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Oxidation of reduced daughter products from 2,4-dinitroanisole (DNAN) by Mn(IV) and Fe(III) oxides

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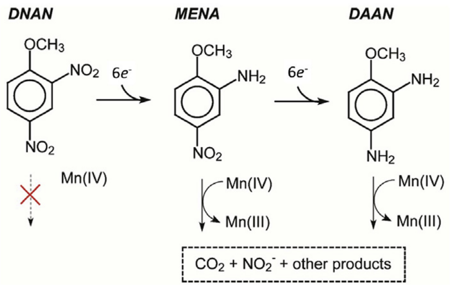
HIGHLIGHTS

- Insensitive munition compound DNAN is resistant to oxidation by soil minerals.
- DNAN reduced daughter products, MENA and DAAN, are oxidized by birnessite.
- DAAN can be oxidized by either ferrihydrite or birnessite.
- MENA reacted with birnessite releases N to nitrite.

GRAPHICAL ABSTRACT



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ABSTRACT

Abiotic transformation of anthropogenic compounds by redox-active metal oxides affects contaminant fate in soil. The capacity of birnessite and ferrihydrite to oxidize the insensitive munitions compound, 2,4-dinitroanisol (DNAN), and its amine-containing daughter products, 2-methoxy-5-nitro aniline (MENA) and 2,4-diaminoanisole (DAAN), was studied in stirred reactors at controlled pH (7.0). Aqueous suspensions were reacted at metal oxide solid to solution mass ratios (SSR) of 0.15, 1.5 and 15 $g\,kg^{-1}$ and solutions were analyzed after 0–3 h by high performance liquid chromatography coupled with photodiode array or mass spectrometry detection. Results indicate that DNAN was resistant to oxidation by birnessite and ferrihydrite. Ferrihydrite did not oxidize MENA, but MENA was susceptible to rapid oxidation by birnessite, with nitrogen largely mineralized to nitrite. This is the first report on mineralization of nonphenolic aromatics and the release of mineralized N from aromatic amines following reaction with birnessite. DAAN was oxidized by both solids, but *ca.* ten times higher rate was observed with birnessite as compared to ferrihydrite at an SSR of 1.5 $g\,kg^{-1}$. At 15 $g\,kg^{-1}$ SSR, DAAN was removed from solution within 5 min of reaction with birnessite. $CO_{2(g)}$ evolution experiments indicate mineralization of 15 and 12% of the carbon associated with MENA and DAAN, respectively, under oxic conditions with birnessite at SSR of 15 $g\,kg^{-1}$. The results taken as a whole indicate that initial reductive (bio)transformation products of DNAN are readily oxidized by birnessite. The oxidizability of the reduced DNAN products was increased with progressive (bio)reduction as reflected by impacts on the oxidation rate.

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1. Introduction

The U.S. Department of Defense (DoD) is evaluating new and safer alternatives to traditional munitions compounds. The insensitive munitions compound (IMC), 2,4-dinitroanisole (DNAN), is one of those being testing to replace the traditional munitions compound, 2,4,6-trinitrotoulene (TNT), because it exhibits lower susceptibility to unintended detonation by shock and heat (Walsh et al., 2013). However, upon detonation, a substantial mass fraction of free product often remains unaltered and DNAN is subsequently passively released into the environment during residue dissolution (Morley et al., 2006; Taylor et al., 2009). The fate and transport of these compounds in soil systems remains poorly understood. Furthermore, recent studies have indicated that, under anoxic soil conditions, DNAN is subjected to microbially-mediated or mineral-surface-catalyzed reduction to form potentially toxic aromatic amine daughter products 2-methoxy-5-nitro aniline (MENA) and 2,4-diaminoanisole (DAAN) (Liang et al., 2013; Hawari et al., 2015, Olivares et al., 2013, 2016a, 2016b). Despite this, there has been very limited study on the fate of these daughter compounds in soil. These potentially toxic aromatic amines that form during different stages of transformation of the parent compound DNAN may also pose environmental threats to the soil and aquatic systems.

Electron transfer reactions at soil mineral surfaces play an important role in the abiotic transformation of organic environmental contaminants (Laha and Luthy, 1990; Pizzigallo et al., 1998; Majcher et al., 2000; Li et al., 2003). Iron-bearing minerals are abundant and have been shown to transform xenobiotics, including explosive compounds (Hofstetter et al., 1999; Boparai et al., 2010; Ou et al., 2015). Despite their lower mass concentration in soils, manganese (III, IV) oxide minerals, such as birnessite ($[Na,Ca,Mn^{2+}][Mn^{3+},Mn^{4+}]_7O_{14}\cdot 2.8H_2O$) have been found to be capable of oxidizing organic compounds including phenolics like catechol, hydroquinone, resorcinol, aniline and its derivatives (Laha and Luthy, 1990; Klausen et al., 1997; Pizzigallo et al., 1998; Majcher et al., 2000; Colon et al., 2002; Li et al., 2003; Chien et al., 2009), eventually leading to reactive intermediates that may undergo polymerization or partial mineralization to $CO_{2(g)}$ (Majcher et al., 2000; Kang et al., 2006; Li et al., 2012). The inherent oxidizing or reducing capability of minerals must be resolved to predict the fate of novel IMCs in soils. Toward that goal, we chose two mineral models (i) birnessite and (ii) ferrihydrite ($Fe^{III}{}_2O_3\cdot 0.5H_2O$) to better understand their reactivity toward the parent compound DNAN and its daughter products MENA and DAAN. These minerals are known for their surface reactivity and are commonly found in soils and sediments (Essington and Vergeer, 2015).

