



Abiotic hydroxylamine nitrification involving manganese- and iron-bearing minerals

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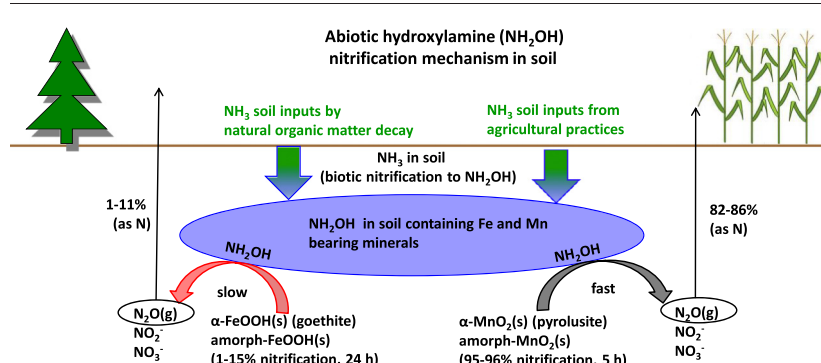
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HIGHLIGHTS

- Abiotic NH_2OH nitrification by Mn minerals was rapid, but not with Fe minerals.
- The total N mass balance was: input = NH_2OH ; outputs = $\text{N}_2\text{O}(\text{g}) + \text{N}_2\text{O}(\text{aq}) + \text{NO}_2^- + \text{NO}_3^-$.
- The total N recovery in 4.5 h using pyrolusite and amorph- $\text{MnO}_2(\text{s})$ was 95–96%.
- Total N recovery in 17 d using goethite and amorph- $\text{FeOOH}(\text{s})$ was 1.1–14.5%.
- NH_2OH nitrification by Mn was \gg Fe, despite similar specific [Mn] and [Fe] (mg/m^2).

GRAPHICAL ABSTRACT



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ABSTRACT

Hydroxylamine (NH_2OH) undergoes biotic and abiotic transformation processes in soil, producing nitrous oxide gas ($\text{N}_2\text{O}(\text{g})$). Little is known about the magnitude of the abiotic chemical processes in the global N cycle, and the role of abiotic nitrification is still neglected in most current nitrogen trace gas studies. The abiotic fate of NH_2OH in soil systems is often focused on transition metals including manganese (Mn) and iron (Fe), and empirical correlations of nitrogen residual species including nitrite (NO_2^-), nitrate (NO_3^-), and $\text{N}_2\text{O}(\text{g})$. In this study, abiotic NH_2OH nitrification by well-characterized manganese (Mn)- and iron (Fe)-bearing minerals (pyrolusite, amorphous $\text{MnO}_2(\text{s})$, goethite, amorphous $\text{FeOOH}(\text{s})$) was investigated. A nitrogen mass balance analysis involving NH_2OH , and the abiotic nitrification residuals, $\text{N}_2\text{O}(\text{g})$, $\text{N}_2\text{O}(\text{aq})$, NO_2^- , NO_3^- , was used, and specific reactions and mechanisms were investigated. Rapid and complete NH_2OH nitrification occurred (4–5 h) in the presence of pyrolusite and amorphous $\text{MnO}_2(\text{s})$, achieving a 95–96% mass balance of N byproducts. Conversely, NH_2OH nitrification was considerably slower by amorphous $\text{FeOOH}(\text{s})$ (14.5%) and goethite (1.1%). Direct reactions between the Mn- and Fe-bearing mineral species and NO_2^- and NO_3^- were not detected. Brunauer–Emmett–Teller surface area and energy dispersive X-ray measurements for elemental composition were used to determine the specific concentrations of Mn and Fe. Despite similar specific concentrations of Mn and Fe in crystalline and amorphous minerals, the rate of NH_2OH nitrification was much greater in the Mn-bearing minerals. Results underscore the intrinsically faster NH_2OH nitrification by Mn minerals than Fe minerals.

