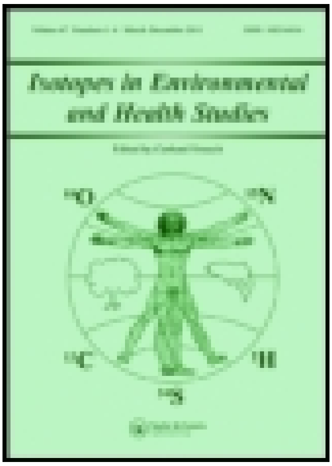
This article was downloaded by: [Greg Michalski]
On: 21 July 2015, At: 09:26
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: 5 Howick Place, London, SW1P 1WG



Click for updates

Isotopes in Environmental and Health Studies

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gieh20

Oxygen and nitrogen isotopic composition of nitrate in commercial fertilizers, nitric acid, and reagent salts

Greg Michalski[a][b], Michelle Kolanowski[b] & Krystin M. Riha[a]

[a] Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, IN, USA

[b] Department of Chemistry, Purdue University, West Lafayette, IN, USA

Published online: 16 Jul 2015.

To cite this article: Greg Michalski, Michelle Kolanowski & Krystin M. Riha (2015): Oxygen and nitrogen isotopic composition of nitrate in commercial fertilizers, nitric acid, and reagent salts, Isotopes in Environmental and Health Studies, DOI: 10.1080/10256016.2015.1054821

To link to this article: http://dx.doi.org/10.1080/10256016.2015.1054821

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Isotopes in Environmental and Health Studies, 2015
http://dx.doi.org/10.1080/10256016.2015.1054821

Oxygen and nitrogen isotopic composition of nitrate in commercial fertilizers, nitric acid, and reagent salts

Greg Michalski[a,b*], Michelle Kolanowski[b] and Krystin M. Riha[a]

[a]*Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, IN, USA;* [b]*Department of Chemistry, Purdue University, West Lafayette, IN, USA*

(*Received 4 November 2014; accepted 13 April 2015*)

Nitrate is a key component of synthetic fertilizers that can be beneficial to crop production in agro-ecosystems, but can also cause damage to natural ecosystems if it is exported in large amounts. Stable isotopes, both oxygen and nitrogen, have been used to trace the sources and fate of nitrate in various ecosystems. However, the oxygen isotope composition of synthetic and organic nitrates is poorly constrained. Here, we present a study on the N and O isotope composition of nitrate-based fertilizers. The δ^{15}N values of synthetic and natural nitrates were 0 ± 2 ‰ similar to the air N_2 from which they are derived. The δ^{18}O values of synthetic nitrates were 23 ± 3 ‰, similar to air O_2, and natural nitrate fertilizer δ^{18}O values (55 ± 5 ‰) were similar to those observed in atmospheric nitrate. The Δ^{17}O values of synthetic fertilizer nitrate were approximately zero following a mass-dependent isotope relationship, while natural nitrate fertilizers had Δ^{17}O values of 18 ± 2 ‰ similar to nitrate produced photochemically in the atmosphere. These narrow ranges of values can be used to assess the amount of nitrate arising from fertilizers in mixed systems where more than one nitrate source exists (soil, rivers, and lakes) using simple isotope mixing models.

Keywords: fertilizer; nitrate; nitric acid; nitrogen-15; oxygen-17; oxygen-18

1. Introduction

Nitrate is an important compound in healthy natural, agricultural, and urban ecosystems but it can have negative impacts at elevated levels. Excess nitrate can lead to eutrophication in lake, riverine [1], estuary, and coastal waters [2,3], which can result in hypoxia [3] and the destruction of fisheries and other aquatic life. In terrestrial ecosystems, plants that have evolved to more effectively take up excess nitrate have a competitive advantage over other species, which can lead to shifts in biodiversity [4,5]. Nitrates in drinking water have been linked to a number of negative health effects in humans [6–8] and livestock [9], and it is a regulated groundwater pollutant by the United States Environmental Protection Agency. Nitrate is a major component of acid rain [10,11] and harmful, respirable particulate matter [12–14] in urban areas [15,16]. Therefore, understanding the sources of nitrate is important from ecological, economic, and human health perspectives.

Nitrate is produced in a number of ways, both naturally and by human activities, and stable isotopes have proven useful as tracers of these pathways. Nitrification is the main source of

---

*Corresponding author. Email: gmichals@purdue.edu nitrate; it is a broad category that refers to the process of microbial oxidation of ammonia (NH_3) found in the soil, water, sewage, and manure [17]. Synthetic fertilizers are another major source of nitrate both directly, as nitrate contained in the fertilizer, and from the post application nitrification of NH_3 fertilizers in soils [18,19]. The third major source is atmospheric nitrate, which is formed when nitrogen oxide, produced by lightning, fossil fuel combustion, and as a by-product of nitrification/denitrification, is oxidized to nitrate by photochemical radical chemistry in the atmosphere [16,20].