Birnessite (denoted from here simply as $MnO_{2(s)}$) is a common representative of Mn(III, IV) containing secondary mineral forms produced as a result of primary mineral weathering in soils. It exhibits both permanent and pH-dependent surface charge, the former as a result of Mn(IV) vacancy sites in the crystal structure, and the latter because of proton adsorption-desorption on Mn-OH surface functional groups (Essington, 2015). Synthetic “acid birnessite” prepared from reduction of potassium permanganate has been widely used as surrogate for naturally-occurring biogenic birnessite (Chorover and Amistadi, 2001; Villalobos et al., 2003). Ferrihydrite is a poorly-crystalline and highly-reactive hydrous Fe(III) oxide that serves as an important sink for contaminant metals and an oxidizing agent for some organic compounds (Waychunas et al., 2005). The high surface-reactivity of ferrihydrite includes the capacity for either reductive or oxidative transformation, wherein it promotes Fe(II)-sorbate-induced reduction of DNAN (Niedzwiecka and Finneran, 2015) or the surface Fe(III)-induced oxidative transformation of aromatic amine biotransformation products.

The objectives of the study were to (i) assess the oxidation potential of IMCs and their daughter products by birnessite and ferrihydrite, and (ii) identify the inorganic oxidation products. The ability of birnessite and ferrihydrite to abiotically transform the IMC parent compound DNAN in comparison with its daughter products, MENA and DAAN, was studied under well-controlled laboratory conditions.

2. Materials and methods

All chemicals used were ACS reagent grade or better, and all solutions were prepared from ultrapure (Barnstead nanopure, 18.2 MΩ) water. The details of mineral synthesis and characterization methods, including mineral purity, specific surface area and particle size distribution, are described in Supplementary Information (section A.1).

2.1. IMCs and daughter products

2,4-dinitroanisole (DNAN; CAS #119-27-7, 98% purity) was purchased from Alfa Aesar (Ward Hill, MA). 2-methoxy-5-nitroaniline (MENA; CAS #99-59-2, 98% purity) and 2,4 diaminoanisole (DAAN; CAS #615-05-4, 99.6% purity) were purchased from Sigma–Aldrich (St Louis, MO). The physico-chemical properties of the compounds are listed (Table A.1).

2.2. Time series kinetic experiments

Time series experiments were conducted to quantify the abiotic transformation potential of IMCs by birnessite and ferrihydrite at solid to solution ratios (SSR) of 0.15, 1.5 and 15 g kg^{-1}. One hundred mL of 1 mM DNAN, MENA or DAAN solution (in 10 mM NaCl as background electrolyte) at pH 7.0 were placed in a reactor with a magnetic stirrer and the appropriate dry mass of birnessite or ferrihydrite was added with rapid mixing to initiate the reaction at the desired SSR ratios. The pH was controlled at 7.0 by titration of 10 mM HCl or NaOH throughout the reaction. Samples were taken at time intervals of 0, 5, 10, 20, 40, 60 and 180 min for birnessite reaction and at 0, 15, 30, 60 and 180 min for ferrihydrite. Solids were separated via centrifugation at 41,500 g for 5 min using an Eppendorf 5417C bench top micro-centrifuge. The supernatant solution was analyzed for equilibrium concentration of IMCs using ultra high performance liquid chromatography with photodiode array detection (UHPLC-PDA) for target compounds. All time series experiments were conducted under oxic conditions (in equilibrium with atmospheric air) at 25 °C. Surface-area normalized pseudo first order rate coefficients [for oxidation kinetics were determined from the magnitude of the slope of the regression line resulting from plotting the log of normalized reactant concentration (C_t/C_0) vs time (h) for first three data points, where C_t is the concentration of compound at time *t*, and C_0 is the initial concentration of the compound at time zero, normalized to specific surface area.

2.3. CO_2 evolution experiments

A separate set of experiments was conducted in closed serum bottles to measure the extent to which IMC and daughter product oxidation resulted in compound mineralization to $CO_{2(g)}$. These experiments were carried out in closed serum bottles in 10 mM NaCl background and initial pH 7.0, at 25 °C. Forty mL of 1 mM DNAN, MENA or DAAN solution were added to 0.6 g mineral in a serum bottle (Volume = 155.5 cm^3) in triplicate at SSR of 15 g kg^{-1}. The samples were allowed to react for 3 h, and $CO_{2(g)}$ released to the headspace was measured using gas chromatography after