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Monitoring Stable Nitrogen and Oxygen Isotope Compositions of Nitrate in Atmospheric Precipitation

Final Report of a Coordinated Research Project

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MONITORING STABLE NITROGEN AND OXYGEN ISOTOPE COMPOSITIONS OF NITRATE IN ATMOSPHERIC PRECIPITATION

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FINAL REPORT OF A COORDINATED RESEARCH PROJECT

INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

Increases in food production and energy use worldwide have in turn led to higher anthropogenic emissions of reactive inorganic nitrogen compounds into the atmosphere. These emissions contribute to atmospheric pollution that is transported and deposited through atmospheric precipitation in terrestrial and aquatic systems. Nitrogen deposition that exceeds the remediation capacity or critical load in aquatic systems may disrupt the nitrogen balance and can result in the eutrophication and/or acidification of local water bodies such as rivers, lakes and streams. For the past four years, the IAEA has promoted the use of stable nitrogen and oxygen isotope analyses for tracing sources of nitrates in the atmosphere and hydrosphere to address water quality issues. This publication is a result of the studies conducted during a coordinated research project entitled Global Monitoring of Nitrogen Isotopes in Atmospheric Waters in 2018–2023. It is intended to promote the analysis of stable nitrogen and oxygen isotopes in nitrates by providing monitoring procedures and illustrative case studies of successful applications. This knowledge transfer is expected to improve the capability and expertise of participating Member States.

The coordinated research project focused on the determination of the spatio-temporal distribution of the stable nitrogen isotope composition in precipitation as a potential source of nitrogen pollution to water resources sensitive to eutrophication. The principal research method was based on the combined application of stable nitrogen and oxygen isotope analyses in nitrate, chemical analysis and hydrometeorological techniques to better understand nitrogen deposition and to characterize the origin and transformations of nitrogen loadings.

This publication was supported by specialists in stable isotope hydrology, and atmospheric and water sciences from various countries. The case studies included provide an overview of the methods for monitoring stable nitrate isotopes in atmospheric precipitation and their use for nitrogen source tracing across a range of different environmental and climate settings.

The IAEA officer responsible for this publication was Y. Vystavna of the Division of Physical and Chemical Sciences.

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CONTENTS

1. INTRODUCTION

1.1. BACKGROUND

Seventy-eight percent of air is molecular nitrogen (N_2) that can enter the water cycle after being converted into reactive inorganic nitrogen (N) compounds, such as ammonium (NH_4^+), nitrogen oxides (NO_x) and nitrate (NO_3^-) through natural processes, such as lightning and biological N_2 fixation [1]. Natural N entering the biological cycle constitutes only a small fraction of N cycled by the biosphere. Human activities have doubled the amount of reactive N in the atmosphere compared to pre-industrial times [2]. These anthropogenic N loads originate from different sources [2]:

(a) combustion of fossil fuels;
(b) production and excessive application of synthetic and organic fertilizers;
(c) animal livestock, such as pigs and cattle breeding.

Global NO_x industrial emissions are believed to originate mostly from fossil fuel combustion (63%), which far exceeds natural NO_x sources, such as lightning, biogenic soil processes, and wildfires [3]. More recently, it was found that sources other than fuel burning may contribute up to half of industrial NO_x emissions [4]. Estimation of N contribution from agricultural sources to the N reactive compounds in the atmosphere is highly uncertain, and varies widely respectively to the type of farming, climate, and local policies on fertilizer use [5]. Therefore, local air pollution surveys and continued monitoring are required for more accurate estimations of the relative contributions from different N sources.

Both coastal and terrestrial ecosystems are affected by N deposition from various sources related to ocean and/or marine and terrestrial processes, whereas terrestrial sites are mostly affected by land-based N sources. Due to rising anthropogenic N loads (e.g., agriculture, sewage, industrial discharges, and urban areas), water quality in many lakes and rivers around the globe is deteriorating, thus causing changes to their ecosystems [6]. However, the deposition of NO_3^- with precipitation and its transformation are often overlooked in N budgets of aquatic systems. N emissions in the form of N_2O, NH_3, NO_x and NO_3^- can occur by atmospheric circulation and are deposited onto ecosystems hundreds of kilometres from the source. Excessive loads in sensitive aquatic ecosystems may lead to the acidification[1] of surface water and soil and the eutrophication[2] of rivers and lakes. This can subsequently lead to harmful algae blooms, loss of biodiversity, water quality deterioration, and also potential alteration of the global nitrogen and carbon budget [7–12]. Nitrogen limitation often restricts primary productivity in aquatic and terrestrial ecosystems; therefore, excessive N deposition resulting from water pollution may cause undesired fertilization, frequently busting undesired productivity. However, in certain situations when loads are very high, productivity increases are suppressed by negative effects associated with acidification and damage to the stomata of terrestrial plants. Thus, a better understanding of how N pollutant forms are transformed and introduced to terrestrial and aquatic environments with atmospheric precipitation is important for the determination of atmospheric N sources.

Existing precipitation monitoring networks, such as the Global Network of Isotopes in Precipitation, do not include stable nitrogen and oxygen isotope analyses in NO_3^- ($\delta^{15}N$-NO_3

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[1] Acidification – the process of lowering pH in a system, e.g., soils, freshwaters, and oceans.

[2] Eutrophication – the enrichment of an ecosystem with a limiting nutrient. It can occur in terrestrial and aquatic ecosystems. For example, too much nitrogen in aquatic ecosystems can lead to algal blooms, dead zones, and fish kills.

and δ^{18}O-NO_3, respectively). Thus, the spatial distribution of stable isotope composition of NO_3^- in precipitation remains poorly defined and understood.

1.2. OBJECTIVE

The CRP F32008 project aimed to establish a programme for spatial and temporal monitoring of δ^{15}N-NO_3 and δ^{18}O-NO_3 in precipitation at several locations worldwide to understand the relative contributions from various N sources to atmosphere pollution. This programme was designed to test methods, understand logistical and analytical challenges and to standardize sampling methods.

The purpose of this document is to provide guidance on monitoring of NO_3^- in rainwaters using δ^{15}N-NO_3 and δ^{18}O-NO_3 and chemical compound concentrations that can be used for N source tracing and estimation of N loads in water.

1.3. SCOPE

The scope of this document is to provide readers with the necessary information to start δ^{15}N-NO_3 and δ^{18}O-NO_3 monitor in precipitation. The use of δ^{15}N-NO_3 and δ^{18}O-NO_3 allows insights into the origins and transformation pathways of N beyond traditional chemical analyses and helps to better understand the importance of different sources of N pollution. The identification of NO_3^- sources is a first step in partitioning NO_3^- loads of different origins. This knowledge can then be applied to develop more effective monitoring strategies and approaches for managing N pollution in the environment.

The presented methodology is based on a combined δ^{15}N-NO_3 and δ^{18}O-NO_3, and chemical tracers because the analysis of the chemical composition of precipitation alone is unable to accurately partition the NO_3^- sources. The quantification of δ^{15}N-NO_3 and δ^{18}O-NO_3 can help discriminate between sources and trace pathways of NO_3^- formation by providing a unique isotope fingerprint for major sources and processes.

This document is targeted at water managers, practitioners and technicians working at environmental organisations, state agencies, and academia. This TECDOC is focused on a better understanding of the impact of atmospheric pollution on water quality and thereby enhance sustainable water management in Member States.

1.4. STRUCTURE

This publication discusses different approaches for δ^{15}N-NO_3 and δ^{18}O-NO_3 and chemical composition monitoring in precipitation, as well as data interpretation to support the decision-making process to address air and water N pollution. The publication includes a general overview of N sources in the atmosphere, transformation processes, and the impact on air and water quality (Sections 2.1 and 2.2). The detailed methodology of N monitoring based on δ^{15}N-NO_3 and δ^{18}O-NO_3 and hydrochemical tools is described in Section 3, with a special focus on the development of sampling strategies, analysis, data reporting and basic interpretation. Successful applications of these methodologies are illustrated by four case studies of N monitoring in atmospheric waters and their broader conclusions (Section 4). Discussions and future directions are presented in Section 5.

2. NITROGEN COMPOUNDS, THEIR SOURCES, AND TRANSFORMATION PROCESSES

2.1. NITROGEN SOURCES AND THEIR ISOTOPIC SIGNATURES

Human activities have elevated the amount of N_2O, NO_x, NH_x (ammonium and ammonia) in the atmosphere compared to pre-industrial times. The elevated concentrations of NH_x are generally released as a side effect of fertilizer application. Nitrogen oxides originate mainly from the combustion of fossil fuels used for energy production and transportation. Nitrogen oxides and NH_x are also released through the generation and use of manure. Atmospheric N from natural and human emissions is deposited on land and waters, typically in the form of NO_3^- ion dissolved in rainwater or snow (wet deposition) or in the forms bonded to particles (dry deposition) [13, 14]. Nitrate contamination in freshwaters commonly arises from commercial fertilizers and human or animal waste. The determination of their relative contribution to water contamination can be resolved through the analysis of $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$.

In principle, the $\delta^{15}N\text{-}NO_3$ in rainwaters reflects $\delta^{15}N$ of NO_x in emission sources, assuming limited change of the stable isotope signature during the conversion of NO_x to NO_3^-. Different sources of NO_x emission showed different ranges of the $\delta^{15}N$ value. For example, the NO_x emissions derived from power generators typically show higher $\delta^{15}N$ values (> +5‰) than N emissions from soil and fertilized areas (down to -20‰) [15] or natural lightning [4]. The $\delta^{15}N\text{-}NO_x$ values of vehicle emissions typically range between -20‰ and +10‰, whereas those of biomass burning range between -10‰ and +10‰.

Commercial NO_3^- fertilizers, being derived from atmospheric N, have an isotope composition close to the atmospheric ambient N_2 (0‰). On the other hand, organic wastes lose N through NH_3 volatilization or nitrification and the denitrification cycle. This process preferentially removes the lighter ^{14}N isotopes from the solution. Thus, NO_3^- derived from human and animal waste that represent the residual part of undenitrified and frequently refractory nitrogen (e.g., septic systems, animal waste from feedlots) has a significantly higher $\delta^{15}N\text{-}NO_3$. Nitrate, which is associated with increased NO_x emissions, is a potential source of bioavailable N in aquatic systems. The high surplus of N loads may lead to eutrophication of rivers and lakes, lake and stream acidification, and consequently, loss of biodiversity and alteration of global nitrogen and carbon budget [10].

