ABIOTIC DEALKYLLATION AND HYDROLYSIS OF ATRAZINE BY BIRNESSITE

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Abstract—Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and its degradation products are important contaminants of world water systems and have effects on aquatic life. These effects are modulated by the degradation of atrazine, which depends, in part, on its reactivity with soil minerals. We have studied the degradation reaction of atrazine on synthetic birnessite (δ-MnO₂) in the aqueous phase using a batch reactor and a developed high-performance liquid chromatography method. The reaction was studied in the absence of light at 25°C and between pH 2.3 to pH 8.3. The reaction rates increased with decreasing pH and increasing δ-MnO₂ loading, and they did not follow simple first-order kinetics. The major products are hydroxylated and mono- and didealkylatrazine. Ammeline and cyanuric acid also were detected. The half-life (t½) for the degradation of atrazine was approximately 16.8 d and independent of oxygen. Manganese(II) evolution was a minor product. The mechanism of dealkylation involved proton transfer to Mn(IV)-stabilized oxo and imido bonds, with no net oxidation and reduction. Oxidation was a secondary reaction. The proposed abiotic pathway for the transformation of atrazine on δ-MnO₂ was identical to the reported biotic pathway. Thus, δ-MnO₂, a common soil component, facilitated the efficient N-dealkylation and hydrolysis of the herbicide atrazine at 25°C, possibly via a nonoxidative mechanism. The N-dealkylation has been attributed strictly to a biological process in soils.

Keywords—Abiotic Atrazine Degradation Nonredox Manganese oxide

INTRODUCTION

The herbicide atrazine (AT; 2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine), one of the most widely used selective herbicides in the United States, has drawn renewed interest because of recent data indicating widespread atmospheric transport and deposition [1–3]. In June 2000, the U.S. Environmental Protection Agency Scientific Advisory Panel voted to recommend that AT be reclassified as “not likely” to be a human carcinogen. More recently, however, AT has been identified as a potent disrupter of cell chromosome structure and estrogen metabolism [4–6]; thus, its reactivity with soil minerals and removal from the environment remain important issues.

Atrazine can be degraded by both biotic and abiotic processes in soil environments. Biological contributions to the degradation of AT in soil environments are well known [7–11]; however, abiotic transformations are poorly understood and often ignored in remediation scenarios. Since the early work on AT degradation, researchers have suggested that microbial degradation may not be the only major factor in the detoxification and loss of s-triazine herbicides from field soils [12]. The literature does show a consensus [13], however, that the three principal metabolites found in soils from biotic processes are hydroxyatrazine (HA) [14,15], deisopropylatrazine (DEA), and deethylatrazine (DIA). Hydroxylation of these products has been suggested as an initial step to complete degradation to CO₂, which is a slow process in soil environments [16]. A well-known product of abiotic reactions is HA [17–20]. By contrast, N-dealkylation is classified strictly as a biological transformation [21,22], with time scales on the order of weeks to months in field soils.

Transformation of organic pollutants adsorbed to the surface of metal oxides, particularly manganese oxides, is well established [23,24], although abiotic transformations of herbicides by this pathway rarely have been investigated [24]. Cheney et al. [25] have shown that AT is rapidly degraded (hours) at ambient temperature on the surface of air-dried (10% water content) birnessite (δ-MnO₂), which is similar to manganese oxides found in soils [26]. In a more recent study, Shin et al. [27] demonstrated that AT can be N-dealkylated while adsorbed on the surface of air-dried (10% water content) δ-MnO₂, cryptomelane 2, cryptomelane 1, and pyrrolusite at 30°C. They employed a novel combination of tribologic, microcalorimetric, manometric, chromatographic, and spectroscopic methods to demonstrate that the manganese oxide surface catalyzes the adsorbed herbicide in a nonredox reaction that produced the dealkylated products DEA, DIA, and dealkylated AT (DDA) as well as heat (exothermic reaction), with no soluble manganese detected following extraction. A novel nonredox dealkylation mechanism was proposed involving proton transfer to Mn(IV)-stabilized oxo and imido bonds [23]; however, those results did not identify any hydrolyzed and/or other dealkylated forms of AT except for those discussed above.

