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pH-dependence of organic matter solubility: Base type effects on dissolved organic C, N, P, and S in soils with contrasting mineralogy

Denis Curtin *, Michelle E. Peterson, Craig R. Anderson

The New Zealand Institute for Plant & Food Research Limited, Private Bag 4704, Christchurch, New Zealand

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ABSTRACT

Dissolved organic matter (DOM) is an important substrate for soil biological processes. Raising pH is known to cause release of DOM but less is known of the impact of different bases on the quantity and quality of DOM in soils. Three acid (pH 5.3–5.7) soils of contrasting mineralogy were used to examine how the quantity and quality of DOM changes when soil pH is raised using lime ($Ca(OH)_2$) or KOH (chemical analog of NH_4OH, a product of urea hydrolysis). Dissolved organic carbon (DOC) increased as the base addition rate increased, with the response to KOH being up to 9 times larger than to $Ca(OH)_2$. The proportion of carbohydrate-C (hexose- and pentose-C) in DOM did not show consistent effects of base rate or type and was similar for the three soils (35% of DOC, on average). Dissolved phenol-C increased as base addition rate increased. Only monomeric phenols were solubilized in $Ca(OH)_2$-treated soils whereas polyphenols were solubilized in increasing amounts as the KOH rate was raised. Although the quantity of DOM differed considerably between treatments, its bioavailability (45% on average; measured using a 7-day bioassay at 20 °C) was similar across treatments and soil types, with good correspondence between carbohydrate-C and bioavailable C. Large base type effects on organically bound nutrients (dissolved organic N, P, and S) were also observed (KOH $\gg$ $Ca(OH)_2$). A distinguishing feature of DOM released by KOH was the presence of large amounts of complexed Al and Fe. We concluded that KOH (and, by extension, NH_4OH) may render stable organic matter accessible to microbes by liberating it from the protective influence of soil minerals. Our results emphasize the importance of choosing an appropriate base when examining pH effects on DOM and associated biological processes.

1. Introduction

Much of the organic matter in soil is stable and only a small part is active in C and nutrient cycling. The active component includes the dissolved organic matter (DOM) (Chantigny et al., 2014; Sanderman et al., 2008). Although DOM usually makes up a very small fraction of total SOM, its high turnover rate and mobility means that it can influence a broad range of biogeochemical processes in both terrestrial and aquatic environments (Bolan et al., 2011). For example, it is recognized as a key driver of denitrification in topsoil and subsoil (Burford and Bremner, 1975; Jandl and Sollins, 1997; McCarty and Bremner, 1993; Peterson et al., 2013; Siemens et al., 2003).

Many factors can influence the quantity of DOM in soil, including land use (DOM is usually greater under pasture than arable cropping) and management (e.g., fertilizer and lime use). Research suggests that organic matter is solubilized primarily as a result of abiotic processes (Toosi et al., 2014). DOM is released after re-wetting of dry soil (so-called Birch effect (Birch, 1958)), though the underpinning mechanism and sources remain elusive. DOM is also affected by temperature (positive response; Chantigny et al. (2010) and references therein) and by changes in the chemical environment. Addition of inorganic salts (e.g., fertilizers) can either have a positive or negative effect depending on the nature of the salt; chloride and nitrate salts decrease DOM whereas phosphate may increase it (Curtin et al., 1999).

The soil mineral matrix has a strong influence on the adsorption and desorption of DOM. Mineralogical characteristics determine how much DOM can be adsorbed and protected from microbial attack (Baldock and Skjemstad, 2000). Soils containing a substantial amount of amorphous and poorly crystalline Al and Fe oxides or allophane can have a particularly large capacity to adsorb and stabilize DOM (Beare et al., 2014; Percival et al., 2000).

