



Use of Isotope Techniques to Determine The Source of Nitrogen Compounds in Grounwater

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ABSTRACT

Rapidly growing population and the accompanying urbanization, industrialization, increase in agricultural activities, to the decrease in available water resources and pollution is caused.

Nowadays, nitrogen compounds significantly pollute water sources and nitrogen sources in determining pollutants has increased the use of isotope techniques. Determine the source of pollutants, water pollution prevention, controlling and plays an important role in water management.

Nitrogen has long been unregarded by isotope geologists perhaps because most of its compounds are soluble in water. Stable isotope abundances of ^{15}N have been used extensively to provide information on the origins and transformations of inorganic N in surface and groundwaters. The isotopic composition of inorganic N in soils and groundwater influenced by microbial or physical processes such as denitrification, nitrification, and ion exchange.

Nitrate (NO_3^-) is found naturally at moderate concentrations in many aquatic environments, but is often enriched to high levels by anthropogenic activities involving nitrogenous compounds such as mineral fertilizer and by-products of organic compounds from agriculture, septic systems, and poultry, hog or cattle manure.

The nitrogen isotopes (^{15}N and ^{14}N) are useful anthropogenic tracers. The biogenic isotopic fractionations are complex, but often allow to determine the source of organic pollution in groundwater .

Combined isotope analyses of nitrogen and oxygen in NO_3^- leaves fingerprints on natural and anthropogenic sources of nitrate, on the microbial denitrification, nitrification and biological fixation processes and the nitrogen budget in the groundwater.

Keywords: Groundwater, Isotope Techniques, Nitrogen, Pollution Source.

1. INTRODUCTION

1.1. Nitrogen and Nitrogen Cycle

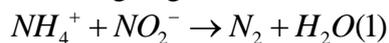
Nitrogen (N) is a very common element which is essential for almost all forms of life found on earth. For plants, nitrogen is an important nutrient and often limits the primary production in ecosystems, both on land and sea. In living tissues nitrogen is important because it is part of enzymes needed for respiration and photosynthesis. Compounds

containing N is commonly found both in liquid, solid and gaseous forms. Not counting nitrogen bound in rocks, the most common nitrogen compounds found in nature are, N₂ (nitrogen gas), N₂O (nitrous oxide), NH₄⁺ (ammonium), nitrite (NO₂⁻) and NO₃⁻ (nitrate). Nitrogen compounds are found at valence states ranging from -3 (NH₄⁺) to +5 (NO₃⁻). Many microbes use the potential energy of transformations of these compounds to sustain them with energy resulting in a complex geochemical cycle with many possible transformations [1].

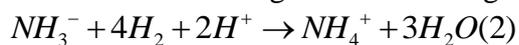
Nitrogen, originating from agricultural sites, animal feedlots, septic tanks and other waste disposal sites, is one of the most common contaminants in groundwater.

Of all the nitrogen found on earth, 97.76% is bound in rocks, 2.01% is found in the atmosphere while the remaining 0.23% is located in the hydrosphere and biosphere [2]. The atmospheric nitrogen is however not available to most of the biosphere. There are two natural possible pathways for nitrogen to enter the biosphere, see Figure 1. N₂-gas in the atmosphere can be oxidised to the biologically more available form NO during thunderstorms, which is then dissolved in water and falls to the ground with precipitation [3]. Some plants are also able to directly fixate N₂ from the atmosphere [1].

