} \) values tend to be lower than those in Arequipa. Average Northern Hemisphere NO\(_3^-\) atm \( \delta^{15}\text{N} \) cluster around 0 ± 3‰ (SI Supplementary Figure S3) with urban values tending to slightly elevated relative to suburban values. East Asia values tend to be higher that North America and Europe, probably due to fewer NO\(_x\) reduction systems on coal burning power plants that are prevalent in East Asia. Arequipa’s NO\(_3^-\) atm \( \delta^{15}\text{N} \) values appear to be generally higher than those in the northern hemisphere where NO\(_x\) emissions are significantly higher than in the southern hemisphere.

Arequipa NO\(_x\) Source Apportionment Using \( \delta^{15}\text{N} \) Mass Balance

In order to try and explain the \( \delta^{15}\text{N} \) values of Arequipa NO\(_3^-\) atm and its variation, we first test the NO\(_x\) “source hypothesis” by comparing to the measured NO\(_3^-\) atm \( \delta^{15}\text{N} \) values to NO\(_x\) sources using an isotope mixing model. The source hypothesis claims that NO\(_x\) is converted into NO\(_3^-\) atm relatively quickly and completely, resulting in \( \delta^{15}\text{N} \) values of the product NO\(_3^-\) atm identical to the source NO\(_x\). According to a 2004 regional NO\(_x\) inventory (DIGESA, 2005), the two main anthropogenic sources of NO\(_x\) in Arequipa are vehicles that account for 8,114 tonne NO\(_x\) yr\(^{-1}\) and industry, contributing 1,072 tonne NO\(_x\) yr\(^{-1}\) and roughly 80% of this is from coal combustion used during cement production. Arequipa vehicle NO\(_x\) is generated primarily (DIGESA, 2005) by old trucks and buses without catalytic converters (70%) and newer automobiles with NO\(_x\) reduction controls (30%). The \( \delta^{15}\text{N} \) values of vehicle NO\(_x\) is mainly determined by whether the vehicle has NO\(_x\) reduction technology such as 3-way catalytic converters. Gas and diesel combustion is derived from natural gas that is typically enriched in 15N, and thus has a positive \( \delta^{15}\text{N} \) value. Industries typically burn coal that is depleted in 15N, leading to negative \( \delta^{15}\text{N} \) values, and fossil fuels like gas and diesel are a major source of NO\(_x\) emissions over the region.
engines without NOx reduction technology generate isotopically light NOx of around -15‰, due to the KIE of 14N reacting faster than 15N as N2 fragments in the engine cylinder during combustion (Walters et al., 2015). In contrast, newer vehicles with NOx reduction catalytic converters tend to produce NOx of around -2‰ (Walters et al., 2015; Miller et al., 2017) because for the same mechanistic reason, the KIE of 14N reacting faster than 15N as NOx is reduced by the catalytic converter (for details see Walters et al., 2015). We used a simple two component isotope mixing model to predict the δ15N from vehicles (δ15Nveh).

$$\delta^{15}N_{\text{veh}} = f_{\text{cat}} \delta^{15}N_{\text{cat}} + f_{\text{nc}} \delta^{15}N_{\text{nc}}$$

(2)

$$f_{\text{nc}} + f_{\text{cat}} = 1$$

(3)

Where $f_{\text{cat}}$ and $f_{\text{nc}}$ are the molar fractions of NOx from vehicles with catalytic converters and without, respectively, and $\delta^{15}N_{\text{cat}}$ and $\delta^{15}N_{\text{nc}}$ are the δ15N values of NOx emitted by those same vehicles. This yields a vehicle NOx δ15N of approximately -11‰. Industrial NOx is primarily from coal burning during cement production and brick kiln operations that lack emission control technology. Previous research has shown that without emission controls, coal burning generates NOx with a δ15N of ~ +14 to +18‰ (Felix et al., 2012), similar to the highest δ15N value in Arequipa NOx ∼ +12‰. Using another two-component mixing model and assuming industry ($f_{\text{ind}} = 0.12$, $\delta^{15}N = +16$) and vehicles ($f_{\text{veh}} = 0.88$) are the dominant anthropogenic NOx sources, isotope mass balance gives an expected anthropogenic NOx in Arequipa a δ15N of -8‰ (Figure 3). This is significantly lower than the Arequipa average (+5.3‰) or even the lowest value (~1.8‰) and would suggest that either industrial (coal burning) NOx is significantly underestimated, there is an uncounted for NOx source with high a15N/14N ratio, or that chemistry has altered the δ15N during the conversion of NOx into NOx via kinetic, equilibrium, or photolysis isotope effects (Fang et al., 2021).