In the present study, we further investigated δ-MnO₂ to determine if the new developed high-performance liquid chromatography (HPLC) method is able to detect hydrolyzed and other dealkylated products of AT degradation in suspension of the oxide, to see if the nonredox AT dealkylation mechanism observed in air-dried δ-MnO₂ prevails in wet conditions, and to develop a new abiotic degradation pathway for AT. We report here five other hydrolyzed and dealkylated forms of AT degradation and confirm that the mechanism of dealkylation observed in air-dried MnO₂ prevails in wet conditions as well. The mechanism of the dealkylation reaction was studied by...
measuring both the surface properties of the synthetic δ-MnO₂ and the effect of pH on the reaction. The effects on the rate of the reaction of oxide loading and added cosolute were studied as well, and the ligand promoted dissolution of δ-MnO₂ was studied in relation to oxidation of the products. The results obtained in the present study may prove to be useful not only in the design of remediation scenarios but also in the calibration of in situ microbiological studies, which heretofore have considered abiotic N-dealkylation to be an insignificant pathway of AT degradation in soils. Further studies are needed to determine the influence of environmental parameters on the mechanism and its relevance under natural soil conditions.

MATERIALS AND METHODS

Materials

Atrazine (purity, 97.9%), DIA (purity, 96%), DEA (purity, 94%), DDA (2-chloro-4, 6-diamino-s-triazine; purity, 97%), HA (purity, 97%), deisopropylatrazine; DIA = deisopropylhydroxyatrazine; DEA = deethylhydroxyatrazine; DDA = deisopropylhydroxyatrazine; HA = hydroxyatrazine; DIHA = deisopropylhydroxyatrazine; DEHA = deethylhydroxyatrazine; DDHA = didealkylhydroxyatrazine.

δ-MnO₂ was synthesized according to the methods described by McKenzie [28] from Ciba-Geigy (Columbia, MO, USA) (Table 1). Alkaline manganese dioxide suspensions were prepared with Milli-Q® water.

Table 1. Chemical structure and acronyms of atrazine and its metabolites

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Batch reactor

Experiments were conducted in the dark at 20°C in a 250-ml jacketed glass reactor that was connected to a temperature-controlled chiller. To obtain a consistent aging time and hydration equilibrium, 2.0 g of δ-MnO₂ were suspended in 200 ml of 0.01 M NaCl prepared with Milli-Q® water in the presence of oxygen. The δ-MnO₂ was maintained in suspension by magnetic stirring. To measure the role of oxygen on the reaction, the δ-MnO₂ was suspended as described above with helium gas sparging for 36 h before starting the experiments and during the time course of the experiment to keep oxygen out. To adjust or keep a constant pH during the reaction, small amounts of 0.01 M HCl and 0.01 M NaOH were added to the suspension via a peristaltic pump connected to a pH controller box (Cole Parmer, Vernon Hills, IL, USA). The pH was monitored continuously during the time course of the reaction using a pH meter.

A kinetic experiment was performed by adding an aliquot of a 100 mg L⁻¹ AT stock solution to the above-described suspension of δ-MnO₂, reaching a final concentration of 4.68 μM in AT. Samples of 5 ml were withdrawn from the suspension with a syringe 30 min after the AT was added and at different time intervals. The samples were then quickly filtered into an amber vial through a membrane filter (pore size, 0.1 μm; diameter, 1 inch; Millipore, Billerica, MD, USA). The amber vials were then sealed with aluminum screw caps with septa and kept at −20°C in a refrigerator before analysis by HPLC and/or by graphite furnace atomic absorption spectrometry for dissolved Mn(II). Frozen storage did not appear to affect the characterization of AT degradation products. Control experiments were run by adding an aliquot of the 100 mg L⁻¹ AT stock solution to a suspension containing only Milli-Q® water at pH 2.6, 4.3, 6.2, and 8.0, respectively, and treated as described above.

Analytical methods

Atrazine and its degradation products were analyzed by HPLC with a variable-wavelength, photodiode-array Ultraviolet/Vis detector (Waters 996, Milford, MA, USA), a pumping system (Waters 660), and an auto sampler (Waters 717). Separation of the metabolites was achieved by a two-gradient mobile phase with a C-18 reversed-phase column (150 × 3.9 mm; Waters) equipped with a precolumn (4 × 4 mm) and compared with standards.

