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# Dissolved trivalent manganese in forest soils – interactions of natural organic ligands with manganese oxides

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The presence of dissolved trivalent manganese ( $\text{Mn}^{3+}$ ) in soils has been neglected largely due to its rapid disproportionation. However, natural organic ligands (NOLs) complex and stabilize  $\text{Mn}^{3+}$  by the formation of stable  $\text{Mn}^{3+}$ –NOL complexes. Our objectives were (i) to investigate the influence of NOLs on the dissolution of synthetic Mn oxides, (ii) to perform the speciation analysis of the resulting dissolved total Mn ( $\text{Mn}_T$ ) pool, and (iii) to elucidate the principles governing abiotic formation of  $\text{Mn}^{3+}$ –NOL complexes. NOLs were obtained by extraction (0.001 M  $\text{CaCl}_2$ , 24 h) from a terrestrial forest floor Oe horizon (moder-like raw humus). In batch operations, NOLs reacted with either birnessite (containing  $\text{Mn}^{\text{IV}}$  and minor  $\text{Mn}^{\text{III}}$ ) or manganite (containing solely  $\text{Mn}^{\text{III}}$ ). The interaction between NOLs and Mn (hydr)oxides was investigated as a function of time (1–168 h, 7 steps), and pH (3–7, 5 steps). Mn speciation analysis was performed using a spectrophotometric protocol based on kinetic modeling. Results show that the dissolution of the Mn oxides increased with decreasing pH and increasing time. Mean proportions of  $\text{Mn}^{3+}$ –NOL complexes relative to the  $\text{Mn}_T$  pool ranged from 0 to  $87 \pm 18\%$  (birnessite), and from 0 to  $69 \pm 14\%$  (manganite). A pH-dependent formation of  $\text{Mn}^{3+}$ –NOL complexes was observed, highlighting pH as the critical parameter. Complex stability decreased with decreasing pH, while an influence of time was only assumed for strongly acidic conditions. Overall,  $\text{Mn}^{3+}$ –NOL complexes appeared to be metastable at pH 3–5 (birnessite) and below pH 7 (manganite). In addition, the formation of  $\text{Mn}^{3+}$ –NOL complexes was influenced by the individual properties of the Mn oxides as they were differing in their average oxidation state, point of zero charge, specific surface area and morphology and structure. These properties influence the formation mechanisms of  $\text{Mn}^{3+}$ –NOL complexes and, consequently, the Mn speciation. For example, they affect NOL adsorption rates and capacities, as well as the transformation and degradation of NOLs. We suggest (i) ligand-promoted non-reductive dissolution, (ii) ligand-promoted reductive dissolution, (iii)  $\text{H}^+$ -promoted dissolution, and (iv) ligand exchange as the four possible abiotic dissolution mechanisms for Mn release and  $\text{Mn}^{3+}$ –NOL complex formation. Following dissolution, either  $\text{Mn}^{3+}$ –NOL complexes were released, or released  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  may be complexed by additional NOLs with and without oxidation. We demonstrate that  $\text{Mn}^{3+}$ –NOL complexes are important, previously underestimated, constituents of the  $\text{Mn}_T$  pool in forest floor solutions and propose that they are a non-negligible component in terrestrial environments.

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## Environmental significance

Dissolved trivalent manganese ( $\text{Mn}^{3+}$ ) participates in geochemical processes such as the decomposition of organic compounds, and thus affects carbon storage. In soils, however, this species has been neglected. It is, therefore, a valuable subject to study both quantitatively and qualitatively, in order to draw conclusions about its formation and stabilization. We investigated the influence of soil-derived natural organic ligands (NOLs) on the pH- and time-dependent dissolution of two synthetic Mn oxides. Subsequently, the speciation of the resulting total dissolved Mn pool was performed based on kinetic modeling. Our results demonstrate that terrestrial NOLs complex and stabilize  $\text{Mn}^{3+}$  as  $\text{Mn}^{3+}$ –NOL complexes. We propose that  $\text{Mn}^{3+}$ –NOL complexes are a non-negligible compound in soils, and that this species should be considered in biogeochemical modeling.

## 1 Introduction

Manganese (Mn) is a versatile and ubiquitous element. As a product of weathering, Mn accumulates in global surface soils at concentrations ranging from  $<7$  to  $>9000 \text{ mg kg}^{-1}$  with mean

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values between 270 and 530 mg kg<sup>-1</sup>.<sup>1</sup> Its oxidation states range from -3 to +7.<sup>2</sup> In soils, the oxidation states +2, +3 and +4 dominate.<sup>3</sup>

Dissolved divalent Mn (Mn<sup>2+</sup>) has been assumed to be predominant in aquatic environments, while dissolved trivalent Mn (Mn<sup>3+</sup>) was considered unstable due to its rapid disproportionation.<sup>4,5</sup> However, various studies have shown that natural organic ligands (NOLs) complex and stabilize Mn<sup>3+</sup> in marine and estuarine environments, water treatment works, and acidic forest floor solutions as well as soil solutions.<sup>6-14</sup> Analyses of the binding strengths between Mn<sup>3+</sup> and organic model ligands allow further discrimination between weakly (Mn<sup>3+</sup>-NOL<sub>weak</sub>) and strongly bound Mn<sup>3+</sup> (Mn<sup>3+</sup>-NOL<sub>strong</sub>) complexes.<sup>10</sup> Despite the evidence presented so far for its occurrence and dynamics, the formation, persistence, and reactivity of Mn<sup>3+</sup>-NOL complexes in soils remain largely unexplored. The geochemical behavior of Mn is highly dependent on parameters such as pH and redox potential (*E*<sub>H</sub>),<sup>15</sup> as well as the variability of soil composition, *e.g.*, with respect to Mn oxides.<sup>3</sup>

More than 15 known Mn (oxyhydr)oxide minerals exist,<sup>16,17</sup> and they are widespread in soils. The Mn<sup>III/IV</sup> (oxyhydr)oxides play the largest role in terms of precipitation/dissolution processes, and Mn bioavailability.<sup>18,19</sup> Birnessite (δ-Mn<sup>III/IV</sup>O<sub>2</sub>) is a mixed-valence Mn<sup>III/IV</sup> oxide classified as a phyllosilicate.<sup>20</sup> It is one of the most abundant Mn oxides in the clay-size fraction (<2 μm) of soils.<sup>21</sup> Due to its high oxidation potential, birnessite oxidizes a wide range of natural organic and inorganic compounds.<sup>22</sup> Manganite (γ-Mn<sup>III</sup>O(OH)) is the most abundant and stable natural polymorph of Mn oxy(hydroxide) (MnO(OH)) minerals.<sup>17</sup> We selected these two Mn oxides because of their ubiquity in natural environments and their varying physico-chemical properties. These properties include the average oxidation state (AOS), the point of zero charge (PZC), the specific surface area (SSA), and the *E*<sub>H</sub>, as well as the minerals' morphology and structure.

Dissolved organic matter (DOM) is a complex pool of NOLs with various functional groups, *e.g.*, carboxyl (R-COOH) and phenolic (R-OH) groups, and metal-binding affinities.<sup>23</sup> Low molecular weight organic acids (*e.g.*, citric, oxalic or acetic acid) have carboxyl groups that bind Mn<sup>3+</sup>.<sup>24-27</sup> Phenolic compounds, such as catechol or 2,3-dihydroxybenzoic acid, are known to form Mn<sup>3+</sup>-NOL complexes.<sup>10</sup> In addition, amino acids and peptides (*e.g.*, siderophores) provide suitable binding sites for Mn<sup>3+</sup>.<sup>28,29</sup> NOLs are the key component because stable Mn<sup>3+</sup> can only be formed in the presence of ligands.<sup>30</sup> Nevertheless, the molecular complexity of DOM makes it challenging to predict the formation of Mn<sup>3+</sup>-NOL complexes.

In soils, the principle mechanisms for Mn release<sup>3</sup> are (i) proton (H<sup>+</sup>)-promoted dissolution,<sup>31</sup> (ii) biological reduction (dissimilatory reductive dissolution),<sup>32-34</sup> (iii) abiotic reduction (reductive dissolution), and (iv) ligand-promoted dissolution of Mn oxides.<sup>26</sup>

In this study, the examined abiotic mechanisms for Mn oxide dissolution are defined as (i) proton (H<sup>+</sup>)-promoted dissolution (Mn<sup>IV</sup>O<sub>2</sub> + 4H<sup>+</sup> + 2e<sup>-</sup> → Mn<sup>2+</sup> + 2H<sub>2</sub>O), (ii) ligand-promoted reductive dissolution (*e.g.*, Mn<sup>IV</sup> + NOL + 2e<sup>-</sup> →

Mn<sup>2+</sup> + NOL<sub>ox</sub>), (iii) ligand-promoted non-reductive dissolution (Mn<sup>III</sup> + NOL → Mn<sup>3+</sup>-NOL), and (iv) ligand exchange (Mn<sup>III</sup>-OH + NOL<sup>-</sup> → Mn<sup>III</sup>-NOL + OH<sup>-</sup> → Mn<sup>3+</sup> + NOL → Mn<sup>3+</sup>-NOL). Because H<sup>+</sup>-promoted dissolution of both Mn oxides begins at pH ≤ 5, background dissolution rates were quantified in this study in the absence of NOLs to determine NOL-induced dissolution. The gradual H<sup>+</sup>-promoted release of Mn<sup>2+</sup> is assumed to occur in parallel in the presence of NOLs. Looking at ligand-promoted reductive dissolution, if the NOL has reductive properties, surface-bound Mn<sup>IV</sup> and Mn<sup>III</sup> are converted to Mn<sup>3+</sup> and Mn<sup>2+</sup>. These reduced Mn species may be complexed by the same NOL or by additional NOLs, forming either Mn<sup>3+</sup>-NOL or more soluble Mn<sup>2+</sup>-NOL complexes,<sup>26</sup> with or without subsequent oxidation. The formation rate of Mn<sup>3+</sup>-NOL complexes by abiotic oxidation rate is strongly dependent to the pH of the solution and the properties and concentrations of NOLs.<sup>30</sup> Alternatively, after adsorption onto the surface of the Mn oxides, NOLs may non-reductively detach surface-bound Mn<sup>III</sup> as Mn<sup>3+</sup>-NOL complexes. We assume that these mechanisms affect the formation of Mn<sup>3+</sup>-NOL complexes.