Dissolved organic N (DON) is another important compound in the atmosphere N budget. For example, water-soluble organic N can account for 8 to 50% of total reactive nitrogen in the atmosphere, with an average of 30% of the total N in the wet deposition in many regions [16–18]. Therefore, the wet deposition of total N is often underestimated without considering DON, but currently there is no N controlling legislation addressing the importance of DON. Atmospheric DON can originate from terrestrial and oceanic, natural and anthropogenic, and primary and secondary sources [17, 18]. The lack of understanding of the chemical forms of DON in the atmosphere is an obstacle to the identification of DON sources and to further emissions control.

2.2. NITROGEN ATMOSPHERIC PROCESSES AND TRANSFORMATIONS

To effectively utilize $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ in precipitation for tracing NO_x sources, it is essential to have a comprehensive understanding of how $\delta^{15}N\text{-}NO_3$ are partitioned during N photooxidation in the atmosphere and the formation of NO_3^- from NO_x (Fig. 1). This understanding is fundamental for the accurate interpretation of stable isotope data and the partitioning of different sources of N compounds. By studying δ^{15}N-NO_3 fractionation insights into the processes that create the final stable isotopic composition of NO_3^- observed in atmospheric precipitation can be gained.

This isotope fractionation involves complex chemistry, where various N compounds are oxidised to higher oxidation states, and the final sum of all compounds, respectively, to the progress of oxidation, can be expressed as NO_y, where:

$$NO_y = NO_x + NO_3^- + N_2O_5 + N_2O + HONO + HNO_3(NO_3^-) + NO_3^-(\text{organic}) \\ + NO_3^-(\text{peroxyacyl}) + \text{others}$$

In most environments, NO_y consists of mainly $NO_x + HNO_3$ (NO_3^-), with the other compounds present at negligible trace levels. In clean environments NO_y contains mostly NO_x, while in urban air, most NO_y are NO_3^- (as HNO_3 or particulate NO_3^-). Consequently, in urban environments, the measured δ^{15}N-NO_3 is very close to the initial δ^{15}N in the NO_x source, which means that δ^{15}N-NO_3 in rainwater reflects the NO_x sources of atmospheric N pollution. Dinitrogen monoxide (N_2O) is primarily associated with emissions from agriculture sources [5].

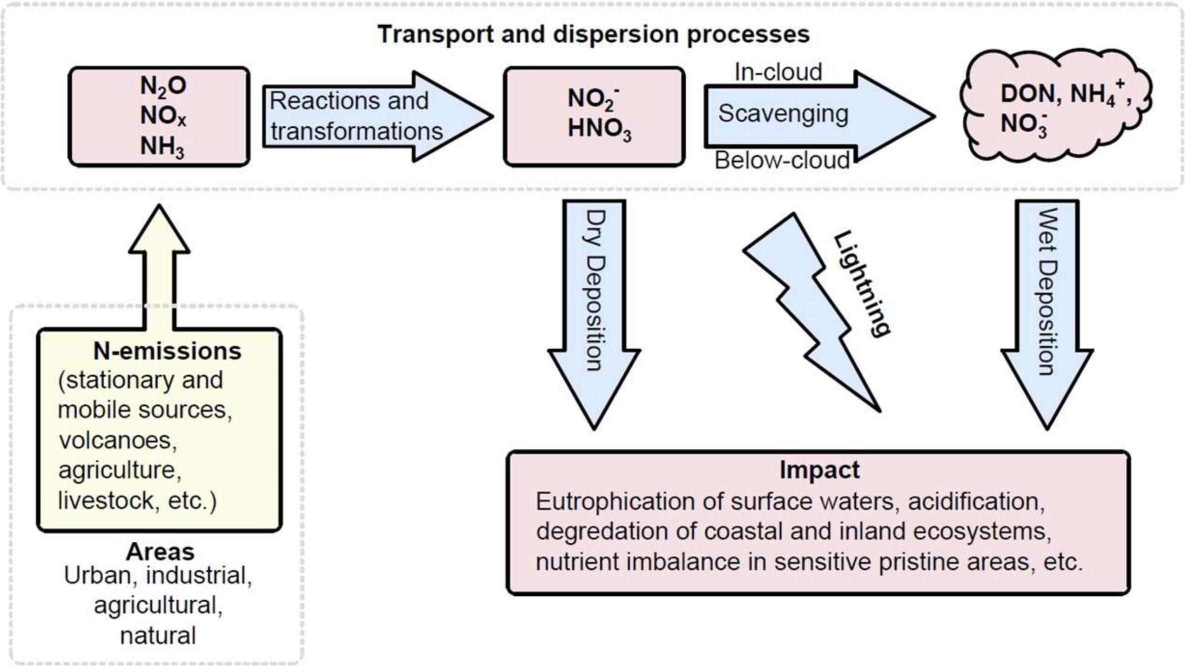

FIG. 1. Nitrogen transport and transformation processes in the atmosphere

In pristine environments, the δ^{15}N of the NO_x source is controlled by nitrogen stable isotope fractionation processes [19]. Fractionation is related to photochemical reactions during NO_x multistep conversion into NO_3^- and results in the deviation of measured δ^{15}N-NO_3 from δ^{15}N of the NO_x source. This fractionation can be accurately calculated using an isotope enabled photochemical box model [19].

Similar fractionations impact stable oxygen isotope composition during NO_x oxidation, but they are more complex because multiple oxygen (O) species participate in these reactions, including ozone (O_3), molecular oxygen (O_2), and water (H_2O). In general, O_3 contribution has the largest effect, and ozone concentrations tend to vary with season, resulting in temporal $\delta^{18}O$ variations. The high $\delta^{18}O$ values are used to trace the natural atmospheric deposition of NO_3^- on the surface and determine the relative importance of NO_3^- deposition in soil, lakes, and stream systems [20].

After NO_x is oxidised into highly soluble or reactive NO_3^- (HNO_3, particulate NO_3^-), and can be deposited on land or water, either through wet deposition when dissolved in rain or mist, or through dry deposition when the gas comes into direct contact with a receiving medium (Fig. 1). The oxidation reactions are influenced by many natural factors, including temperature, humidity, solar radiation, and the availability of reactive aerosol surfaces [21], which results in spatial-temporal variability of N deposition. For example, the oxidation of NO_x is favoured during the summer and in areas that experience extended and perpetual daylight [22, 23].

2.3. NITROGEN DEPOSITION IMPACTS ON WATER AND AIR QUALITY

Elevated concentrations of N-bearing compounds in freshwaters are mainly of terrestrial anthropogenic origin, e.g., wastewater and discharge from agriculture, sewage, industrial, or urban areas. The impact of N species on aquatic ecosystems (e.g., eutrophication) and human health (e.g., methemoglobinemia, cancer, and thyroid disease) is of high concern. However, rivers and lakes located in remote regions are not usually the recipients of terrestrial N, but they are mostly affected by the chronic input of atmospheric N through dry and wet atmospheric depositions. Nitrogen deposition involves the removal of N pollutants from the atmosphere by water droplets, which are then deposited on soil, vegetation, or water bodies. Atmospheric N can enter surface runoff and be transferred by runoff on a catchment scale [24]. Atmospheric circulation can transport N pollutions with air masses much further than surface runoff, and precipitation can be deposited in pristine areas hundreds of kilometres from emission sources [25]. Therefore, partitioning transboundary and local air pollution is critical for the pollution budget evaluation and mitigation.

3. MONITORING PRECIPITATION FOR STABLE NITROGEN AND OXYGEN ISOTOPES

Overall, the workflow for monitoring stable isotope compositions and concentrations of NO_3^- in precipitation includes the following four steps:

(a) proper selection and setup of the monitoring sites;
(b) rainwater sampling (preservation and storage if shipment is required);
(c) monitoring of meteorological parameters; and
(d) chemical and stable isotope analysis.

All these steps are necessary to ensure the representativeness of the monitoring sites, the accuracy of the produced data and the correct interpretation of the findings.

3.1. SAMPLING STRATEGY

Different sampling strategies are required for different applications; however, each project requires consideration of: 1) general sampling criteria, 2) sampling intervals, periods and frequency, 3) sampling collector selection, 4) availability of field data, and 5) sample short-term or long-term storage.

3.1.1. Sampling site criteria

Sampling sites should be selected considering the World Meteorological Organisation (WMO) and Global Atmospheric Watch precipitation chemistry guidelines (i.e., for urban, industrial, rural, and coastal areas) (Fig. 2) [26, 27]. The sample collector should be installed on a flat area (slopes up to ± 15%), ensuring that structures do not project onto the sampler at an angle greater than 45° from the horizontal (30° is considered optimal) (Fig. 2), to avoid impacts of nearby objects. The collector should be placed approximately 1.0–1.2 m above the ground.

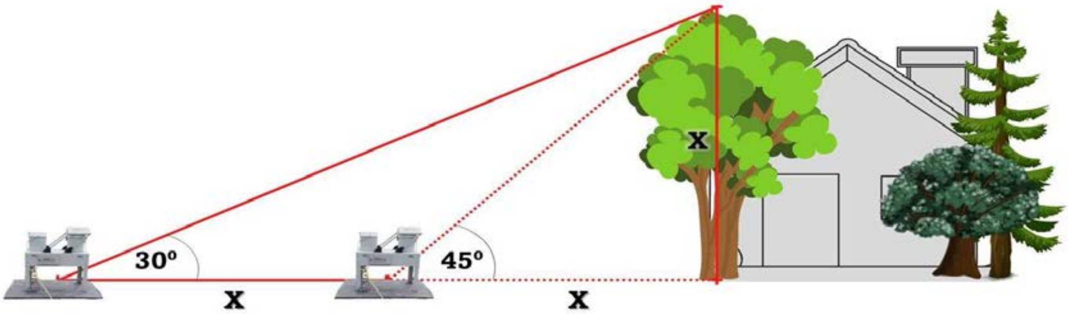

FIG. 2. Recommendations and criteria for setting up rainwater collectors for chemical and stable isotope analyses (adapted from [27]).

3.1.2. Sampling frequency

Consistent sampling frequency and collection of environmental and meteorological parameters at all study sites are recommended to improve datasets for the representative estimation of N deposition and N-source analysis. The sampling frequency may determine the technique for precipitation collection, although section 3.1.3. discusses standardised collectors that can be used across all sampling sites. Usually, 24 hour or event-based precipitation sampling frequencies are used. The WMO highly recommends 24-hour sampling at 09:00 local time. For bulk collectors, sampling periods longer than 24 hours are discouraged due to the risk of sample contamination and stable isotope fractionation during an extended holding time in the sampler [27].