The different mechanisms that produce nitrate are often accompanied by isotope effects. Nitrate production by any pathway can differentially incorporate $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios (R) resulting in unique $\delta^{15}N$ and $\delta^{18}O$ values, where δ (‰) $= [R_{\text{sample}}/R_{\text{standard}} - 1]\cdot 1000$. The $\delta^{15}N$ values are by convention reported with respect to air N_2 and $\delta^{18}O$ according to the Vienna Standard Mean Ocean Water (VSMOW). If unique, these δ values can be used relative to determine the mole fraction of each nitrate source in systems where two or more source contributes to the nitrate load [21–24] and no secondary isotope fractionating process such as denitrification is significantly occuring. For example, nitrate produced photochemically in the atmosphere has elevated $\delta^{18}O$ values [25,26], while those by microbial nitrification are near 0 ‰ [27,28]; $\delta^{15}N$ values in nitrate derived from manure [29] are distinct from synthetic N fertilizers [30]. The ^{17}O has also proven useful for portioning nitrate sources, in particular atmospheric nitrate [31]. During most chemical and biological reactions, isotopes fractionate in a manner dependent on relative mass differences, and the relationship $\delta^{17}O \sim 0.52\,\delta^{18}O$ is normally observed [32]. This relationship is not observed in nitrate produced photochemically; this deviation is quantified approximately as $\Delta^{17}O = \delta^{17}O - \lambda\delta^{18}O$ and exactly as $\Delta^{17}O = 1000\ln(\delta^{17}O/1000 + 1) - \lambda 1000\ln(\delta^{18}O/1000 + 1)$, where λ is the isotope mass-dependent proportionality factor that can range from 0.49 to 0.53 depending on whether the system is controlled by kinetics and/or equilibrium. Atmospheric nitrate has $\Delta^{17}O$ values that typically range from 20 to 34 ‰ [31–34], making them isotopically unique relative to microbial nitrate.

Although a major source of nitrate in agro-ecosystems is nitrate directly applied as fertilizer, surprisingly the oxygen isotope composition of this source remains poorly constrained. The main forms of fertilizer nitrate are ammonium nitrate (NH_4NO_3) and urea ammonium nitrate (UAN), but $NaNO_3$ and $Ca(NO_3)_2$ are sometimes used, albeit to a much lesser extent. In the USA, 652,607 tons of NH_4NO_3 and 10,396,439 tons of UAN were applied in 2010, accounting for 47 % of applied N [35]. To our knowledge, only two studies have published oxygen isotope data on commercial fertilizers and consisted of only a small number of samples from European manufacturers [36,37]. There is no $\delta^{18}O$ for NO_3^- based US fertilizers, synthetic salts, or commercially available HNO_3. Furthermore, there are no $\Delta^{17}O$ data for synthetic NO_3^- other than for a few isotopic standards [38]. There may be significant oxygen isotope variability within fertilizer types and brands, as well as differences between the molecular forms (i.e. UAN vs. NH_4NO_3) and place of origin. Therefore, if oxygen isotopes are to be used to help constrain the fraction of synthetic nitrate in mixed systems, a better understanding of the variability of oxygen isotopes within them is warranted. Presented herein are an O and N isotope analysis of UAN, reagent-grade nitric acid, NH_4NO_3, reagent-grade nitrate salts and natural nitrate salts approved as organic fertilizers. Also, we suggest the origin of these isotopic compositions based on the nitrate manufacturing process.

2. Methods

Fertilizer and reagent-grade nitrates were analysed for oxygen and nitrogen isotopes using several methods. Samples ($n = 270$) of liquid UAN (32 % N, 25 % of total N as NO_3^-) were obtained from the Office of the Indiana State Chemist and diluted with deionized water to a concentration of 5 µM, and 1 mL of solution was used in the analysis (500 nmol). The δ^{15}N and δ^{18}O values of nitrate in the UAN solution were analysed by conversion to N_2O using the denitrifier method [39] and calibrated using a set of working isotope reference nitrates that were calibrated to the international nitrate reference materials USGS32, USGS34, and USGS35. A subset of the UAN, nitric acid and reagent-grade solid metal/ammonia nitrate salts were analysed for Δ^{17}O and δ^{18}O by conversion to O_2 using the $AgNO_3$ decomposition method [40]. Briefly, ∼1 g of each nitrate salts was dissolved in 50 mL of DI water and passed through a cation exchange resin (Biorad AG 50). The resulting HNO_3 solution was neutralized with pre-cleaned Ag_2O. The product $AgNO_3$ solution was freeze dried, and 3–5 mg was thermally decomposed, and analysed using a dual inlet peripheral on a Thermo Delta V isotope ratio mass spectrometer. Precision using the bacteria method is ±0.3 ‰ and 0.6 ‰ for δ^{15}N and δ^{18}O, respectively, and dual inlet Δ^{17}O precision based on replicate sample analysis was ±0.04 ‰.

3. Results and discussion

The distribution of δ^{15}N values of nitrate found in commercial UAN, a common field fertilizer in the USA ($n = 270$), is shown in Figure 1. The nitrate in the UAN fertilizers was determined to have δ^{15}N of 0.2 ± 3.6 ‰ (2σ), which is similar to the δ^{15}N values of total N in other synthetic nitrates [30]. The δ^{15}N values of commercial UAN nitrate and total N in commercial fertilizers can be explained by the chemical processes used in their production. Synthetic nitrates are produced by the oxidation of NH_3 that in turn is produced by the reduction of atmospheric nitrogen (N_2). The Haber-Bosch process reacts atmospheric N_2 with hydrogen (H_2) at high pressure over an iron-based catalysts at an initially high temperature (823 K) to form NH_3: $N_2 + 3H_2 \leftrightarrow 2NH_3$ [41]. Successive recycling of products and reactants at lower temperatures (final temperature ∼ 300 K) typically results in an NH_3 yield of 97 %. The high rate of N_2 conversion into NH_3, the high temperatures, and the use of catalysts suggest that there should be little isotope fractionation between the product NH_3 and the reactant N_2. Total N in ammonium, nitrate, and urea-based fertilizers [30,36] has δ^{15}N values of −0.2 ± 2.1 ‰ ($n = 29$), demonstrating that indeed little fractionation between N isotopes occurs during the Haber-Bosch process. The synthetic ammonia is then primarily used to produce urea and nitrate, which are also used in commercial synthetic fertilizers; this is consistent with nitrate in UAN having a range of