Various studies have investigated the interactions between Mn oxides and NOLs including model ligands, focusing on (i) H<sup>+</sup>- and ligand-promoted reductive dissolution of Mn oxides,<sup>26,28,29,31,35-37</sup> or (ii) oxidative degradation of organic pollutants.<sup>38</sup> However, a quantitative speciation analysis of the resulting total dissolved Mn (Mn<sub>T</sub>) pool is absent from the literature.

Our main objectives were (i) to determine Mn<sub>T</sub> solution speciation, including Mn<sup>2+</sup> (sum of Mn<sup>2+</sup> and Mn<sup>2+</sup>-NOL complexes) and Mn<sup>3+</sup>-NOL complex (sum of Mn<sup>3+</sup>-NOL<sub>weak</sub> and Mn<sup>3+</sup>-NOL<sub>strong</sub>) concentrations, and (ii) to elucidate the principles of the Mn<sup>3+</sup>-NOL complex formation as a result of the abiotic dissolution of Mn oxides. A thorough understanding of the Mn<sup>3+</sup>-NOL complex formation in soil solutions is highly relevant, as the strong oxidant Mn<sup>3+</sup> affects the decomposition of organic matter (OM) and the associated release of carbon dioxide (CO<sub>2</sub>).<sup>39-44</sup> Furthermore, it contributes to the degradation of organic pollutants,<sup>45,46</sup> such as methylmercury,<sup>38</sup> and is redox-active in water treatment works.<sup>6</sup>

In order to address these issues, a spectrophotometric method (porphyrin method), employing α,β,γ,δ-tetrakis(4-carboxyphenyl)porphine (T(4-CP)P), was applied.<sup>7</sup> This analysis enables direct qualification and quantification of the dissolved Mn species by kinetic modeling. The principal mechanism behind the porphyrin method is a metal substitution reaction. Divalent cadmium (Cd<sup>2+</sup>) bound to the porphyrin (Cd<sup>2+</sup>-T(4-CP)P) is replaced by free or NOL-bound Mn<sup>2+</sup> and Mn<sup>3+</sup> present in the sample. Thus, the method allows differentiation of the dissolved Mn<sub>T</sub> pool based on ligand binding affinities and strengths to Mn<sup>2+</sup> and Mn<sup>3+</sup>.<sup>7,8,10</sup> From this, the proportions of Mn<sup>2+</sup>, Mn<sup>3+</sup>-NOL<sub>weak</sub> complexes and Mn<sup>3+</sup>-NOL<sub>strong</sub> complexes are derived by fitting the experimental data using kinetic modeling equations. Two series of batch operations were conducted under oxidizing conditions to evaluate the influences of pH and time on NOL-Mn oxide interactions. A normalized, 'native' Mn and (trace) metal cation free, DOM-stock solution from an acidic spruce site was extracted and



freshly prepared for each batch experiment. Subsequently, the extract was reacted with either birnessite or manganite. The synthesized Mn oxides offer the possibility of studying different dissolution mechanisms that can be accessed by Mn speciation analysis.

## 2 Materials and methods

### 2.1 Sampling of the forest floor

Forest floor samples were collected at the permanent environmental monitoring station #101 at Idar-Oberstein (49° 44'33.38"N, 7°11'47.61"E), Rhineland-Palatinate, Germany, which is managed by the federal state authority Research Institute for Forest Ecology and Forestry of the state of Rhineland-Palatinate in Trippstadt.<sup>47</sup> The soil is classified as a Dystric Cambisol<sup>48</sup> and covered by stands of spruce (*Picea abies* (L.) H. Karst.).

From the Oe horizon (+5–+9 cm),<sup>49</sup> characterized as moderate-like raw humus,<sup>50</sup> about 5 kg of fresh material was obtained over an area of 15 m<sup>2</sup>. In the laboratory, the material was sieved to <2 mm and stored in polypropylene (PP) bags in the dark at 4 °C to minimize changes in composition.<sup>51</sup> A subsample was dried at 60 °C and finely ground in an agate ball mill (PM 400, Retsch, Haan, Germany).

### 2.2 Experimental methods

**2.2.1 Forest floor.** The pH of the Oe horizon was examined potentiometrically in a 0.01 M calcium chloride (CaCl<sub>2</sub>) solution and ultrapure water using a glass electrode (SenTIX 81, WTW, Weilheim, Germany). A conductivity electrode (SevenEasy, Mettler Toledo, Giessen, Germany) was used to measure electrical conductivity (EC) in a suspension of the Oe material and deionized water (1 : 5 w : v). Total carbon (TC) and nitrogen (N) were determined in duplicate by dry combustion of ground samples using a CNS analyzer (Vario EL cube, Elementar, Hanau, Germany) equipped with a thermal conductivity conductor.

**2.2.2 Extraction of the DOM-stock solution.** A fresh DOM-stock solution (3.75 ± 0.17 mmol C L<sup>-1</sup>) was obtained for each batch operation by 0.001 M CaCl<sub>2</sub> extraction of the Oe horizon. The extraction was modified on the basis of CaCl<sub>2</sub> extractions described in the literature, which employed various methodological approaches.<sup>52–54</sup> 40 g of forest floor material and 200 mL of a 0.001 M CaCl<sub>2</sub> solution (1 : 5 w : v) were put in a 500 mL amber glass flask. The glass was then shaken constantly at 9 rpm on an overhead shaker (Reax 20/21, Heidolph Instruments, Schwabach, Germany) for 24 h at 22 ± 1 °C. Centrifugation at 4000 g (Rotina 420 R, Hettich, Kirchlingern, Germany) for 10 min was followed by filtration through a <2 µm ashless blue ribbon filter (589/3, Whatman®, Maidstone, United Kingdom). Next, the extract was passed through a 0.2 µm filter (cellulose acetate, Sartorius, Göttingen, Germany) using acid-cleaned filtration units (polycarbonate, Sartorius, Göttingen, Germany). In order to remove 'native' Mn and (trace) metal cations from the DOM-stock solution, it was passed four times through a cation exchange column (2.5 × 50 cm) filled with an

acidic cation exchange resin (Dowex® 50W-X8 cation exchange resin, mesh 16–50, Dow Chemical, Michigan, USA). A flow rate of 13 mL min<sup>-1</sup> was applied following the protocol presented by Strobel *et al.* (2001).<sup>55</sup> Subsequently, the H<sup>+</sup>-saturated extract was refiltered through 0.2 µm cellulose acetate filters in order to remove potential residues of the cation exchange resin. The removal of 'native' Mn and (trace) metal cations was checked by inductively coupled plasma optical emission spectrometry (ICP OES). Sodium azide (NaN<sub>3</sub>) was added at a concentration of 0.01 M to the DOM-stock solution in order to suppress biological activities.<sup>56</sup>

To determine the total dissolved organic C (DOC) concentration in the DOM-stock solution, a sample volume of 100 µL was injected into a small glass tube and subjected to high-temperature catalytic oxidation to CO<sub>2</sub> at 850 °C. The DOC content was quantified using a non-dispersive infrared TOC analyzer (Dimatoc 2000, Dimatec, Essen, Germany). All samples were analyzed in triplicate.

**2.2.3 Characterization of the DOM-stock solution.** Excitation-emission matrix (EEM) spectroscopy was applied on the DOM-stock solution using a fluorescence spectrometer (FLS 980, Edinburgh Instruments, Livingston, United Kingdom) equipped with a 450 W xenon lamp as the excitation source and a photomultiplier (PMT) detector (R928P, Hamamatsu Photonics, Shizuoka, Japan) at the Department of Chemistry, University of Cologne. Excitation (Ex) wavelengths (200–500 nm, 10 nm steps) and emission (Em) wavelengths (250–700 nm, 1 nm steps) were recorded in a 1 cm quartz cuvette at 22 ± 1 °C. The slits of excitation and emission were set to 2.5 nm and 3.0 nm, respectively. Before the EEM recording, all samples were checked for their absorbance at 254 nm and were diluted with ultrapure water (18.2 MΩ cm) to an absorbance of <0.3 A in order to avoid inner filter effects.<sup>57</sup> The dilution factor was considered in the further calculations. Subtracting the ultrapure water blank spectrum eliminated Raman scattering.<sup>58</sup> In order to further characterize the initial DOM pool, three indices were calculated according to literature: (i) the fluorescence index (FI),<sup>59</sup> (ii) the humification index (HIX),<sup>57,60</sup> and (iii) the biological index (BIX)<sup>61</sup> (see SI). Additionally, four major fluorescent DOM (FDOM) component peaks (B, T, A, C) characterizing terrestrial FDOM were determined. Peak B is at  $E_x/E_m = 275/310$  nm and includes tyrosine-like and protein-like signals; peak T, at  $E_x/E_m = 275/340$  nm, indicates tryptophan-like and protein-like signals. Peak A is at  $E_x/E_m = 260/380$ –460 nm and peak C is at  $E_x/E_m = 350/420$ –480 nm – both mark humic-like FDOM components.<sup>62</sup> Calculating the FDOM data was done in R (version 4.2.2)<sup>63</sup> using RStudio (version 2022.12.0)<sup>64</sup> and the package *staRdom* (version 1.1.25).<sup>65</sup>

### 2.3 Preparation of Mn oxides

The preparation of the birnessite followed the protocol by Rabenhorst and Persing (2017).<sup>66</sup> Manganite synthesis was performed according to the method of Giovanoli and Leuenberger (1969),<sup>67</sup> modified after Lee *et al.* (1980).<sup>68</sup> Detailed descriptions of the syntheses are provided in the SI.



**2.3.1 Characterization of Mn oxides.** The synthesized Mn oxides were analyzed by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and the Brunauer–Emmett–Teller method (BET) at the Federal Institute for Geosciences and Natural Resources (BGR, Hannover, Germany). Additionally, attenuated total reflection Fourier-transform infrared spectroscopy (ATR FT-IR) was performed at the Department of Chemistry, University of Cologne (Cologne, Germany). The AOS and the PZC were determined at the Institute of Geography, University of Cologne. More detailed information can be found in the SI.