Samples, 30–100 mL in volume (method dependent), should be preserved by filtration using at least a 0.45 µm nylon syringe disc filter. When conducting an analysis in 48 hours after the sample collection, it is recommended to store the samples in a refrigerator at a temperature range of 4–5°C. If samples will not be analysed for more than 48 hours, they need to be frozen. For samples to be frozen, it is recommended to keep 10–20% of the headspace in vials to prevent breaking from water expansion during freezing. Chemical preservation methods could be used for selected analytical methods and should be communicated with the laboratory in advance. For sample transportation, insulated boxes with chilling blocks are recommended to maintain a low temperature.

The precipitation amount and type (snow and/or rain and/or solid and/or convective and/or stratiform rain) should be recorded. Wind speed and wind direction can be noted for a better understanding of sources, mixing, and washout processes during the data analysis. In addition to δ^{15}N-NO_3 and δ^{18}O-NO_3, simultaneous analyses of stable isotopes in water molecule (δ^2H-H_2O and δ^{18}O-H_2O) are recommended. In addition, sampling for sulphur and oxygen isotopes in sulphates (δ^{34}S-SO_4 and δ^{18}O-SO_4) can be considered if contributions from fossil fuel combustion are expected to be significant [28]. Supplementary information on the concentration of N compounds, O_3, and major cations and anions is also relevant for the N source tracing. These data can provide additional information on moisture sources and hydroclimate processes.

3.1.3. Sample collectors

Different collectors can be used for different types of sampling. Presented here are precipitation collectors commonly used for monitoring stable hydrogen and oxygen isotope composition of rainfall water that could also be appropriate for precipitation collection for stable nitrogen and oxygen analysis of nitrates.

a) An automated wet-only collector

For event-based or 24-hour sampling, it is recommended to analyse wet deposition only; for dry deposition, usually longer periods are required to obtain a sufficient sample size. A wet-only collector typically consists of a collecting bucket covered by a moveable lid. The lid is activated by a precipitation sensor to open the collector only during precipitation events and prevent dry deposition (Fig. 3A). This excludes dry deposition in a dry period and opens whenever precipitation is detected by a precipitation sensor (Fig. 3A). However, this approach requires a power supply and potable sensors.

Separation of wet and dry depositions is important for more accurate partitioning of pollution sources. Dry and wet depositions could have different stable nitrate isotope and chemical compositions. In addition, the loads of N delivered by dry and wet deposition could vary according to the region and types of pollution present in the atmosphere. If bulk precipitation collectors are used (Fig. 3B), an assessment of the local dry deposition contribution should be performed separately to exclude the impact of dry deposition on the wet deposition results.

b) A bulk precipitation collector

A bulk precipitation collector is a cheaper and less complex solution for rainwater collection (Fig. 3B). However, when using bulk precipitation collectors, the contribution of dry deposition should be considered. Different types of collectors for bulk precipitation sampling are summarised in the IAEA Global Network of Isotopes in Precipitation manual [27]. The bulk precipitation collectors are prone to contamination from bird droppings, so protection measures (e.g., steel wires) should be taken. Periodical cleaning and funnel replacement are recommended. The funnel diameter should be adjusted to the precipitation volume expected during the sampling period to ensure that the water sample volume will be sufficient.

A) B)

FIG. 3. A) Wet and dry precipitation collector (Mae Hia Meteorological Station, Chiang Mai University, Thailand) Photograph courtesy of Somporn Chantara B) bulk precipitation collector (IAEA headquarters, Vienna, Austria). Photograph courtesy of Stefan Terzer-Wassmuth.

3.1.4. Field data and sample containers

To support data interpretation, it is necessary to record basic meteorological data at each sampling station, such as precipitation amount, precipitation type, air temperature, relative humidity, wind direction, event duration (start and end), lightning, haze, hail, snow or smoke occurrence, or any other atmospheric event like dust, pollen, etc.

For all precipitation samples, laboratory-grade high-density polyethylene (HDPE) vials or bottles are recommended. To remove the risk of bacterial contamination, when necessary, sample containers can be cleaned with laboratory detergents, washed with acid (4% HCl), rinsed with deionised water, and dried and stored in a dust-free area prior to use. Sample containers should be hermetically sealed to avoid the loss of samples or the entry of air. It is also recommended to collect 30–50 mL of water for analyses on stable isotopes in water molecules. A higher amount can be needed for the supplementary compound analyses (chemistry, O_3, etc.), and for low concentrations (total dissolved solids < 100 mg L^{-1}) volume up to 1 L could be required.

3.2. CHEMICAL AND STABLE ISOTOPES ANALYSIS

Nitrogen species (such as nitrite) are generally short-lived and undergo rapid oxidation. In addition, some bacteria mediate the fast conversion of NO_3^- into gaseous N through denitrification. Therefore, the samples should be analysed for N species shortly after collection or stored at -20°C.

The analytical techniques δ^{15}N-NO_3 and δ^{18}O-NO_3 in precipitation samples are the same as those used for surface and groundwater (e.g., bacterial denitrification, chemical methods; see subsection 3.2.2.). For rainwater samples, there may be a limitation in measuring NO_3^- concentrations below 0.1 mg L^{-1} (given as N-NO_3^-) due to instrument detection limits. Thus, it is important to contact the laboratory to confirm detection limits prior to sample collection and shipment. Therefore, knowing the range of concentrations of the analysed compounds is essential (nitrate, nitrite, and ammonium) prior to stable isotope analyses. The additional chemical parameters that could be important are pH, electrical conductivity, and sulphate, chloride, sodium, potassium, calcium, magnesium, and ammonia concentrations. Cation and anion balance should be assessed at each monitored station. The procedures stated in the manual for the Global Atmospheric Watch precipitation chemistry programme from the WMO provide a detailed overview of good laboratory practices for wet deposition monitoring [26]. The glass membrane method and conductivity cell instruments are recommended for pH and electrical conductivity analyses. Flow injection analysis and ion chromatography are the most common techniques for ionic composition characterization, since they are fast, accurate, and relatively inexpensive methods [20].

3.2.1. Analytical techniques for stable isotope analyses

Various laboratory methods have been developed for the preparation of NO_3^- for stable isotope analyses. The primary technical challenges are quantitative extraction of NO_3^- from water, isolation of NO_3^- from other N and O bearing species, and conversion of NO_3^- to gases suitable for $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ analyses [29–31]. Usually, NO_3^- is converted to N_2O gas. The N_2O from the reaction vial headspace is usually measured for $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ using either a continuous flow isotope ratio mass spectrometer (IRMS) or laser spectroscopy. The analytical uncertainties for the isotope ratio mass spectrometer method are lower than ± 0.1‰ for $\delta^{15}N\text{-}NO_3$ and ± 0.2‰ for $\delta^{18}O\text{-}NO_3$ with an analytical limit of 0.4 mg L^{-1} $N\text{-}NO_3^-$ [34]. The combined analytical uncertainties for the laser spectroscopy method, meanwhile, are lower than ± 0.2‰ for $\delta^{15}N\text{-}NO_3$ and ± 0.4‰ for $\delta^{18}O\text{-}NO_3$ and the laser methodology also provides the opportunity to analyse also $\delta^{17}O$ to an analytical precision of ± 0.1‰ [34].

Several analytical methods can be used for obtaining N_2O from water samples (e.g., chemical precipitation, bacteria denitrification, chemical reduction methods) [31–33]. The most common is the microbial denitrification method. This method includes cultivating denitrifying bacteria lacking an enzyme to reduce N_2O to N_2. The final metabolite of denitrification is N_2O that can be measured using isotope ratio mass spectrometry or laser absorption spectrometry [31]. Another method is the Cd-Az technique, which uses the chemical conversion of nitrate to nitrite (NO_2) via cadmium reduction, followed by its conversion to nitrous oxide (N_2O) using azide and acetic acid solutions [35]. Unlike microbial denitrification, the Cd-Az method is not influenced by toxic substances in the sample that may prevent bacterial reduction. However, there is a potential risk of exposure to hazardous chemicals (cadmium and sodium azide) during sample preparation. The IAEA Isotope Hydrology Laboratory predominantly uses the titanium (Ti(III)) reduction method. This reduction method [34] directly converts aqueous NO_3^- to N_2O headspace gas in septum-capped vials. The method is faster and less labour intensive than the bacterial denitrification method. This method also produces fewer toxic wastes compared to the azide method [36]. Another alternative method is the silver nitrate precipitation method. Samples undergo preconcentration, elution, and purification using ion exchange resins to create $AgNO_3$ precipitate [37]. This precipitate is subsequently freeze-dried and combined with graphite before analysis using the oxidation method and elemental analyser (EA) for $\delta^{15}N\text{-}NO_3$ and high temperature reduction thermal conversion/elemental analyser (TC/EA) for $\delta^{18}O\text{-}NO_3$. In the EA method N_2 is generated and analysed with high accuracy, usually < 0.10‰. The TC/EA meanwhile produces CO (carbon monoxide analysed with accuracy of < 0.40‰ [38, 39].

Rain samples usually have a low range of NO_3^- concentrations, frequently between 0.05 and 1.00 mg L^{-1} ($N\text{-}NO_3^-$) [40, 41]. Therefore, the detection limits and analytical uncertainties with respect to the analytical method should be considered before the start of the sampling campaign. Collection of samples with low NO_3^- concentrations also requires additional precautions to avoid potential sample contamination during collection or laboratory analyses. To ensure data quality, control protocols such as field blanks, procedural blanks, and duplicates need to be implemented. In addition, laboratory quality control actions, such as keeping records of blanks, calibration, validation standards, sample duplicates, and reference material results, are necessary. Regular participation of isotope hydrology laboratories in interlaboratory comparison exercises is also advised.