In our developed HPLC method, the initial mobile phase (phase A) consisted of 0.0771 g/L of NH₄OAc (ammonium acetate) and 1/L of HOAc (acetic acid from 1 N standard solution) in 5% methanol and 95% water, resulting in a pH of 4.7. The second mobile phase (phase B) consisted of a mixture of 5% methanol and 95% acetonitrile. The gradient began at 100% phase A, increased exponentially to 20% phase B in 0.5 min, and remained at 20% phase B for 5 min. Then, the gradient ramped linearly to 75% phase B in 25 min and 90% phase B in 26 min. The mobile phase was then linearly returned
Abiotic dealkylation and hydrolysis of atrazine by δ-MnO₂

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Fig. 1. (A) Effect of pH on the degradation of atrazine. Experimental conditions: 4.69 μM atrazine, 10 mM NaCl, 2 g/200 ml of birnessite (δ-MnO₂), 20°C, and pH 4.3 in the dark. (B) Linear plot of ln C/C₀, where ln is the natural logarithm and C and C₀ are the final and initial concentrations, respectively, as a function of time for the initial rates from (A). The solid lines are based on a linear-regression equation. Error bars represent ±1 standard deviation from the mean.

Analysis of manganese

The analysis of dissolved Mn(II) concentration was conducted in a graphite furnace atomic absorption spectroscope (Model 4100ZL; Perkin-Elmer, Wellesley, MA, USA) using a Pd/Mg(NO₃)₂ modifer as a masking agent for the manganese solution [29]. The dissolved Mn(II) was separated from the solid manganese oxide–AT mixture by filtering immediately after the sample was withdrawn from the batch-reactor experiment. One of the filtered samples was acidified with 1 ml of 0.1 N HCl before analysis. Detection limits were 10 ppb, and the precision of replicate runs was within 10%. In our experiments, the amount of adsorbed Mn(II) in the membrane filter was very small, which is consistent with the results of earlier work [25,27] and, thus, was neglected. A control experiment consisted of 18 Mega-Ohm Water plus δ-MnO₂ at pH 4.3 and 20°C and was sampled and analyzed as described above.

RESULTS

Mineral characterization

The synthesized δ-MnO₂ was characterized by x-ray powder diffraction and the Brunauer, Emmett, and Teller surface-area method. The x-ray diffraction (d) spacing and intensities of the synthesized δ-MnO₂ are in good agreement with the results for natural δ-MnO₂ [30]. The oxide proved to be amorphous, as indicated by the observed x-ray diffraction pattern, showing only three weak lines at d values of approximately 7.33, 3.64, and 2.44, respectively [31]. The specific surface area was 39 m²/g.

Effect of pH on the degradation reaction

Figure 1A shows the results from the HPLC analysis of a typical batch-reactor experiment for the disappearance of AT over time in a suspension of δ-MnO₂ (10 g L⁻¹, ~1.1 × 10⁻¹ M δ-MnO₂) at a constant pH from 2.6 to 8.5. The δ-MnO₂ was effective in degrading AT. The fastest rate of AT disappearance on this mineral occurred at pH 2.6, followed by a decrease in rates at pH 4.3, 6.2, and 8.5, respectively. Figure 1B shows a linear plot of ln C/C₀ (where C and C₀ are final and initial concentrations, respectively) as a function of time for the initial rates from Figure 1A. The solid straight lines in Figure 1B were obtained by fitting the data through a linear-regression equation. This decision was made because of the difficulty in obtaining a good-fitting line through the scattered data points after the first half-life. Figure 2 shows a plot of the log k₀ (k concentrations, respectively) as a function of time for the initial rates from Figure 1A. The solid straight lines in Figure 1B were obtained by fitting the data through a linear-regression equation. This decision was made because of the difficulty in obtaining a good-fitting line through the scattered data points after the first half-life. Figure 2 shows a plot of the log k₀ (k
observed; initial rates) versus pH for the degradation of AT on δ-MnO₃. A pH dependence of the rates was observed, with no significant difference between the unbuffered and acetate-buffered suspension. The reaction order with respect to the hydrogen-ion concentration was derived from the slope of this line, where the rate was assumed to be pseudo–first-order for the initial part of the kinetics (Table 2). Because the rate of AT disappearance was not significantly different at pH 4.3 and at pH 6.2, the lower pH value was used to study further the reaction, because it can be extrapolated to some eastern U.S. soil system [32].