## 2.4 Batch experiments

Batch operations were chosen in order to investigate the effects of pH (3–7, 5 steps) and time (1–168 h, 7 steps). Initially, 20 ± 0.1 mg of Mn oxide was weighed into a 50 mL PP centrifuge tube (Sarstedt, Nümbrecht, Germany) and covered in aluminum foil to block ambient light. Subsequently, a 30 mL aliquot of the freshly prepared DOM-stock solution (3.75 ± 0.17 mmol C L<sup>-1</sup>) was adjusted with 10 M HNO<sub>3</sub> (≤100 µL) or 10 M NaOH (≤100 µL) based on preliminary experiments to maintain the desired pH, then added to the tube. The suspension was shaken on a horizontal shaker (GFL-3006, Lauda, Lauda-Königshofen, Germany) at 200 rpm for a predefined batch operation time at constant atmospheric conditions ( $T = 20 \pm 0.1$  °C,  $p = 0.1013$  MPa). The suspension was then immediately passed through a 0.2 µm cellulose acetate filter. After filtration, pH (827 pH Lab, Metrohm, Herisau, Switzerland) and EC (SevenEasy™, Mettler-Toledo, Columbus, USA) values were recorded. Experimental samples (in triplicate) were prepared for Mn speciation analysis (in triplicate for each sample), subsequent DOM measurements by UV/Vis spectroscopy (in duplicate) and determination of the DOC concentrations (in triplicate). The H<sup>+</sup>-promoted background dissolution rates were separately determined in the absence of NOLs at pH 3, 4, and 5. Total Mn concentrations in this experiment were quantified by ICP OES.

## 2.5 Mn speciation analysis by kinetic modeling

Dissolved Mn speciation analysis was performed using the spectrophotometric porphyrin method, following the protocols outlined in Madison *et al.* (2011)<sup>7</sup> and Oldham *et al.* (2015).<sup>10</sup> The extended protocol for acidic forest soil solutions and soil solutions was applied as described in Lux and Mansfeldt (2023).<sup>9</sup> In summary, the spectrophotometric analyses included the determination of Mn<sup>2+</sup>, Mn<sup>3+</sup>–NOL<sub>weak</sub> complexes, Mn<sup>3+</sup>–NOL<sub>strong</sub> complexes, and Mn<sub>T</sub> based on kinetic modeling. They were conducted at a specific Soret band (468 nm) using (T(4-CP)P). All absorbance measurements were performed on a Lambda 25™ spectrophotometer (PerkinElmer®, Rodgau, Germany) using a 1 cm pathlength glass cuvette with 3 mL of total volume. Prior to the analyses, the absorption coefficient ( $\epsilon = 95\,340$  M<sup>-1</sup> cm<sup>-1</sup>) for the Mn<sup>3+</sup>–T(4-CP)P complex was determined using manganese chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O) standards (0.1–10 µM). The concentrations of T(4-CP)P and cadmium chloride (CdCl<sub>2</sub>) in the cuvettes were 24 µM each, as proposed by Madison *et al.* (2011).<sup>7</sup> The method

requires a controlled pH range of 7.5–8 to facilitate the metal substitution reaction between Cd<sup>2+</sup>–T(4-CP)P and Mn<sup>2+</sup> or Mn<sup>3+</sup>–NOL<sub>weak</sub> complexes. In order to maintain this pH range, a borate buffer mix was used.

The pipetting volumes of the samples were adapted to the expected Mn<sub>T</sub> concentrations in the cuvette and ranged from 50 to 2360 µL to comply with the method's detection range. Subsequently, the absorption was recorded every 5 seconds over a period of 10 minutes. The recording was stopped earlier depending on kinetics and the formation of a sufficient plateau, which indicated that the absorbance maximum was reached and the metal substitution reaction had ended.

In DOM-rich solutions, inherent coloration can interfere with the Soret band at 468 nm. Therefore, a background correction was performed.<sup>9</sup> The same sample quantity used in the porphyrin method was placed in a cuvette and diluted with ultrapure water to a final volume of 3 mL. Absorbance was measured against 3 mL of ultrapure water at 468 nm for the same duration as the corresponding Mn speciation analysis. The resulting background absorbance was then subtracted from the Mn absorbance measurement to correct for interference.

For each sample, a 10 mL aliquot was mixed with 10 µL of concentrated HNO<sub>3</sub> (suprapur®, 65%) for subsequent ICP OES analysis. It should be noted that acidification of humic-rich samples to a pH value <2 leads to precipitation of humic substances and thus to an underestimation of metal concentrations.<sup>12</sup>

As described by Madison *et al.* (2011),<sup>7</sup> the kinetic modeling approach was tested on several Mn<sup>2+</sup>/Mn<sup>3+</sup>–pyrophosphate mixtures with varying species concentrations. Initial Mn<sup>2+</sup> and Mn<sup>3+</sup> concentrations were predicted within 0.4–2% of their known values. These results suggest that the method can be a reliable tool for Mn speciation analysis. However, it must be considered that unknown environmental samples contain a diverse DOM pool and a complex solution matrix, characterizing them as a 'black box'.

The kinetic modeling of the dissolved Mn<sub>T</sub> pool was carried out as outlined in Lux and Mansfeldt (2023).<sup>9</sup> In order to determine the dissolved Mn<sub>T</sub> pool, two separate measurements were performed: one in the absence (non-reduced samples) and one in the presence of the strong reducing agent hydroxylamine (reduced samples). The modeling equations proposed by Madison *et al.* (2011)<sup>7</sup> were extended by introducing an additional parameter ( $t_0$ ) to estimate the reaction start time, as it did not coincide with the first absorbance measurement due to manual operation [eqn (1) and (2)]. Initially, kinetic modeling of the non-reduced samples provides the concentrations of Mn<sup>2+</sup> and Mn<sup>3+</sup>–NOL<sub>weak</sub> complexes [eqn (1)], where Mn<sup>2+</sup>, Mn<sup>3+</sup>–NOL<sub>weak</sub> complexes,  $k_1$ ,  $k_2$  and  $t_0$  are parameterized. Mn<sup>3+</sup>–NOL<sub>weak</sub> complexes comprise NOLs with different binding affinities and strengths, which most strongly influence the reaction kinetics and thus the recorded absorbance curves. In order to clearly differentiate Mn<sup>3+</sup>–NOL<sub>weak</sub> complexes from Mn<sup>2+</sup>, the condition  $k_1 \geq 3 \cdot k_2$  has to be satisfied.<sup>14</sup>

In the second modeling step, the concentration of Mn<sub>T(hydroxylamine)</sub>, representing Mn<sup>2+</sup> and all forms of Mn<sup>3+</sup>–NOL complexes, was determined by parameterizing Mn<sup>2+</sup>,  $k_1$ ,



and  $t_0$  [eqn (2)]. The addition of the reducing agent was necessary to model the concentration of  $\text{Mn}^{3+}$ , which is methodically defined as  $\text{Mn}^{3+}\text{-NOL}_{\text{strong}}$  complexes, since the ligand-bound  $\text{Mn}^{3+}$  cannot be outcompeted by T(4-CP)P.<sup>10</sup> The concentration of  $\text{Mn}^{3+}\text{-NOL}_{\text{strong}}$  complexes was determined by calculating the difference between the reduced and the non-reduced sample [eqn (3)]. Together, the modeling equations require the estimation of eight parameters for each speciation analysis.

Five-parameter equation:

$$\text{Mn}_T = (\text{Mn}^{3+}\text{-T(4-CP)P})_T = \text{Mn}^{2+} \cdot (1 - e^{-k_1 \cdot (t-t_0)}) + \text{Mn}^{3+}\text{-NOL}_{\text{weak}} \cdot (1 - e^{-k_2 \cdot (t-t_0)}) \quad (1)$$

where  $\text{Mn}^{2+} = \text{Mn}^{2+}$  concentration ( $\mu\text{mol L}^{-1}$ );  $\text{Mn}^{3+}\text{-NOL}_{\text{weak}} = \text{Mn}^{3+}\text{-NOL}_{\text{weak}}$  concentration ( $\mu\text{mol L}^{-1}$ );  $k_1 = \text{Mn}^{2+}$  rate constant ( $\text{s}^{-1}$ );  $k_2 = \text{Mn}^{3+}\text{-NOL}_{\text{weak}}$  rate constant ( $\text{s}^{-1}$ );  $t =$  reaction time (s); and  $t_0 =$  reaction start (s).

Three-parameter equation:

$$\text{Mn}_{T(\text{hydroxylamine})} = \text{Mn}^{2+} \cdot (1 - e^{-k_1 \cdot (t-t_0)}) \quad (2)$$

where  $\text{Mn}^{2+} = \text{Mn}^{2+}$  concentration ( $\mu\text{mol L}^{-1}$ );  $k_1 = \text{Mn}^{2+}$  rate constant ( $\text{s}^{-1}$ );  $t =$  reaction time (s); and  $t_0 =$  reaction start (s).

$$\text{Mn}^{3+}\text{-NOL}_{\text{strong}} = \text{Mn}_{T(\text{hydroxylamine})} - (\text{Mn}^{2+} + \text{Mn}^{3+}\text{-NOL}_{\text{weak}}) \quad (3)$$

An R code written in RStudio (version 2022.12.0)<sup>63</sup> using R (version 4.2.2)<sup>62</sup> and the *nlmrt* package (version 2016.3.2)<sup>69</sup> was executed. The initial parameter estimation [eqn (1) and (2)] was performed using the *wrapnls* method, which attempts to solve the nonlinear sum of squares problem by employing the *nlxb* algorithm and introducing predefined lower and upper limits for each parameter. Thereafter, the nonlinear least squares (nls) method based on the stats package (version 4.2.2)<sup>63,70</sup> was executed in order to estimate the parameters more precisely. To verify the goodness of fit to the recorded data, the root mean square error (RMSE) was determined. As reported by Johnson *et al.* (2018)<sup>6</sup> and by Lux and Mansfeldt (2023),<sup>9</sup> smaller rate constants for the  $\text{MnCl}_2$  standards (reaction end in approximately 90 s) were determined in contrast to Madison *et al.* (2011),<sup>7</sup> and considered in the modeling process.