3.3 DATA REPORTING, BASIC DATA TREATMENT AND INTERPRETATION

3.3.1. Data reporting

Each reported stable isotope dataset needs to be accompanied by the minimum information required for publishing the stable isotope results to ensure the longevity and reusability of published data. These requirements were published as the International Union of Pure and Applied Chemistry Technical Report with the aim of standardising reporting requirements [42]. Information about (1) analytical procedure, (2) traceability, (3) data processing, and (4) uncertainty evaluation is required to avoid inconsistencies and biases arising from the use of different standards or protocols [43]. The minimum information should include the following:

(1) description of analytical procedure should include details of sample preparation procedure, together with type and model of instrument and peripheral device, including critical operational parameters of the measurement (e.g., gas flows, temperatures) and analytical materials;
(2) metrological traceability description should include isotope-delta values of the used standards and the identity of the international standard used for their determination, along with information about their combined analytical uncertainty;
(3) publications should disclose how stable-isotope data were processed, the results were normalized to the international isotope delta scale, and what other corrections were applied (e.g., blank, memory effects, drift, linearity and/or mass effects, isobaric, and other interferences);
(4) the reported isotope-delta value needs to be accompanied by analytical uncertainty, with information on how it was calculated.

3.3.2. Basic data treatment and interpretation

The $\delta^{15}N\text{-}NO_3$ value in precipitation can provide information about nitrogen sources and atmospheric transport processes. The $\delta^{18}O$ value of atmospheric NO_3^- is elevated relative to all other ‘terrestrial’ NO_3^- pollution sources (Fig. 4). This enables $\delta^{18}O\text{-}NO_3$ to be used to identify locations and times when surface water or terrestrial environments are affected by atmospheric N deposition rather than anthropogenic sources (for examples, see [44, 45]).

These significantly elevated $\delta^{18}O\text{-}NO_3$ values result from the exchange between intermediate nitrogen oxides and stratospheric O_2 and O_3 molecules, which have high $\delta^{18}O\text{-}NO_3$ values (O_2 constant value of +23‰ and O_3 between +70 and +120‰) [46, 47]. These reactions are discussed in more detail in Section 2.2.

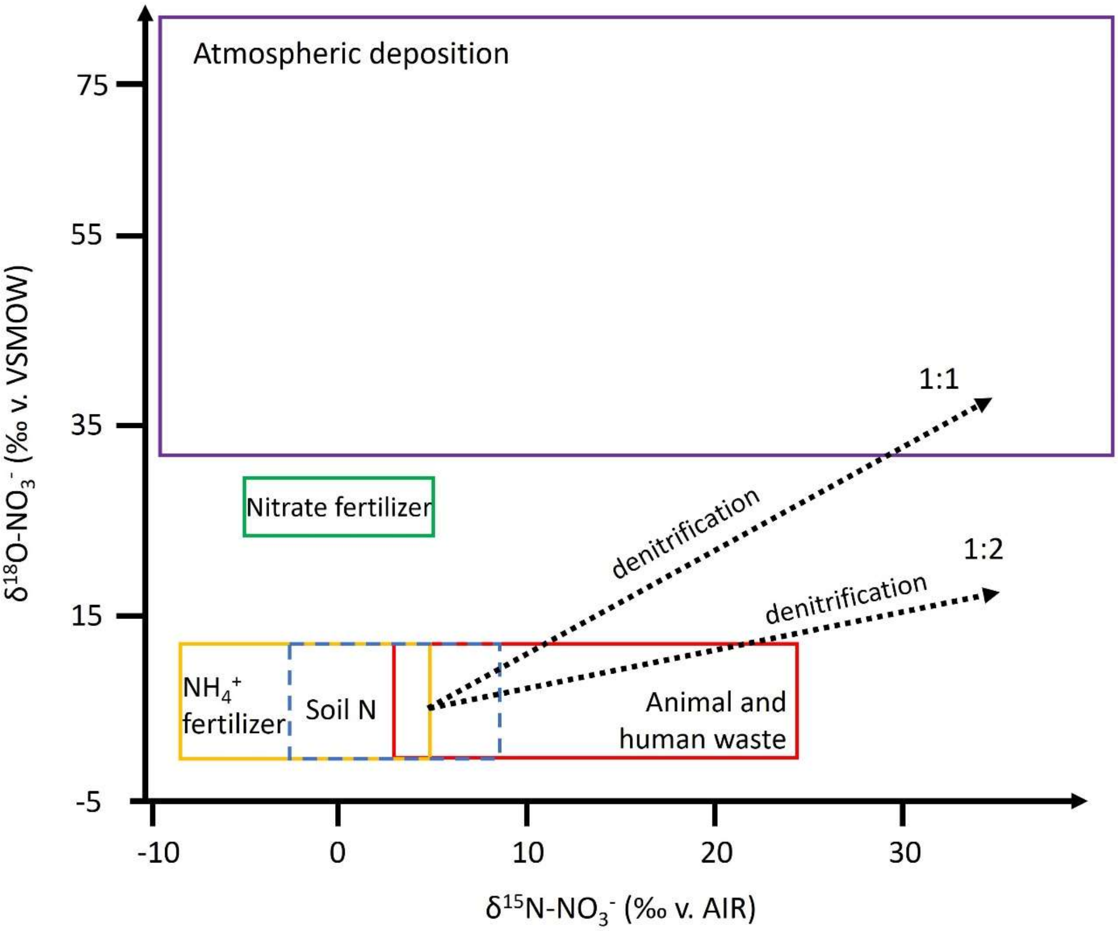

FIG. 4. The reported ranges of $\delta^{15}N-NO_3$ and $\delta^{18}O-NO_3$ values in NO_3^- originating from different terrestrial (NH_4^+ fertilizers, soil N, animal, and human waste) and atmospheric deposition sources, as well as NO_3^- fertilizers produced from atmospheric N_2. Note that the $\delta^{15}N$ range of NO_3^- from atmospheric deposition is wider than the axes in this diagram. The values are from [48–50].

The $\delta^{15}N-NO_3$ in precipitation varies approximately between -60‰ and +30‰ and can be used for identification of the major sources of emissions (Fig. 5). Local (washout) and long-range (rainout) atmospheric depositions may reflect influences from different emission sources. NO_3^- derived from fossil fuel combustion by electricity generation and industry generally yields high $\delta^{15}N-NO_3$ values compared to 'natural' NO_x sources like lightning, biogenic and/or fertilized soil emissions and biomass burning. For example, the $\delta^{15}N-NO_3$ from coal combustion in power plants ranges from +6 to +26‰, whereas much lower isotope delta values from -20 to +10‰ are observed from vehicle NO_x emissions. Biogenic nitrogenous emissions from soil N volatilization are more depleted in ^{15}N, with $\delta^{15}N-NO_3$ values as low as -60‰ after soil fertilization. Consequently, the $\delta^{15}N$ in rainwaters in highly polluted areas is generally higher than in pristine non-urban regions, and the relative proportions between natural and industrial sources can be estimated based on the characteristic source stable isotope fingerprint despite significant overlap.

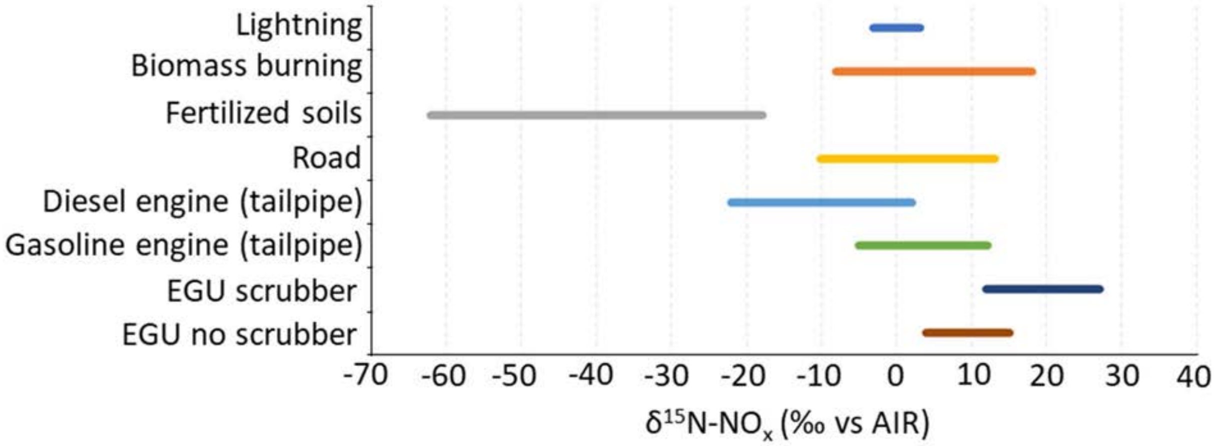

FIG. 5. Stable isotopic signatures of NO_x emissions sources from [48]. EGU stands for Electric Generating Units.

The stable isotope composition of NO_3^- in rainwater is not just affected by the mixing of different pollution sources, but also by complex chemical reactions that affect the initial chemical composition of pollution and NO_3^- transport through the atmosphere. Thus, sources and reactions should be acknowledged when interpreting NO_3^- isotopic data (Fig. 6).

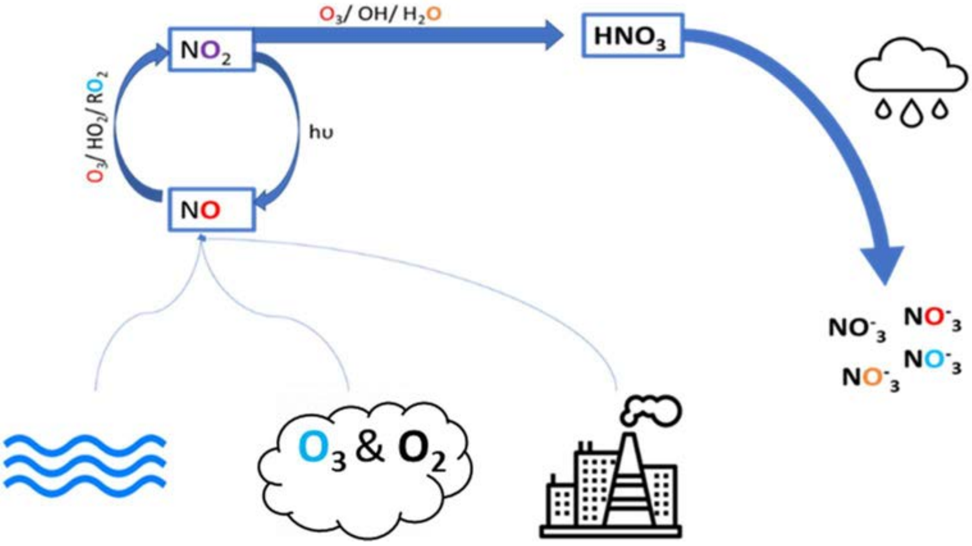

FIG. 6. Different sources of oxygen in atmospheric NO_3^-. The colours of O reflect the source molecule of oxygen (water, ozone and source compounds).

