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Abiotic hydroxylamine nitrification involving manganese- and iron-bearing minerals

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Abstract

Hydroxylamine (NH₂OH) undergoes biotic and abiotic transformation processes in soil, producing nitrous oxide gas (N₂O(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 NH₂OH in soil systems is often focused on transition metals including manganese (Mn) and iron (Fe), and empirical correlations of nitrogen residual species including nitrite (NO₂⁻), nitrate (NO₃⁻), and N₂O(g). In this study, abiotic NH₂OH nitrification by well-characterized manganese (Mn)- and iron (Fe)-bearing minerals (pyrolusite, amorphous MnO₂(s), goethite, amorphous FeOOH(s)) was investigated. A nitrogen mass balance analysis involving NH₂OH, and the abiotic nitrification residuals, N₂O(g), N₂O(aq), NO₂⁻, NO₃⁻, was used, and specific reactions and mechanisms were investigated. Rapid and complete NH₂OH nitrification occurred (4–5 h) in the presence of pyrolusite and amorphous MnO₂(s), achieving a 95–96% mass balance of N byproducts. Conversely, NH₂OH nitrification was considerably slower by amorphous FeOOH(s) (14.5%) and goethite (1.1%). Direct reactions between the Mn- and Fe-bearing mineral species and NO₂⁻ and NO₃⁻ 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 NH₂OH nitrification was much greater in the Mn-bearing minerals. Results underscore the intrinsically faster NH₂OH nitrification by Mn minerals than Fe minerals.

Graphical Abstract

Keywords

Hydroxylamine; Abiotic nitrification; Manganese; Iron; Nitrous oxide

1. Introduction

1.1. Nitrous oxide byproduct from the abiotic transformation of hydroxylamine

Nitrous oxide (N_2O) 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). N_2O 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 N_2O emissions from natural sources (Anderson et al., 2010) with an estimated 50–60% of global N_2O emissions (US EPA, 2010).

Ammonia (NH_3) released from the decay of organic matter, the reduction of atmospheric nitrogen (N_2) to the ammonium ion (NH_4^+) 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 (NH_2OH) during nitrification (Arp and Stein, 2003). Once the NH_2OH is microbiologically produced, it may leak from autotrophic and heterotrophic nitrifiers into the soil matrix (Heil et al., 2015). Abiotic nitrification of NH_2OH in soil, including by iron (Fe) and manganese (Mn), forms $\text{N}_2\text{O(g)}$ as a major byproduct (Bremner et al., 1980; Bremner, 1997; Heil et al., 2014, Heil et al., 2015, Heil et al., 2016; Liu et al., 2016). The simultaneous occurrence of biotic nitrifier pathways and abiotic nitrification mechanisms in N_2O formation introduces challenges in differentiating the role of each. Studies that determine the relative contributions of N_2O formation by abiotic NH_2OH nitrification and nitrifier-denitrification are urgently needed to assess the importance of NH_2OH 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 NH_2OH fate mechanisms and nitrogen residuals in soil systems. The fate of NH_2OH in soils ($n = 19$) was investigated where NH_2OH transformation produced more N_2O than N_2 (Bremner et al., 1980). N_2O formation increased over a 5 d period, and was positively correlated with pH, CaCO_3 equivalent, exchangeable Ca^{2+} , and oxidized manganese (Mn). The production of N_2O via chemical decomposition of NH_2OH in the soils greatly exceeded production of $\text{N}_2\text{O(g)}$ through decomposition of nitrite (NO_3^-), and no formation of nitrogen oxide (NO) was measured. Results indicated that the abiotic reaction between NH_2OH and NO_2^- was limited. Soil from different ecosystems were amended with NH_2OH and monitored to assess biotic and abiotic sources of $\text{N}_2\text{O(g)}$ formation (Heil et al., 2015). Soil parameters including Fe and Mn were measured for each soil type. In sterilized soil, $\text{N}_2\text{O(g)}$ formation was not completely inhibited indicating that abiotic NH_2OH transformation occurred. It was concluded that the Fe in soil was weakly correlated with NH_2OH -related N_2O formation, and a higher correlation between Mn and $\text{N}_2\text{O(g)}$ formation, despite lower Mn concentrations relative to Fe. It was proposed that the difference in redox potential of the two redox pairs, $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{4+}$, favored the reaction of NH_2OH and helped explain why lower levels of Mn can exert a higher rate of NH_2OH oxidation than Fe. It was also proposed that Fe might be complexed too tightly in soil to be available as a reaction partner with NH_2OH .