The solubility of DOM is pH-dependent and significant increases in DOM have been observed when pH is raised by addition of lime (as $Ca(OH)_2$) (Curtin et al., 1998). Formation of NH_4OH following urea application or deposition of livestock urine can result in large increases in soil pH (Clough et al., 2003; O'Callaghan et al., 2010). Although elevated pH in urea-/urine-affected areas are transient (last for days to weeks only), they can have important effects on the solubility and leaching of soil C (Lambie et al., 2012a,b). The solubilization of organic

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* Corresponding author.
E-mail address: denis.curtin@plantandfood.co.nz (D. Curtin).

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matter in urea- and urine-affected areas can lead to increased soil respiration (Kelliher et al., 2005) as well as fuelling denitrification (Monaghan and Barraclough, 1993; Wachendorf et al., 2005).

The effect of elevated pH on the solubility of organic matter is likely to depend on the nature of the base that causes the pH increase. Solubility of organic matter may be greater in the presence of monovalent cations such as NH_4^+ or K^+ compared with a multivalent cation (Baldock and Skjemstad, 2000; Nelson et al., 1998). Thus, DOM concentrations may be greater when pH is raised by NH_4OH than with an equivalent addition of $Ca(OH)_2$. Knowledge of the pH × cation interaction on organic matter solubility is needed to understand how important biological processes (respiration, denitrification) respond when a base is applied (e.g., lime) or generated (e.g. NH_4OH) in the soil. One aim of this work was to provide a mechanistic understanding of base type effects on organic matter solubility using soils with contrasting mineralogy. Dissolved organic matter may range in complexity from simple monomers to highly complex bio-polymers and variation in biochemical composition will likely influence its biodegradability and thus biogeochemical processes. A second objective was to determine if there are qualitative differences between the organic matter solubilized in the presence of $Ca(OH)_2$ versus the base of a monovalent cation.

2. Materials and methods

2.1. Soil sampling

Three sites in New Zealand were sampled to provide soils of contrasting mineralogy. A Wakanui silt loam (Udic Dystrocrept) was sampled under a no-tillage, arable cropping rotation at Lincoln, Canterbury (43°40′3.5″S, 172°28′11.0″E). This soil contains predominantly 2:1 clays and has a low anion storage capacity (ASC). A Patumahoe clay loam (Andic Palehumult) under outdoor vegetable cultivation was sampled at Pukehohe, south of Auckland (37°12′17.0″S, 174°51′43.3″E). It is high in sesquioxides (Fe and Al) and has moderately high ASC. A Dunmore silt loam (Typic Hapludand) under permanent pasture was sampled at Aramiro near Hamilton (37°53′27.0″S, 175°02′19.3″E). This soil has significant allophane content and an extremely high ASC.

2.2. Soil characterization

At each site, multiple soil cores were taken to a depth of 7.5 cm (A horizon), and mixed thoroughly into one composite sample. Soils were passed through a 4-mm sieve and air-dried. pH was measured at a 1:2 soil:water ratio. Total soil N and C were determined by Dumas combustion (LECO TruMac, Leco Corporation, St. Joseph, MI, USA). Mineral N was extracted with 2 M KCl and determined using an automated colorimeter (QuickChem 8000 FIA+, Lachat Instruments, Loveland, CO). Sulfate-S was extracted with 0.02 M KH_2PO_4 and determined by ion chromatography. Available P was determined by the method of Olsen et al. (1954). Anion storage capacity (ASC) was determined by equilibrating the soils with 0.02 M KH_2PO_4 (1:10 soil: solution ratio; 16 h extraction) and measuring the proportion of added P retained by the soils (Saunders, 1965). Aluminum and Fe were extracted by overnight shaking of soil in 0.1 M potassium pyrophosphate (1:100 *w*/*v* soil:extractant ratio) (Courchesne and Turmel, 2008). Aluminum and Fe in the extracts were measured by Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES — Varian 720, Varian Australia Pty Ltd., Victoria, Australia).

