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Review

Synthetic fertilizer and livestock manure differently affect $\delta^{15}N$ in the agricultural landscape: A review

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A B S T R A C T

Synthetic fertilizers and raw or composted livestock manure are typical nitrogen (N) sources in intensive cropping and livestock-farming systems. The distinct N isotope ratios ($^{15}N/^{14}N$, expressed as $\delta^{15}N$) of the N sources make it possible to use the $\delta^{15}N$ of soil, plant and groundwater samples to trace the N derived from the two N sources in the agricultural landscape. However, N isotope fractionation during N cycling may hamper the usefulness of the $\delta^{15}N$ technique for tracing N. This paper reviews the changes in the $\delta^{15}N$ of soil, plant and groundwater samples in the agricultural landscape as affected by synthetic fertilizer and raw or composted manure applications with consideration of the effect of N source and N fractionation during N cycling on variations in $\delta^{15}N$. First, this review summarizes the fundamental N isotope fractionation theory with an emphasis on the critical role of nitrification in changing $\delta^{15}N$ through N loss. Second, the differences in the $\delta^{15}N$ of synthetic fertilizer and raw or composted manure are discussed with an emphasis on mechanisms that increase $\delta^{15}N$ in raw or composted manure. Third, the effects of synthetic fertilizer and raw or composted manure applications on the variations of $\delta^{15}N$ in soil, plant and groundwater samples across different scales of experiments from laboratory to watershed are discussed. We conclude that in spite of N isotope fractionation, the feasibility of the $\delta^{15}N$ technique in tracing N originated from synthetic fertilizer and raw or composted manure in soil, plant and groundwater in the agricultural landscape can be strengthened when site-specific information on the $\delta^{15}N$ of N sources as well as the dominant N processes is available.

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1. Introduction

More than 99% of the known nitrogen (N) on or near the earth's surface is present either as atmospheric N_2 or as dissolved N_2 in the ocean, and only a small amount of N is combined with other elements, mainly carbon (C), oxygen (O) and hydrogen (Liu et al., 2010) to form a diverse range of compounds. However, this small fraction of N plays a pivotal role in the biological world as N is an essential element for all living organisms (Ollivier et al., 2011). In the agricultural landscape, the most important sources of N are synthetic fertilizer and organic inputs such as raw or composted livestock manure and green manure (Schlesinger, 2009). Globally, synthetic fertilizer N application is the single largest source of N input to croplands, accounting for 50% of the total N input (150 Tg N), followed by N_2 fixation (16%) and organic inputs (8–13%) (Schlesinger, 2009). Of the applied N, about 55% is taken up by crops, and the remainder is subject to loss via leaching (16%), surface runoff (15%), and gaseous emissions (14%), with all of those three processes result in environmental pollution (Liu et al., 2010). Due to the biologically reactive nature of the N, together with the existence of a variety of N sources and the complexity of the N cycling processes in agricultural systems, the identification of the sources of N in sinks such as soil, plant and water bodies is important in the management of N for sustaining agricultural productivity and minimizing the impact of N on the environment.

The natural abundance of N ($^{15}N/^{14}N$, expressed as $\delta^{15}N$) has served as an indicator of N source due to the distinct $\delta^{15}N$ signatures among N sources such as synthetic fertilizer and raw or composted manure (Choi et al., 2003a). Kohl et al. (1971) were the first to report the potential use of $\delta^{15}N$ to identify N sources by estimating the contribution of fertilizer N to nitrate (NO_3^-) contamination in river water based on the fact that $\delta^{15}N$ of synthetic fertilizer N is lower than that of native soil N. Thereafter, many studies applied the $\delta^{15}N$ technique to identify dominant sources of N in specific sinks such as soil, plant and groundwater (Bateman et al., 2005; Xue et al., 2009). For example, in crop fields, the $\delta^{15}N$ technique is applied in differentiating conventional agricultural produce grown with ^{15}N-depleted synthetic fertilizers vs. organic produce grown with ^{15}N-enriched organic N sources such as raw or composted manure (Bateman et al., 2005; Inácio et al., 2015). For groundwater in the agricultural landscape, the $\delta^{15}N$ of NO_3^- has been widely used to elucidate sources of groundwater contamination with land-use types including crop field and livestock farming area (Choi et al., 2007b; Kellman, 2015). The $\delta^{15}N$ of NO_3^- in groundwater (particularly unconfined shallow groundwater) is more likely to reflect the land-use type overlying the aquifer than surface water which receives NO_3^- that originates from many other sources including municipal and industrial areas (Choi et al., 2007b; Xing and Liu, 2016). However, $\delta^{15}N$ is not yet a quantitative indicator of the source of N because the $\delta^{15}N$ signal is not conservative but subject to change due to N isotope fractionation associated with N cycling and N loss (Robinson, 2001). It is now accepted that the $\delta^{15}N$ is an integrator of the effect of N sources and N cycling, suggesting that the N source in a certain sink should be estimated in the context of the dominant N processes that cause deviations in the $\delta^{15}N$ of N in a sink from that in a source (Lim et al., 2015; Robinson, 2001).