Nitrogen re-enters the atmosphere from the soil or the sea through the multistep process of denitrification in which NO₃⁻ is reduced to N₂ by microbes under anaerobe conditions, with NO₂⁻, N₂O and NO as intermediate forms, see Figure 1. Nitrogen can also be returned to the atmosphere through the process of anaerobic ammonium oxidation, abbreviated annamox. Annamox is an important process in anaerobic freshwater lakes and the oceans where microbes oxidize NH₄⁺ with the help of NO₂⁻ to form nitrogen gas and water according to [1];



If the redox-conditions are strongly reducing (i.e. anaerobic) combined with high amounts of carbon and limited amounts of nitrate, microbes may reduce nitrate to ammonium according to the following reaction;



This reaction is known as dissimilatory nitrate reduction to ammonium or DNRA. An important difference between DNRA and the processes of denitrification and annamox is that nitrogen is retained in the system during DNRA while it is lost to the atmosphere during denitrification and annamox. The role of DNRA in the nitrogen cycle is however typically minor compared to that of denitrification [4]. Still recent studies have shown that it may be the dominant process of nitrate reduction in some environments [5].

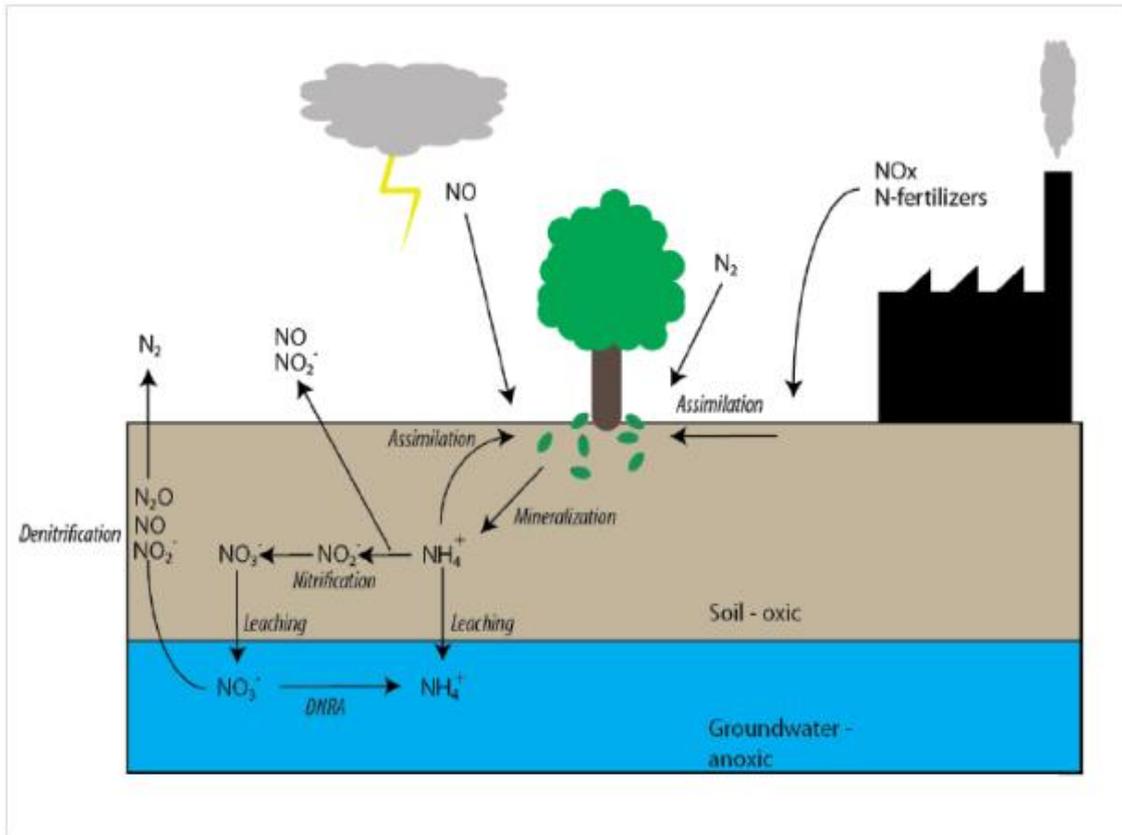


Figure 1. Simplified cartoon of pathways by which nitrogen enters the soil and groundwater by and possible reactions that occur in the soil.