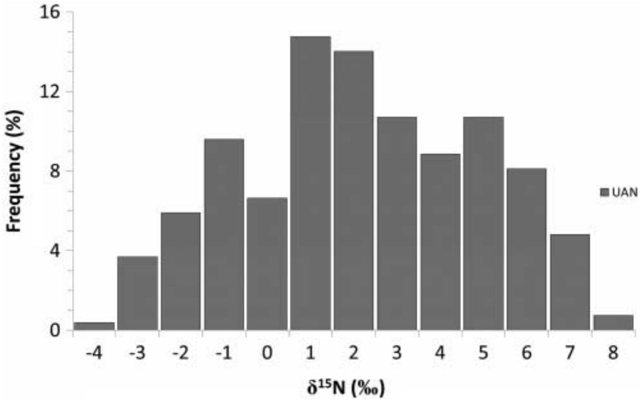


Figure 1. The δ^{15}N distribution, as percentages, of nitrate contained in 270 samples of urea-ammonium-nitrate (UAN) fertilizers. Roughly 80 % of the UAN nitrate δ^{15}N values fall between −3 ‰ and +3 ‰.

δ^{15}N values of 0.2 ± 3.6 ‰ which is similar to the δ^{15}N values of total N in other synthetic fertilizers analysed by Bateman and Kelly [30]. Therefore, the three N compounds in UAN have equivalent δ^{15}N values, thus limiting the use of δ^{15}N as a tracer of nitrate derived from different components of fertilizer N.

The δ^{18}O values in 10 different bottles of commercial-grade nitric acid (HNO_3) ranged from 23.7 to 27.5 ‰, which can be explained by the HNO_3 manufacturing process. Roughly, half of all ammonia produced in the USA by the Haber-Bosch process is converted into HNO_3 (US Environmental Protection Agency, 1995) via the Ostwald process, and insights into the expected isotopic composition of HNO_3 can be gained by understanding the steps of this process. The Ostwald process uses a Pt/Rh catalyst and high temperature (1170 K) to oxidize NH_3 into nitrate using air oxygen (O_2) and water as the oxygen reagents. This process has a 96 % conversion rate [42]. Following similar arguments made about minimal isotope fractionation occurring during NH_3 synthesis in the Haber-Bosch process, the high temperature, the near quantitative yield, and the use of catalysts make any significant ^{15}N discrimination unlikely during the Ostwald process.

Understanding the sources and isotopic composition of oxygen incorporated into HNO_3 during the Ostwald process and determining their relative fraction are more complex. From a stoichiometric point of view, the overall reaction is

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O. \tag{1}$$

However, a more accurate step-wise account of the Ostwald process is

$$4NH_3 + 7O_2 \rightarrow 2HNO_3 + 5H_2O + NO_2 + NO \tag{2}$$

with the remaining nitrogen oxides (NO_X) cycled back into the system for further oxidation into HNO_3 [42]. During the initial NH_3 oxidation (Equation (1)), the product water is generated as steam because of the high reaction temperature and subsequent exothermicity of the reaction. The steam is condensed through a heat exchanger, and a fraction of the water reacts with nitrogen dioxide (NO_2) to form HNO_3. The remainder is cooled and used in a counter column reaction tower in order to further react with NO_2 [42]. Based on the simple stoichiometry (Equation (1)), the resulting nitric acid solution should be 77 % by weight, which is above its azeotropic point (68 %) [42]. Therefore, external water sources amounting to 37–67 % of the total water must be added to the system to attain the typical HNO_3 concentrations of 55–68 % (but as low as 30 %). Waste water and water loss as steam in the vent gas account for less than 1 % of the total water [42,43], therefore isotope fractionation during water loss should have a minimal impact on the oxygen isotope composition of the HNO_3. The water deficit is partially eliminated using the water vapour present in the intake air used during the ammonia oxidation step, and the remainder through the addition of locally sourced deionized ground water. Therefore, the mole fraction of oxygen from air O_2 in HNO_3 would typically range between 0.95 (68 % HNO_3) and 0.85 (53 % HNO_3).

The δ^{18}O of the product nitric acid can be estimated assuming the δ^{18}O of the reaction water (Equation (1)) and that of nitrogen oxides are the same as air O_2 (minimal isotope fractionation at 1100 K over catalysts) by

$$\delta^{18}O_{mix} = f_{O_2}(23.5‰) + f_{H_2O}(\delta^{18}O_{H_2O}), \tag{3}$$

where f_{H_2O} and $\delta^{18}O_{H_2O}$ are the oxygen fraction and δ^{18}O value of the external water added and f_{O_2} is the fraction derived from air O_2 that has a constant δ^{18}O value of 23.5 ‰ [44,45]. The δ^{18}O value of the external water would depend on the location of the manufacturing plant and season. For the continental US where the annual δ^{18}O of precipitation ranges between 0 and –15 ‰ [46], the resulting possible values of $\delta^{18}O_{mix}$ have only a minor spread, ranging from 20.0 to 23.8 ‰.