Recent developments in sensitive methods to accurately measure low concentrations of NH_2OH in soil have enabled a more quantitative determination of NH_2OH abundance in soils (Liu et al., 2014), and to disentangle the roles of biotic and abiotic fate of NH_2OH in soil (Liu et al., 2016). Liu et al. (2016) used multiple regression analysis and concluded that Mn was an important factor explaining $\text{N}_2\text{O(g)}$ emission rates from soil, emphasizing the importance of MnO_2 transformation of NH_2OH to $\text{N}_2\text{O(g)}$ in the Norway spruce forest ecosystem. A negative correlation in $\text{N}_2\text{O(g)}$ emission rates was reported for soil samples containing organic matter and pH values near or above the pK_a of NH_2OH ($\text{pK}_a = 5.95$). Under these conditions the de-protonated form of NH_2OH reacted with carbonyl groups to form oximes. Thus, NH_2OH became less available for the oxidation by MnO_2 .

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 NH_2OH transformation, $\text{N}_2\text{O(g)}$ production, and the formation of nitrite (NO_2^-) and nitrate (NO_3^-) 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 NH_2OH 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 NH_2OH 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 ((1), (2), (3), (4), (5), (6), (7), (8), (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 ((2), (3), (4)) where MnO₂(s) initiates NH₂OH transformation and is converted to N₂O(g). In specific reactions, intermediates include NO₂[−] and NO₃[−] ((2), (3), (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

1.2.1.2 Specific reactions

1.2.2. Fe-bearing minerals—Goethite (α -FeOOH) is a common iron oxyhydroxide found in aquifer material and soil, and was used in NH_2OH nitrification reactions. The source of goethite was derived from a naturally occurring source mineral. Amorphous FeOOH(s) (ferrihydrite), a poorly structured form of FeOOH, is more amenable to dissolution than goethite, and will be referred to as amorph-FeOOH(s). Ferrihydrite and goethite share similar elemental composition, but these minerals exhibit different physical and chemical characteristics (Villacís-García et al., 2015).

The *proposed* overall reaction between NH_2OH and undifferentiated mineral forms of iron results in N_2O formation (reaction 6). The *proposed* oxidation reactions lead to NO_2^- and NO_3^- intermediates ((7), (8)), and a reduction reaction leads to $\text{N}_2\text{O(g)}$ formation (reaction 9). During the reactions, Fe(III) is reduced to undifferentiated reduced forms of Fe, represented as Fe^{2+} and FeO. The reduction step may be carried out by surface reactions involving $\equiv \text{Fe(II)}$, or soluble Fe^{2+} . In environmental systems exposed to air, $\equiv \text{Fe(II)}$ and Fe^{2+} could become oxidized (i.e., $\equiv \text{Fe(III)}$, Fe^{3+}) by oxidized species in the test system, including $\text{O}_2(\text{g})$ or dissolved oxygen.

1.2.2.1. Overall reaction

1.2.2.2. Specific reactions

1.3. Objectives

The proposed fundamental reactions were investigated as a guideline to better understand abiotic NH_2OH nitrification. Specific objectives included, (1) examine the rate and extent of reaction between NH_2OH and Mn- and Fe-bearing minerals (pyrolusite, amorph-MnO₂(s), goethite, and amorphous FeOOH(s)), (2), identify predominant reaction byproducts and assess whether the proposed reactions and mechanism are viable, and, (3) assess the role of mineral surface characteristics and the mineral Fe and Mn content in NH_2OH nitrification.

2. Methods and materials

2.1. Chemicals and preparation

Goethite and pyrolusite ore were obtained from D.J. Mineral Company (Butte, Montana); crushed using a mortar and pestle and sieved through a 140 mesh (0.150 mm, 0.0041 in) sieve. Due to Fe impurities found in pyrolusite, a laboratory synthesized, Fe-free, amorphous $\text{MnO}_2(\text{s})$ was used to help differentiate between Mn- and Fe-initiated nitrification reactions. Amorph- $\text{MnO}_2(\text{s})$ was prepared using NaMnO_4 (0.282 M; 0.1 L), slowly adding H_2O_2 (10%) until the Mn^{+7} was reduced to Mn^{4+} . The amorph- $\text{MnO}_2(\text{s})$ precipitate was rinsed with de-ionized water (DIW), dried (105 °C), and stored in a desiccator. Due to the Mn impurities found in the goethite, a laboratory synthesized, Mn-free, amorph- $\text{FeOOH}(\text{s})$ was used to help differentiate between Fe- and Mn-initiated nitrification reactions. Ferrihydrite (amorph- $\text{FeOOH}(\text{s})$) was synthesized using similar methods described by Villacís-García et al. (2015). $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in DIW (13.3 g/0.3 L; 0.11 M) and neutralized (pH 7) with NaOH to precipitate amorph- $\text{FeOOH}(\text{s})$. The solid suspension was washed with DIW (4×), decanted, filtered, dried (104 °C), and stored in a desiccator until used.