Denitrification may play an important role in influencing nitrate concentrations and its isotopic composition in environments where reducing conditions are found at shallow depths. [6].

The forms of nitrogen generally measured in groundwater include nitrate (NO_3^-), nitrite (NO_2^-), and ammonia (NH_4^+) ions. Most analyses combine NO_3^- and NO_2^- and investigators report this as NO_3^- because NO_2^- occurs in substantially smaller concentrations in groundwater than NO_3^- . Nitrite also is an intermediate product of both nitrification and denitrification, that is, relatively unstable which helps explain its limited occurrence in groundwater [7].

Nitrogen is an essential macronutrient, second only to water availability in its importance for plant growth. Unfortunately, increases in N use have had detrimental effects such as eutrophication of surface water and increases of NO_3^- in groundwater [8].

2. ISOTOPES CHEMISTRY

Isotopes are chemical elements that have the same atomic number, but different atomic mass. The chemical identity of a given atom is determined by its atomic number. While the atomic number remains fixed for a given elemental (atomic) species, the number of neutrons do not. For example, nitrogen has an atomic number of 7, but the number of neutrons in the nucleus may be 7 or 8. This means different nitrogen isotopes exist which have an atomic mass of 14 [^{14}N] and 15 [^{15}N], respectively. These isotopes behave differently during certain chemical or biochemical reactions.[9]

Isotopes can be fractionated. Isotopic fractionation refers to a natural change in isotopic composition of a chemical element during a reaction. This includes radiogenic and stable isotopes. Radiogenic isotopes are those isotopes whose abundance are primarily a function of the radioactive decay of a parent atom.

Stable isotopes are those isotopes of a lower atomic weight whose abundance is the principle cause of isotopic fractionation among stable isotopes [9].

Stable isotopes have been used effectively in ecological studies to trace the impact of different components, and consequently potential pollutants, on ecosystems, as well as to trace food webs. They provide a powerful tool for source determination and following anthropogenically derived material (from animal waste, septic systems, sewage treatment plants, etc.) from their source to different segments in the environment [10,11,12,13,14,15,16,17, 18].

2.1. Nitrogen isotopes as environmental tracers

Stable isotopic data are reported as "delta values" or per mil values (‰), which is shorthand for parts per thousand. Isotopic compositions are reported as a deviation from a standard value. Nitrogen isotopic compositions are reported as delta ¹⁵N, the deviation from standard atmosphere, using the following equation;

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

Positive delta ¹⁵N values (delta ¹⁵N greater than 0) indicate that the sample has a higher ¹⁵N / ¹⁴N ratio than the atmosphere standard. Negative delta ¹⁵N values (delta ¹⁵N less than 0) indicate a lower ¹⁵N / ¹⁴N ratio than the atmosphere standard [19]

The majority of N in the atmosphere is composed of ¹⁴N (99.6337%) and the remainder is composed of ¹⁵N (0.3663%) [8].

The isotopic composition of the dissolved nitrogen (N) species has been used extensively to better constrain the sources and fate of N in groundwater [20].

Nitrogen cannot be considered conservative because it is biologically modified through nitrification and denitrification reactions, both during infiltration of the water and in the groundwater body, causing isotopic fractionation that modifies the δ¹⁵N signatures of the dissolved N species [21].

Discriminating multiple NO₃⁻ sources by their N isotopic composition alone becomes impossible wherever heterogenic or autogenic denitrification occurs, thus there is a need for establishing co-migrating discriminators of NO₃⁻ sources [20].

Stable isotopes of nitrogen compounds in theory can be used to discriminate between sources of nitrogen in field settings, as nitrogen compounds originating from different sources has characteristic isotopic ratios [22].

