Soil Biology & Biochemistry 67 (2013) 70–84

Contents lists available at ScienceDirect

Soil Biology & Biochemistry

journal homepage: www.elsevier.com/locate/soilbio

Differences in carbon and nitrogen mineralization in soils of differing initial pH induced by electrokinesis and receiving crop residue amendments

Kongcao Xiao [a], Jianming Xu [a,*], Caixian Tang [b], Jiabao Zhang [c], Philip C. Brookes [a]

[a] *College of Environmental and Natural Resource Sciences, Zhejiang Provincial Key Laboratory of Subtropical Soil and Plant Nutrition, Zhejiang University, Hangzhou 310058, China*

[b] *Department of Agricultural Sciences, La Trobe University, Bundoora (Melbourne), Vic. 3086, Australia*

[c] *Chinese Academy of Sciences, Institute of Soil Science, State Key Lab Soil & Sustainable Agriculture, Nanjing 210008, China*

ARTICLE INFO

Article history:
Received 1 February 2013
Received in revised form
15 August 2013
Accepted 20 August 2013
Available online 30 August 2013

Keywords:
Acidic soil
Crop residue
CO_2 emission
Nitrification
Mineralization
Initial soil pH

ABSTRACT

Initial soil pH has been reported to have a great impact on the decomposition of added organic materials and hence to determine the direction and magnitude of subsequent soil pH changes. However, most previous investigations have been conducted on different soil types differing in initial pH and other soil properties. Here, we investigated the effects of initial soil pH on the subsequent soil pH and N mineralization changes caused by addition of crop residues to two soils (a Paleudalf and a Plinthudult) with different pHs induced by treatment with direct electric current. This produced pH gradients of 6.50–3.20 and 6.74–3.81, respectively. Three typical field crop residues differing in C/N ratio, i.e. rice straw C/N = 42, canola residue C/N = 36 and Chinese milk vetch C/N = 14 (vetch), were incubated with the soils for 102 days. With both soils, total CO_2 fluxes differed between the type of added crop residues, with vetch > canola residue > rice straw, and decreased with decreasing initial soil pH. The incorporation of crop residues into the two soils at all pHs increased soil pH except for the Paleudalf at pH 3.81 and 4.25 amended with rice straw and canola residue, where pH slightly decreased. As expected, vetch incorporation caused a greater pH increase than the two non-legume residues (rice straw and canola residue), but this effect was transient in soils of higher initial pH. The pH declined rapidly with time in soils of initial pH $\geq$ 4.40 treated with vetch, while addition of rice straw and canola residue maintained stable pHs. Irrespective of crop residue addition, soil pH continuously increased or remained steady over the 102-day incubation period in the highly acidic soils (pH $\leq$ 4.25). While NH_4^+ accumulated in highly acidic soils, NO_3^- accumulated in higher pH soils. Contrasting effects on nitrification and subsequent pH changes occurred between soil pH $\leq$ 4.25 and pH $\geq$ 4.40. However, no clear relationship between net N mineralization and soil pH was found. This study demonstrated that low soil pH greatly inhibited nitrification, while net N mineralization was generally less affected. This, in turn, affected the direction and extent of soil pH changes after addition of crop residues.

1. Introduction

Soil acidification is of world-wide concern as it significantly affects agricultural sustainability (Guo et al., 2010; Yang et al., 2012). It has been greatly accelerated by anthropogenic activities including atmospheric acid deposition (Stevens et al., 2009), application of ammonium-based fertilizers (Xu et al., 2002; Huang et al., 2010; Schroder et al., 2011), plant uptake of base cations (Duan et al., 2004; Randall et al., 2006), tea plantations (Alekseeva et al., 2011) and even elevated atmospheric CO_2 (Oh and Richter, 2004). Cost-effective and environmentally friendly measures for amelioration of acid soils are in demand to ensure the sustainability of ecosystems.

Plant materials, including crop residues, are generally considered to have some liming potential since large amounts of base cations are absorbed during plant growth and, importantly, the return of plant residues to soil can play a dual role as fertilizer and "lime" (Naramabuye and Haynes, 2006). Previous studies have reported disparate responses of soil pH after incorporation of plant residues, e.g. increased pH (Tang et al., 1999; Marx et al., 2002; Naramabuye and Haynes, 2006; Wang et al., 2009a), decreased pH (Owen et al., 1999; Rosolem, 2011), or increased pH early and

---

* Corresponding author. Tel./fax: +86 571 8898 2069.
E-mail address: jmxu@zju.edu.cn (J. Xu).

0038-0717/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.soilbio.2013.08.012

then decreased (Yan et al., 1996; Tang and Yu, 1999; Paul et al., 2001a; Xu and Coventry, 2003; Yuan et al., 2011). Paradoxically, no changes in soil pH after addition of plant residues were observed in other investigations (Xu and Coventry, 2003). Reasons for these discrepancies are largely attributed to the differences in inorganic nutrient composition and types of added plant residues, also, soil properties and experimental conditions may also have been involved (Xu et al., 2006b). Dominant pH effects influencing soil processes include the release of alkalinity from plant residues decomposition, net N mineralization, and subsequent nitrification (Paul et al., 2001), with the final soil pH determined by the relative contributions of these processes (Xu et al., 2006b).