2.3. Effect of base addition on dissolved organic matter

The soils were treated with five or seven rates of either KOH or $Ca(OH)_2$, including a control with no base addition (seven rates for the Pukekohe and Aramiro soils; five for the weakly buffered Lincoln soil). The intention was to raise soil pH to ~8 at the highest addition rate (pH can increase to 8–8.5 after bovine urine deposition; (O'Callaghan et al., 2010)). We used KOH, a chemical analog of NH_4OH (K and NH_4 ions are similar in size and in their physical chemistry in soil (DeSutter and Pierzynski, 2005; Evangelou and Phillips, 2005)) to avoid potential complicating effects associated with NH_4-N transformations (e.g., volatilization, nitrification). The two bases were applied at equi-molar rates, i.e., the same amount of OH^- was applied in the KOH and $Ca(OH)_2$ treatments. There were three replicates of each treatment.

DOM was extracted by shaking 30 g of air-dried soil with 60 mL of deionized water containing either KOH or $Ca(OH)_{2.}$ As $Ca(OH)_2$ is relatively insoluble, it was added to the soil in solid form prior to addition of 60 mL of deionized water. For the KOH treatments, aliquots of 0.2 M KOH were diluted in deionized water to a total volume of 60 mL before addition to the soils. The soil suspensions were shaken at room temperature (20 °C) for 16 h in 85-mL centrifuge tubes. The tubes were centrifuged for 5 min at 40,000 g and the supernatants filtered through a 0.45 μm nylon filter.

2.4. Characterization of soil water extracts

The extracts were analyzed for pH and electrical conductivity. Concentrations of cations (Ca, Mg, K, Na, Al, Fe) were determined using ICP-OES. Dissolved anions (Cl, Br, SO_4, PO_4) were measured using a Dionex DX-2100 Ion Chromatograph (Thermo Scientific, Sunnyvale, CA, USA).

Dissolved organic and inorganic C were determined using a Total Organic Carbon Analyzer (Shimadzu TOC-$V_{CSH,}$ Shimadzu Corp, Japan). Total dissolved N was determined by persulfate oxidation, as described by Cabrera and Beare (1993). Dissolved organic N was estimated by subtracting mineral N (NH_4^+ and NO_3^- determined using an automated colorimeter, as described above) from total dissolved N. Total amounts of dissolved P and S in the extracts were also determined (by ICP-OES). Dissolved organic P (P_o) and dissolved organic S (S_o) were estimated by subtracting dissolved inorganic P and S (measured by ion chromatography) from total dissolved P and S.

The biodegradability of DOM tends to increase as its carbohydrate content increases whereas aromatic compounds, including phenolics, are more recalcitrant (Marschner and Kalbitz, 2003).Total dissolved phenols were measured with Folin's–Ciocalteu reagent (Ohno and First, 1998). Monomeric phenols were determined after precipitating polyphenols using casein; polyphenol concentration was then estimated as the difference between total and monomeric phenol concentration (Kuiters and Denneman, 1987). Concentrations of hexoses and pentoses in the extracts were determined by anthrone-sulfuric acid and orcinol-ferric chloride-hydrochloric acid hydrolysis, respectively (Brink et al., 1960; Kawahigashi et al., 2003). The biodegradability of dissolved organic C in the extracts was assessed using the seven-day incubation assay described by McDowell et al. (2006). Briefly, the extract was diluted to ~20 μg DOC mL^{-1}, then 30 mL of diluted extract was transferred to a vial, amended with nutrients and inoculum (prepared from a fresh sample of topsoil), and incubated in the dark for 7 days at 20 °C. Non-purgable organic C (NPOC) was quantified before and after the incubation following filtration (0.45 μm); NPOC was determined using the TOC-V_{CSH} analyzer described above. Biodegradable C was estimated from the decrease in NPOC during the incubation.

2.5. Data analysis

Correlations and scatter plot matrices were used to examine the behavior of response variables. A linear mixed model fitted with Restricted Maximum Likelihood (REML) was used to estimate means and 95% least significant differences (LSD) for the interaction between soil, base type and base addition rate with degrees of freedom reported for each soil. Where required, a log transformation was used to help ensure homoscedasticity; the variation associated with back-transformed estimates