Reactive N compounds undergo a multitude of chemical reactions in the atmosphere, which can be generally grouped into two different pathways: 1) the hydroxyl (OH) pathway (Eq. 1) and 2) the N_2O_5 pathway (Eq. 2), both imprinting their isotopic signature into the resulting NO_3^-.

$$\delta^{18}\text{O-NO}_3^- = 2/3[\delta^{18}\text{O-O}_3] + 1/3[\delta^{18}\text{O-OH}] \text{ (OH pathway)} \quad (1)$$

$$\delta^{18}\text{O-NO}_3^- = 5/6[\delta^{18}\text{O-O}_3] + 1/6[\delta^{18}\text{O-H}_2\text{O}] \text{ (N}_2\text{O}_5\text{ pathway)} \quad (2)$$

where δ^{18}O-O_3 ranges between +70‰ and +120‰, δ^{18}O-OH around -44‰, and δ^{18}O-H_2O between -70‰ and 10‰ [47]. δ^{18}O-H_2O can be easily determined by analysing the stable isotope composition of precipitation or ambient moisture in the atmosphere.

Most chemical and physical reactions occur at slightly different rates for heavy and light isotopes, leading to preferential use of certain isotopes, with some reactions preferentially using heavier and others lighter isotopes. This process is called isotope fractionation. The reactions within the atmosphere that affect the formation and breakdown of NO_3^- occur with different degrees of kinetic and equilibrium fractionation. In kinetic fractionation, lighter isotopes react faster than heavy isotopes, meaning that the product will have a lower δ^{18}O-NO_3 than the substrate. At the same time, residual substrate becomes relatively 'enriched' in heavy isotopes as the reaction progresses, resulting in increasing δ^{18}O-NO_3 of remaining substrate during the reaction progress [51, 52].

Equilibrium fractionation primarily occurs in exchange reactions, but similar to kinetic reactions, it unevenly partitions heavy and light isotopes between multiple chemical species or physical phases. Although δ^{15}N-NO_3 is assumed to be a conservative tracer, isotope fractionation via photochemical transformations creates a wider range of δ^{15}N-NO_3 values. For example, the nitrogen isotope exchange between NO and NO_3^- (Eq. 1) has significant isotope fractionation (ε = +18‰) resulting in ^{15}N enrichment in the more oxidised form. This oxidation process is strongly dependent on O_3 and direct sunlight, with distinct diel and seasonal variations [47].

The stable oxygen isotope composition in nitrate can also be affected by the degree of exchange between different oxidised N intermediate compounds in the atmosphere, as many of these reactions also impart equilibrium fractionation (Fig. 6). A kinetic reaction is imparted during N transformations between particulate and gaseous forms. For a more comprehensive review of the isotope reactions involved in NO_3^- formation see [47].

A detailed understanding of these processes is critical for a complete explanation of the complex variability in δ^{15}N-NO_3 and δ^{18}O-NO_3 in rainwater. Possible changes in transport mechanisms (e.g., rain during the day versus during the night) should also be considered. Changes in atmospheric conditions are likely to create diurnal and seasonal fluctuations in rainwater NO_3^- isotopes. This variability should inform both the design of monitoring campaigns and the interpretation of the data.

4. APPLICATIONS OF STABLE ISOTOPES IN NITRATES

The combustion of fossil fuels emits NO_x into the atmosphere, which lowers pH in rain and creates 'acid rain' causing negative effects in natural environments. Furthermore, NO_x can lead to the photochemical formation of O_3 and NO_3^- aerosols that cause health issues. Similarly, to combustion processes, agricultural activities also release N_2O, NH_3 and NO_x, which can form aerosols and after chemical transformations contribute to rain acidification. These aerosols can be transported and deposited via dry and wet depositions. Nitrogen pollution transported in the atmosphere with air mass movements expands far beyond its point of geographic origin, and anthropogenic N pollution is detected even on remote coral atolls [53]. This 'extra' N added to water and soil alters ecosystem functions and has negative impacts on potable water quality, biodiversity, carbon storage, and greenhouse gas emissions [54]. Thus, identifying and managing atmospheric N sources is critical for mitigating air and rain quality degradation.

Improved pollution distribution forecasts can help decision-makers adjust their measures against air pollution. Data collection and mapping are useful for the generation of total deposition maps, and efforts on a global scale are needed to address transboundary pollution issues. These can reduce uncertainty in confirming the geographic distribution of air pollution sources. To improve these methods and the underlying models, more measurements of wet deposition are required, particularly where monitoring remains geographically sparse (e.g., Africa). Such steps towards better air quality management will play an important role in sustainable environmental management.

This overview presents four case studies where stable isotope methods were successfully applied to analyse nitrogen sources contributing to nitrates in precipitation. The case studies cover a broad range of climates, environments, and geographic locations from (1) 'pristine' places at high altitudes far from cities (see case study from Italy, section 4.1), (2) rapidly growing cities (see case study from India, section 4.2), and (3) intensive industrial and agricultural areas (see case studies from the United States of America and Brazil, sections 4.3 and 4.4).

4.1. PRISTINE LOCATIONS IN ITALY

The study area is located in the northwest Italian Alps at an elevation of 2,901 m above sea level, close to the Monte Rosa massif (Fig. 7). The station site is a node of the Long-Term Ecological Research program (LTER) established in Italy as a monitoring network of alpine tundra biome. The glaciers and snowpack of these mountains serve as 'water towers' for lowlands, and the meltwater is a major source of water for some of the major lakes in northern Italy. Chemical and the stable isotope methods are applied to obtain insights into the role of atmospheric deposition in nitrogen cycling and to assess the potential impact of the long-range transport of nitrogen species on soil and aquatic ecosystems.

Extreme weather conditions in high-elevation alpine environments are the main challenges constraining in-field activities and resulting in low temporal resolution data sets. The presence and/or absence of snow requires specific sampling techniques to monitor wet deposition. Nutrient concentrations and chemical characterizations have rarely been investigated in wet depositions and surface waters in alpine tundra. This pilot study aims to fill this knowledge gap.

FIG. 7. Long Term Ecological Research (LTER) site at Angelo Mosso Scientific Institute, Italy. Photograph courtesy of Michele Freppaz.

In this study area, the seasons were defined by the presence/absence of the snowpack. The snow season commonly starts in November and ends at the beginning of July, and the snow-free season covers only July to September. The total annual sum of precipitation (snow and rain) ranged from 1200 mm to 1800 mm during the 2018–2020 observation period. The contribution of rain to the total amount of precipitation was about 30%.

The analysis of backward trajectories revealed that the most frequent clusters contributing to precipitation were regional, and mostly came from i) north and northwest, ii) south, with a Mediterranean origin, and iii) from east and northeast, including Po valley.

Chemical analysis of rainwater and snow showed that Ca^{2+} was the dominant ion in precipitation. Ammonium was the main inorganic N form in rain samples, contrary to NO_3^- that was prevailing in snow. The rain samples had higher concentrations of all chemical species compared to snow, including N compounds. The rain concentrations of NO_3^- were 2.9, NH_4^+ were 5.4, and SO_4^{2-} 4.9 times greater than in the snow.

In rain and snow, the significant correlation observed between Na^+ and Cl^- and Ca^{2+} and Mg^{2+} suggested a contribution of marine aerosols, as well as crust and soil dust. The correlation between NO_3^- and SO_4^{2-} in rain but not in snow revealed that contributions from anthropogenic sources were greater during the summer than during the snow-covered season.

For most analysed chemical compounds, the contribution of the snow component to the total deposition fluxes was substantial, reflecting loads, respectively, to concentration and the precipitation volumes. For NO_3^-, the rain contribution ranged between 31% and 56% annually, respectively, to the year of observation. For NH_4^+ the rain contributed about 50% in 2018 and 2019, while it reached 79% in 2020. Despite the relatively low NO_3^- and NH_4^+ concentrations recorded in rain and snow, a large amount of precipitation leads to the formation of a high N annual load, exceeding the critical load equal to 1.5 kg ha^{-1} y^{-1} [55]. This load makes alpine tundra aquatic ecosystems vulnerable to structural and functional alterations.

The δ^{15}N-NO_3 composition of NO_3^- ranged between -10.6 to -2.2‰ for rainwater and between -0.7‰ and -5.2‰ for snow samples. The temporal change in δ^{15}N-NO_3 in rainwater samples showed a clear decreasing trend from July to August and an increasing trend from August to September (Fig. 8). The high δ^{15}N-NO_3 values in snow samples, compared to rainwater samples, likely result from NO_3^- loss through post depositional processes, such as photolysis and volatilization as HNO_3 which trigger isotopic enrichment in ^{15}N.

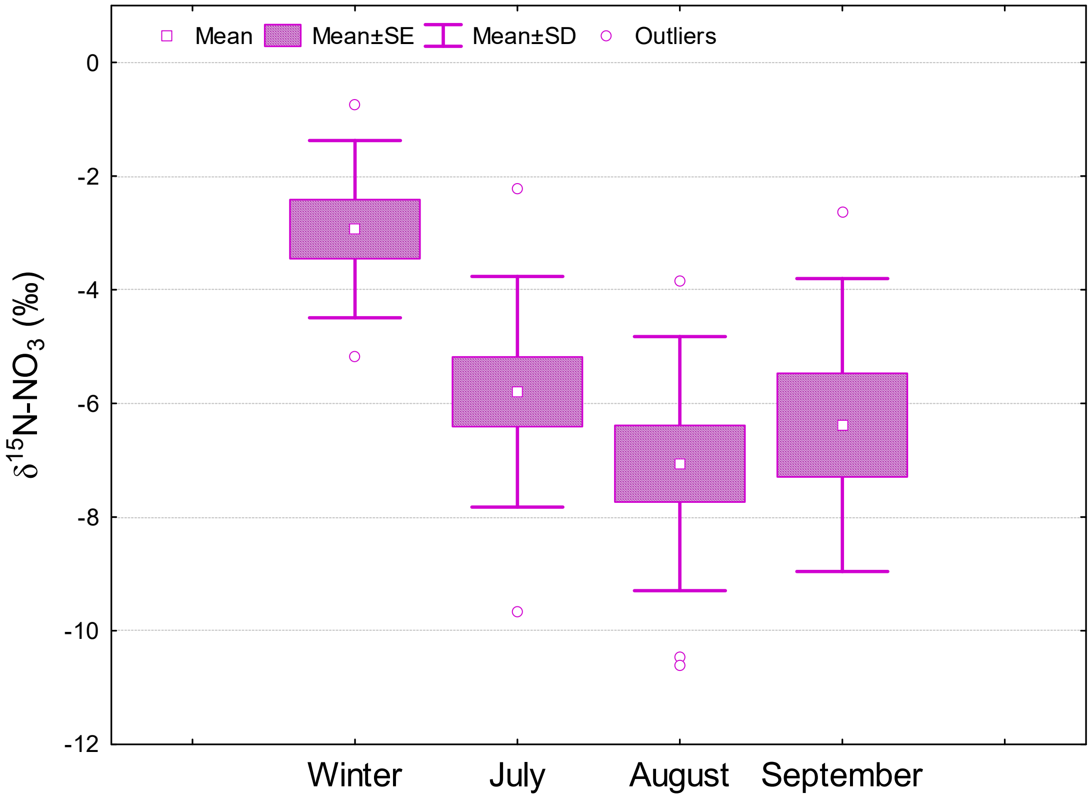

FIG. 8. Box plots of δ^{15}N-NO_3 for the summer months and the mean for winter. For snow samples, it was not possible to assign monthly values because the snowpack was collected at the maximum accumulation phase from the deposited snow.