2.2. Test reactor configuration and testing

The baseline testing configuration included serum vials (50 mL) containing amorph- $\text{MnO}_2(\text{s})$, pyrolusite, goethite, or amorph- $\text{FeOOH}(\text{s})$ (0.07 g), DIW (1.5 mL), and NH_2OH solution (35 mL; $[\text{NH}_2\text{OH}]_{\text{INITIAL}} = 50 \text{ mg/L as N}$), leaving approximately 25 mL of air-filled headspace (i.e., total volume 50 mL serum vial is ~60 mL). Teflon-faced septa (20 mm) were immediately placed on the vials, and crimp sealed with aluminum caps. The vials were laid down horizontally allowing only fluid contact with the septa to limit gaseous diffusion losses. The headspace of unopened vials was sampled (24 h) through the septa with a gas-tight syringe and analyzed for $\text{N}_2\text{O}(\text{g})$. Aqueous samples were collected and measured for pH, NO_2^- , and NO_3^- . Due to slow formation of $\text{N}_2\text{O}(\text{g})$ in test reactors amended with iron minerals (i.e., goethite and amorph- $\text{FeOOH}(\text{s})$), long-term testing was performed and reactors were sacrificed at 1, 4, 10 and 17 d. Mineral-free and NH_2OH -free vials were used to establish quality assurance and quality control under all conditions tested.

Controls were conducted to investigate whether pyrolusite or goethite reacted with NO_2^- to NO_3^- , and whether Mn^{2+} reacted with NO_3^- to form N_2O ((3), (4), (8)). NO_2^- , NO_3^- , Mn^{2+} were amended to the test reactors for short term and long-term periods of reaction to assess whether NO_3^- reacted with pyrolusite or goethite. Aqueous samples were analyzed to measure the final concentration of nitrogen species (i.e., NO_2^- , NO_3^- , N_2O) relative to the total nitrogen added as NH_2OH . The contact period for reactors containing Mn-species (Mn^{2+} or pyrolusite) was 24 h. Longer reaction times were provided for reactors containing goethite (1–17 d) due to the slower reaction rates. Pyrolusite or goethite (0.07 g), DIW (1.5 mL), and NO_2^- or NO_3^- solution (35 mL; $[\text{NO}_2^-]_{\text{INITIAL}}$ or $[\text{NO}_3^-] = 50 \text{ mg/L as N}$), were amended into these test systems. The $[\text{Mn}^{2+}]$ in test reactors was 3.4, 6.9 and 10.3 mmol/L (i.e., 1×, 2×, and 3× the $[\text{NO}_3^-]_{\text{INITIAL}}$, respectively).

NH_2OH has been reported to react with various forms of soil organic matter (SOM) to produce oximes (Porter, 1969), another potential form of nitrogen. In SOM-free systems,

including the test reactor configurations used here, this mechanism would be negligible, and would not constitute a significant loss of nitrogen. Consequently, oxime was not measured, nor considered in the N mass balance.

2.3. Analytical methods

Nitrate and nitrite were determined by capillary electrophoresis, method 4140 B capillary ion electrophoresis with indirect UV detection (American Public Health Association et al., 1998). Total nitrogen was measured using the Shimadzu TNM-1, Total Nitrogen Module. Nitrogen is combusted to NO and NO₂, reacted with ozone and measured with a chemiluminescence detector as total N (MDL ~ 0.1 mg/L) (ASTM, 2008). Total nitrogen measurements of the NH₂OH stock solution (n = 3) confirmed the initial concentration of 50 mg/L (as N) (i.e., 103% recovery of nitrogen). pH was determined by EPA Method 150.1 using the Orion Star A215 pH meter.