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1. Introduction

1.1. Nitrous oxide byproduct from the abiotic transformation of hydroxylamine

Nitrous oxide (N₂O) is a long-lived greenhouse gas present in the atmosphere, is chemically stable, persists in the atmosphere for centuries or longer, and will have a long-term influence on the climate (Anderson et al., 2010). N₂O is the 4th most important anthropogenic greenhouse gas (Davidson, 2009), and is a major contributor in the destruction of stratospheric ozone (Ravishankara et al., 2009). Upland soil and riparian areas, in conjunction with manmade agricultural activities, account for the majority of the estimated global N₂O emissions from natural sources (Anderson et al., 2010) with an estimated 50–60% of global N₂O emissions (US EPA, 2010).

Ammonia (NH₃) released from the decay of organic matter, the reduction of atmospheric nitrogen (N₂) to the ammonium ion (NH₄⁺) by certain species of bacteria (i.e., nitrogen fixation), and ammonia from nitrogen-based fertilizer input to croplands are three predominant sources of nitrogen (N) in environmental systems. A large part of the soil ammonium pool will form as hydroxylamine (NH₂OH) during nitrification (Arp and Stein, 2003). Once the NH₂OH is microbiologically produced, it may leak from autotrophic and heterotrophic nitrifiers into the soil matrix (Heil et al., 2015). Abiotic nitrification of NH₂OH in soil, including by iron (Fe) and manganese (Mn), forms N₂O(g) as a major byproduct (Bremner et al., 1980; Bremner, 1997; Heil et al., 2014, 2015, 2016; Liu et al., 2016). The simultaneous occurrence of biotic nitrifier pathways and abiotic nitrification mechanisms in N₂O formation introduces challenges in differentiating the role of each. Studies that determine the relative contributions of N₂O formation by abiotic NH₂OH nitrification and nitrifier-denitrification are urgently needed to assess the importance of NH₂OH oxidation in soil (Snider et al., 2015). Further, little is known about the magnitude of abiotic nitrification processes in the global nitrogen cycle (Heil et al., 2016), and the role of abiotic nitrification is still neglected in most nitrogen trace gas studies (Heil et al., 2015).

Laboratory studies have been successfully used to gain insight into NH₂OH fate mechanisms and nitrogen residuals in soil systems. The fate of NH₂OH in soils (n = 19) was investigated where NH₂OH transformation produced more N₂O than N₂ (Bremner et al., 1980). N₂O formation increased over a 5 d period, and was positively correlated with pH, CaCO₃ equivalent, exchangeable Ca²⁺, and oxidized manganese (Mn). The production of N₂O via chemical decomposition of NH₂OH in the soils greatly exceeded production of N₂O(g) through decomposition of nitrite (NO₂⁻), and no formation of nitrogen oxide (NO) was measured. Results indicated that the abiotic reaction between NH₂OH and NO₂⁻ was limited. Soil from different ecosystems were amended with NH₂OH and monitored to assess biotic and abiotic sources of N₂O (g) formation (Heil et al., 2015). Soil parameters including Fe and Mn were measured for each soil type. In sterilized soil, N₂O(g) formation was not completely inhibited indicating that abiotic NH₂OH transformation occurred. It was concluded that the Fe in soil was weakly correlated with NH₂OH-related N₂O formation, and a higher correlation between Mn and N₂O(g) formation, despite lower Mn concentrations relative to Fe. It was proposed that the difference in redox potential of the two redox pairs, Fe²⁺/Fe³⁺ and Mn²⁺/Mn⁴⁺, favored the reaction of NH₂OH and helped explain why lower levels of Mn can exert a higher rate of NH₂OH oxidation than Fe. It was also proposed that Fe might be complexed too tightly in soil to be available as a reaction partner with NH₂OH.