The δ^{15}N values were within ranges overlapping with values typical for vehicle emissions (-20 to +17‰) and biomass burning (-10 to +10‰) (Fig. 9). Although, NH_4^+/NO_3^- ratios higher than 1.0 are indicative of agricultural influence, this was not reflected in the δ^{15}N-NO_3 values, which could be due to masking from different sources or atmospheric oxidation processes.

To assign hypothetical mean δ^{15}N values to the air mass trajectories, the contributions of air masses of different origins (Mediterranean, Po valley, polar, oceanic, and arctic) were calculated for weekly periods according to the precipitation amount associated with each trajectory. Next, the weeks showing higher than 80% representation for air masses from one of the described origins were selected, and the δ^{15}N-NO_3 value of that week was assigned. Precipitation derived from air masses with long-range trajectories presented the highest δ^{15}N-NO_3 values, while those with more local influence, particularly air masses coming from the east (e.g., Po valley), were characterised by the lowest δ^{15}N-NO_3. The low δ^{15}N-NO_3 could indicate the influence of emissions derived from agriculture. The increase of δ^{15}N-NO_3 shows influence of combustion sources from power generators and industries.

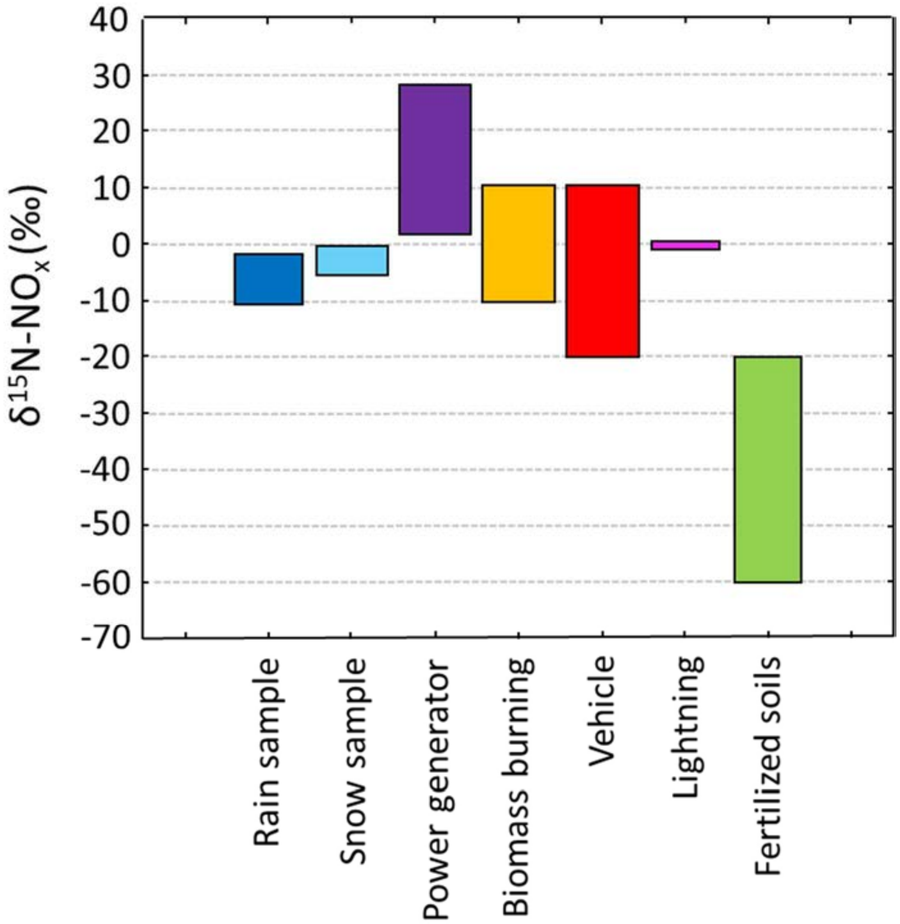

FIG. 9. Precipitation range of $\delta^{15}N\text{-}NO_3$ values in this study versus literature range ($\delta^{15}N$ in NOx) values by emission source [48].

The study displays that combined chemical and stable isotope analyses of nitrogen compounds in snow and rain deposition combined with hydrometeorological techniques were useful in identifying the sources of inorganic N loadings and the possible influence on terrestrial ecosystems.

4.2. AGRICULTURAL IMPACT IN INDIA

The economy of India depends on agricultural productivity, and the fertile land of the eastern part of India is one of the most important hubs for agricultural activity globally. To understand the impact of agricultural activity on the chemical composition of the atmospheric precipitation, a study was conducted in the Mohanpur area (Fig. 10). This region is situated 50 km north of Kolkata, which is a mega city in the eastern part of the country with a population >15 million (2023). The area in and around Mohanpur is characterised by multi-crop production, although rice and vegetables are the major cash crops produced.

FIG. 10. Area of the case study, Mohanpur area *in India. Photograph courtesy of Ajay Ajay.*

To increase agricultural productivity, the use of urea fertilizers has increased almost three times over the last 30 years [56]. Although the overall impact of excess use of urea in agricultural practice remains to be tested, its impact on groundwater has already been observed in several places in India, resulting in elevated NO_3^- concentrations in groundwater [57]. It is also important to test how agricultural activities impact the chemical composition of atmospheric precipitation and the contribution of urea from agricultural application to NO_x emissions.

Dissolved NO_3^- was measured in precipitation for the period 2019–2021. Precipitation samples were collected during the day and at night. During 2019, samples were collected once every 24 hours and during 2020 and 2021, samples were collected based on rain events and categorised as day or night (Fig. 11C). The stable nitrogen and oxygen composition was analysed in nitrates and the stable hydrogen and oxygen composition in water. The monsoon season (June to September) was characterised by lower NO_3^- concentrations (2.68 ± 2.71 mg L^{-1}) compared to non-monsoon months (4.08 ± 2.75 mg L^{-1}), as the NO_x is more frequently removed from the atmosphere due to the high frequency of precipitation (Fig. 11A).

On the seasonal scale, the monsoon season is characterised by a lower $\delta^{18}O$ value in NO_3^- in precipitation (from +30 to +66‰; Fig. 11D). The $\delta^{18}O$-NO_3 depends upon the oxidation pathway of NO_x to NO_3^- and the source of oxygen (Section 3.3.). Nitrogen oxides can be oxidised by tropospheric O_3 which itself is characterised by a high $\delta^{18}O$ (from +90 to +122‰; Fig. 11D). This results in higher $\delta^{18}O$-NO_3 in rainwaters (from +50 to +76‰; Fig. 11D). This oxidation pathway is significant when the water vapour concentration in the atmosphere is low, such as during the non-monsoon season. Atomic oxygen formed from the photolysis of O_3 reacts with water vapour (with typically very low $\delta^{18}O$ in high precipitation events) in the atmosphere to generate OH radicals. Thus, during the monsoon season NO_x is dominantly oxidised by the OH radicals due to the high concentration of water vapour in the atmosphere and its low $\delta^{18}O$ values.

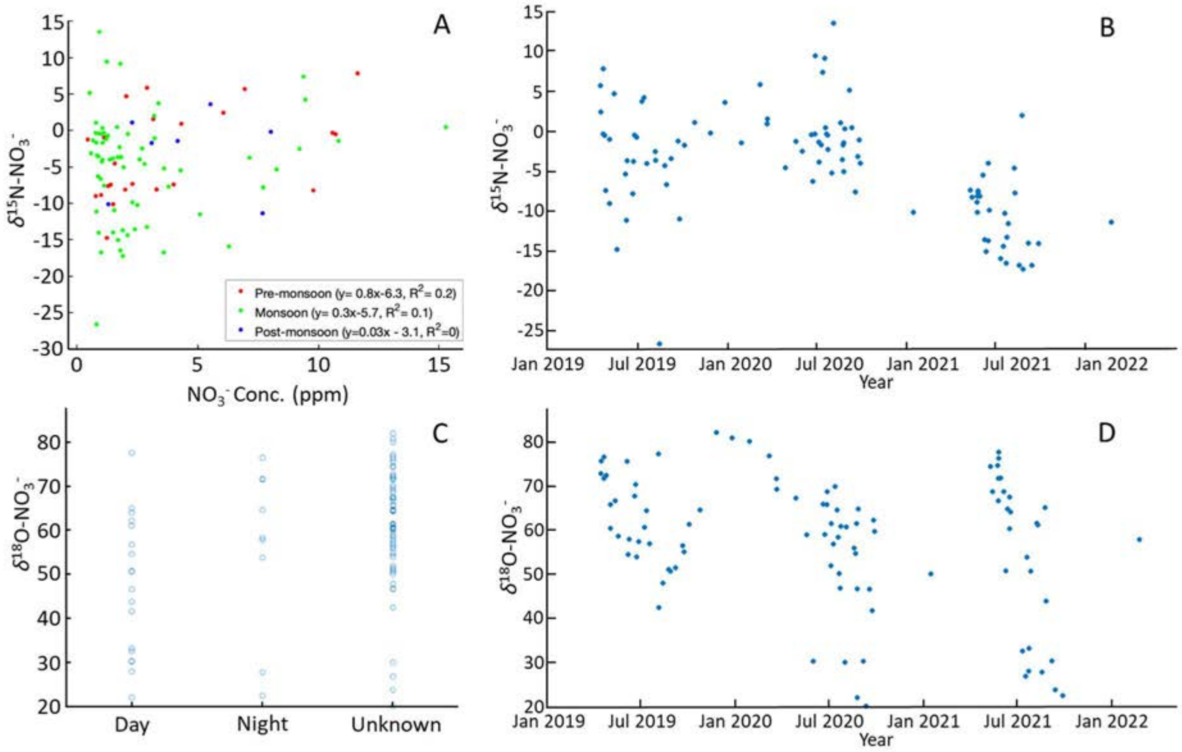

FIG. 11. A) Comparison of δ^{15}N-NO$_3$ with NO$_3$ concentrations split into seasonal groups of pre-monsoon, monsoon, and post-monsoon; B) Measurements of δ^{15}N-NO$_3$ during the 2019-2022 time period; C) Measurements of δ^{18}O-NO$_3$ values organised by time of day sampled; D) Measurements of δ^{18}O-NO$_3$ during the 2019-2022 time period (Sanyal, unpublished).