The serum vial headspace was analyzed for N₂O using a static equilibration method. N₂O concentrations were determined by gas chromatography, refer to Supporting information (Section S.2, Details of Analytical Methods). The dissolved N₂O (as N) in the aqueous phase (N₂O(aq)) was based on the gas phase measurements and the N₂O Henry's law constant. In a created headspace condition where gas concentrations are derived from the aqueous solution, the total dissolved N₂O concentration in the aqueous phase is calculated by first measuring the N₂O concentration in the headspace. The N₂O concentration in the headspace is converted to the partial pressure of N₂O which is used to calculate the portion of aqueous gas concentration that partitioned into the gas phase, and aqueous phase concentration that remained in the aqueous phase. Both parameters are used to calculate the concentration of dissolved N₂O in the aqueous phase of the serum vial, refer to the Supporting information (Section S.3, Calculation of dissolved N₂O gas concentration in test reactors).

Metals in minerals were determined by inductively coupled plasma, optical emission spectroscopy (ICP-OES) using Perkin Elmer Optima 8300DV ICP-OES, based on EPA Method 200.7 (U.S. EPA, 1994). The metals were extracted by microwave digestion in a 10% HNO₃ solution. The suspension was sealed in a pressurized liner and microwaved (175 °C). After digestion, the solids settled overnight prior to analysis, or were filtered (0.45 µm membrane filter) if solids remained in suspension.

Analysis of pyrolusite and goethite ore involved samples that were crushed and sieved (140 mesh; 0.150 mm; 0.0041 in). The ICP-OES detection limit and quantitation limit for Fe and Mn were 4.0 and 8.1 mg/kg, respectively. Quality control results for the calibration checks, method blanks, digestion blanks, interference checks, digestion duplicates, and serial dilutions met criteria established in EPA Method 200.7 (US EPA, 1994). The Brunauer–Emmett–Teller (BET) surface area of the minerals was determined using the QuantiChrome NOVA 4200e Surface Area Analyzer (Boynton Beach, FL). Mineral composition was determined by the Rigaku MiniFlex X-ray Diffractometer which provides a qualitative identification of minerals present in solid matrices based on comparison to reference diffraction data for known compounds. Imaging and microanalysis of Mn and Fe minerals were conducted using scanning electron microscopy (SEM) with energy dispersive X-ray

spectrometry (EDS). Refer to the Supporting information (Section S.2, Details of Analytical Methods) for details associated with X-ray Diffractometer, SEM, and EDS. Quality control standards, blanks, spikes, and duplicates indicated proper function of all analytical methods used.

3. Results and discussion

3.1. Surface area and mineral analysis

The surface area of pyrolusite ($5.5 \text{ m}^2/\text{g}$) and goethite ($5.3 \text{ m}^2/\text{g}$) were approximately equal (Table 1). The surface area of the amorphous $\text{MnO}_2(\text{s})$ ($123 \text{ m}^2/\text{g}$) and $\text{FeOOH}(\text{s})$ ($185 \text{ m}^2/\text{g}$) minerals was significantly greater than the crystalline forms (Table 1). The concentrations of Mn and Fe were elevated in the pyrolusite and goethite ore, respectively (Table 1). The majority of pyrolusite was comprised of Mn, but contained appreciable quantities of Fe impurities (Table 1). Goethite contained approximately 3% by weight Fe, with low concentrations of Mn (Table 1). The lab-synthesized amorph- $\text{MnO}_2(\text{s})$ and amorph- $\text{FeOOH}(\text{s})$ were predominantly comprised of Mn and Fe, respectively. Only 2.91% by weight Mn was measured in amorph- $\text{MnO}_2(\text{s})$ whereas the theoretical Mn content was 63%. This result indicated incomplete extraction of Mn, and possibly the pyrolusite too. The amorph- $\text{FeOOH}(\text{s})$ was 51.3% Fe by weight. Despite the extraction inefficiency of Mn minerals, amorph- $\text{MnO}_2(\text{s})$ was nearly Fe-free, and reactions with NH_2OH were dominated by Mn. Similarly, amorph- $\text{FeOOH}(\text{s})$ contained negligible quantities of Mn and reactions with NH_2OH were dominated by Fe.

X-Ray diffraction (XRD) analysis of the amorph- $\text{MnO}_2(\text{s})$ used in these experiments indicated disordered $\text{MnO}_2(\text{s})$ (data not included). XRD of the amorph- $\text{FeOOH}(\text{s})$ indicated a mixture of 2-line ferrihydrite which comprised a majority of the Fe content (data not included). Energy dispersive X-ray (EDX) analysis of the 4 minerals provided a quantitative measure of the Mn and Fe content of the mineral surfaces (Table 1). These results indicated that both the pyrolusite and amorph- $\text{MnO}_2(\text{s})$ exhibited 1–2 orders of magnitude higher Mn content than the results obtained by sample digestion followed by ICP OES analysis. To a lesser extent, EDX results also indicated 20 $\times$ higher concentrations of Fe in goethite, and 27% higher concentrations in the amorph- $\text{FeOOH}(\text{s})$. Overall, EDX results indicated incomplete extraction of Mn and Fe from pyrolusite, amorph- $\text{MnO}_2(\text{s})$, and goethite.