Non-conservative behavior in the δ¹⁵N of NO₃⁻ is most often the result of microbial processes. The direction of an isotope shift during microbial reactions can indicate the process that causes alteration. For example, loss of NO₃⁻ through denitrification can result in a marked enrichment in the ¹⁵N content of the remaining NO₃⁻. In contrast, during nitrification, the light isotope is preferentially incorporated into NO₃⁻ and a decrease in δ¹⁵N during this process is frequently observed Delwiche and Steyn, 1970; Mariotti et al., 1981; Yoshida, 1988. Fractionation during nitrification is most marked

when NH_4^+ is abundant in soils, as occurs following the application of NH_4^+ based fertilizers, and may be small or negligible when NH_4^+ is not readily available [1974; Freyer and Aly, 1975; Heaton, 1986 [24].

2.2 Isotopic signature of N sources

The fractionation of ^{15}N through biotic and abiotic processes contributes to different range of $^{15}\text{N}/^{14}\text{N}$ ratios for different N sources. Common sources of NO_3^- include animal waste, soil N, and inorganic fertilizer. Animal waste $\delta^{15}\text{N}$ is generally between 10 and 20 ‰, which is higher than the $\delta^{15}\text{N}$ of most of the vegetation animals consume. Metabolic processes lead to ^{15}N enrichment in the animal and concurrent ^{15}N depletion of the excreted N. Volatilization, a major pathway of N losses from manure, may increase the $\delta^{15}\text{N}$ of manure-N, resulting in ^{15}N -enriched compounds. Groundwater NO_3^- - ^{15}N typically falls between 0 and 10‰, but values as low as -15‰, and as high as 80 ‰ have been reported [8].

The ^{15}N values of groundwater vary widely, depending on the sources that may locally dominate the inputs of N to groundwater [9]. The typical range of NO_3^- - ^{15}N is similar to the range to the ^{15}N of soil organic N, which reflects the relative rate of the mineralization and nitrification processes. Fertilizer- $\delta^{15}\text{N}$ ranges from 0.5 to 5 ‰ for oxidized N (NO_3^-), with lower values for the reduced form [8].

The identification of the sources of nitrate water contamination in a particular area is becoming a matter of growing interest, especially with the application of the principle that the 'polluter pays'. Consequently, a reliable method is needed to achieve this objective. Basically there are two kinds of tool available: (i) computerised mapping techniques, and (ii) isotope methods [24]. In some cases, a combination of both is used. The mapping techniques are based on an overlapping of data relating to various different factors – i.e. drainage, crops, fertiliser rates, livestock farms, ground water samplings – on a composite map. The isotope methods, on the other hand, are based on the fact that the isotopic composition of a particular compound (nitrates, in this case) is related to its origin [25].

The use of the N isotope ratio values for the identification of the sources of nitrate contamination dates back to the decade of the 1970s. Kohl et al. (1971) used that method to estimate the fertiliser contribution to nitrate in the Sangamon River [26]. Their work was heavily criticised at the time [27], but essentially, the method worked. The method consists of measuring the isotopic ratio of nitrogen ($^{15}\text{N}/^{14}\text{N}$) in the sample and comparing the values obtained with the values of the contaminant sources. A description of the scope of this method can be found in Kendall (1998) [28]. Some studies also include measurements of the ratio of oxygen ($^{18}\text{O}:^{16}\text{O}$) in the nitrate sample [29]. The ratio of $^{15}\text{N}/^{14}\text{N}$ is nearly constant in the atmosphere but certain biological, chemical and physical processes result in changes (nitrogen isotope fractionation) in the isotopic composition of the substrate and the product. Commonly there is an enrichment in ^{15}N in the substrate and a depletion in ^{15}N in the product [24]. The stable isotopic ratio of nitrogen has been recognised as a useful tool for the identification of the sources of nitrate contamination in North America since the 1970s [30,31]. In spite of this, the use of the isotope method is not very widespread [31].

Different reactions will cause different fractionations of N, meaning that $\delta^{15}\text{N}$ values can possibly be used to identify the origin of the nitrogen in a sample. Stable nitrogen isotopes has been used by many to identify sources of nitrate or ammonium in

groundwater. Following here is a description of which $\delta^{15}\text{N}$ values that can be expected from samples containing nitrogen of different origin and how different processes affect N isotope fractionation, see also Figure 2.