The seasonal cycle of δ^{15}N-NO$_3$ values showed intra-annul variation, characterised by the two minima occurred in January to February (from -15 to -10‰) and May to June (from -15 to -5‰) (Fig. 11B). Contrary to δ^{18}O in NO$_3$, the δ^{15}N-NO$_3$ values do not have pronounced seasonal cycles that can be used for the NO$_x$ sources identification. Nitrogen oxides are emitted into the atmosphere as an intermediate product during nitrification and denitrification. Nitrification results in lower δ^{15}N-NO$_x$, whereas denitrification results in higher δ^{15}N-NO$_x$ values in the emission [58]. However, it has been shown that, after a couple of days, fertilizer denitrification becomes a dominant process [59]. In this case study, fertilizers are sprayed in excessive amounts for rice cultivation just before the onset of the monsoon, which may cause progressive enrichment in δ^{15}N in rainwater throughout the monsoon period. During the pre-monsoon season, air parcels travel through the Ganga plain, where most of NO$_x$ is coming from the biomass burning resulting in δ^{15}N-NO$_3$ ranging from -7 to +12‰. During monsoon season, the air parcel comes from the southeast direction, where most of the NO$_x$ is emitted from coal combustion carrying δ^{15}N-NO$_3$ of +19.5‰, and therefore variation in δ^{15}N-NO$_3$ value reflected a change in the NO$_x$ from these two sources [60, 61].

Although the δ^{15}N-NO$_3$ show variation, overall low values suggest atmospheric NO$_3^-$ contribution from soil fertilizer decomposition. Therefore, it is important to regulate the excess use of fertilizer in agricultural practices to the optimal level required by crops. This practice will not only improve the quality of groundwater, but also improve the air quality and will reduce overall fertilizer costs.

4.3. TRAFFIC VERSUS AGRICULTURE IN THE MIDWESTERN UNITED STATES OF AMERICA

Environmental planners, regulators, and governmental officials often use 3D chemical transport models (e.g., see Fig. 12) for forecasting air quality and developing remediation best-practice solutions to remediate poor air quality. However, for this to be effective, air quality models must be accurate in their prediction of air pollutant concentrations.

The accuracy of air quality models is generally based only on their ability to simulate observed ozone (O_3) and particulate matter concentrations, ignoring other pollutants like NO_x, SO_2 and organic compounds. Most models cannot predict within 50% of the observed levels of O_3 and particulate matter. This uncertainty is often related to the chain of chemical reactions and transformation processes used in the models. The selection of the best method to validate these models remains problematic and requires a new approach for models' correction and evaluation. To address this issue, a stable nitrogen isotope composition of NOx has been added to the chemical transport models.

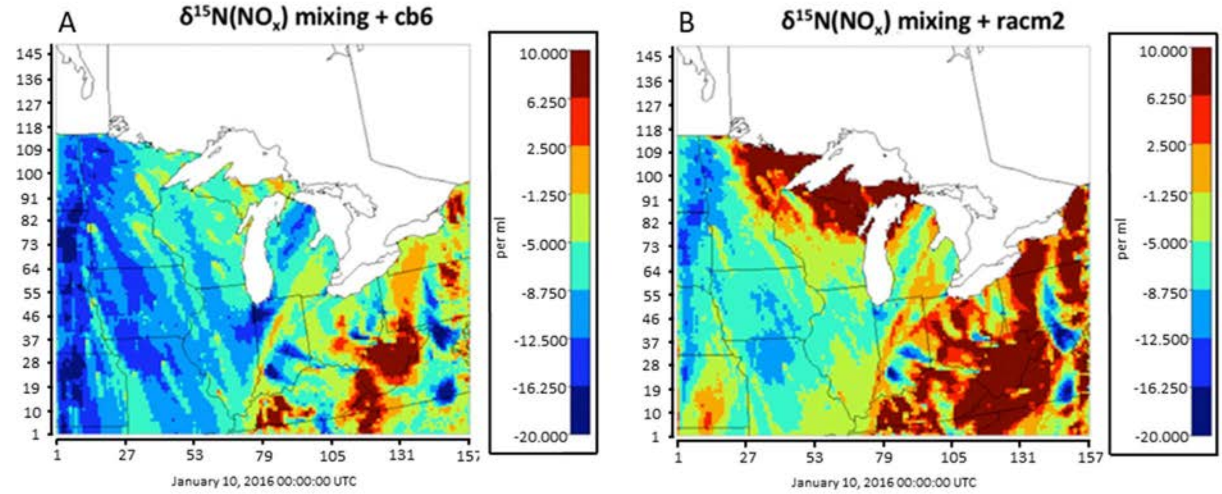

FIG. 12. 3D chemical transport modelling of the $\delta^{15}N$-NO_3 using two different chemical mechanisms with all other factors drawn from the same datasets: A) pollutant emissions and B) meteorological transport [24]. Displayed are the Carbon Bond VI (cb6) mechanism (A) and the Regional Atmospheric Chemical Mechanism (racm2) (B) [62, 63].

The $\delta^{15}N$-NO_3 models [24, 62, 63] show their relevance for a better understanding of how two different chemical mechanisms can predict very different $\delta^{15}N$ of compounds like NO_x and NO_3^- (Fig. 12). The two models displayed above are the carbon bond VI (cb6) mechanism (the newest variant of Carbon Bond atmospheric transport modelling mechanisms; Fig. 12A) [62] and the Regional Atmospheric Chemical Mechanism (racm2) (built upon the regional atmospheric chemistry mechanism (RACM) through the inclusion of ^{15}N into the pre-established atmospheric organic and inorganic chemistry processes; Fig. 12B) [63]. Therefore, measuring $\delta^{15}N$ in rain across broad spatial and temporal scales provides a new means of proving the accuracy of certain mechanisms in these important models.

Stable isotope-enabled 3D chemical transport models are useful in three ways. The first is to evaluate the accuracy of the models for predicting air pollutants and diagnosing their limitations. Second, they can be used to validate current pollution emission estimates (emission inventories). Third, they predict the isotope composition of compounds like NO_3^- that can then be used as tracers as the deposited pollutants move through the biosphere, soils, and waters. To maximise the utility of this $\delta^{15}N-NO_3$ model validation approach, more measurements across a range of spatial and temporal scales are required.

4.4. MARINE TRANSPORT EMISSIONS IMPACT ON AIR QUALITY IN BRAZIL

In this study, different techniques are being used to assess the origin of N in air pollution on a continental scale and its wet deposition as NO_3^- in a tropical region (southeast Brazil), including assessments of seasonal patterns. The stable nitrogen and oxygen compositions in nitrates and stable hydrogen and oxygen compositions in water were analysed during a one-year monitoring period. These stable isotope results were used in conjunction with concentration data of other chemical components in rainwater, backward trajectory analysis of air masses from the monitoring point, meteorological data, geospatial mapping of possible sources and atmospheric NO_x, and source apportionment analysis models. This integrated approach is intended to contribute new insights into the sources of atmospheric N in a tropical urban region of a country that has a vast territory and diversified economic and industrial activities. Several data sets were used to explain observed values, including: (i) quantitative reports on wet deposition of N species; (ii) identification of seasonal patterns; and (iii) processes that may be related to the dynamics of NO_3^- wet deposition.

Systematic monitoring of $\delta^{15}N-NO_3$ and $\delta^{18}O-NO_3$ in precipitation was carried out in 2019–2020 in the city of Belo Horizonte. The city is a metropolitan tropical region in Brazil (Fig. 13). Air pollution control is a major challenge and priority in Brazil, as air quality issues are considered responsible for > 50,000 deaths per year [64]. NO_x air pollutants originate predominantly from fossil fuel burning from industrial plants, vehicles, biomass burning, and agriculture [65].

The main challenge in the region is the lack of data to identify the origin of air pollutants in the city and the region to take necessary mitigation measures. Another challenge is emissions originating from the Amazon, Pantanal, and Cerrado regions, that represent important ecosystems, but have been severely affected by land use changes and suffered from 'slash and burn' practices. In addition, despite the intense activity of ports along some regions of the Brazilian coast, the contribution of ship emissions to atmospheric pollution has not yet been investigated.

FIG. 13. Area of the case study from Brazil. Photograph courtesy of Ricardo Gomes Passos.

The mean N-NO_3 concentrations in rainwater were weighted by the precipitation amount. For the whole monitoring period N-NO_3 concentrations varied between 0.063 and 0.959 mg L^{-1}. The general trend indicated that higher NO_3^- concentrations were present during the dry season and were lower in the wet season. A total wet N-deposition of ~12 kg N ha^{-1} per year confirmed high air pollution, with 37% of N-pollution originating from nitrate (4.6 kg N-NO_3 ha^{-1} per year).

The δ^{15}N-NO_3 values observed in precipitation, ranged from -8.46 to +4.05‰ and δ^{18}O-NO_3 values varied between +25.93‰ and +63.48‰. The δ^{15}N-NO_3 values were within the common range typical for precipitation (from -16 to +10‰). However, the wide range and temporal and spatial variations in δ^{15}N-NO_3 indicated that multiple sources of NO_x contributed to air pollution. These sources varied seasonally, reflecting dominant air mass movements and differences in the spatial distribution of pollution sources. A decreasing trend in NO_3^- and NH_4^+ concentrations and in δ^{18}O-NO_3 were observed during the wet season and can be explained by "precipitation amount effect" that means the strong correlation between isotope delta values and precipitation amount.