3.2. Hydroxylamine transformation by pyrolusite, amorph- $\text{MnO}_2(\text{s})$, goethite and amorph- $\text{FeOOH}(\text{s})$

The basis for nitrogen in the mass balance was the initial NH_2OH (35 mL, 50 mg/L as N) amendment to test reactors, and the post-reaction nitrogen residuals. These residuals included the final concentrations of N_2O in the gas phase ($\text{N}_2\text{O}(\text{g})$), dissolved N_2O in the aqueous phase ($\text{N}_2\text{O}(\text{aq})$), and NO_2^- and NO_3^- in the aqueous phase.

High concentrations of $\text{N}_2\text{O}(\text{g})$ were measured, and a high level of total nitrogen (i.e., $\text{N}_2\text{O}(\text{g}) + \text{N}_2\text{O}(\text{aq}) + \text{NO}_2^- + \text{NO}_3^-$) recovery was achieved with both pyrolusite (96%) and amorph- $\text{MnO}_2(\text{s})$ (95%) after a 1 d reaction period (Table 2; Fig. 1). The recovery of measured nitrogen species in the pyrolusite- and amorph- $\text{MnO}_2(\text{s})$ -amended systems was

similar. Lower concentrations of $\text{N}_2\text{O}(\text{g})$ were measured, and lower total nitrogen was recovered in goethite and amorph- $\text{FeOOH}(\text{s})$ amended systems. Specifically, only 1.1% and 14.5% recovery was achieved in goethite and amorph- $\text{FeOOH}(\text{s})$ amended reactors, respectively, after a 1 d reaction period (Table 2; Fig. 1). The initial pH (0.07 g mineral, 35 mL DIW) was 7.7, 10.0, 7.5, and 9.0 in pyrolusite, amorph- $\text{MnO}_2(\text{s})$, goethite and amorph- $\text{FeOOH}(\text{s})$, respectively. NH_2OH amendment and abiotic nitrification resulted in a pH decline in the test reactors (Fig. 1). Due to a slow reaction between Fe minerals and NH_2OH , and incomplete recovery of total N, a longer reaction period (10 d) was evaluated (Table 2; Fig. 2). After 10 d, the concentration of $\text{N}_2\text{O}(\text{g})$ was low and the total N recovered was limited in goethite-amended reactors. Conversely, greater concentrations of N_2O were measured, and greater total nitrogen was recovered in amorph- $\text{FeOOH}(\text{s})$ amended reactors. Despite the same mass (0.07 g) of goethite and amorph- $\text{FeOOH}(\text{s})$ amended to the test reactors, greater Fe content and surface area of the amorph- $\text{FeOOH}(\text{s})$, relative to goethite (Table 1), was partially responsible for these differences in the NH_2OH transformation rate.

Greater concentrations of NO_2^- were measured in test reactors amended with Mn minerals, than with Fe minerals (Table 2). NO_3^- concentrations were variable under all conditions, and no clear trend could be established with either Mn or Fe bearing minerals. The amount of NO_2^- and NO_3^- were generally equal, and their concentrations were higher in reactors amended with amorph- $\text{FeOOH}(\text{s})$, relative to goethite. In summary, the total nitrogen recovered in amorph- $\text{FeOOH}(\text{s})$ - and goethite-amended systems was limited relative to Mn-amended systems.

3.3. Rate of N_2O formation

The rate of NH_2OH transformation and $\text{N}_2\text{O}(\text{g})$ formation using pyrolusite was significantly faster than goethite (Fig. 3). Complete transformation of NH_2OH was achieved by pyrolusite within 4.5–5 h (Fig. 3). The recovery of total N was 96.3%, and the predominant reaction byproduct was recovered as N_2O (82.1%), and the average concentrations ($n = 5$) of NO_2^- (6.7 mg/L) and NO_3^- (0.1 mg/L) accounted for 14.2%. The mass balance recovery of nitrogen indicated that other forms of nitrogen gas species (i.e., NO , NO_2) were absent. $\text{N}_2(\text{g})$ may have formed as a product of these reactions, but would have been difficult to measure given the high background concentrations. Given the relatively complete mass balance on total nitrogen results, $\text{N}_2(\text{g})$ was determined to be minimal, and would be of limited environmental concern.