## 2.6 Characterization of DOM-stock and DOM-batch solutions

The pH- and time-dependent, qualitative and quantitative, changes of the batch DOM pool in relation to the DOM-stock solution after interaction with the Mn oxides were investigated. Prior to the experiments, the DOM-stock solution was adjusted to a DOC concentration of  $3.75 \pm 0.17 \text{ mmol C L}^{-1}$  using a 0.01 M  $\text{CaCl}_2$  solution as a background electrolyte. Various parameters, including the DOC concentration, the molar absorption (MA), the absorption ratio (A), the spectral slope (S), and the spectral slope ratio ( $S_R$ ) were determined for reacted DOM-batch samples using a TOC analyzer and UV/Vis spectroscopy. UV/Vis spectra were collected for samples using an UV/Vis spectrometer (Lambda 25™, PerkinElmer®, Rodgau,

Germany). Scans were performed from 800 to 200 nm with a 1 nm decrement to prevent UV-induced DOM degradation. All samples were analyzed in a 1 cm pathlength cuvette against a 3 mL ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}$ ) reagent blank at  $20.0 \pm 0.1 \text{ }^\circ\text{C}$ .<sup>71</sup> Molar absorptions at 254, 280, and 350 nm were calculated in order to elucidate the aromaticity of DOM, *e.g.*, humic substance aromaticity<sup>71–73</sup> and relations to molecular weight (MW).<sup>74</sup> The absorbance ratio  $A_{280}/A_{350}$  is reported as a well correlating parameter for both aromaticity and MW.<sup>73</sup> Spectral slopes were determined over the wavelength ranges 275–295 nm ( $S_{275-295}$ ), 290–350 nm ( $S_{290-350}$ ), and 350–400 nm ( $S_{350-400}$ ). These are related to phototransformation of low molecular weight (LMW) material to more humic-like material as well as information about LMW material and aromaticity.<sup>72,75,76</sup> Finally, the  $S_R$  ( $S_{275-295}/S_{350-400}$ ) was calculated as a proxy of DOM MW and photobleaching.<sup>76</sup> Calculations of the DOM parameters were performed using the R package *starDom*.<sup>65</sup>

## 3 Results

### 3.1 Forest floor

The Oe horizon showed a strongly acidic pH of  $3.6 \pm 0.008$  in 0.01 M  $\text{CaCl}_2$  and  $4.7 \pm 0.006$  in ultrapure water. An EC of  $153 \pm 11.2 \mu\text{S cm}^{-1}$  was determined. Elemental analysis revealed proportions of  $47.0 \pm 0.8\% \text{ C}$  and  $1.7 \pm 0.0\% \text{ N}$  resulting in a C/N ratio of  $27.1 \pm 0.3$ , indicating a moder-like raw humus.<sup>50</sup>

### 3.2 Characterization of the DOM-stock solution

The DOM-stock solution had a strongly acidic pH of 2–3 and the ICP OES analysis revealed Mn concentrations  $<0.182 \mu\text{mol L}^{-1}$ . DOC concentrations averaged  $3.75 \pm 0.17 \text{ mmol C L}^{-1}$  after protonation by the cation exchange resin, which is similar to forest floor solutions reported in the literature.<sup>77</sup> A substantial loss of DOC was not observed. Further analysis by EEM spectroscopy revealed humic-like peaks (denoted as A and C), while distinct protein-like (B and T) and fulvic-like (D and E) FDOM peaks were absent (Fig. S4). An A/C peak ratio of 1.83 confirmed a blue-shifted humic-like FDOM. Additionally, calculated values for the BIX (0.400), FI (1.58), and HIX (0.966) were derived from the 3D scan.

### 3.3 Batch experiments

**3.3.1 Total manganese concentrations.** Fig. 4 shows the development of the dissolved  $\text{Mn}_T$  concentrations as a function of pH and time analyzed by ICP OES (see Tables S2 and S3). The  $\text{H}^+$ -promoted background dissolution ( $\text{pH} \leq 5$ ) of the Mn oxides was subtracted in order to determine the exclusively NOL-induced dissolution ( $\text{Mn}_{T(\text{NOL})}$ ).

For birnessite (Fig. 1a), the following general trends were observed: (i) a decrease in pH results in higher Mn concentrations, (ii) a longer reaction times promote an increased Mn release, and (iii) the lower the pH the lower the NOL-induced dissolution relative to the  $\text{H}^+$ -promoted dissolution. Mean  $\text{Mn}_{T(\text{NOL})}$  concentrations ranged from  $0.884 \pm 0.212$  to  $899 \pm 108 \mu\text{mol L}^{-1}$  (Table S2) and peaked at pH 3 after 168 h (Fig. 1a).





Fig. 1  $Mn_{T(NOL)}$  concentrations of pH-dependent and NOL-induced Mn oxide dissolution over time for (a) birnessite, and (b) manganite.  $H^+$ -promoted background dissolution was subtracted. Each experiment was conducted in triplicate and analyzed by ICP OES.  $Mn_{T(NOL)}$  = total dissolved Mn by NOL-induced dissolution; NOL = natural organic ligand.

The largest proportions of  $Mn_{T(NOL)}$  (100%) were revealed at pH 6 and 7 (Table S2). By contrast, the lowest proportions were observed at pH 4 ranging between  $37.8 \pm 3.9$  and  $73.9 \pm 0.1\%$  with an overall mean of  $58.5 \pm 10.7\%$  (Table S2). The highest dissolution rates were identified within the first 24 h. Prolonged batch operations revealed considerably slower dissolution kinetics.

Manganite showed similar general trends to birnessite (Fig. 1b). In comparison, the mean  $Mn_{T(NOL)}$  concentrations ranged from  $13.6 \pm 0.675$  to  $567 \pm 22.4 \mu\text{mol L}^{-1}$  (Table S3) and revealed an almost halved maximum concentration at pH 3 after 48 h. The highest proportions (100%) of NOL-induced dissolution were observed at pH 6 and 7 (Table S3). On the other hand, the lowest means were recorded at pH 3 ranging from  $20.9 \pm 4.3$  to  $47.1 \pm 1.1\%$  with an overall mean of  $38.1 \pm 9.2\%$  (Table S3). This indicates a further significant reduction in NOL-induced dissolution under strongly acidic conditions compared to the birnessite batch experiments. Particularly noteworthy is the increased release of Mn at pH 6 and 7. Equally, the manganite batch experiments showed that increasing acidic conditions and a prolonged batch operation contributed to an increased dissolution. Looking at the dissolution kinetics, the dissolution of manganite was most rapid in the first 12 h, in particular with decreasing pH. Subsequently, the dissolution decreased sharply.

Considering the additional  $H^+$ -promoted dissolution, mean  $Mn_T$  concentrations during the birnessite batch experiments ranged from  $0.884 \pm 0.212$  to  $1418 \pm 108 \mu\text{mol L}^{-1}$  (Table S2) and revealed a higher solubility of birnessite compared to manganite. The  $Mn_{T(Porph)}/Mn_{T(ICP\ OES)}$  ratio for birnessite ranged from 0.87 to 1.27 with a mean of  $1.03 \pm 0.08$  ( $n = 35$ ,  $r =$

$0.996$ ,  $R^2 = 0.991$ ,  $p < 0.001$ ). The manganite batch experiments revealed a narrower range of mean  $Mn_T$  concentrations ( $13.6 \pm 0.675$  to  $1338 \pm 77.4 \mu\text{mol L}^{-1}$ ) (Table S3). For manganite, the  $Mn_{T(Porph)}/Mn_{T(ICP\ OES)}$  ratio ranged from 0.85 to 1.17 with a mean of  $1.02 \pm 0.06$  ( $n = 35$ ,  $r = 0.998$ ,  $R^2 = 0.995$ ,  $p < 0.001$ ).

The results show that NOL-induced dissolution ( $pH \leq 5$ ) appears to be an important process. However, the relative contribution to the overall dissolution decreased with decreasing pH, rendering  $H^+$ -promoted dissolution more effective especially during manganite batch experiments. Based on these findings, possible abiotic dissolution mechanisms are outlined in Section 4.1.

**3.3.2 Kinetic modeling.** Fig. 2 presents experimental data from the Mn speciation analysis of a single birnessite (non-reduced) and a single manganite (non-reduced) sample in the presence of NOL at pH 7 after 1 h. For each sample, two representative analytical measurements (A and B) are depicted in order to highlight clear differences in reaction kinetics. Kinetic modeling was conducted to fit the data including  $Mn^{2+}$  and  $Mn^{3+}$ -NOL<sub>weak</sub> complexes [eqn (1)]. For clarity, the modeled  $Mn^{3+}$ -NOL<sub>strong</sub> complexes are not shown, as weakly binding ligands primarily influence the reaction kinetics when employing the porphyrin method. Fig. 3 depicts the modeled proportions of  $Mn^{2+}$ ,  $Mn^{3+}$ -NOL<sub>weak</sub> and  $Mn^{3+}$ -NOL<sub>strong</sub> complexes relative to  $Mn_T$  for both samples. Notable differences in the reaction kinetics between the Mn oxides were observed, as indicated by distinct curve shapes (Fig. 2) and substantial variations in the modeled  $Mn^{3+}$ -NOL<sub>weak</sub> complex proportions (Fig. 3).

In particular, the recorded curves for the NOL-birnessite interactions appear flattened (Fig. 2a) compared to those for manganite (Fig. 2b), indicating slower reaction kinetics. Kinetic





Fig. 2 Kinetic modeling of (a) a single birnessite (non-reduced) and (b) a single manganite sample (non-reduced) at pH 7 after 1 h. The analysis of the non-reduced sample represents the Mn speciation analysis without the hydroxylamine treatment. The modeling includes complexes of  $Mn^{2+}$  and  $Mn^{3+}-NOL_{weak}$  (Tables S2 and S3), excluding  $Mn^{3+}-NOL_{strong}$  complexes. Two analytical measurements (A and B) are demonstrated for each sample, along with the corresponding fits: measurement A (black crosses) with fit A (red line), and measurement B (black crosses) with fit B (blue line). NOL = natural organic ligand;  $Mn^{3+}-NOL_{weak}$  = weakly bound  $Mn^{3+}$ ;  $Mn^{3+}-NOL_{strong}$  = strongly bound  $Mn^{3+}$ .