A period of high NH_4^+/NO_3^- molar ratios was registered during the middle of the wet season with values close to 8. After the mid-wet season, the values decreased to < 1. Two other high NH_4^+/NO_3^- molar ratio values were observed during the period of partial lockdown due to the COVID-19 pandemic. These high values and the period with a decreasing trend with values below unit may reflect changes in contributions from different N-sources. In contrast to concentrations and to δ^{18}O-NO_3, no clear seasonal pattern in δ^{15}N-NO_3 was identified within one year of monitoring, and likely the isotope variation was mostly related to the changes in pollution sources (Fig. 14).

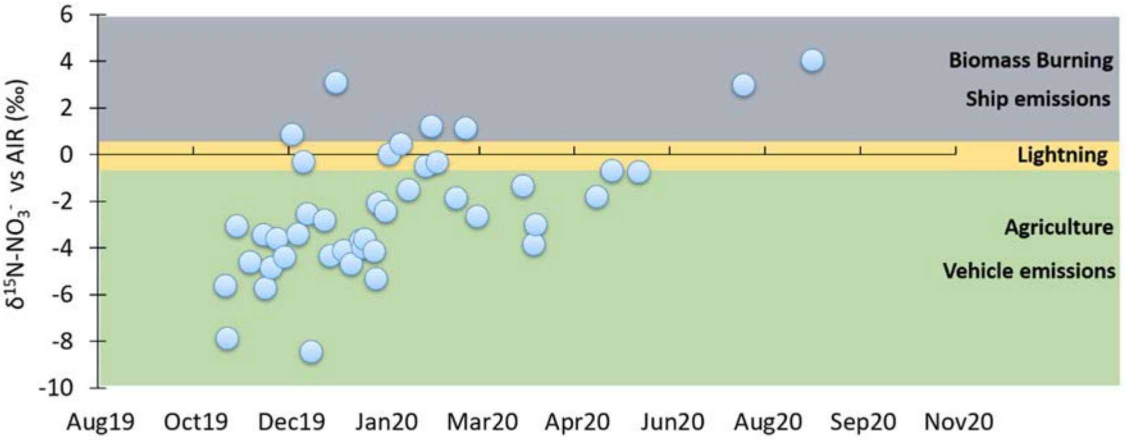

FIG 14. δ^{15}N-NO_3 data reflect the typical ranges of the expected sources.

The analysis of all calculated 96-hour air masses backward trajectories that arrived at the monitoring site shows spatial differences in air mass origin. A long-range transport in all directions was observed, but the most frequent air masses arrived from the direction of the Minas Gerais state. These masses were mainly from the east and northwest, reflecting coastal and central areas of the country. The clustering analysis based on the latitude and longitude of the air mass origin resulted in three different clusters that differed in distance and direction of air mass movements (Fig. 15). The green cluster includes air masses of southern origin, transporting air through the region of the country with the highest density of polluting sources, including transport, industries, and agriculture. Red cluster air masses from an eastern origin, with a marine impact (Atlantic Ocean), and passing through a region of intense ship traffic and port activity at the coast. The red cluster represents trajectories carrying higher NO_3^- concentrations and higher $\delta^{15}N$-NO_3. The blue cluster covers a range of trajectories that start from the most central region of the country, with the intensive mixing of several N-sources.

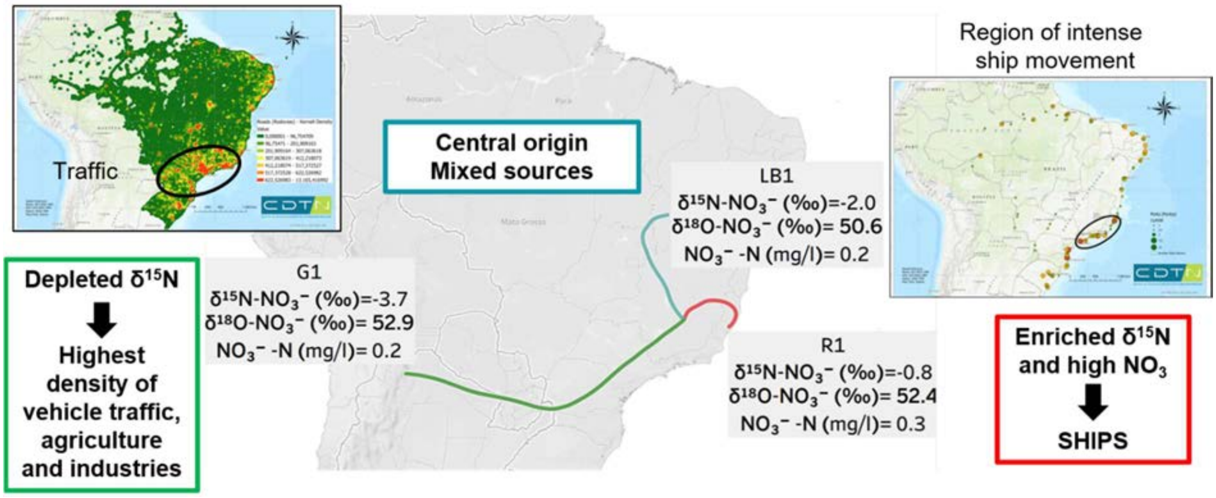

FIG 15. Trajectories clusters based on latitude and longitude data with average values of NO_3^- concentration and $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3.

Stable isotope composition of nitrates combined with meteorological, hydrochemical, and spatial distribution data was applied to trace the influence of local and distal emission sources in rainwater, the amount of the total deposited N, and the causes of temporal variation of NO_3^- concentration in rainwater. The survey revealed two major origins of NO_3^- in rainwater: 1) urban emissions (including vehicles and industries) and 2) long-range transported emissions from ships located in coastal zones [66].

Individual rain events also revealed the influence of wildfire emissions coming mainly from the Pantanal and Amazon areas. The total N deposition load showed intermediate to low air pollution, but at the levels potentially causing water quality degradation. Stable nitrogen and oxygen isotope composition of nitrates revealed that the air quality degradation in the city of Belo Horizonte is not only related to local N emissions but also to N air pollutants released far from the monitoring site.

5. DISCUSSION AND FUTURE DIRECTIONS

Atmospheric emissions impact air and water quality across local, regional, and global scales. Despite the recent reduction in global N emissions [67] NO_x still significantly contributes to acidification and eutrophication of soil and water and requires appropriate mitigation and adaptation actions [68]. Mitigation strategies targeting the further reduction of atmospheric N emissions, including N_2O greenhouse gases in the atmosphere, need to be implemented to reduce the health risks for humans and improve environmental outcomes. Therefore, further development of monitoring strategies, more accurate analysis and quantification of pollution sources, evaluation of data interpretation, and a translation of science into policy are necessary. Long-term observations of stable N and O stable isotope compositions and concentrations of NO_3^- in precipitation at global, regional, and local scales are currently very limited. However, the impact of the proposed future emission reduction policies should be assessed to quantify their efficacy under changing climate conditions.

Implementation of long-term studies requires dedicated logistics for sampling on a global scale and harmonization of research strategies, sampling protocols, and analytical techniques. The experience obtained during this CRP is an important step in developing guidelines and protocols that could serve as a reference for future efforts. Establishing a global network for monitoring N isotopes in atmospheric waters can be a major targeted outcome to enable long-term observations. IAEA programmes, such as the IAEA Global Network of Isotopes in Precipitation (https://www.iaea.org/services/networks/gnip) or the Global Network of Isotopes in Rivers (https://www.iaea.org/services/networks/gnir), can serve as templates for future efforts in developing these monitoring strategies. Further strengthening and developing analytical capacities through the IAEA Technical Cooperation Programmes on a regional scale is needed, especially in developing countries, where these analytical techniques are limited.

The stable N and O isotope compositions in NO_3^- depends on the isotopic signature of the NO_x sources and the changes due to isotopic fractionation. Therefore, while isotopes can improve the estimation of N source contribution in the atmosphere at the local, regional, and global scales, better determination of N sources transformation is still required. This will improve the accuracy of the calculation of fractionation factors for key N-related chemical processes. These efforts could be supplemented by developing comprehensive models, such as the Regional Atmospheric Chemistry Mechanism model (RACEM) that incorporates $\delta^{15}N$-NO_3 into the simulation of N reactions in the atmosphere. This model was made open access and offers a simple online graphical user interface that can improve data interpretation.

A development of stable N and O in atmospheric NO_3^- precipitation networks will help to improve data interpretation on a global scale and further determine the fate of atmospheric N and the proportional contribution of emitting sources. Isotopes can also improve the delineation of local and distal N sources. Air pollution is not limited by the boundaries of cities, states or countries. Therefore, the regulation of emissions and responsibilities cannot be managed solely at the local scale but requires the development of a global observation network for stable NO_3^- isotopes in precipitation. To ensure better understanding of the local and distal sources, high-frequency sampling campaigns are necessary [69]. Current investigations have largely focused on the stable isotope composition of inorganic species. Organic N is another important component of atmospheric N, which can account for 30% of the total N in wet deposition in many regions but is usually not monitored at all.

Over the long term, climate change will worsen air pollution, even in areas where it has recently been improving [70]. Particularly, climate change is resulting in hotter and drier conditions, leading to increased frequency and intensity of wildfires that release large quantities of smoke, which is carried long distances by wind. Therefore, climate change and air quality are strongly connected, and attention should be paid to the reduction of atmospheric emissions (e.g., reduction fossil fuel use and associated emissions, and a shift towards low-carbon energy production).

Decision makers require comprehensive datasets to underpin decisions. However, modelling efforts of atmospheric NO_3^- is currently limited. A better understanding of air quality pollution sources, processes, transformations, and impacts in the water and soil should be translated into action that could support prevention, mitigation, and control strategies for atmospheric N pollution. Economic activities, such as farming, industries, and fossil fuel combustion processes (e.g., automobiles and electrical generation), are the main contributors of anthropogenic atmospheric N pollution. Therefore, different actions have to be taken to minimise the contribution of local pollution sources to the atmosphere. These include more sustainable use of fertilizers in agriculture or controlling fossil fuel emissions.

This publication was developed based on the results of the CRP F32008 – Global Monitoring of Nitrogen Isotopes in Atmospheric Waters, which gathered participants from 16 countries with different study areas and approaches. The overall aim of the CRP project was to evaluate the use of stable nitrogen and oxygen isotope compositions of NO_3^- isotopes in precipitation to partition N sources contributing to atmospheric N wet deposition.

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