Goethite involved a longer reaction period (17 d) where incomplete NH_2OH transformation was achieved. Only 8.8% of total N had been recovered, including 8.7% as N_2O , and 0.1% as nitrite and nitrate residuals ($[\text{NO}_2^-] = 0.033 \text{ mg/L}$; $[\text{NO}_3^-] = 0.0 \text{ mg/L}$). The range in pH (4.0–6.5) of the Fe-mineral suspension did not appear to impact the rate of N_2O formation (Fig. 3).

Due to the incomplete digestion and extraction of Mn using ICP OES analysis, a critical analysis was based on the EDX elemental composition results (Table 1). The BET-based specific surface concentrations of Mn and Fe were calculated using results from the EDX surface concentrations and the surface area measured for each mineral. The BET-based specific surface concentrations of iron in goethite and amorph- $\text{FeOOH}(\text{s})$ were 7.99 and 0.23

mg Fe/m², respectively; and Mn in pyrolusite and amorph-MnO₂(s) are 7.67 and 0.34 mg Mn/m², respectively.

Despite significant differences in specific surface concentrations of Mn in pyrolusite and amorph-MnO₂(s), nearly complete recovery of NH₂OH (as N) was achieved within a 24 h reaction period (Fig. 1). The rate of NH₂OH nitrification was rapid in both cases, and differences in nitrification rates were indistinguishable over this reaction period. In the Fe-bearing minerals, a higher NH₂OH nitrification rate was measured in the amorphous-FeOOH(s) than the goethite (Fig. 2) and was attributed to greater surface area and contact between Fe reaction sites and NH₂OH. Comparable BET-based specific surface concentrations of Mn and Fe were measured for both crystalline and amorphous Mn- and Fe-bearing minerals. However, the rate of NH₂OH nitrification was much greater in the Mn-bearing minerals than in the Fe-bearing minerals. These results underscore the intrinsically faster reaction of Mn mineral species with NH₂OH, relative to Fe mineral species.

Four sequential applications of NH₂OH to pyrolusite were conducted to assess whether the abiotic nitrification of NH₂OH could be sustained through repeated exposures. High concentrations of N₂O and high levels of total nitrogen recovery (88.2–96.7%) were measured indicating the consistency in this abiotic mechanism (refer Supporting information, Section 4, Repeated NH₂OH amendment to pyrolusite).

3.4. Reaction mechanism testing

Test reactors containing pyrolusite, MnSO₄ (i.e., Mn²⁺), or goethite were amended with NO₂⁻ or NO₃⁻ to assess whether *proposed* (3), (4), (8) played a role in the NH₂OH nitrification mechanism. Results indicated complete recovery of the NO₂⁻ and NO₃⁻ amended to pyrolusite, 96–107% and 102–105%, respectively (i.e., 95% confidence interval); complete recovery of NO₂⁻ and NO₃⁻ amended to goethite, 100–104% and 94–101% respectively; and 99–104% recovery of NO₃⁻ amended to MnSO₄. The concentration of N₂O(g) was negligible and was at or below background levels. Complete recovery of NO₂⁻ and NO₃⁻, and no N₂O(g) formation in these test systems indicated that *proposed* (3), (4), (8) did not occur under the conditions of these experiments.

NH₂OH nitrification by pyrolusite, amorph-MnO₂(s), goethite, and amorph-FeOOH(s) resulted in varying concentrations of NO₂⁻ and NO₃⁻ residuals (Table 2). These results are consistent with previous studies involving residuals from the abiotic transformation of NH₂OH (Bremner et al., 1980). However, the results from testing of these specific reactions are in general disagreement with *proposed* (1), (2), (3), (4), (5), (6), (7), (8), (9), and suggests alternate reactions and/or mechanisms play a role. For example, NH₂OH nitrification and formation of NO₂⁻ and NO₃⁻ may be directly coupled with oxidation reactions involving Mn(IV) or Fe(III) and NH₂OH nitrification. However, NH₂OH was not amended in these control reactors. Currently, a firm explanation cannot be provided and additional investigation is needed to clarify the roles of NO₂⁻ and NO₃⁻ intermediates and/or end products in the overall mechanism. Mechanistic uncertainty ranges from the possibility that the reaction does not involve any free nitrogenous intermediates and that N₂O is formed directly from an iron-nitrogen complex (Butler and Gordon, 1986), to the mechanism may involve a series of rapid sequential isomerization steps and proton transfer

(Heil et al., 2014). Recently, rapid NH_2OH nitrification was measured in synthetic ocean water using birnessite where the main reaction byproduct was N_2O . The proposed mechanism included nitroxyl (HNO), and possibly the aminoxyl radical ($\text{H}_2\text{NO}\cdot$) that could be involved in other coupled reactions in the nitrogen cycle (Cavazos et al., 2018).