In intensive cropping and livestock farming systems, synthetic fertilizer and raw or composted manure are the dominant N sources, and the presence of the two dominant N sources with distinct $\delta^{15}N$ signal may differently affect the $\delta^{15}N$ in soil, plant and groundwater (Choi et al., 2007b). There have been a few excellent reviews that aim to address the usefulness and limitation of the $\delta^{15}N$ technique in tracing the sources of N in soil and plant (Bateman et al., 2005; Inácio et al., 2015) and water systems (Xu et al., 2016; Xue et al., 2009). However, a comprehensive review on the impact of N sources on $\delta^{15}N$ across soil, plant and groundwater systems in the agricultural landscape is lacking. Considering the inter-connection of soil, plant and groundwater in terms of N cycling, a comprehensive understanding of the variations in $\delta^{15}N$ with N cycling through soil, plant and groundwater is required for the use of $\delta^{15}N$ to assess the impact of synthetic fertilizer and raw or composted manure on the environment at the agricultural landscape scale.

Targeting the agricultural landscape that is intensively managed with cropping and livestock farming, this review provides a synthesis of how synthetic fertilizer and raw or composted manure differently change the $\delta^{15}N$ in soil, plant and groundwater samples. We will focus on 1) the fundamental N isotope fractionation processes associated with N cycling, with a special emphasis on nitrification which triggers N loss via leaching and denitrification, 2) the difference in the $\delta^{15}N$ of synthetic fertilizer and raw or composted manure with emphases on the progressive ^{15}N-enrichment of manure N, and 3) the changes in the $\delta^{15}N$ in soil, plant and groundwater samples as affected by synthetic fertilizer and raw or composted manure across different scales of experiments from laboratory to watershed. We conclude the review by highlighting the need for site-specific $\delta^{15}N$ information for assessing the effect of synthetic fertilizer and raw or composted manure on the $\delta^{15}N$ of soil, plant and groundwater samples in intensively managed agricultural systems.

2. The $\delta^{15}N$ theory

2.1. Definition of $\delta^{15}N$

Isotopes are atoms whose nuclei contain the same number of protons but a different number of neutrons (Ingerson, 1953). Of the N atoms on earth, 99.6337% of them are the lighter ^{14}N with the remainder (0.3663%) as the heavier ^{15}N, and the ratio between the two stable N isotopes ($^{15}N/^{14}N$) is expressed as ^{15}N atom% (Mariotti, 1983). The ^{15}N atom% varies in the biosphere as a result of isotope fractionation during physical, chemical, and biological processes, and the atmospheric N_2 (0.3663 atom%) is accepted as the standard (Junk and Svec, 1958; Mariotti, 1983). In natural ecosystems, the ^{15}N atom% usually varies within a narrow range from 0.355 to 0.377 atom% (Macko and Ostrom, 1994; Moore, 1974; Nadelhoffer and Fry, 1994). Because the variation in the absolute abundance of ^{15}N is small, N isotope composition is expressed using the δ notation in parts per thousand (‰) as:

$$\delta^{15}N\,(‰) = [(R_{sample} - R_{standard})/R_{standard}] \times 1000 \quad (1)$$

where R_{sample} and $R_{standard}$ are the atom% of the sample and the standard (atmospheric N_2, 0.3663%), respectively. This equation indicates that the $\delta^{15}N$ of atmospheric N_2 is 0‰ by definition and that the more ^{15}N-enriched a sample is, the more positive its $\delta^{15}N$ and *vice versa*. Most N compounds found in agricultural ecosystems have $\delta^{15}N$ between −30 and +30‰ that are equivalent to 0.355 and 0.377 atom%, respectively (Robinson, 2001).