Review paper

The nitrogen cycle: A review of isotope effects and isotope modeling approaches

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ABSTRACT

The nitrogen (N) cycle involves a set of N compounds transformed by plants and microbes. Some of these N compounds, such as nitrous oxide (N_2O) or nitrate (NO_3^-), are environmental pollutants jeopardizing biodiversity, human health or the global climate. The natural abundances of the common (^{14}N) and rare (^{15}N) stable N isotopes in a given compound, i.e. the isotopic composition, depend on individual production and consumption processes. As each process has an individual preference for the common or rare isotope (isotope effect) the measurement of the isotopic composition has been identified as a powerful tool for improved process understanding and source process identification. Both are key requirements for the development of strategies aiming at mitigating the release of environmental harmful N compounds. However, up to now, no comprehensive compilation of N cycle isotope effects is available.

A compilation of isotope effects is also in high demand for testing biogeochemical models as such models are increasingly used to study N cycling in ecosystems and across landscapes and regions. Biogeochemical models are usually calibrated and validated only with single, easily accessible quantities. The isotopic composition of N compounds has a high potential to be used as additional, integrative parameter for a more thorough assessment of simulation results. For instance, the isotopic composition of soil N is determined by fractionation of the most relevant processes and, thus, integrates several N cycle processes, some of which cannot be accessed easily by direct measurement. To implement isotopic fractionation in ecosystem models and to utilize those for model validation, the magnitude of the isotope effects associated with individual transformations in the N cycle need to be assessed.

This review summarizes the available methods to determine N isotope effects of various key ecosystem processes, thereby systematically comparing isotope effects for different experimental conditions and processes, exploring the accuracy of theoretical calculations of isotope effects and finally, addressing concepts to implement isotope effects into biogeochemical modeling.

Our review shows that published isotope effects for N processes in soil incubations seem to be stronger as compared to those in water saturated systems. In addition to the choice of isotope effects adequate for the respective ecosystem, the challenge for modeling approaches is the sequential calculation of isotopic compositions. Associated numerical inaccuracies can be minimized by controlling the share of reacted substrates, i.e. the time step. The criterion to determine the time step needs to consider the strongest isotope effect, required accuracy of the calculations and the share of substrate consumed from or provided to the compound pool.

The combination of biogeochemical models with $\delta^{15}N$ methods and novel measures like site preference (SP) of N_2O is a promising approach for improving process understanding at various spatial and

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temporal scales. Nevertheless, the compilation of isotope effects in this review may not only be of benefit for modelers, but also for experimentalists, as measurement and modeling of isotope effects may eventually help to test and validate our current process understanding of the N cycle.

1. Introduction

As essential compound of the DNA, proteins or enzymes, nitrogen (N) is a key component of life and a fundamental nutrient. Its most abundant form, atmospheric dinitrogen (N_2), is unavailable for most organisms, making nitrogen a limiting nutrient (Galloway et al., 2003; Vitousek and Howarth, 1991). Therefore, the conversion of N_2 into reactive nitrogen (N_r) directly or indirectly supports biomass growth. In the environmental context, reactive nitrogen compounds include oxidized nitrogen species, such as nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), nitrate (NO_3^-), nitrite (NO_2^-) as well as the reduced nitrogen species, ammonia (NH_3) and ammonium (NH_4^+) salts, as well as organic bound N e.g. in its simplest form of urea, amine derivatives or as organic N in proteins or other substances. The main natural processes creating biologically available N_r are lightning (globally approx. 5 Tg N yr^{-1}) and biological N_2-fixation (BNF) in terrestrial and aquatic ecosystems (globally approx. 198 Tg N yr^{-1}) (Fowler et al., 2013). However, in most ecosystems the demand of N_r by far exceeds natural N_2-fixation by both processes, so that ecosystems are in general N limited (Aber et al., 1989). This shortage was revoked following the invention of the Haber-Bosch process, which allowed the conversion of N_2 into NH_3/NH_4^+ at industrial scale (Erisman et al., 2008). NH_4^+ was used at the beginning for the production of explosives with the focus changing to the production of synthetic fertilizers. The increasing use of synthetic N fertilizers in the mid of the last century boosted global agricultural production and facilitated an ever growing world population, with approx. 50% of the global world population currently being fed due to the availability of the Haber-Bosch technology (Erisman et al., 2008). However, the use and overuse of N fertilizers is also associated with detrimental effects on the terrestrial and aquatic environment, climate and human health as N_r is driving eutrophication (increasing mineral and organic N in ecosystems), acidification (as a consequence of oxidizing NH_4^+ to NO_3^-), radiative forcing (mainly by the greenhouse gas N_2O), stratospheric ozone depletion (stratospheric degradation of N_2O to NO with the latter acting as O_3 depleting substance), tropospheric ozone production (due to soil emissions of NO and its chemical reactions in the troposphere) and formation of particulate matter up to 2.5 μm size ($PM_{2.5}$), as, e.g., NH_4NO_3 is a major particle forming substance (for a detailed overview see Galloway et al. (2003) or Fowler et al. (2013) and references therein).