The resulting HNO_3–H_2O mixture will come to isotopic equilibrium and the ending $\delta^{18}O$ of the HNO_3 is found from

$$\delta^{18}O_{H_2O} = \delta^{18}O_{HNO_3} - \varepsilon_{NO_3-H_2O}, \tag{4}$$

$$f_{NO_3}\delta^{18}O_{HNO_3} - (1 - f_{NO_3})\delta^{18}O_{H_2O} = \delta^{18}O_{mix}. \tag{5}$$

Substituting Equation (4) into Equation (5) and rearranging yield

$$\delta^{18}O_{HNO_3} = \frac{[\delta^{18}O_{mix} - \varepsilon_{NO_3-H_2O}(1 - f_{NO_3})]}{(2f_{NO_3} - 1)}, \tag{6}$$

where f_{NO_3} is the fraction of oxygen as HNO_3 which ranges from 0.78 (53 % HNO_3) to 0.86 (68 % HNO_3), and $\varepsilon_{NO_3-H_2O}$ is the water–nitrate isotope equilibrium enrichment factor. Calculating $\varepsilon_{NO_3-H_2O}$ based on reduced partition function ratios [47,48] yields an enrichment factor that is a linear function of T(K) over typical ambient temperatures (273–340 K) and fit the function $\varepsilon_{NO_3-H_2O} = -0.2T(K) + 82.3$. At 295 K this yields a $\varepsilon_{NO_3-H_2O}$ of 22.5 ‰ that is in good agreement with the observed $\varepsilon_{NO_3-H_2O}$ of 22.0 ‰ [38]. This oxygen isotope enrichment would be expected for bottles of HNO_3 at room temperature. The range of $\delta^{18}O_{HNO3}$ values predicted by this model, given the spread in precipitation $\delta^{18}O$ values across the continental US and the possible HNO_3 strength, is relatively narrow, between 23.6 and 27.6 ‰. This is remarkably close to the $\delta^{18}O$ of our observed values in 10 different bottles of commercial-grade HNO_3 that ranged from 23.7 to 27.5 ‰ (Figure 2).

The $\delta^{18}O$ value of nitrate in UAN ($n = 270$; Figure 3) and reagent-grade NH_4NO_3 ($n = 12$) spanned a narrow range (23 ± 2 ‰), similar to [36] and the $\delta^{18}O$ of synthetic HNO_3 ($n = 10$), which can also be explained by the manufacturing process. Ammonium nitrate is synthesized by the neutralization reaction, $NH_3 + HNO_3 \rightarrow NH_4NO_3$, and its isotopic composition largely reflects the effects of the Haber-Bosch and Ostwald processes (Figures 1–3). Water in the NH_4NO_3 solution is evaporated to form crystalline NH_4NO_3 that is either packed as solid NH_4NO_3 or mixed with urea to form UAN. This would suggest that exchange between NO_3^- and H_2O ceases upon neutralization, since evaporation would increase the remaining solution

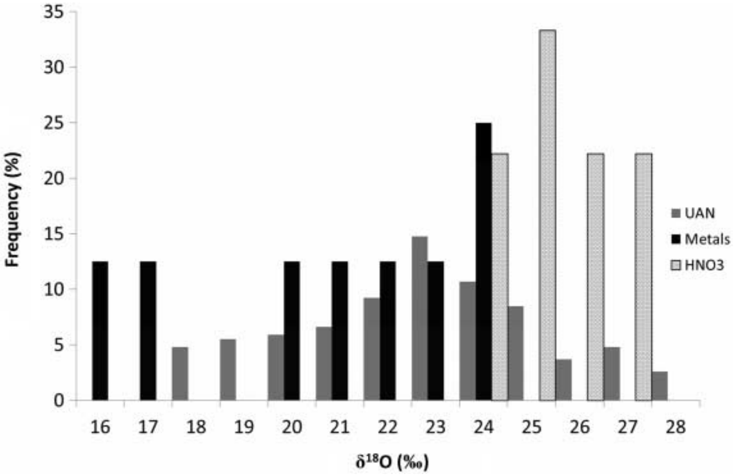


Figure 2. The frequency distribution, as percentage, of $\delta^{18}O$ values of nitrate found in UAN ($n = 270$), reagent–grade nitric acid ($n = 10$), and commercial nitrate salts, including NH_4NO_3 ($n = 12$). Most commercially made nitrate compounds have $\delta^{18}O$ values between 20 and 28 ‰ and averaging 25 ‰. Frequencies were determined by binning all measured $\delta^{18}O$ values that were ± 0.5 ‰ of the whole number value indicated by the bar.