Recent developments in sensitive methods to accurately measure low concentrations of NH₂OH in soil have enabled a more quantitative determination of NH₂OH abundance in soils (Liu et al., 2014), and to disentangle the roles of biotic and abiotic fate of NH₂OH in soil (Liu et al., 2016). Liu et al. (2016) used multiple regression analysis and concluded that Mn was an important factor explaining N₂O(g) emission rates from

soil, emphasizing the importance of MnO₂ transformation of NH₂OH to N₂O(g) in the Norway spruce forest ecosystem. A negative correlation in N₂O(g) emission rates was reported for soil samples containing organic matter and pH values near or above the pK_a of NH₂OH (pK_a = 5.95). Under these conditions the de-protonated form of NH₂OH reacted with carbonyl groups to form oximes. Thus, NH₂OH became less available for the oxidation by MnO₂.

Studies conducted to better understand the role of abiotic nitrification in the global nitrogen cycle have involved an array of soil types, Fe and Mn content, soil physiochemical characteristics, reagents amended to soil, redox potential, methods of analysis, pH, and organic carbon content (Zhu-Barker et al., 2015; Heil et al., 2016). The range in the concentration of Mn and Fe, and the undifferentiated mineral forms of the Mn and Fe species used in these studies have also had a measurable impact on NH₂OH transformation, N₂O(g) production, and the formation of nitrite (NO₂⁻) and nitrate (NO₃⁻) reaction intermediates (Bremner et al., 1980; Zhu-Barker et al., 2015; Heil et al., 2016). Often, acid digested soil samples, used to extract metals from the soil, are analyzed but may not accurately reflect available metals involved in NH₂OH nitrification. Detailed information regarding geochemical composition, elemental composition, and surface characteristics of the Mn- and Fe-bearing minerals would be beneficial to understand their correlation with NH₂OH nitrification.

1.2. Reactions and mechanism for Mn- and Fe-mediated abiotic NH₂OH transformation

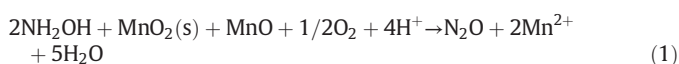
Given the reports of abiotic transformation of NH₂OH to N₂O, and NO₂⁻ and NO₃⁻ reaction intermediates (Bremner et al., 1980), a series of balanced oxidation-reduction reactions involving Mn and Fe mineral species was proposed as a technical guideline for the study (reactions 1–9). Gibbs free energy calculations were used to assess the thermodynamic feasibility of these reactions. Based on data provided in Diakonov et al. (1994) and Dean (1979), the thermodynamic analysis indicated that all reactions are energetically favorable and a summary of the analysis and calculations are provided in the Supporting information (Section S.1 Summary of Thermodynamic Calculations).

1.2.1. Mn-bearing minerals

There are several crystallographic structures (i.e., polymorphs) of MnO₂. Pyrolusite, the most common naturally occurring mineral form of MnO₂, was used in this study. Amorphous MnO₂(s), is poorly structured and more amenable to dissolution than pyrolusite, and will be referred to as amorph-MnO₂(s). Contrasting results between the two mineral forms provides insight regarding the potential role of surface characteristics, Mn content, and Fe impurities found in the pyrolusite.

In nitrification reactions involving Mn, the proposed overall reaction (reaction 1) represents the sum of the proposed specific reactions (reactions 2–4) where MnO₂(s) initiates NH₂OH transformation and is converted to N₂O(g). In specific reactions, intermediates include NO₂⁻ and NO₃⁻ (reactions 2–4), where NH₂OH is oxidized to NO₂⁻ (reaction 2), and subsequently NO₂⁻ is oxidized to NO₃⁻ (reaction 3). The final step involves the reduction of NO₃⁻ to N₂O(g) by reduced Mn. During the reactions, ≡Mn(IV) is reduced to undifferentiated reduced forms of Mn, represented as Mn²⁺ and MnO. Reduced Mn has been represented as undifferentiated MnO (reaction 5) (Bremner, 1997). The reduction step may be carried out by surface reactions involving ≡Mn(II), or soluble Mn²⁺. In environmental systems exposed to air, ≡Mn(II) or Mn²⁺ could become oxidized (≡Mn(IV)) by oxidized species in the test system, including O₂(g) or dissolved oxygen.

1.2.1.1. Overall reaction.



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