Theoretically, any factors which affect the above processes will ultimately affect the pH change pattern after addition of plant residues. The chemical composition of plant residues *per se* primarily determines the liming potential. It has been widely documented that the difference in potential liming ability between different plant residues is related to the alkalinity (i.e. concentration of excess cations), total basic cations, N and $CaCO_3$ concentrations, and proton neutralization capacity (Noble et al., 1996; Tang et al., 1999; Yan and Schubert, 2000; Marx et al., 2002; Naramabuye and Haynes, 2006; Wang et al., 2009a; Butterly et al., 2011). Pocknee and Sumner (1997) pointed out that the basic cations are the major cause of soil pH increases, and their concentrations are significantly correlated with pH changes. However, the increase in soil pH may also be attributed to the microbial decarboxylation of organic acids in which H^+ ions react with the newly formed organic anions and other negatively charged chemical functional groups thereby leading to an increase in pH (Yan et al., 1996; Marschner and Noble, 2000; Butterly et al., 2011; Rukshana et al., 2011). Additionally, the chemical composition of plant residues plays an important role during the initial stages of residue decomposition (Xu et al., 2006a), and affects the mineralization of organic N and the release of alkalinity (Tian et al., 2007; Nicolardot et al., 2007).

The plant C/N ratio is the most frequently used predictor of the decomposition rate of plant residues and N mineralization in soil (Janssen, 1996). In general, plant C/N ratios below about 25 are considered to favor N mineralization while C/N ratios much above 30 favor N immobilization (Trinsoutrot et al., 2000; Kumar and Goh, 2003). However, soil properties, such as soil texture, soil organic matter (SOM) content, soil pH and moisture content, also have great influences on the decomposition of added organic materials (Van Bergen et al., 1998; Paul et al., 2001) and thus on soil pH changes. Among these, soil pH is one of the most dominant variables and has profound influences on the microbial biomass (Aciego Pietri and Brookes, 2008b, 2009), microbial activity (Kemmitt et al., 2006) and microbial community structure (Bååth and Anderson, 2003; Fierer and Jackson, 2006; Rousk et al., 2009, 2010). Nitrogen transformations during decomposition can influence soil pH change and vice versa. For instance, nitrification is more sensitive to low pH than ammonification and other processes (Arora et al., 1986; Robson and Abbott, 1989). Furthermore, soil pH also influences the association and dissociation of organic compounds, and the initial soil pH is considered to determine the direction and magnitude of soil pH change after incorporation of plant residues (Tang and Yu, 1999). However, soil pH is often correlated with many other factors such as nutrient availability and so causality among factors is not easily determined (Fernández-Calviño et al., 2011).

In most previous studies, acidic soils, over a wide range of soil pH but also varying in soil type, land use and climatic conditions, were sampled from different zones to compare the amelioration of soil acidity by plant residues, so that soil physical, chemical and biochemical properties were inevitably confounded (Tang et al., 1999; Xu et al., 2006b; Fernández-Calviño et al., 2011). Thus, information on the effects of plant residues on pH changes along a sequential pH gradient from a single soil, in which most variables are minimized other than soil pH, is still lacking (Xu and Coventry, 2003). Studies along continuous pH gradients within a single soil type are rare because such soils are rarely encountered in nature (Aciego Pietri and Brookes, 2008a). Since soil physicochemical and biological properties are accordingly altered with changing soil pH, there really are no soils which differ only in soil pH while their other properties remain identical.

In contrast to the traditional pH studies using soils of differing pH, soil type, and cultivation history, or pH differences produced by addition of different amounts of acid or alkali (Fu et al., 1987; Tietema et al., 1992), soil pH gradients in this study were produced after electrokinetics, which is one of the recently developed methods for remediation of soils containing inorganic and organic contaminants (Maini et al., 2000; Virkutyte et al., 2002; Gomes et al., 2012). In this technology, a direct electric current is applied to promote the movement of contaminants towards the electrodes through electromigration, electroosmosis and electrophoresis. Electrokinetics is commonly applied to remove contaminants from soil, but the process inevitably impacts other soil properties, especially soil pH. This is due to the electrolysis of water that occurs at the anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ and at the cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$, which causes pH increases in the soil region near the cathode while pH decreases in the soil region near the anode, with a resulting pH gradient between the electrodes (Saichek and Reddy, 2003).

To our knowledge, there have been no reported studies of applying electrokinetics to produce soil pH gradients aimed at evaluating the effect of initial soil pH on liming potential and N mineralization following crop residue incorporation. Here, we test the hypothesis that low initial soil pH will inhibit nitrification but not ammonification and examine how initial soil pH values from a pH gradient within a single soil type affects the subsequent changes of soil pH after addition of crop residues differing in C/N ratio. Our assumption is that the liming effect of plant residues is greater and persists much longer in highly acidic soils (i.e. $pH < 4.5$) than in slightly acidic soils (i.e. $4.5 < pH < 7$).

2. Materials and methods

2.1. Preparation of soils and crop residues

Two cultivated soils, i.e. a Plinthudult (clayey kaolinitic thermic plinthaqualf) and a Paleudalf (clayey illitic thermic typic umbraqualf), were collected from the 0–20 cm depth on selected field sites in Longyou county and Jiaxing city, respectively, both located in Zhejiang province, China. The soils were air-dried and milled <2 mm. Their initial physical and chemical characteristics are presented in Table 1. Soil samples with various initial pH values were produced after application of direct electric current (DC). An electrokinetic apparatus similar to that described by Lear et al. (2004) was used. It consisted of a DC power supply, a reactor, two electrode chambers, and a pump. The electrokinetic reactor was made from PVC material and had a soil compartment (50 × 20 × 10 cm) and two electrode chambers (dimensions 20 × 2 × 8 cm) each of which contained four compressed plate-type graphite electrodes (8 cm × 3 cm × 0.8 cm). The electrokinetic compartment was first packed with air-dried soil to a depth of 6 cm and subsequently saturated with water and allowed to equilibrate for 24 h prior to DC application, when a constant voltage gradient of 1 V/cm was applied to the electrode. After the electrokinetic process was run for 72 h, the soil was removed from the compartment and was cut into four parts (divided by the distance from anode to cathode, 5–15 cm (S1), 15–25 cm (S2), 25–35 cm