4. Conclusions and discussion

4.1. NH_2OH transformation mechanism

Rapid and complete NH_2OH transformation occurred in the presence of crystalline and amorphous manganese mineral species. Analysis of nitrogen residuals used in a nitrogen mass balance indicated nearly complete abiotic NH_2OH nitrification, where N_2O was the predominant reaction byproduct, and to a lesser extent, NO_2^- and NO_3^- . NO_2^- and NO_3^- residuals did not react directly with pyrolusite, goethite, and Mn^{2+} , indicating *proposed* (3), (4), (8) do not occur under these experimental conditions. Reduced iron (Fe^{2+}), but not Mn^{2+} , may react with NO_2^- under acidic conditions ($\text{pH} \approx 4$), and in the presence of elevated $[\text{Fe}^{2+}]$ (Wullstein and Gilmour, 1966; Nelson and Bremner, 1970; Jones et al., 2015). Reactions between Fe^{2+} and NO_3^- are very slow at lower temperatures, and reduction rates of this magnitude may be able to remove NO_3^- from groundwater in natural areas where the NO_3^- input is low and reaction time long, but would be of little significance when the NO_3^- load is high, such as below agricultural areas (Postma, 1990). Although the thermodynamics of Fe(II) oxidation are favorable when coupled to either NO_3^- or NO_2^- reduction, the kinetics of abiotic Fe(II) oxidation by NO_3^- are relatively slow (Picardal, 2012). Overall, acidic and reduced conditions, in conjunction with long reaction periods did not occur in this study and helps to explain the presence of NO_2^- and NO_3^- residuals.

NH_2OH nitrification by goethite was limited, and the low concentrations of $\text{N}_2\text{O(g)}$ measured in the goethite/ NH_2OH system (Table 2) may have been partially attributed to Mn impurities in the goethite (Table 1). Conversely, the NH_2OH nitrification rate by the Mn-free, amorph- FeOOH(s) , was greater than goethite, and was attributed to greater surface area of the amorph- FeOOH(s) . The range of reaction pH (4.0–6.5) did not impact NH_2OH transformation (Fig. 3).

Excess Fe (5–10 $\times$), relative to NH_2OH , is needed for $\text{N}_2\text{O(g)}$ to form, otherwise the nitrogen byproduct is $\text{N}_2\text{(g)}$ (Bengtsson et al., 2002). In this study, both Fe and Mn were present in excess (i.e., EDX Mn and Fe results; $\text{Mn/NH}_2\text{OH} = 5.9\text{--}6.1$ mol/mol; $\text{Fe/NH}_2\text{OH} = 6.3\text{--}7.0$ mol/mol) and nearly complete conversion of NH_2OH to $\text{N}_2\text{O(g)} + \text{NO}_2^- + \text{NO}_3^-$, was measured. Ammonia-oxidizing bacteria are prevalent in soil environments and are responsible for the release of significant amounts of NH_2OH when in the presence of excess ammonia (Liu et al., 2017). In many environmental systems, Fe and/or Mn are present in abundance, suggesting that rapid, complete, and sustained nitrification of NH_2OH could occur. Consequently, rapid abiotic NH_2OH nitrification may be a contributing factor to the very low NH_2OH concentrations often measured in soil (Liu et al., 2014, Liu et al., 2016, Liu et al., 2017), and to N_2O being the predominant reaction byproduct.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Notice

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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).

Fig. 1.

Nitrogen recovery as a result of the reaction between NH_2OH and Mn and Fe mineral species (0.07 g mineral, $[\text{NH}_2\text{OH}]_{\text{INITIAL}} = 50 \text{ mg/L}$ (as N); 36.5 mL solution; 25 mL headspace; 1 d reaction).

Fig. 2.

Nitrogen recovery as a result of mineral reaction with hydroxylamine in test reactors containing goethite (Top) and amorphous-FeOOH(s) (Bottom) (0.07 g mineral; $[\text{NH}_2\text{OH}]_{\text{INITIAL}} = 50 \text{ mg/L (as N)}$; 36.5 mL solution; 25 mL headspace).