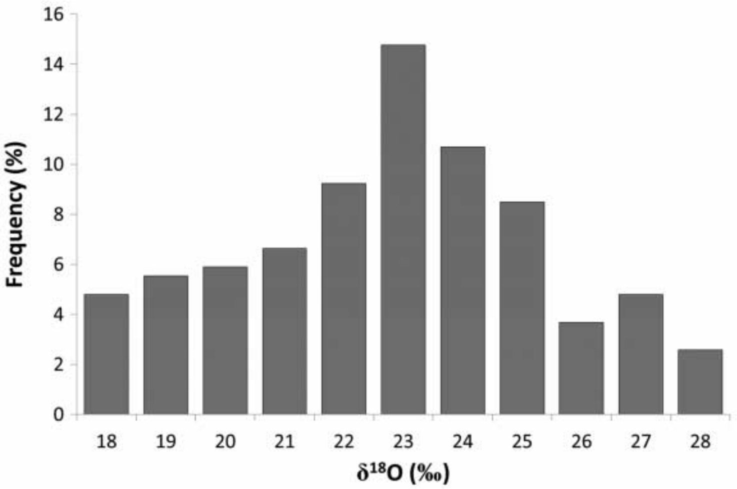


Figure 3. The frequency distribution of $\delta^{18}O$ values of nitrate found in UAN ($n = 270$) that were determined by binning all measured $\delta^{18}O$ values that were ±0.5 ‰ of the whole number value.

water $\delta^{18}O$ values, and exchange would lead to elevated $\delta^{18}O$ values in NO_3^- with respect to the initial HNO_3, which is not observed.

Metal nitrate (MNO_3) synthesis typically uses dilute HNO_3, and the $\delta^{18}O$ value of a number of commercial-grade metal nitrates reflects this dilution (Table 1). Concentrated HNO_3 can create an oxidation layer when reacting on metallic surfaces slowing the intended reaction $M + HNO_3 \rightarrow MNO_3 + ½H_2$. Commercial strength acid is therefore diluted during the synthesis of most MNO_3, and the HNO_3 should come into new isotopic equilibrium. The resulting

Table 1. Isotopic composition of commercial fertilizers, reagent-grade nitrate salts, nitric acid, and organic labelled fertilizer.

Nitrate source	$\delta^{15}N$ (‰)	$\delta^{18}O$ (‰)	$\delta^{17}O$ (‰)	$\Delta^{17}O$ (‰)
Commercial fertilizers				
UAN ($n = 270$)	0.3	24.2 ± 3.0	11.4	− 0.15 ± 0.30
$NH_4(NO_3)$ (12)	ND	28.8	14.7	− 0.24 ± 0.027
Reagent-grade nitrate				
$Cu(NO_3)_2$	ND	22.8	11.2	− 0.17 ± 0.040
$Mg(NO_3)_2$	ND	17.3	8.4	− 0.019 ± 0.037
$Al(NO_3)_3$	ND	15.7	7.5	− 0.096 ± 0.013
$Co(NO_3)_2$	ND	21.6	10.4	− 0.25 ± 0.024
$Zn(NO_3)_2$	ND	23.9	11.9	− 0.016 ± 0.04
$LiNO_3$	ND	23.0	11.3	− 0.13 ± 0.045
KNO_3	ND	24.4	12.0	− 0.14 ± 0.058
$Fe(NO_3)_3$	ND	20.4	10.1	0.040 ± 0.027
HNO_3 (10)	ND	25.7 ± 1.3	12.7	− 0.22 ± 0.02
Organic fertilizers				
Bonide Nitrate of Soda	− 1.5	49.7	44.7	18.9 ± 0.2
Hoffman Nitrate of Soda	0.5	52.6	47.2	19.8 ± 0.3
Drammatic One liquid	− 4.4	50.5	45.3	19 ± 0.4
Hi-Yield Nitrate of Soda	− 1.2	51.7	46.3	19.4 ± 0.3
USGS35	− 2	57.5	51.5	21.1 ± 0.2

Notes: Standard deviations for the analysis of the same compound but different origins (UAN, NH_4NO_3, and HNO_3) represent the range of values for that compound. $\Delta^{17}O$ standard deviation for metal nitrates reflects replicate analysis of the same sample. No $\delta^{15}N$ was determined for metal nitrates because the use of thermal decomposition (see Section 2) produces O_2.

dilute HNO_3 will have a $\delta^{18}O$ value dependent on the amount of added water and its $\delta^{18}O$ value (Equation (6)). Generally, one would expect a decrease in the $\delta^{18}O$ value in the dilute HNO_3 used to make the MNO_3 since the $\delta^{18}O$ value of meteoric water is well below that of concentrated HNO_3 (Table 1). The observation that MNO_3 $\delta^{18}O$ values range from 15.5 to 23.0 ‰ compared to concentrated HNO_3 (23.7–27.5 ‰) appears to confirm this hypothesis. Only one KNO_3 sample had a $\delta^{18}O$ value (24.4 ‰) in the range of concentrated HNO_3, and it is similar to the KNO_3 isotope standard USGS32 (25.7 ‰). This suggests that some common alkali metal nitrates may have been synthesized by neutralizing HNO_3 with hydroxides such as KOH and NaOH. These reactions would not require acid dilution and would likely happen quickly enough to inhibit any further HNO_3–H_2O exchange during the reaction.