Due to the delicate coexistence of beneficial and detrimental effects, a profound understanding of N cycle processes is required to develop efficient mitigation strategies sustaining agricultural productivity (Butterbach-Bahl et al., 2013). The fundamental process in N cycling is *nitrogen fixation*: The conversion of atmospheric N_2 to NH_3 by nitrogen-fixing microorganisms which oxidize ("burn") carbohydrates to gain energy and thereby reduce N_2 to NH_3 (biological nitrogen fixation). Once fixed, N is transformed to microbial or plant biomass (*immobilization and uptake, respectively*), eventually ending up in the soil organic matter pool (SOM) after senescence, littering and decomposition. Microbes are involved in a process called *mineralization*, which represents the breakdown of complex organic matter molecules into monomeric organic nitrogen compounds *(depolymerization)* and inorganic NH_4^+ (Schimel

and Bennett, 2004). NH_4^+ can be utilized by microbes to gain energy in a two-step process called *nitrification*. In the first step, $NH4^+$ is oxidized to NO_2^- via the intermediate hydroxylamine (NH_2OH); in the second step NO_2^- is oxidized to NO_3^-. Both reactions can be carried out by chemo-lithotrophic ammonium or nitrite oxidizers. However, also heterotrophic bacteria, fungi and archaea are capable of nitrification, though without gaining energy from the process, thereby using monomeric organic nitrogen compounds for growth. NO_3^- can be lost to ground water through leaching and at high pH NH_4^+ can *volatilize* and be lost to the atmosphere in gaseous form as NH_3. In the anoxic process of *denitrification*, NO_3^- is used as alternative electron acceptor instead of O_2, and be stepwise reduced via NO_2^-, NO and N_2O to N_2. Two other notable processes are *dissimilatory nitrate reduction to ammonium* (DNRA), and *anaerobic ammonia oxidation* (ANAMMOX). During DNRA, NO_3^- is first reduced to NO_2^- and then reduced to NH_4^+, with many organisms at the same time also producing N_2O, probably to avoid toxic NO_2^- concentrations (Rütting et al., 2011; Stevens et al., 1998). ANAMMOX produces N_2 from both NH_4^+ and NO_2^- (Harris et al., 2015). Additionally to these biotic processes in soils, also *abiotic N_2O production* can happen in soils with the nitrification byproducts NH_2OH and NO_2^- as substrate (Bremner, 1997) or hypersaline ponds (Ostrom et al., 2016; Peters et al., 2014; Samarkin et al., 2010) (see Fig. 1).

N transformation processes in aquatic and terrestrial ecosystems have been studied extensively from laboratory to global scales by means of various different measuring approaches (e.g., microbial pure culture experiments, analysis of N_r concentrations and fluxes) including isotope techniques (Bai et al., 2012; Groffman et al., 2006; Houlton et al., 2015). Experimental techniques are supported by modeling approaches, which assess environmental impacts of N cycling on regional and global scale using process-oriented
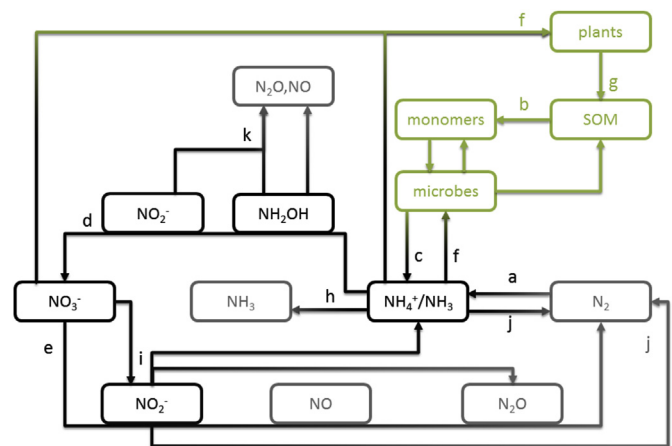
Fig. 1. : Processes involved in terrestrial ecosystem N cycling: a) biological N_2 fixation, b) depolymerization, c) mineralization, d) nitrification, e) denitrification, f) immobilization and plant uptake, g) senescence, h) volatilization, i) dissimilatory nitrate reduction to ammonium, j) anaerobic ammonia oxidation, k) abiotic N_2O production. Soil N compounds are shown in black, gaseous compounds in grey and organic N in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)