It is unlikely that the discrepancy between the measured Arequipa NOx ∼ δ15N and that expected from NOx accounting can be resolved by assuming higher industrial emissions. Industrial emissions would need to be more than half of total NOx emissions to achieve isotope mass balance. Yet coal burning, the main industrial NOx source in the region, accounts for roughly 10% of total NOx (DIGESA, 2005) and this is from a single massive modern cement production plant (Yura S.A.) with quantified production rates and emission factors. Thus, industrial NOx emission uncertainty is low (DIGESA, 2005) and certainly not a factor of five higher than current estimates.

There is also no known natural NOx source with high δ15N/14N ratio that could explain the elevated δ15N values of NOx ∼ +16‰ in Arequipa. Natural NOx is almost exclusively from either emission by soils during microbial nitrification and denitrification, produced by lightning, or biomass burning (natural or anthropogenic). None of these has significantly positive δ15N values to lead to elevated δ15N in PM nitrate. In fact soil NOx has the lowest δ15N (-25‰ to -40‰) of all known NOx sources (Li & Wang, 2008; Yu & Elliott, 2021). Further, soils are a considered minor source of NOx southern Peru because of the desert environment, minimal natural vegetation, and low amounts of rainfall. Indeed, a recent high resolution (0.25°lat. × 0.3125°long.) global NOx inventory (Weng et al., 2020) shows that in the Arequipa region less than 72 × 103 TgN yr −1 is attributed to soil emissions, less than 10% of the city anthropogenic emissions. Likewise, lightning has low δ15N values (-0‰) and is also considered a small source of NOx in the area. Recent satellite analysis of lightning by Bond et al. (2002) found that while lightning accounted for roughly 23% of NOx in the tropics, it accounted for less that 1% over Peru west of the Andes including the Arequipa region. Thus, neither lightning nor soil NOx emissions can explain the positive δ15N value of NOx ∼ +5‰ observed in Arequipa.

Biomass burning derived NOx, either local or transported into the Arequipa region, is potential source, but both its δ15N values and other evidence suggest it cannot explain the observed elevated PM δ15N values. Biomass burning emissions are due to agricultural practices, forest clearing, and natural fires and the δ15N of NOx derived from biomass burning is nearly identical to the δ15N of the foliage being burned (Fibiger & Hastings, 2016). There is some local biomass burning in the Arequipa region used as means of removing crop residues and for pest management (field observations). The δ15N of crops are largely reflect a combination of the δ15N of the soil in which they grow (Hogberg, 1997) and the δ15N of applied fertilizer. Agriculture soil in the Arequipa district have δ15N of -2‰ (Filley, personal communication) and inorganic fertilizers are -0 ± 2‰ (Bateman & Kelly, 2007; Michalski, Kolanowski, & Riha, 2015). This suggests that local biomass burning NOx δ15N values would be just slightly positive and cannot significantly elevate the local NOx δ15N. Likewise, large biomass burning events that are seasonal occurrences in the Amazon Basin east of the Andes burn biomass with average δ15N of only +5‰ (Ometto et al., 2006). Some of these aerosols are known to be transported over the Andes by advected air masses (Bourgeois et al., 2015) yet the vast majority are removed by deposition and cloud chemistry as they pass...
through the planetary boundary layer (PBL) into the free troposphere as they surmount the Andes. After reaching the western side of the Andes they are diluted as they mix across the Pacific over a lifetime of 7-8 days and are quite slow to mix back into the PBL (Bourgeois et al., 2015). Amazon biomass burning occurs predominately in the dry season from June to November (Reddington et al., 2019), but our $\delta^{15}N$ of PM NO$_3^-$ in April-May is not significantly different relative to the biomass burning months of August-November. In addition, biomass burning aerosols are predominately organic carbon and the sum of Cl$^-$, NO$_3^-$, and NH$_4^+$ make up less than 5% of the aerosol mass (Reddington et al., 2019).