Analysis of ^{17}O abundances also supports the hypothesis that synthetic nitrates are composed of oxygen primarily from atmospheric O_2 and a small fraction of water (Figure 2 and Table 1). All of the reagent-grade nitrates and most of the nitrate fertilizers had $\Delta^{17}O$ values near the terrestrial oxygen isotope fractionation line, ranging from $+0.04$ to -0.25 ‰ (± 0.04 ‰). The $\Delta^{17}O$ values were anti-correlated with $\delta^{18}O$ values, with $\Delta^{17}O$ values approaching zero as $\delta^{18}O$ values decreased. Measurements of modern air O_2 have shown that its $\Delta^{17}O$ value is constant at -0.223 ‰ [45,49]. In contrast, oxygen isotope variation in meteoric water induced by evaporation and condensation follows mass-dependent isotope fractionation rules and has a $\Delta^{17}O$ value of 0.0 ‰ [50]. Thus, a greater contribution of air O_2 during HNO_3 synthesis should result in higher $\delta^{18}O$ values and negative $\Delta^{17}O$ values in the HNO_3. Conversely, $\Delta^{17}O$ values should approach zero, and $\delta^{18}O$ values should decrease as the fraction of HNO_3–H_2O exchange increases with acid dilution. These trends are observed in the acid and metal nitrates (Table 1) and are therefore consistent with the hypothesis that air O_2 is the major and meteoric water a minor source of oxygen in synthetic nitrates. This mixing of primarily mass-dependent oxygen reagents and mass-dependent equilibrium reactions results in a well-defined mass-dependent isotope composition in dual isotope ratio space (Figure 4) yielding $\lambda = 0.513$.

While the majority of fertilizers and reagent-grade nitrates tested had $\Delta^{17}O$ values near the terrestrial oxygen isotope fractionation line, a subset was anomalously enriched in ^{17}O (Table 1). These fertilizers were either solid $NaNO_3$ or liquid organic fertilizers that contain nitrate and they had a narrow range of $\Delta^{17}O$ values from 19 to 21 ‰, elevated $\delta^{18}O$ values (48–55 ‰) but

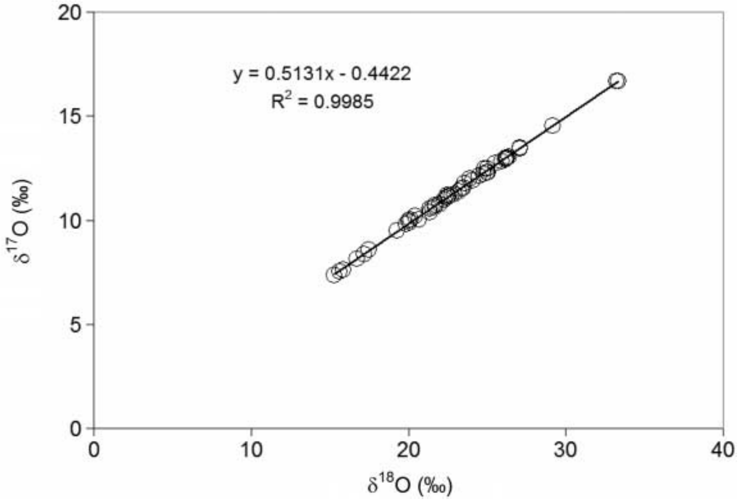


Figure 4. The $\delta^{18}O$ versus $\delta^{17}O$ of metal nitrates, nitric acid, and several UAN samples demonstrating the mass dependent isotope fractionation that occurs during nitrate synthesis yielding a $\lambda = 0.513$.

δ^{15}N values more characteristic of synthetic nitrates. The origin of these fertilizers was traced back to nitrate that was mined from naturally occurring ores located in the Atacama (Chile) and Turpan (China) deserts [51,52]. Since these are natural nitrate deposits they are considered 'organic' by regulators who certify organic agriculture practices. They are used either as pure $NaNO_3$ fertilizer or the $NaNO_3$ is added to some organic fertilizer brands as an N source. The origin of the Atacama and Turpan deposits has been linked to the deposition of HNO_3 and nitrate aerosols produced by photochemistry in the atmosphere that has accumulated in these deserts over million-year timescales [33]. Chilean nitrates had widespread use in the USA and Europe during the early 1900s prior to the expansion of synthetic fertilizer production that occurred after the Haber-Bosch and Ostwald processes were developed. In 1913, 54.7 % of the world consumption of fixed nitrogen was produced by the Chilean nitrate industry, but by 1923 production had dropped to 32.2 %, and was only 7 % by 1934. The unique Δ^{17}O and δ^{18}O compositions of Chilean nitrate have been used as isotopic 'fingerprints', pinpointing the source of nitrate in ground waters under some landscapes [53,54] that were used in agriculture during the early 1900s.

4. Conclusion

The stable isotope composition of most nitrate-based fertilizers spans a very narrow range and reflects the reagents and processes used in nitrate synthesis or its natural origin. The δ^{15}N values of synthetic and natural nitrates were 0 ± 2 ‰ similar to the air N_2 from which they are derived. The δ^{18}O values of synthetic nitrates were 23 ± 3 ‰, similar to air O_2 and natural nitrate fertilizers, δ^{18}O values (55 ± 5 ‰) were similar to those observed in atmospheric nitrate. The Δ^{17}O values of synthetic fertilizer nitrate were approximately zero following a mass-dependent isotope relationship, while natural nitrate fertilizers had Δ^{17}O values of 18 ± 2 ‰ similar to nitrate produced photochemically in the atmosphere. These narrow ranges of values can be used to assess the amount of nitrate arising from fertilizers in mixed systems where more than one nitrate source exists (soil, rivers, and lakes) using simple isotope mixing models.