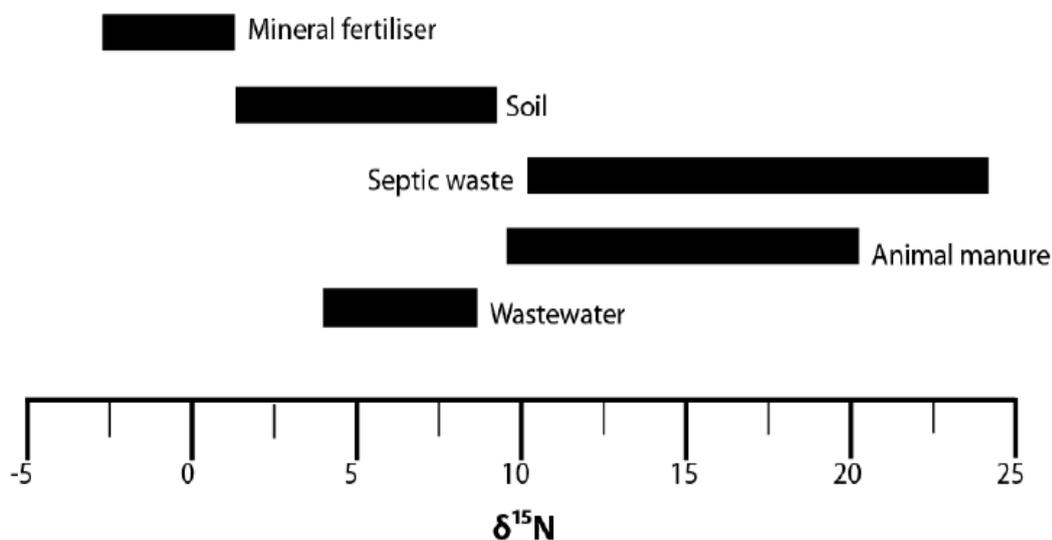


Figure 2. Reported ranges of $\delta^{15}\text{N}$ -values expressed in ‰ for different anthropogenic sources of N [29].

Curt and others (2004) reported to their study, animal waste sources and WWTP sources (sludge and/or effluent) are isotopically indistinguishable but the $\delta^{15}\text{N}$ method can be successfully used to distinguish between organic and synthetic nitrogen sources [29].

In their study of Ostrom and others (1998), were reported to the probable sources of NO_3^- were limited to soil organic matter and precipitation, and precipitation, and the primary process expected to cause variation in $\delta^{15}\text{N}$ were mineralization, nitrification and denitrification [23].

In study of Lindenbaum (2012) researched ammonium sources in Nam Du Hanoi groundwater by using isotopes of nitrogen and boron. This study results, indications that wastewater or animal manure is infiltrating down to the groundwater in some places, locally contributing to the high ammonium concentrations [32].

The isotopic composition of nitrates which percolate to groundwater is the result of complex processes. Therefore, it is difficult to relate the isotopic composition of the various nitrogen compounds in groundwater to atmospheric and agricultural inputs without considering the isotope fractionation caused by nitrification and denitrification processes as well as mixing of nitrates and ammonium from soil and atmospheric sources.

Hypothetical relationship between the $\delta^{15}\text{N}$ value and the concentration of dissolved nitrate derived from soil and fertilisers. Solid bars (X and Y) represent soil and fertiliser mixing end members. The grey area shows the effect of mixing. The broken lines were calculated and stand for the fractionation during denitrification of fertiliser nitrate (NO_3^-) = -30 and -10‰ with the initial point Y) and due to mineralization of soil organic nitrogen (line X – C using NO_3^- Norg) = -

30‰). A, B, C are hypothetical isotopic compositions of nitrate resulting from mixing and/or nitrogen mineralisation [33].