Effect of initial oxide concentration on the degradation reaction

Figure 3A presents the effect of δ-MnO₃ concentration on the disappearance of AT at a constant pH of 4.3. The rate of AT disappearance was faster for the higher concentration of added δ-MnO₃. For the first 6 d of the reaction, increasing the δ-MnO₃ concentration from 2.87 \( \times 10^{-2} \) to 2.3 \( \times 10^{-1} \) M increased the rate constant proportionally, from 3.50 \( \times 10^{-2} \) to 8.87 \( \times 10^{-2} \) d⁻¹. The rate constants obtained from the different concentration of added δ-MnO₃ are summarized in Table 3. Figure 3B is a plot of the log \( k_o \) versus the log δ-MnO₃ concentration of the data in Figure 3A. This graph indicates that the reaction order at pH 4.3 has a linear relationship with respect to δ-MnO₃ concentration, with a slope of approximately 0.43 (\( r^2 = 0.9159 \)).

Reduction of δ-MnO₃

Figure 4A shows the time-course concentration of evolved Mn(II) observed during the experimental run shown in Figure 1A at pH 4.3. An initial increase was observed in the concentration of evolved Mn(II) that appeared to level off at approximately 0.5 \( \mu \)M in 6 d, followed by a small decline in concentration in 30 d.

Atrazine and its degradation products

To determine the degradation pathway of AT on δ-MnO₃, experiments were conducted in a batch reactor as described in the experimental section. Figure 4B shows a plot of the disappearance of AT and the appearance of hydrolyzed and dealkylated products formed on δ-MnO₃ over time at pH 4.3 in the dark at 20°C. Seven dealkylated forms of AT were detected by our developed HPLC method. However, difficulty occurred in quantifying two of the reaction products, ammeline and cyanuric acid, because they eluted with the solvent front and not separated. Hydroxyatrazine was produced at a higher concentration than the dealkylated forms, DEA and DIA. The

Table 3. Initial rates of atrazine disappearance calculated using the assumption of pseudo–first-order kinetics

<table>
<thead>
<tr>
<th>δ-MnO₃ M</th>
<th>k_o (d⁻¹)</th>
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<tbody>
<tr>
<td>No acetate</td>
<td>10 mM Acetate</td>
</tr>
<tr>
<td>2.87 ( \times 10^{-2} )</td>
<td>3.50 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>5.75 ( \times 10^{-2} )</td>
<td>4.16 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>1.10 ( \times 10^{-1} )</td>
<td>5.01 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>2.30 ( \times 10^{-1} )</td>
<td>8.87 ( \times 10^{-2} )</td>
</tr>
</tbody>
</table>

\( ^a \) Experimental conditions: 4.69 \( \mu \)M atrazine, 10 mM NaCl, 10\( g/L \) δ-MnO₃, 20°C, and pH 4.3.
where \( q \) and \( r \) are the reaction order with respect to \( d_5 \) of AT protonation [32]. The first and second rates of this reaction with respect to \( [\text{H}^+] \) and \([\text{MnO}_2]\), as shown by the straight lines in Figures 2 and 3B, varied from 0.11 to 0.23 for \( r \) and depended on \( \text{MnO}_2 \) loading (\( q = 0.4, r^2 = 0.9159 \)) in the present study. The apparent order, although slightly lower than the values reported for the model organic compounds aniline and \( p \)-methylphenol [34,35], followed the same trend. We acknowledge that traces of Mn(III) occurred recently under investigation) was surprising: It was chosen because of its low affinity for the surface and dissolved divalent metal cations. On the other hand, no significant inhibitory effect was found on the kinetics observed when 36 \( \mu \text{M} \) Mn(II) was added to the reaction mixtures.