Fig. 3.
 (Top) N₂O(g) formation in the headspace of test reactors containing pyrolusite (0.07 g), and NH₂OH (50 mg/L as N); (Bottom) N₂O(g) formation in the headspace of test reactors containing FeOOH(s) (0.07 g), and NH₂OH (50 mg/L as N).

Table 1.

Average surface area results^a; average ICP OES metals concentrations^b in pyrolusite and goethite ore, and amorphous MnO₂(s) and amorphous FeOOH(s); EDX surface elemental composition results^c.

Mineral Surface area ^a (m ² /g)	ICP OES ^b [Mn] (mg/kg)	ICP OES ^b [Fe] (mg/kg)	EDX ^c	
			Mn (%)	Fe (%)
Pyrolusite				
5.5 (5.4–5.6)	6580 (5690–7460)	3320 (3150–3500)	60.3 (60.1–60.5)	ND
Amorph-MnO ₂ (s)				
123 (121–125)	29,120 (20,040–38,200)	8 (8–8) ^d	58.0 (57.8–58.2)	ND
Goethite				
5.3 (4.9–5.7)	150 (130–180)	30,980 (27,500–34,450)	ND	62.8 (62.6–63.0)
Amorph-FeOOH(s)				
185 (180–189)	11 (1–20)	512,720 (322,370–703,070)	ND	70.0 (69.8–70.2)

^a Surface area of pyrolusite and goethite ore (n = 3), and amorph-MnO₂(s) and amorph-FeOOH(s) (n = 4); 95% confidence interval reported in parentheses.

^b Average concentration (n = 6, pyrolusite and goethite; n = 3 amorph-MnO₂(s) and amorph-FeOOH(s)); 95% confidence interval reported in parentheses was the average (n = 3) ± standard error; where standard error = $t_{0.05} \times \text{standard deviation} / n^{0.5}$, and $t_{0.05} = 4.303$ (i.e., standard t-table 0.05 level of significance, 2 degrees of freedom).

^c Average surface concentrations of Mn and Fe; 95% confidence interval reported in parentheses are the average ± standard error; where standard error = $t_{0.05} \times \text{standard deviation} / n^{0.5}$, and $t_{0.05} = 2.021$; ND – not detected.

^d All samples reported 8 mg/kg (below quantitation limit).

Table 2.

The concentrations of nitrogen species (mg/L, as N) remaining after NH_2OH nitrification represent the average value; 95% confidence intervals are in parentheses^a.

Nitrogen species	Pyrolusite	Amorph-MnO ₂ (s)	Goethite	Amorph-FeOOH(s)
Day 1				
N ₂ O(g)	16,650 (16,350–16,940)	17,250 (17,120–17,390)	220 (195–250)	3580 (3530–3630)
NO ₂ [−]	6.2 (6.0–6.4)	4.5 (4.3–4.6)	0.18 (0.17–0.19)	0.77 (0.64–0.90)
NO ₃ [−]	0.6 (0.57–0.62)	0.31 (0.22–0.39)	0.0–	0.70 (0.63–0.76)
Day 4				
N ₂ O(g)	NT	NT	990 (680–1300)	8260 (8100–8420)
NO ₂ [−]	NT	NT	0.25 (0.24–0.27)	1.57 (1.43–1.71)
NO ₃ [−]	NT	NT	0.0–	0.73 (0.76–0.91)
Day 10				
N ₂ O(g)	NT	NT	1630 (1350–1900)	12,100 (11,910–12,290)
NO ₂ [−]	NT	NT	0.25 (0.21–0.3)	1.29 (1.11–1.48)
NO ₃ [−]	NT	NT	0.16 (0.0–0.53)	1.12 (0.83–1.40)
Day 17^b				
N ₂ O(g)	NT	NT	1680	NT
NO ₂ [−]	NT	NT	0.34	NT
NO ₃ [−]	NT	NT	0.00	NT

NT not tested.

^a95% confidence interval = average ($n = 5$) $\pm$ standard error; standard error = $t_{0.05} \times \text{standard deviation} / n^{0.5}$, where $t_{0.05} = 2.776$ (i.e., standard t-table 0.05 level of significance, 4 degrees of freedom).

^bAverage values for replicate reactors with goethite (0.07 g), hydroxylamine (36.5 mL, 50 mg/L as N), 25 mL headspace, and a 17-day reaction period.