Back trajectory analysis and ion data also suggest biomass burning (local or distant) in a minor NO$_x$ source in Arequipa. 48-h HYSPLIT back trajectory ensemble runs show that the origin of most air masses reaching Arequipa are from the ocean (43%) and the northern desert (34%), and only 18% of air masses are derived from the Andean highlands or Amazon (Supplementary Figure S4). The $\delta^{15}N$ of NO$_3$ in PM derived from the eastern air masses (8‰) is not different from the average. Potassium cations (K$^+$) are a geochemical tracer of biomass burning (Andreae, 1983). PM$_{2.5}$ K$^+$ concentrations in Arequipa were 0.42 ± 0.19 mg/m$^3$ and were not significantly higher in the biomass burning season (Supplementary Figure S2). Further K$^+$ is best correlated with Na$^+$ ($R^2 = 0.45$) suggesting dust derived from local desert surface is the main K$^+$ source (Olson et al., 2021; Li et al., 2021). We conclude that based on the small positive $\delta^{15}N$ value of biomass NO$_x$, the limited transport from biomass burning regions, and the lack of significant potassium variations that biomass burn can be considered a negligible NO$_x$ source and cannot account for the elevated $\delta^{15}N$ values of NO$_3$ observed throughout the year in Arequipa. Thus, the $\delta^{15}N$ of Arequipa NO$_3$ is difficult to reconcile from the perspective of NO$_x$ sources controlling the $\delta^{15}N$ values.

A two NO$_3$ source mixture to explain elevated values (or the annual $\delta^{15}N$ variation) is also not supported by an isotope Keeling plot. In a two source system, regressing $\delta^{15}N$ values versus 1/[NO$_3$] should yield a correlation with a y-intercept that defines the $\delta^{15}N$ of one of the sources, in this case an unknown source(s) with elevated $\delta^{15}N$ (Keeling, 1961). The Keeling plot for Arequipa $\delta^{15}N$ vs. 1/[NO$_3$] showed no correlation with an $R^2$ of 0.07. This indicates that there is not an unknown $\delta^{15}N$ enriched NO$_x$ source (or combination of enriched sources) mixing with the combined known local NO$_x$ sources. These considerations suggest that the elevated $\delta^{15}N$ of NO$_3$ in Arequipa PM$_{2.5}$ is due, in part, to kinetic, equilibrium, and photolysis isotope effects occurring during the oxidation of NO$_x$ in NO$_3$.

Calculations of isotope equilibrium suggest that during the oxidation of NO$_x$, NO$_x$ compounds, including NO$_3$ should become isotopically enriched relative to the initial NO$_x$, which qualitatively explains the elevated $\delta^{15}N$ values for NO$_3$ in Arequipa relative to other southern hemisphere locations. At equilibrium, N compounds tend to incorporate $^{15}N$ preferentially into molecules with stronger bonds, which is usually a function of the compound’s oxidation state. For example, calculated isotope fractionation factors ($\alpha$) of nitrogen oxides at 298 K (Walters and Michalski, 2015) increase (relative to NO) as the N oxidation state increases (Figure 4) from 2 (NO) to 5 (HNO$_3$, N$_2$O$_5$, and HNO$_4$). Here, the isotope enrichment is defined as $\delta^{15}N = (\alpha - 1) x 1,000$. The result would be the $\delta^{15}N$ of NO$_3$ would be elevated relative to the emission source, leaving behind NO$_x$ with lower $\delta^{15}N$ that could be transported away from the source area. This isotope photochemistry effect would explain elevated NO$_3$ $\delta^{15}N$ values near emission sources (Arequipa) and low NO$_3$ $\delta^{15}N$ values in remote ocean regions (Morin et al., 2009; Li et al., 2021) since it would form from the residual NO$_x$ transported from the continent. This is analogous to water vapor isotopes becoming depleted as a function of the rainout fraction and

$\delta^{15}N$ (‰) of NO$_x$ (NO, NO$_2$, NO$_3$, HONO, NO$_2$, N$_2$O$_5$, HNO$_3$, H$_2$O, and HNO$_4$ at 298 K, respectively.

FIGURE 4 | The isotope fractionation factors for $^{15}N$ in nitrogen oxides with different oxidation states. The $^{15}N$ were calculated as $\beta_N/O/\beta_{NO}$ where $\beta_{NO}$ and $\beta_{NO}$ are the calculated values using coefficients from Table 1 in Walters and Michalski (2015) for NO and NO$_2$, NO$_2^-$, HONO, N$_2$O$_5$, HNO$_3$, N$_2$O$_5$, and HNO$_4$ at 298 K, respectively.