At \( pH 2.6 \), competition exists between protons and protonated forms of AT for surface sites. The structure of the surface precursor complex formed and of its binding (inner- or outer-sphere) to the surface is unknown, but the rate of formation is influenced by the leaving group and electrostatic interactions on the surface. In the present study, at any \( pH \) examined, \( \delta \)-\( \text{MnO}_2 \) did not adsorb significant amounts of AT in aqueous suspension, suggesting that the equilibrium-binding constant for AT is lower than that for the precursor complex. The decreased reaction rates from \( pH 4 \) to \( pH 8 \) can be explained in terms of a decrease in acidity of the surface hydroxyl groups along with less protonated forms of AT. Surface hydroxyl groups also can act as nucleophiles in the reaction, and increasing \( pH \) decreases their nucleophilicity. The three possible protonation structures (at low \( pH \)) based on delocalization of lone-pair electrons from the electron-abundant isopropylamino, ethylamino nitrogen, and chlorine atoms into the adjacent \( \pi \)-electron system in the triazine ring have been given by Pospisil et al. [32]. Welhouse and Bleam [33] reported delocalization to be more predominant in a polar solvent and in acid solution. Thus, not surprisingly, the highest initial rate was found to be at \( pH 2.6 \) (Fig. 1). The apparent order \( (r \) and \( q \)) of this reaction with respect to \( [\text{H}^+] \) and \([\text{MnO}_2]\), as shown by the straight lines in Figures 2 and 3B, varied from 0.11 to 0.23 for \( r \) and depended on \( \text{MnO}_2 \) loading (\( q = 0.4, r^2 = 0.9159 \)) in the present study. The apparent order, although slightly lower than the values reported for the model organic compounds aniline and \( p \)-methylphenol [34,35], followed the same trend. We acknowledge that traces of Mn(III) occurred recently under investigation) was surprising: It was chosen because of its low affinity for the surface and dissolved divalent metal cations. On the other hand, no significant inhibitory effect was found on the kinetics observed when 36 \( \mu \text{M} \) Mn(II) was added to the reaction mixtures.

A more technically defensible higher-order rate expression that was used for data analysis is of the type

\[
\text{rates} = k_1 [\text{AT}] = k_2 [\text{AT}][\text{MnO}_2][[\text{H}^+]]^q
\]

where \( q \) and \( r \) are the reaction order with respect to \( \delta \)-\( \text{MnO}_2 \) and \( \text{H}^+ \), respectively, and \( k \) is the rate constant, with units of \( \text{M}^{-2} \text{s}^{-1} \).

The \( pH \) of the reaction mixture plays an important role in both the charge of the manganese oxide surface and the extent of AT protonation [32]. The first and second \( pK_a \) (log of the acidity constant) values of AT are 1.6 and 1.95 [32], respectively, and the point-of-zero-charge value for \( \text{MnO}_2 \) is 2.7. The increase in activity of \( \text{MnO}_2 \) toward observed as the \( pH \) is decreased (Fig. 1A) can be attributed to more favorable conditions for the formation of surface precursor complexes with protonated AT (Fig. 5). We hypothesize that the surface precursor complex formed in our reaction is of the type

\[
\rightarrow \text{MnO}^+ + \text{H}_2 \text{N}^+ \cdot \text{R} \rightarrow \text{MnO}^+ \cdot \text{H}_2 \text{N}^+ \cdot \text{R}
\]

where \( -\text{NH}_2^+ \) is a protonated-ring nitrogen (Fig. 5, structure 1).
was added to the unbuffered suspension at the same pH. The values of the initial rates under these conditions are summarized in Tables 2 and 3. The small size of Mn(II) compared to acetate may not allow it to compete with AT for adsorption sites on the oxide surface. Although it was not possible to compare directly the exact inhibition effects of Mn(II) (36 μM) and acetate buffer (10 mM) without using the same cosolute concentration, dissolution of the mineral clearly does not affect the degradation rate of AT on the manganese oxide surface. In real environmental conditions, the reaction rate may be influenced further by the presence of various inhibitors, such as humic substance, dissolved metal ion, and other organic substances.