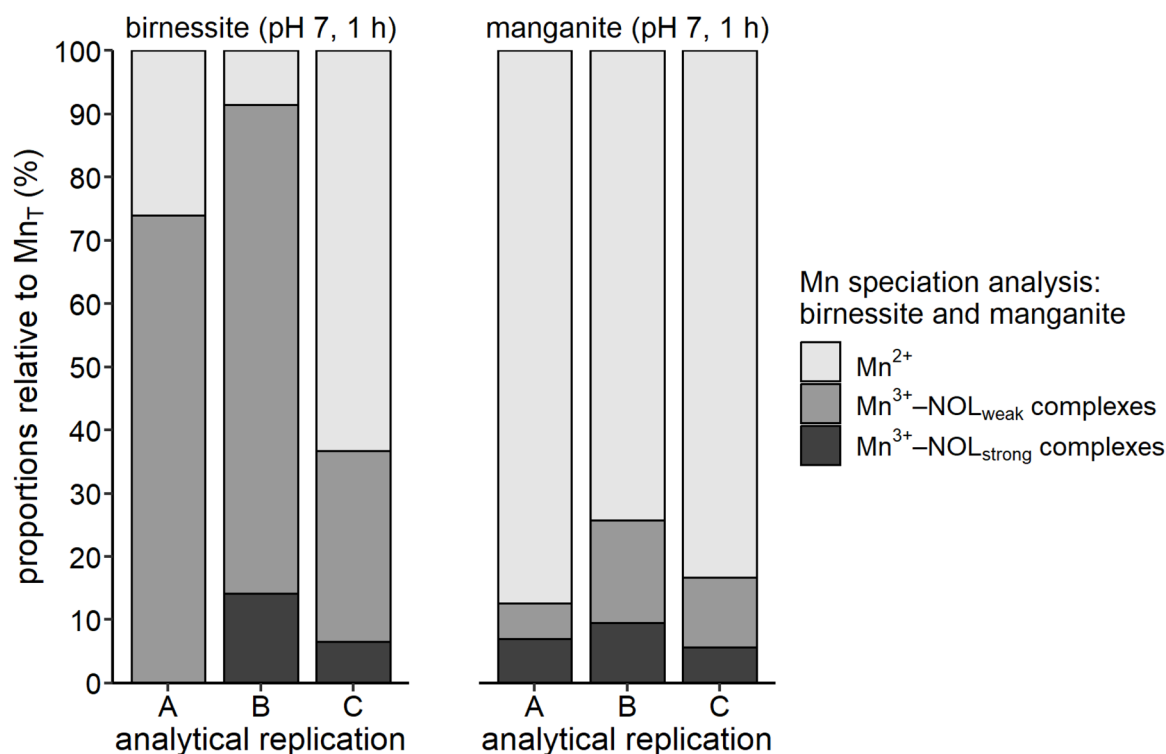


Fig. 3 Mn speciation analysis in triplicate (A–C) of a single birnessite and manganite sample at pH 7 after 1 h.  $Mn_T$  = total dissolved Mn;  $Mn^{3+}-NOL_{weak}$  = weakly bound  $Mn^{3+}$ ;  $Mn^{3+}-NOL_{strong}$  = strongly bound  $Mn^{3+}$ .

modeling of the analytical replicates A and B revealed sample-specific dominant proportions of  $Mn^{3+}-NOL_{weak}$  complexes, accounting for 73.9 and 77.2% relative to  $Mn_T$  (Fig. 3). Proportions of  $Mn^{2+}$  contributed 26.1 and 8.6%, while  $Mn^{3+}-NOL_{strong}$  complexes accounted for 0 and 14.2%, respectively (Fig. 3).

Manganite, in contrast, exhibited faster reaction kinetics (Fig. 2b), as the curves plateaued more quickly. After 1 h, only minor traces of  $Mn^{3+}-NOL_{weak}$  complexes (16.2 and 5.6%) were

detected, while  $Mn^{2+}$  was the dominant species (74.3 and 86.9%) (Fig. 3). The sample-specific proportions of  $Mn^{3+}-NOL_{strong}$  complexes were 8.5 and 10.3% (Fig. 3). Notably, the  $k_2$  values were an order of magnitude lower than the  $k_1$  values, confirming distinct kinetic behavior (Fig. 2b).

For both NOL–Mn oxide interactions, the modeled Mn species proportions vary across individual measurements (Fig. 3). Additionally, the modeled rate constants satisfied the

condition  $k_1 \geq 3k_2$ , which is used to differentiate ligands based on their binding affinities and strengths.<sup>14</sup>

**3.3.3 Manganese speciation analysis.** In this study, the speciation analysis of  $Mn_T$  was performed including  $Mn^{2+}$ ,  $Mn^{3+}$ -NOL<sub>weak</sub> complexes, and  $Mn^{3+}$ -NOL<sub>strong</sub> complexes. Fig. 4 shows the percentage of  $Mn_T$  that are  $Mn^{3+}$ -NOL complexes (sum of  $Mn^{3+}$ -NOL<sub>weak</sub> and  $Mn^{3+}$ -NOL<sub>strong</sub> complexes) for the NOL–birnessite and the NOL–manganite interaction as a function of pH (3–7) and time (1–168 h). The formation and stabilization of  $Mn^{3+}$ -NOL complexes was dependent on the individual Mn oxide, showing sharp decreases with lowering pH and increasing reaction time (strongly acidic conditions) (Fig. 4). Notably, our analysis of molar  $Mn_T$ :DOC ratios indicates that values  $\geq 0.08$  resulted in a sharp decrease in  $Mn^{3+}$ -NOL complex proportions (Tables S4 and S5). The molar ratios exceeded this threshold multiple times, especially under strongly acidic conditions and reaction times  $\geq 6$  h.

For the birnessite batch experiments, the  $Mn^{3+}$ -NOL complex proportions ranged from 0 to  $87 \pm 18\%$  across all pH and time steps (Fig. 4a). The highest proportion of  $Mn^{3+}$ -NOL complexes was observed at pH 7 after 24 h. Under circumneutral conditions,  $Mn^{3+}$ -NOL complexes predominated at all time steps ranging from  $68 \pm 9$  to  $87 \pm 18\%$ . A strong contrast with low  $Mn^{3+}$ -NOL complex proportions ( $6 \pm 4$  to  $11 \pm 7\%$ ) was observed at pH 5 between 1 and 6 h. The sharp decrease in  $Mn^{3+}$ -NOL complexes within the NOL–birnessite interactions resulted from the modeling process. The parameterization of the rate constants narrowly missed the condition  $k_1 \geq 3k_2$  (Table S2). The  $Mn^{3+}$ -NOL<sub>weak</sub> complexes could not, therefore, be modeled. Subsequently, the proportions ( $35 \pm 4$  to  $86 \pm 5\%$ ) increased sharply from 12 h onwards. An opposite pattern was

identified under strongly acidic conditions.  $Mn^{3+}$ -NOL complexes dominated at pH 4 from 1 to 6 h; and at pH 3 only at 1 h but with a high proportion of  $85 \pm 9\%$ . Remarkably,  $Mn^{3+}$ -NOL complexes decreased with decreasing pH and increasing time, becoming negligible after 6 h (pH 3 and 4). Interestingly, the proportions of  $Mn^{3+}$ -NOL complexes were mainly assigned to the  $Mn^{3+}$ -NOL<sub>weak</sub> complexes, as shown in Table S3, which is in contrast to the NOL–manganite interaction.

In summary, birnessite batch experiments indicate that  $Mn^{3+}$ -NOL complexes can be predominant under all pH conditions, but the formation and stability is strongly dependent on the reaction time under strongly acidic conditions.

Fig. 4b shows the proportions of  $Mn_T$  that are  $Mn^{3+}$ -NOL complexes observed in the manganite batch experiments. Overall, the  $Mn^{3+}$ -NOL complex proportions ranged from 0 to  $69 \pm 14\%$ . Looking closely at the pH steps, a different pattern of the  $Mn^{3+}$ -NOL complex distribution becomes apparent. The highest  $Mn^{3+}$ -NOL complex proportions were detected at circumneutral pH. A pH  $\leq 6$  already leads to a sharp decrease in the  $Mn^{3+}$ -NOL complex proportions. Similar to birnessite, the proportions decreased with time. In particular, the maximum proportion of  $Mn^{3+}$ -NOL complexes ( $69 \pm 14\%$ ) was recorded at pH 7 after 12 h. Furthermore, a consistent but decreasing dominance of  $Mn^{3+}$ -NOL complexes was observed only at pH 7 from 12 to 48 h ( $69 \pm 14$  to  $65 \pm 7\%$ ). Under both moderately and strongly acidic conditions, the  $Mn^{3+}$ -NOL complex proportions decreased drastically, ranging between 0 and  $21 \pm 7\%$  (pH 6, 1 h). Exceptions were observed at pH 4 after 3 h ( $39 \pm 6\%$ ) and at pH 3 after 1 h ( $57 \pm 4\%$ ). All modeled proportions of  $Mn^{3+}$ -NOL complexes were predominantly attributed to  $Mn^{3+}$ -NOL<sub>strong</sub> complexes (Table S3).



Fig. 4 Proportions of  $Mn^{3+}$ -NOL complexes (%) (sum of  $Mn^{3+}$ -NOL<sub>weak</sub> and  $Mn^{3+}$ -NOL<sub>strong</sub> complexes) for (a) the NOL–birnessite and (b) the NOL–manganite interaction as a function of pH (–) and time (h) relative to  $Mn_T$ . NOL = natural organic ligand;  $Mn^{3+}$ -NOL<sub>weak</sub> = weakly bound  $Mn^{3+}$ ;  $Mn^{3+}$ -NOL<sub>strong</sub> = strongly bound  $Mn^{3+}$ .



under strongly acidic conditions compared to moderately acidic conditions and circumneutral conditions.

## 4 Discussion

#### 4.1 Possible dissolution mechanisms

Fig. 5 and 6 summarize the possible abiotic pathways enabling the  $\text{Mn}^{3+}$ -NOL complex formation during our batch experiments, while biological reduction was excluded.