Acknowledgements

We would like to thank Dr Bethany Theiling for her technical assistance.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

We would like to acknowledge National Science Foundation (NSF) DEB 0918708 for funding this work, and Robert D. Waltz, the Indiana State Chemist and Seed Commissioner, and the technical staff for providing the UAN samples.

References

[1] McIsaac GF, David MB, Gertner GZ, Goolsby DA. Eutrophication – nitrate flux in the Mississippi river. Nature. 2001;414:166–167.
[2] Paerl HW. Cultural eutrophication of shallow coastal waters. Coupling changing anthropogenic nutrient inputs to regional management approaches. Limnologica. 1999;29:249–254.
[3] Rabalais NN, Diaz RJ, Levin LA, Turner RE, Gilbert D, Zhang J. Dynamics and distribution of natural and human-caused hypoxia. Biogeosciences. 2010;7:585–619.

[4] Fenn ME, Poth MA, Aber JD, et al. Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. Ecol Appl. 1998;8:706–733.

[5] Tilman D, Wedin D, Knops J. Productivity and sustainability influenced by biodiversity in grassland ecosystems. Nature. 1996;379:718–720.

[6] Forman D. Are nitrates a significant risk factor in human cancer? Cancer Surv. 1989;8:443–458.

[7] Mensinga TT, Speijers GJ, Meulenbelt J. Health implications of exposure to environmental nitrogenous compounds. Toxicol Rev. 2003;22:41–51.

[8] Ward MH, Mark SD, Cantor KP, Weisenburger DD, Correa-Villasenor A, Zahm SH. Drinking water nitrate and the risk of non-Hodgkin's lymphoma. Epidemiology. 1996;7:465–471.

[9] Hooda PS, Edwards AC, Anderson HA, Miller A. A review of water quality concerns in livestock farming areas. Sci Total Environ. 2000;250:143–167.

[10] Lynch JA, Bowersox VC, Grimm JW. Acid rain reduced in Eastern United States. Environ Sci Technol. 2000;34:940–949.

[11] Wright RF, Schindler DW. Interaction of acid rain and global changes: effects on terrestrial and aquatic ecosystems. Water Air Soil Pollut. 1995;85:89–99.

[12] Fairley D. Daily mortality and air pollution in Santa Clara County, California: 1989–1996. Environ Health Perspect. 1999;107:637–641.

[13] Kunzli N, Kaiser R, Medina S, et al. Public-health impact of outdoor and traffic-related air pollution: a European assessment. Lancet. 2000;356:795–801.

[14] Samet JM, Dominici F, Curriero FC, Coursac I, Zeger SL. Fine particulate air pollution and mortality in 20 U.S. cities, 1987–1994. New Engl J Med. 2000;343:1742–1749.

[15] Adams PJ, Seinfeld JH, Koch DM. Global concentrations of tropospheric sulfate, nitrate, and ammonium aerosol simulated in a general circulation model. J Geophys Res. 1999;104:13791–13823.

[16] Seinfeld JH, Pandis SN. Atmospheric chemistry and physics: from air pollution to climate change. 1st ed. New York: Wiley; 1998.

[17] Ward BB. Nitrification: an introduction and overview of the state of the field. In: Ward BB, Arp DJ, Klotz MG, editors. Nitrification. Washington, DC: American Society for Microbiology (ASM); 2011. p. 3–8.

[18] Galloway JN, Townsend AR, Erisman JW, et al. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science. 2008;320:889–892.

[19] Galloway JN, Dentener FJ, Capone DG, et al. Nitrogen cycles: past, present, and future. Biogeochemistry. 2004;70:153–226.

[20] Finlayson-Pitts BJ, Pitts JN Jr. Chemistry of the upper and lower atmosphere. San Diego, CA: Academic Press; 2000.

[21] Kendall C. Tracing nitrogen sources and cycling in catchments. In: Kendall C, McDonnell JJ, editors. Isotope tracers in catchment hydrology. Amsterdam: Elsevier Science B.V.; 1998. p. 519–576.

[22] Amberger A, Schmidt HL. Natural isotope content of nitrate as an indicator of its origin. Geochim Cosmochim Acta. 1987;51:2699–2705.

[23] Kaushal SS, Groffman PM, Band LE, Elliott EM, Shields CA, Kendall C. Tracking nonpoint source nitrogen pollution in human-impacted watersheds. Environ Sci Technol. 2011;45:8225–8232.

[24] Wassenaar LI. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of ^{15}N and ^{18}O in NO_3^-. Appl Geochem. 1995;10:391–405.

[25] Durka W, Schulze ED, Gebauer G, Voerkelius S. Effects of forest decline on uptake and leaching of deposited nitrate determined from ^{15}N and ^{18}O measurements. Nature. 1994;372:765–767.

[26] Hastings MG, Sigman DM, Lipschultz F. Isotopic evidence for source changes of nitrate in rain at Bermuda. J Geophys Res. 2003;108:4790.

[27] Mayer B, Bollwerk SM, Mansfeldt T, Hutter B, Veizer J. The oxygen isotope composition of nitrate generated by nitrification in acid forest floors. Geochim Cosmochim Acta. 2001;65:2743–2756.