Our developed HPLC method was able to quantify accurately all products of the abiotic reaction except ammeline and cyanuric acid (Fig. 4B), because these products eluted with the solvent front. The products of AT degradation on δ-MnO₂ at pH 4.3 were consistent with those found in earlier work [27] and were identified to be DEA, DIA, and DDA, possibly produced via a nonredox pathway. Six new degradation products (HA, DEHA, DIHA, DDHA, ammeline, and cyanuric acid) also were detected. To emphasize the complexity of the AT-MnO₂ reaction, Figure 5 shows a detailed hypothesized formation pathway of HA (the major product) catalyzed by δ-MnO₂ at pH 4.3 and 20°C in the dark. Using MnO₂ both as a Lewis acid activator and a source of metal-bound hydroxide as a nucleophile would account for the catalyzed hydrolysis reaction that was observed. Once HA is formed, it can be stabilized immediately by the polar media, thus accumulating as the reaction proceeds. A control experiment in which AT (4.6 μM) was suspended in 18 Mega-Ohm Water at pH 4.3 produced only 1% HA (and no dealkylated products) in 90 d, indicating minimal contribution at this pH to the overall reaction. The formation of the dealkylated forms (DEA, DIA, and DDA) in suspension of the oxide is independent of oxygen. Thus, oxygen is not involved in the dealkylation mechanism, only in secondary oxidation.

Birnessite is a well-known oxidant [36]. However, alkylamine substituents on AT are deactivated from oxidation, because the chlorine-bearing triazine ring draws electron density from them [34]. This observation is supported by the fact that only small amounts of Mn(II) were detected in solution (after subtraction of the control). Thus, dealkylation of AT to olefin products does not involve net oxidation or reduction. How? We think that the key player in this reaction is Mn(IV), which can form double bonds with nitrogen and oxygen atoms by accepting π electrons into empty d orbitals. Thus, oxygen and nitrogen atoms remain basic and can be involved in proton-transfer reactions in a mechanism similar to the one observed on dry δ-MnO₂ [23]. Briefly, Mn(IV) in the oxide structure can coordinate to nitrogen in one of the amine substituents via its lone pair. The terminal oxo ligand on the surface of Mn(IV) then can attract a proton from the β-carbon of the nitrogen-bound alkyl group. Subsequent β-elimination of the olefin is promoted by imido N=Mn(IV) double-bond formation. The -HN=Mn-OH fragment then rearranges to -H₂N-Mn=O, and dissociation of the bound amine completes the dealkylation reaction. Thus, electrons and protons are carried back and forth transiently via the Mn(IV) with no net oxidation or reduction. The olefin products (ethylene and propylene) are short-lived in respect to oxidation and could account for some of the Mn(II) produced only as secondary reactions.
We also hypothesize that delocalization, protonation, coulombic interactions, precursor complex formation, and steric hindrance control the extent of the ratio of product formation in our system (Fig. 4B). This is supported by the highest percentage yield of HA and the higher amounts of DEA over DIA. The DEA to DIA concentration ratio value of less than 1 during the entire time course of the reaction suggests that DEA is relatively more stable than DIA [37–40]. From the DEA, DIA, and HA that are formed, more hydroxylated forms of AT can be produced through hydrolysis (Figs. 4B and 5).

DIA. The DEA to DIA concentration ratio value of less than 1 during the entire time course of the reaction suggests that DEA is relatively more stable than DIA [37±40]. From the DEA, DIA, and HA that are formed, more hydroxylated forms of AT can be produced through hydrolysis (Figs. 4B and 5). Some difficulty occurred in obtaining a complete mass balance during the time course of the reaction on AT concentration. Because a complete mass balance was not obtained, we hypothesize further that AT may be mineralized and/or transformed to other unidentified products that were not detected by our analytical procedure. That AT degradation did not go to completion at pH 4.3 supports, in part, the hypothesis of surface precursor complex formation and is a subject of continuing investigation. Clearly, however, ß-MnO₂, which is a common soil constituent, promoted the degradation, N-dealkylation, and hydrolysis of AT in a nonphotochemical abiotic process, possibly via a non-redox mechanism. These results may be useful not only in the design of remediation scenarios, but also in the calibration of in situ microbiological studies, which heretofore have considered abiotic N-dealkylation to be an insignificant pathway of AT degradation in soils.

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