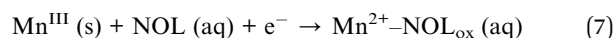
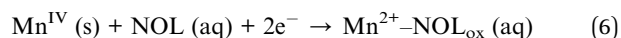
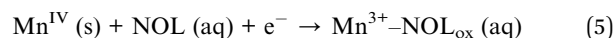
Biotic processes are mostly inactivated by  $\text{NaN}_3$  but the activity of Gram-positive bacteria such as actinomycetes is only partially suppressed or even not affected.<sup>78</sup> Therefore, microbially-mediated processes like DOC degradation, resynthesis, and transformation cannot be completely excluded. Nevertheless, microbial activity should be largely restricted in this study and we focus solely on abiotic processes. These abiotic NOL–Mn oxide interactions can be categorized into four possible dissolution mechanisms (Fig. 5 and 6):

(1) Ligand-promoted non-reductive dissolution, (2) ligand-promoted reductive dissolution, (3)  $H^+$ -promoted dissolution, and (4) ligand exchange.

Looking at the NOL–birnessite interactions (Fig. 5), ligand-promoted non-reductive dissolution is a possible mechanism under circumneutral and moderately acidic conditions. Surface-bound  $\text{Mn}^{\text{III}}$  is dissolved by the adsorption of a near-associated NOL and released as a  $\text{Mn}^{3+}$ –NOL complex,<sup>12</sup> while the NOL is neither oxidized nor reduced [eqn (4)]. Because the AOS of the birnessite used in this study clearly indicates an increased proportion of  $\text{Mn}^{\text{III}}$ , we expect the mechanism to support the  $\text{Mn}^{3+}$ –NOL complex formation (Table S1).

$$\text{Mn}^{\text{III}}(\text{s}) + \text{NOL}(\text{aq}) \rightarrow \text{Mn}^{3+}\text{-NOL}(\text{aq}) \quad (4)$$

The second mechanism involves ligand-promoted reductive dissolution ( $1\text{-e}^-$  or  $2\text{-e}^-$  transfer) of mineral-bound  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{IV}}$  by a directly associated NOL. Consequently, Mn oxide reduction and NOL oxidation proceed in parallel [eqn (5), (6) and (7)] and the same NOL forms either a  $\text{Mn}^{3+}$ -NOL complex or a  $\text{Mn}^{2+}$ -NOL complex. Alternatively, the NOL detaches  $\text{Mn}^{2+}$  or  $\text{Mn}^{3+}$  as it is oxidized, and another NOL from the solution may form a  $\text{Mn}^{3+}$ -NOL complex or a  $\text{Mn}^{2+}$ -NOL complex [eqn (5), (6) and (7)]. Banerjee and Nesbitt (1999, 2001)<sup>22,79</sup> stated that the reduction of birnessite is controlled by a  $1\text{-e}^-$  transfer reaction from  $\text{Mn}^{\text{IV}}$  to  $\text{Mn}^{\text{III}}$ , forming a strong  $\text{Mn}^{3+}$  carboxyl surface complex.



EEM spectroscopy revealed humic proportions containing hydroquinones and thus phenolic groups. We assume that these functional groups contribute to homolytic  $1-e^-$  transfers mediated by the formation of radical semiquinones in the hydroquinone/quinone system, or by intermediate phenoxy radicals. Ligand-promoted reductive dissolution is surface-



Fig. 5 Schematic illustration of the assumed essential (black) and side (gray) NOL–birnessite interactions and the proposed parallel main (black) and minor (grey) ad-/desorption processes that lead to the formation of  $\text{Mn}^{\text{III}}\text{-NOL}$  complexes. NOL = natural organic ligand;  $\text{Mn}^{\text{III}}\text{-NOL}_{\text{weak}}$  = weakly bound  $\text{Mn}^{\text{III}}$ ;  $\text{Mn}^{\text{III}}\text{-NOL}_{\text{strong}}$  = strongly bound  $\text{Mn}^{\text{III}}$ .

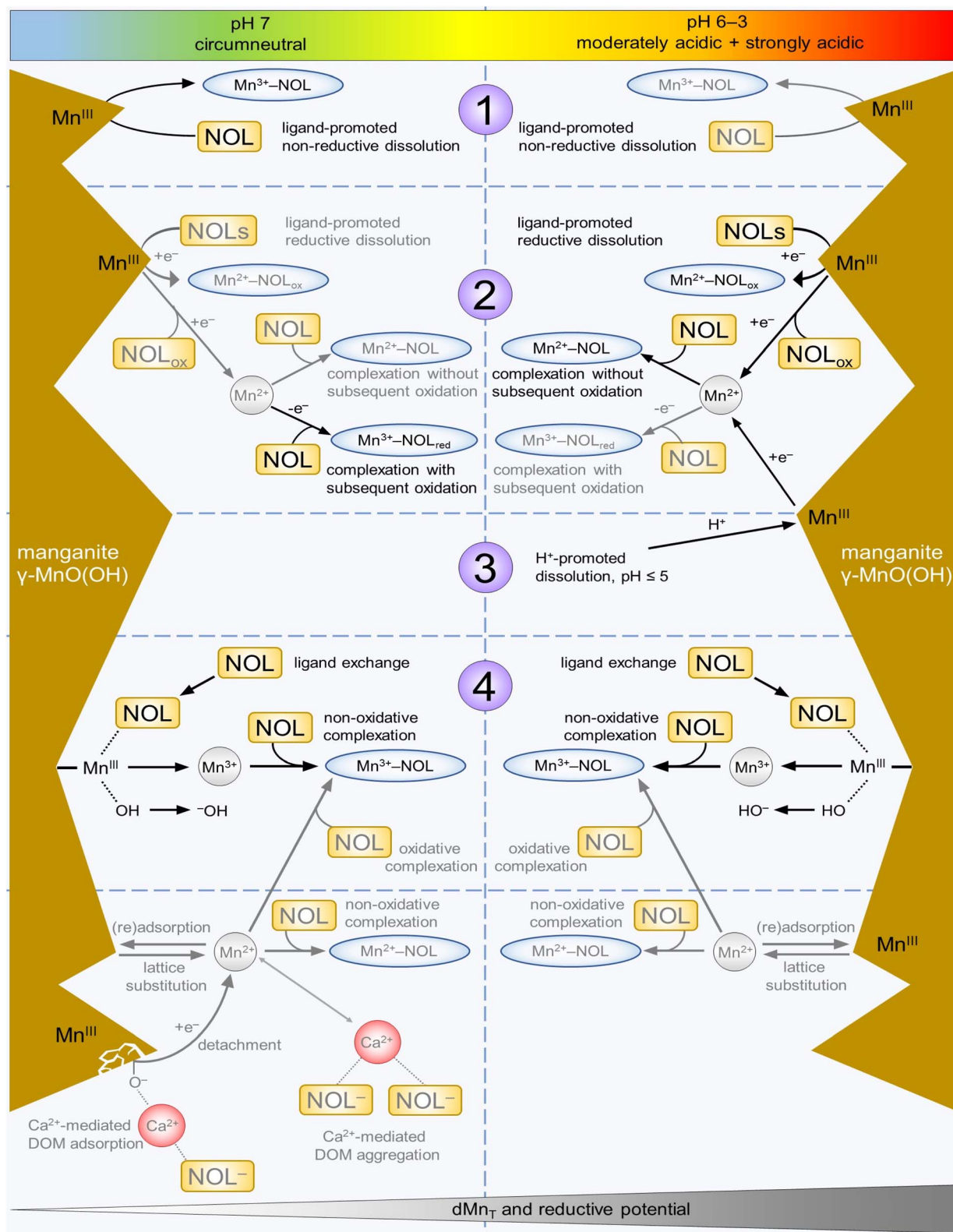
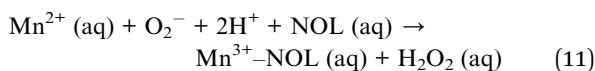
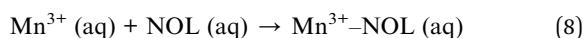
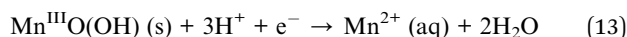
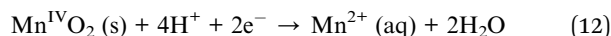


Fig. 6 Schematic illustration of the assumed essential (black) and side (gray) NOL–manganite interactions and the proposed parallel main (black) and minor (grey) ad-/desorption processes that lead to the formation of  $\text{Mn}^{3+}\text{-NOL}$  complexes. NOL = natural organic ligand;  $\text{Mn}^{3+}\text{-NOL}_{\text{weak}}$  = weakly bound  $\text{Mn}^{3+}$ ;  $\text{Mn}^{3+}\text{-NOL}_{\text{strong}}$  = strongly bound  $\text{Mn}^{3+}$ .

controlled, requiring close association of NOLs with surface sites prior to  $e^-$  transfer and metal ion release.<sup>80</sup> Released  $Mn^{2+}$  and  $Mn^{3+}$  may subsequently be complexed by additional NOLs [eqn (8)–(10)]. Terrestrial NOLs are known to inhibit the complete oxidation of  $Mn^{2+}$  to  $Mn^{IV}$  oxides,<sup>11,26</sup> by stabilizing the  $Mn^{3+}$  intermediate through ligand-promoted oxidation, complexation, and simultaneous NOL reduction [eqn (9)]. Following reductive dissolution,  $Mn^{3+}$ –NOL complex formation can occur *via* ligand-promoted oxidative complexation similar to eqn (9). Released  $Mn^{2+}$  is complexed by NOL. The intermediate  $Mn^{2+}$ –NOL complex is then oxidized during a dark reaction promoted by reactive oxygen species, namely superoxide ( $O_2^-$ ) [eqn (11)].<sup>11–13,81</sup> This  $H^+$ -consuming reaction is favored under moderately to strongly acidic conditions, where high Mn oxide dissolution rates, excessive  $H^+$  concentrations and dissolved  $O_2$  are present.



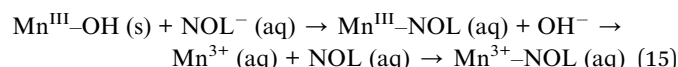
Under increasing acidic conditions, we propose  $H^+$ -promoted dissolution as the third mechanism. The observed increase in  $H^+$ -promoted background dissolution (Table S2) combined with the increasing NOL-induced dissolution (Fig. 1a) results in a decrease in  $Mn^{3+}$ –NOL complex formation. Consequently,  $Mn^{2+}$  concentrations increase, suggesting that  $H^+$ -promoted dissolution of  $Mn^{IV}$  and  $Mn^{III}$  to  $Mn^{2+}$  proceeds *via* a  $2e^-$  or a  $1e^-$  transfer mediated by inorganic or organic reductants [eqn (12) and (13)]. McKendry *et al.* (2015)<sup>82</sup> outlined that  $Mn^{III}$ -enriched active sites promote water oxidation and subsequent  $H^+$  generation, which intensifies  $H^+$ -promoted background dissolution [eqn (12) and (13)]. The low AOS of our triclinic birnessite renders enhanced  $H^+$ -promoted dissolution plausible, as supported by increased initial dissolution rates and a corresponding decrease in pH.