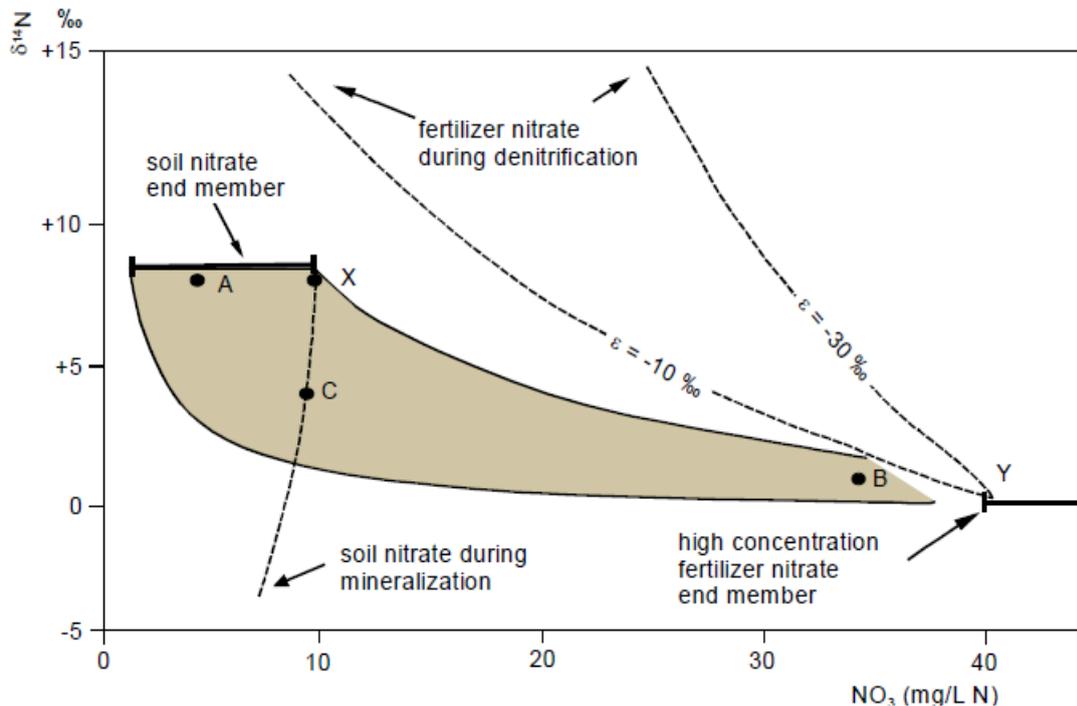


Figure 3. Hypothetical relationship between the $\delta^{15}\text{N}$ value and the concentration of dissolved nitrate derived from soil and fertilisers [33].

3. CONCLUSION

Nowadays, nitrogen compounds significantly pollute water sources and nitrogen sources in determining pollutants has increased the use of isotope techniques. Determine the source of pollutants, water pollution prevention, controlling and plays an important role in water management.

Anthropogenic activities and over-exploitation of groundwater resources has led to degradation of the groundwater quality in many places. There are also several natural contamination sources of groundwater.

Nitrogen has long been unregarded by isotope geologists perhaps because most of its compounds are soluble in water. Stable isotope abundances of ^{15}N have been used extensively to provide information on the origins and transformations of inorganic N in surface and groundwaters.

The isotopic composition of nitrogen compounds in natural environments is controlled by that of its source and processes that cause its production, consumption or exchange.

The Nitrogen isotopes ^{15}N and ^{14}N are useful anthropogenic tracers. The biogenic isotopic fractions are complex, but allow to determine the source of organic pollution in groundwater.

In this study was aimed to indicate isotopic composition of nitrogen sources, classification of nitrogen resources using of isotope techniques in groundwater. For this purpose, in the literature of the past to the present, studies on the subject have been collected.

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