FIGURE 5 | The $\delta^{15}N$ values of NO$_3$ (HNO$_3$, NO, NO$_2$, and HONO) predicted by $\mu$PACM for Arequipa conditions for a NO$_x$ defined as 0% $\delta^{15}N$ shifts between NO and NO$_2$ is due to NO-NO$_2$ isotope exchange (Walters et al., 2016). The enrichment of NO$_3$ is due kinetic, equilibrium, and photolysis isotope effects as discussed in Fang et al., 2021).
depositing isotopically light rain as a function of distance or altitude (Gat, 1996).

**Quantifying the Influence of Photochemical Isotope Effects on Nitrate PM δ^{15}N Using \textit{ NRACM**

We quantitatively explored the photochemistry effect in Arequipa using the isotope enabled \textit{NRACM} photochemical box model (Fang et al., 2021). Briefly, the model accounts for kinetic isotope effects associated with bimolecular reactions such as NO + O \rightarrow NO_2 + O_2 (Walters and Michalski, 2016), equilibrium isotope effects such as NOx isotope exchange (Walters et al., 2016), and photolysis isotope effects, mainly NO2 \rightarrow NO + O (Fang et al., 2021). In addition, the model accounts for the amount of NOx converted to nitrate, and has demonstrated that when conversion reaches 100%, the NO3 \rightarrow δ^{15}N is the same as the NO3 source but that isotope fractionation is greatest when conversion fractions are small, similar to more simplistic Rayleigh models. The \textit{NRACM} model predicts that the NO3 \rightarrow δ^{15}N values are elevated by 10–20‰ relative to the NO3 source, while the residual NO3 becomes 15N depleted (Figure 5). There is a seasonality to the δ^{15}N values, with the southern hemisphere late fall months (May) having higher values and the Summer/Spring months with lower values (Figure 5). This is driven primarily by differences in daylight hours and thus the isotope sensitivity of photolysis reactions. When the initial NO3 source is shifted to -8‰, based on our isotope mass balance mixing model of known NO3 sources (discussion above) the \textit{NRACM} model does a fair job of replicating the data (Figure 6). For example, the spread in NO3 \rightarrow δ^{15}N values observed in the May and Aug–Oct. (±3‰) is captured by the \textit{NRACM} model though the modeled values in May are shifted upward by about six‰ relative to the observed values. The \textit{NRACM} model tends to under predict the observed δ^{15}N values during the summer months (Jan–Mar.), nor does it capture the roughly ±4‰ spread in the values during this period. The root mean square error (RMSE) between the model and data assuming a 0‰ source is 8.9‰, but improves to 3.7‰ when the source is assumed to be -8‰ based on our isotope mass balance mixing model (Figure 3). The accuracy of the \textit{NRACM} model on a day-by-day comparison is less robust, with a model versus observed R^2 = 0.14.

The inability of the \textit{NRACM} model to accurately predict the day by day NO3 \rightarrow δ^{15}N values is not surprising given the assumptions in the model. The main limitation of the \textit{NRACM} model is the assumption that the daily NO3 source mixture δ^{15}N is single valued. This is clearly not the case when considering the main NO3 source, based on the local emission inventory, of vehicle NOx. We defined the NO3 from vehicles without catalyzed NOx reduction technologies as a single value (-15‰), when in fact this is only an average and that individual vehicles can range from -7‰ to -19‰. This range believed to be caused is cause by kinetic isotope effects occurring in the Zeldovich mechanism during fuel combustion in the engine cylinder (Walters et al., 2015). The kinetics and subsequent isotope effect is thus a function of the engine efficiency and running conditions. Likewise, NO3 from vehicles with catalyzed NOx reduction technology also exhibit a significant range (-19‰ to +10‰). This is caused by the NO3 removal efficiency of the catalytic converter which in turn is a function of the converter temperature and drive time, with the NO3 δ^{15}N values becoming less negative and even going positive as NO3 reduction is maximized (Walters et al., 2015). Likewise, other known NOx sources (industry, biomass burning) and natural sources (soil, lightening) are temporally variable. Thus, some of the ±3‰ spread in the observed δ^{15}N values not captured the \textit{NRACM} model could simply be due to variations in NO3 sources with time. Regular and reliable trace gas monitoring (NO3, O3, CO) in Arequipa would help resolve this uncertainty in future studies.