In addition to the mechanisms presented in [eqn (6), (7), (12) and (13)], the sharp decrease in  $Mn^{3+}$ –NOL complex proportions (Fig. 4a) with decreasing pH and longer batch operation (>6 h) necessitates the consideration of additional mechanisms. The decay of  $Mn^{3+}$ –NOL complexes might result from internal redox reactions of organic molecules, as observed for  $Mn^{3+}$ –catechol or  $Mn^{3+}$ –citrate, leading to  $Mn^{2+}$  formation.<sup>10,25</sup> It is conceivable that a reduction of  $Mn^{3+}$ –NOL complexes, coupled with oxidation of ambient NOLs ( $1e^-$  transfer) [eqn (14)], similar to the transformation of organic pollutants,<sup>45,46</sup> contributes to the decrease in  $Mn^{3+}$ –NOL complex proportions relative to  $Mn_T$  with increasing reaction time.



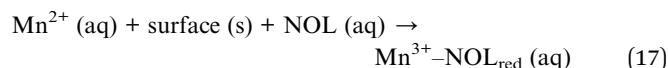
Ligand exchange, the forth possible mechanism, involves the substitution of surface hydroxyl groups ( $-OH$ ) by carboxyl or phenolic groups of DOM.<sup>3</sup> Initial acid/base additions stabilized the pH and compensated for  $-OH$  release. NOLs adsorb to Mn centers, replacing  $-OH$  groups, weakening Mn–OH bonds,<sup>3,83</sup> and altering surface coordination, promoting the release of  $Mn^{3+}$ , which is subsequently complexed by additional NOLs [eqn (15)]. This mechanism is favored by NOLs with high molecular weight (HMW), acidity, and aromaticity,<sup>3</sup> and likely contributes to  $Mn^{3+}$ –NOL complex formation under circumneutral conditions. As noted by Stuckey *et al.* (2018),<sup>83</sup> ligand exchange may be particularly relevant under moderately to strongly acidic conditions, supporting  $Mn^{3+}$ –NOL complex formation in the early stages of the NOL–Mn oxide interactions.



Complementary to the mechanisms discussed above,  $Mn^{3+}$ –NOL complexes may be formed or degraded by additional reactions. Disproportionation of  $Mn^{3+}$ –NOL complexes [eqn (16)], as proposed for neutral pH and citrate as the chelator, may explain the small  $Mn^{2+}$  proportions at circumneutral pH (Fig. 4a).<sup>24</sup>



Surface-catalyzed oxidation of  $Mn^{2+}$  to  $Mn^{3+}$ , followed by complexation through additional ligands, promotes  $Mn^{3+}$ –NOL complex formation [eqn (17)].<sup>11</sup> In combination with eqn (11) and (15),  $Mn^{3+}$ –NOL complex concentrations increase, consistent with the rise observed at pH 5 after 12 h (Fig. 4a).



We conclude that (i) ligand-promoted non-reductive dissolution, (ii) ligand-promoted reductive dissolution either directly or followed by subsequent complexation with and without oxidation, (iii) ligand exchange, and apart from these mechanisms (iv) the observed molar  $Mn_T$ :DOC ratio  $\leq 0.08$  (Table S4) promote the formation of  $Mn^{3+}$ –NOL complexes under circumneutral and moderately acidic conditions. The relatively small  $Mn^{2+}$  proportions resulted from reductive degradation of  $Mn^{3+}$ –NOL complexes, for example through redox-active transformation of additional NOLs. Contrastingly, under strongly acidic conditions (pH 3–4, >6 h), decreased  $Mn^{3+}$ –NOL complex concentrations (Fig. 4a) result from (i) lesser ligand-promoted non-reductive dissolution, (ii) dominant ligand-promoted or  $H^+$ -promoted dissolution, followed by complexation without oxidation, (iii) progressive reduction of  $Mn^{3+}$ –NOL complexes by additional NOLs, and besides these mechanisms (iv) the observed molar  $Mn_T$ :DOC ratio  $\geq 0.08$  (Table S4). Since the experimental setup provides only a temporary, limited insight



into the ongoing solution chemistry, considerable variations in the  $\text{Mn}^{3+}$ -NOL complex concentrations are expected. Overall,  $\text{Mn}^{3+}$ -NOL complexes appear to be metastable under strongly acidic conditions.

Focusing on NOL-manganite interactions (Fig. 6), (i) ligand-promoted non-reductive dissolution [eqn (4)], (ii) ligand-promoted reductive dissolution by direct complexation ( $1\text{-e}^-$  transfer) or detachment of  $\text{Mn}^{2+}$  [eqn (7)] with subsequent oxidation [eqn (9) and (11)], and (iii) ligand exchange [eqn (15)] are assumed to promote the formation of  $\text{Mn}^{3+}$ -NOL complexes under circumneutral conditions (Fig. 4b). Similar to birnessite, the observed pH drift caused by  $-\text{OH}$  release could be initialized by ligand exchange [eqn (12)].<sup>84</sup>

At  $\text{pH} \leq 6$ , the strong decrease in  $\text{Mn}^{3+}$ -NOL complexes indicates a change in the predominating mechanisms. As pH decreases, the synergy between  $\text{H}^+$ -promoted and ligand-promoted reductive dissolution of surface-coordinated  $\text{Mn}^{\text{III}}$  increases.<sup>36</sup> Similar to birnessite, solid  $\text{Mn}^{\text{III}}$  is reductively dissolved and the corresponding NOLs are simultaneously oxidized [eqn (7)]. Additional NOLs then complex  $\text{Mn}^{2+}$  without oxidation [eqn (10)]. Manganite provides a higher  $E_{\text{H}}$  (1.51 V) than  $\text{Mn}^{\text{IV}}$  oxides (1.23 V) and thus, an increased potential to oxidize DOM and to be reduced.<sup>85</sup> Various studies have shown that manganite is reductively dissolved by a myriad of organic compounds.<sup>26–29</sup> The negligible traces of  $\text{Mn}^{3+}$ -NOL<sub>weak</sub> complexes and the small proportions of  $\text{Mn}^{3+}$ -NOL<sub>strong</sub> complexes are consistent with the findings by McArdell *et al.* (1998),<sup>35</sup> who studied the dissolution of  $\text{Mn}^{\text{III}}\text{O}(\text{OH})$  interacting with ligands such as aminocarboxylates.

Another reductive dissolution mechanism that increases the  $\text{Mn}^{2+}$  concentration is the  $\text{H}^+$ -promoted disproportionation ( $\text{pH} < 6$ ) of  $\text{Mn}^{\text{III}}$  [eqn (18)].<sup>29,31</sup> The precipitated  $\text{MnO}_2$  is susceptible to reductive dissolution, potentially further increasing  $\text{Mn}^{2+}$  concentration.



Under strongly acidic conditions, the higher proportions of  $\text{Mn}^{3+}$ -NOL complexes observed during the first 3 h can be attributed to synergistic effects of the four possible dissolution mechanisms. The variability in  $\text{Mn}^{3+}$ -NOL complex proportions highlights the unstable nature of these complexes, which are susceptible to disproportionation at low pH. Additionally, they are prone to degradation *via* intramolecular or intermolecular  $\text{e}^-$  transfer reactions.<sup>10,30,45,46</sup>

In contrast to birnessite, NOL-manganite interactions favor the formation of  $\text{Mn}^{3+}$ -NOL<sub>strong</sub> complexes (Table S3). Whether the high  $\text{Mn}^{3+}$ -NOL<sub>strong</sub> complex proportions result from the individual  $E_{\text{H}}$  of the manganite, its predominant valence state, low SSA, surface charge, or selective NOL adsorption remains uncertain and warrants further investigation.

The formation and stabilization of  $\text{Mn}^{3+}$ -NOL complexes primarily depends on pH (key parameter), as well as on reaction time and the properties of both Mn oxides and NOLs. We assume that the predominant Mn valence of the Mn oxide governs the preferential dissolution mechanisms as a function

of solution pH. However, further studies are required to qualify and quantify the influence of the dominant Mn valence.

Similar to the findings on  $\text{Mn}^{3+}$ -NOM complexes,<sup>3</sup> it can be confirmed from our data that lower molar  $\text{Mn}_{\text{T}}:\text{DOC}$  ratios ( $\leq 0.08$ ) support the formation of  $\text{Mn}^{3+}$ -NOL complexes (Tables S4 and S5). We therefore hypothesize that NOL availability is a decisive factor. The range of  $\text{Mn}^{3+}$ -NOL complex proportions (Fig. 4) determined in this study ( $0$  to  $87 \pm 18\%$ ), particularly under strongly acidic conditions during the first 6 h ( $0$  to  $85 \pm 9\%$ ), aligns with our previous analyses of *in situ* sampled non-limed ( $11$  to  $79\%$ ) and formerly limed ( $10$  to  $87\%$ ) forest floor solutions and soil solutions.<sup>9</sup>

Although  $\text{Mn}^{2+}$  was the predominant species under strongly acidic conditions,  $\text{Mn}^{3+}$ -NOL complexes remain a non-negligible compound in NOL-enriched topsoil layers at the acidic forest site. However, the formation and stabilization of  $\text{Mn}^{3+}$ -NOL complexes are evidently restricted, characterizing them metastable under natural acidic conditions.

**4.1.1 Possible side mechanisms.** Parallel side mechanisms occur during NOL-Mn oxide interactions (Fig. 5 and 6) and affect the Mn speciation analysis.