[28] Mayer B, Boyer EW, Goodale C, et al. Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: isotopic constraints. Biogeochemistry. 2002;57:171–197.

[29] Högberg P. Tansley review No. 95. ^{15}N natural abundance in soil–plant systems. New Phytol. 1997;137:179–203.

[30] Bateman AS, Kelly SD. Fertilizer nitrogen isotope signatures. Isot Environ Health Stud. 2007;43:237–247.

[31] Michalski G, Scott Z, Kabiling M, Thiemens M. First measurements and modeling of Δ^{17}O in atmospheric nitrate. Geophys Res Lett. 2003;30:1870.

[32] Miller MF. Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. Geochim Cosmochim Acta. 2002;66:1881–1889.

[33] Michalski G, Böhlke JK, Thiemens MH. Long term atmospheric deposition as the source of nitrate and other salts in the Atacama Desert, Chile: new evidence from mass-independent oxygen isotopic compositions. Geochim Cosmochim Acta. 2004;68:4023–4038.

[34] Michalski G, Meixner T, Fenn M, et al. Tracing atmospheric nitrate deposition in a complex semiarid ecosystem using Δ^{17}O. Environ Sci Technol. 2004;38:2175–2181.

[35] Slater JV, Kirby BJ. Commercial fertilizers 2010. Lexington, KY: Association of American Plant Food Control Officials; 2011.

[36] Vitoria L, Otero N, Soler A, Canals A. Fertilizer characterization: isotopic data (N, S, O, C, and Sr). Environ Sci Technol. 2004;38:3254–3262.

[37] Amberger A, Schmidt HL. Natürliche Isotopengehalte von Nitrat als Indikatoren für dessen Herkunft. Geochim Cosmochim Acta. 2000;51:2699–2705.

[38] Böhlke JK, Mroczkowski SJ, Coplen TB. Oxygen isotopes in nitrate: new reference materials for ^{18}O:^{17}O:^{16}O measurements and observations on nitrate–water equilibration. Rapid Commun Mass Spectrom. 2003;17:1835–1846.

[39] Casciotti KL, Sigman DM, Hastings MG, Böhlke JK, Hilkert A. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Anal Chem. 2002;74:4905–4912.

[40] Michalski G, Savarino J, Böhlke JK, Thiemens M. Determination of the total oxygen isotopic composition of nitrate and the calibration of a $\Delta^{17}O$ nitrate reference material. Anal Chem. 2002;74:4989–4993.

[41] Appl M. Ammonia. 2. Production processes. In: Ullmann's encyclopedia of industrial chemistry. Amsterdam: Wiley-VCH; 2000.

[42] Thiemann M, Scheibler E, Wiegand KW. Nitric acid, nitrous acid, and nitrogen oxides. In: Ullmann's encyclopedia of industrial chemistry. Amsterdam: Wiley-VCH; 2000.

[43] US EPA. AP 42 compilation of air pollutant emission factors. 5th ed. Washington, DC: US Environmental Protection Agency; 1995. Chapter 8, Inorganic Chemical Industry; p. 8.8-1–8.8-7.

[44] Barkan E, Luz B. High-precision measurements of $^{17}O/^{16}O$ and $^{18}O/^{16}O$ of O_2 and O_2/Ar ratio in air. Rapid Commun Mass Spectrom. 2003;17:2809–2814.

[45] Luz B, Barkan E, Bender ML, Thiemens MH, Boering KA. Triple-isotope composition of atmospheric oxygen as a tracer of biosphere productivity. Nature. 1999;400:547–550.

[46] Bowen GJ, Wilkinson B. Spatial distribution of $\delta^{18}O$ in meteoric precipitation. Geology. 2002;30:315–318.

[47] Monse EU, Spindel W, Stern MJ. Isotope effects in chemical reactions. Vol. 89, Advances in chemistry. New York: American Chemical Society; 1969. Chapter 9, Analysis of isotope-effect calculations illustrated with exchange equilibria among oxynitrogen compounds; p. 148–184.

[48] Urey HC. The thermodynamic properties of isotopic substances. J Chem Soc. 1947;562–581. doi:10.1039/JR94700FP001

[49] Luz B, Barkan E. The isotopic ratios $^{17}O/^{16}O$ and $^{18}O/^{16}O$ in molecular oxygen and their significance in biogeochemistry. Geochim Cosmochim Acta. 2005;69:1099–1110.

[50] Meijer HAJ, Li WJ. The use of electrolysis for accurate $\delta^{17}O$ and $\delta^{18}O$ isotope measurements in water. Isot Env Health Stud. 1998;34:349–369.

[51] Ericksen GE. The Chilean nitrate deposits. Am Sci. 1983;71:366–374.

[52] Ge WS, Keqin C, Shaojie S, Bin Q. Composition and origin of the Kumtag large nitrate deposits in the Turfan-Hami basin. Acta Mineral Sinica. 2009;27:104–106.

[53] Böhlke JK, Hatzinger PB, Sturchio NC, Gu BH, Abbene I, Mroczkowski SJ. Atacama perchlorate as an agricultural contaminant in groundwater: isotopic and chronologic evidence from Long Island, New York. Environ Sci Technol. 2009;43:5619–5625.

[54] Wisniak J, Garcés I. The rise and fall of the salitre (sodium nitrate) industry. Indian J Chem Technol. 2001;8:427–438.