Another limitation of the \textit{NRACM} model’s ability to accurately predict the day by day NO3 \rightarrow δ^{15}N values is that it neither accounts for atmospheric transport nor NO3 removal. Atmospheric transport is important in that the PM sampled may have derived from outside the city and transported in or under low wind conditions be primarily of city origin. If there were a clear difference between non-urban and urban NO3 \rightarrow δ^{15}N values, then this difference should be evident in the Keeling isotope plot (Figure 4) if the two sources are well mixed, which it is not. However, transport cannot be conclusively ruled out. Deposition of NO3 \rightarrow δ^{15}N is single valued. This is clearly not the case when considering the main NO3 source, based on the local emission inventory, of vehicle NO3. The kinetics and subsequent isotope effect is thus a function of the engine efficiency and running conditions. Likewise, NO3 from vehicles with catalyzed NOx reduction technology also exhibit a significant range (-19‰ to +10‰). This is caused by the NO3 removal efficiency of the catalytic converter which in turn is a function of the converter temperature and drive time, with the NO3 δ^{15}N values becoming less negative and even going positive as NO3 reduction is maximized (Walters et al., 2015). Likewise, other known NOx sources (industry, biomass burning) and natural sources (soil, lightening) are temporally variable. Thus, some of the ±3‰ spread in the observed δ^{15}N values not captured the \textit{NRACM} model could simply be due to variations in NO3 sources with time. Regular and reliable trace gas monitoring (NO3, O3, CO) in Arequipa would help resolve this uncertainty in future studies.

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residence time effect. A more accurate modeling system would be a 3-D chemical transport model that incorporates both temporal/spatial NOx emission rates and their $\delta^{15}$N values, 3-D mixing via pressure/temperature gradients, and N isotope effects incorporated into its chemical mechanism. Unfortunately, such a model does not yet exist.

CONCLUSION

We report on the first time series of $\delta^{15}$N in aerosol nitrate (PM$_{2.5}$) from South America. PM$_{2.5}$ was collected at four sites located in Arequipa, a major city in southern Peru. PM$_{2.5}$ nitrate concentrations ranged from a minimum of 0.17 mg/m$^3$ to a maximum of 2.87 mg/m$^3$ and averaged 0.90 mg/m$^3$ and accounted for 9–12% of the ion mass. Nitrate $\delta^{15}$N values ranged from $-1.7$ to $-15.9\%$ and averaged $5.3 \pm 3.0\%$, with no significant difference between the four study sites and no discernable seasonal trend, but this lack of a seasonal trend may be an artifact of gaps in the data and the movement of the sampler over the course of a year. These $\delta^{15}$N values are significantly higher than those in aerosol nitrate from southern hemisphere marine environments and those from the northern hemisphere. An isotope enabled 0-D photochemical box model (in RACM; Fang et al., 2021) was used to estimate the isotope enrichment of nitrate relative to NOx due to kinetic, equilibrium, and photolysis isotope effects occurring during NOx oxidation. After correcting for the photochemical isotope effect, we estimated a NOx sources with $\delta^{15}$N of $-8 \pm 3\%$. Using an isotope mass balance mixing model that utilized known NOx source $\delta^{15}$N it was determined that NOx in Arequipa is derived mainly from anthropogenic sources (vehicles and some industry), in general agreement a recent emission inventory. Without the photochemical isotopes effect correction, the data indicates a NOx source with a significantly positive $\delta^{15}$N value, possibly coal burning or biomass burning, which is unlikely given the sparse vegetation in the region. This suggests that the photochemical isotope effect must be accounted for if nitrate $\delta^{15}$N values are to be used to accurately constrain NOx sources. If it is accounted, then measurements PM nitrate $\delta^{15}$N values could be a new tool to validate NOx emission inventories in other locations. This is of particular relevance in regions where detailed NOx emissions inventories are lacking, such as South America and Africa. Further, the "photochemistry + source" hypothesis can be further tested in regions where NOx sources are more varied and the NOx inventories are the thought to be more accurate (US, Europe) by measuring PM nitrate $\delta^{15}$N at high temporal and spatial scales.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Materials, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

GM is the PI, analyzed the data, and wrote the manuscript. AE and JR collected the PM samples and conducted the gravimetric analysis. HF and JL conducted the modeling and isotope analysis. EO prepared the samples for analysis and conducted ion analysis. LW is Co-Pi and assisted in preparing the manuscript and training students.

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SUPPLEMENTARY MATERIAL

The Supplemental Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2022.916738/full#supplementary-material

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