Adsorption of released  $\text{Mn}^{2+}$  was neither qualitatively nor quantitatively assessed in this study, but it should be considered.  $\text{Mn}^{2+}$  adsorption is particularly favored by negatively charged mineral surfaces and high SSA. This surface-catalyzed process can occur under strongly to moderately acidic conditions, particularly for the synthesized birnessite, as well as under circumneutral conditions (Fig. 5). Upon adsorption onto the mineral surface,  $\text{Mn}^{2+}$  may participate in redox interactions, leading to the formation of various  $\text{Mn}^{3+}$ -containing mineral phases through comproportionation.<sup>86,87</sup> Alternatively,  $\text{Mn}^{2+}$  may undergo oxidation followed by precipitation, however, this process is strongly pH-dependent and thermodynamically unfavorable below pH 8.<sup>88</sup>

Any addition of salts to the DOM-stock solution increases the ionic strength, influences the solubility of (trace) metals, affects the binding affinity of DOM to the surfaces of the Mn oxides, and thus the dissolution kinetics and Mn speciation analysis.<sup>89,90</sup>

During our batch operations, the mean molarities for  $\text{Ca}^{2+}$  ranged from  $0.0003$  to  $0.001$  M (Tables S6 and S7). This cation mediates interactions between negatively charged NOLs, in particular carboxyl groups, and negatively charged Mn oxide surfaces by the formation of inner- and outer-sphere surface complexes and/or electrostatic attraction.<sup>90</sup> Experimental indications of this side mechanism were found during the NOL-Mn oxide interactions at pH 7 for birnessite at all time steps and more limited for manganite at  $\geq 12$  h (Fig. 5 and 6). By this mechanism, the NOLs are (temporarily) removed from the solution and are not available for, amongst others, the complexation of dissolved  $\text{Mn}^{2+}$  with or without oxidation [eqn (8)–(10)]. This effect was indicated by a distinct decrease in the  $\text{Ca}^{2+}$  concentrations (Tables S6 and S7). However, the experimental data do not provide conclusive evidence for this mechanism and further studies are needed. By contrast, this mechanism did not occur reliably under strongly acidic conditions, since  $\text{Ca}^{2+}$  then has a lower sorption affinity towards Mn



oxides<sup>91,92</sup> and is displaced by (excessively) released  $\text{Mn}^{2+}$  and  $\text{H}^+$ .<sup>93</sup> Looking at manganite, its high PZC and smaller SSA limit the readsorption rate.

Another possible side mechanism involves the formation of  $\text{Ca}^{2+}$ -mediated DOM aggregates, leading to HMW organic molecules.<sup>94</sup> It occurs preferentially under circumneutral conditions, as carboxyl groups are mainly deprotonated. Although HMW NOLs are more prevalent under circumneutral conditions, this process cannot be conclusively verified by the data. Similar effects do not occur in  $\text{Na}^+$  and  $\text{Mg}^{2+}$  solutions.<sup>95</sup> For mechanisms such as cation bridging and aggregate formation, the influence of  $\text{NaN}_3$  and  $\text{NaOH}$  which were used in our experiments is negligible. However,  $\text{NaN}_3$  can act as both an oxidant and a reductant, potentially altering DOM molecules (*e.g.*, quinones and phenols) by rapidly reducing redox-active functional groups, thereby decreasing their overall reducing capacity.<sup>96</sup> Since a control experiment without  $\text{NaN}_3$  was not performed, a potential influence of  $\text{NaN}_3$  on the reducing capacity of DOM or the EEM spectroscopy analysis cannot be excluded.

**4.1.2 Interactions of the natural organic ligands.** During the batch experiments, the observed  $\text{DOC}_{\text{loss}}$  proportions may result from (i) adsorption onto mineral surfaces, (ii) surface-catalyzed degradation to  $\text{CO}_2$ ,<sup>97</sup> and (iii) the formation and precipitation of non-filter-passing  $\text{Mn}^{2+/3+}$  colloids stabilized by humic acids.<sup>3,97</sup> These processes alter the DOM composition, thereby influencing  $\text{Mn}^{3+}$ -NOL complex formation and, consequently, Mn speciation analysis.

For birnessite, increased  $\text{DOC}_{\text{loss}}$  proportions ( $\text{pH} \leq 4$ ) are attributed to its high SSA and surface charge, which promote adsorption, higher sorption capacities (*e.g.*,  $\text{Mn}^{2+}$ , DOM),<sup>83,98</sup> dissolution kinetics,<sup>31</sup> and oxidation of many polar organic compounds.<sup>85</sup> Protonated functional groups like carboxyl ( $\text{pK}_a$  3–6)<sup>99</sup> and phenolic groups ( $\text{pK}_a$  8–11)<sup>100</sup> are less repelled by the negatively charged surface. Adsorption is largely governed by carboxyl groups, which are abundant alongside hydroxylic groups in terrestrial DOM.<sup>101</sup> These groups initiate bridging and/or the mono-/bidentate bonds that bind DOM to birnessite.<sup>102</sup> Once adsorbed, DOM is prone to surface-catalyzed oxidation, as indicated by increased  $S_s$  and  $S_R$  values (Table S4). Birnessite is known for its ability to oxidize organic molecules such as catechol to  $\text{CO}_2$ , releasing  $\text{Mn}^{2+}$ . This process contributes to a progressive DOC loss over time, which further shifts the  $\text{Mn}_T$ :DOC ratio, preventing the formation of  $\text{Mn}^{3+}$ -NOL complexes.

For manganite, the almost halved  $\text{DOC}_{\text{loss}}$  ( $\text{pH} \leq 4$ ) compared to birnessite results from its small SSA and repelled functional groups due to the mineral surface charge. Decreased  $\text{MA}_{254}$  and  $\text{MA}_{350}$  values, along with increased  $S_s$  and  $S_R$ s, suggest shrinking aromaticity and a predominance of LMW NOLs (Table S5). This aligns with the preferential adsorption of molecules with HMW, high(er) aromaticity, high content of oxygen, nitrogen and carbohydrates, while unsaturated LMW molecules, defined by less oxygen-containing functional groups, remain dissolved.<sup>3,97,103</sup> Ongoing oxidation of DOM, driven by the strong oxidative potential of manganite as well as the higher reductive potential of the solution, leads to its degradation. Consequently, terrestrial LMW NOLs complex  $\text{Mn}^{3+}$  only to a limited extent and the resulting  $\text{Mn}^{3+}$ -NOL

complexes are metastable, particularly under strongly acidic conditions.

Considering the general binding affinity of NOLs under strongly acidic conditions,  $\text{Mn}^{2+}$  and  $\text{H}^+$  are assumed to compete for binding sites on NOLs, such as humic acids.<sup>104</sup> This competitive binding, resulted by reductive dissolution mechanisms and a molar  $\text{Mn}_T$ :DOC ratio  $\geq 0.08$ , strongly hinders  $\text{Mn}^{3+}$ -NOL complex formation.

In summary, concentration, availability, composition (*e.g.*, functional groups, charge) and potential transformation of DOM during NOL-Mn oxide interactions are crucial for  $\text{Mn}^{3+}$ -NOL complex formation.

## 4.2 Method criticism

The extraction protocol for the forest floor solution affects the duration of extraction, the dissolution ratio,<sup>105</sup> the concentration of the background electrolyte,<sup>77,106</sup> and the intensity of rewetting of the dried forest soil sample.<sup>107</sup> Consequently, the protocol for the extraction of NOLs has a decisive influence on the NOL concentration, composition, and reactivity.<sup>108</sup> In addition, micro- and nano-sized Mn oxides that surpass the filtration steps cannot be completely excluded and might lead to an overestimation of  $\text{Mn}^{3+}$ -NOL<sub>strong</sub> complexes.<sup>30</sup>

Looking at the kinetic modeling process, unknown environmental samples with their individual reaction kinetics are challenging. In particular, a large number of unknown NOLs complicate the modeling and parameterization.<sup>9,109</sup> The equations used for modeling [eqn (1) and (2)] are simplified and represent the diversity of the NOL pool only to a limited extent. More precise kinetic modeling would require extending these equations to account for the individual number of NOLs, as suggested by Kim *et al.* (2022).<sup>109</sup> Furthermore, due to the large variety of NOLs, it remains unclear whether certain NOLs withstand competition from  $\text{T(4-CP)P}^{30}$  or hydroxylamine. Consequently, it is impossible to fully incorporate the variability of unknown NOLs into the modeling process.

Additionally, the use of experimental and analytical triplicates introduces further variability into the  $\text{Mn}_T$  pool data. This variability arises from (i) the individual DOM composition of each replicate (ii) minor inconsistencies in manual procedures (*e.g.*, pipetting), and (iii) the process of fitting experimental data to the model equations.

We are critically aware that, in particular, the removal of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  species by the cation exchange resin excluded prominent binding partners for NOLs. Under natural conditions, these cations form stable complexes with the NOLs of the soil solution<sup>110</sup> and thus compete with dissolved Mn species. It is, therefore, obvious that natural soil solutions exhibit a more variable cation pool. We conclude that additional competitive side reactions potentially decrease  $\text{Mn}^{3+}$ -NOL complex concentrations, resulting in increased  $\text{Mn}^{2+}$  proportions.

## 5. Conclusions

Our results demonstrate that  $\text{Mn}^{3+}$ -NOL complexes are important constituents of the  $\text{Mn}_T$  pool in forest floor solutions. We



further outline fundamental abiotic mechanisms that are assumed to contribute to the formation of  $\text{Mn}^{3+}$ -NOL complexes in terrestrial environments. Since its formation and stability are particularly limited under strongly acidic conditions, it is a metastable species that is subject to a continuous cycle of formation and decay. However,  $\text{Mn}^{3+}$ -NOL complexes remain a non-negligible compound. It is likely that high amounts of reactive  $\text{Mn}^{3+}$ -NOL complexes promote the oxidative degradation of organic compounds as well as altering the acidity and redox capacity of forest floor solutions. Consequently, the role of  $\text{Mn}^{3+}$ -NOL complexes in terrestrial environments has been underestimated. Based on our findings, we hypothesize that different types of Mn oxides react with NOLs to enable the formation of  $\text{Mn}^{3+}$ -NOL complexes over a wide pH range in forest floor solutions, even under oxidizing conditions. Further research should investigate more complex forest floor and soil solution matrices as well as different Mn oxides, and follow the trace of  $\text{Mn}^{3+}$ -NOL complexes.

## Conflicts of interest

The authors declare that there are no conflicts of interest.

## Data availability

The data supporting this article have been included as part of the SI. See DOI: <https://doi.org/10.1039/d5em00388a>.

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