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Changes in soil chemical properties as affected by pyrogenic organic matter amendment with different intensity and frequency

Ruzhen Wang [a], Yulan Zhang [a,*], Artemi Cerdà [b,c], Mingming Cao [a], Yongyong Zhang [a,d], Jinfei Yin [a,d], Yong Jiang [a], Lijun Chen [a]

[a] National Engineering Laboratory of Soil Nutrient Management, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China
[b] Soil Erosion and Degradation Research Group, Department of Geography, University of Valencia, Valencia, Spain
[c] Soil Physics and Land Management Group, Wageningen University, Droevendaalsesteeg 4, 6708PB Wageningen, The Netherlands
[d] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Pyrogenic organic matter (PyOM) has long been used as a soil amendment to improve soil physicochemical properties. However, few studies simultaneously investigated both intensities and frequencies of PyOM addition on soil chemical properties of soil base cations, soil pH buffering capacity (pHBC), and plant available micronutrients. In the main food production area of lower Liaohe River Plain in Northeast China, a field manipulation of PyOM addition was initiated in 2013 to examine how the intensities (0, 1%, 3%, and 5% of 0–20 cm soil mass) and frequencies (3% of soil mass applied once versus yearly for 3 years) of PyOM amendment affected soil chemical properties. Higher intensity of PyOM addition significantly increased soil exchangeable Mg (by 24.2%), which was caused by increase of soil pH, soil exchangeable surfaces, and soil organic matter. Plant available Fe, Mn, and Cu were significantly decreased with increasing PyOM addition intensity by up to 39.4%, 50.8%, and 30.0%, respectively, especially under the highest amount of PyOM amendment (5%). This was possibly due to removal of micronutrients with plant biomass or irreversible binding of available micronutrients on PyOM which decreased the extraction efficiency. Under the same amount of PyOM addition (3% in total), higher frequency of PyOM amendment significantly increased soil exchangeable Mg, while lower frequency showed no impact as compared to control plots (CK). Higher frequency of PyOM amendment significantly decreased plant available Mn and Cu as compared to both lower frequency and CK treatments. Both the intensity and frequency of PyOM addition significantly increased soil pH but showed no influence on soil pHBC. Our results showed that exchangeable Mg increased but available Mn and Cu decreased with both PyOM amendment intensity and frequency. Even though PyOM amendment could enrich soil base cations, it might cause deficiency of available micronutrients and pose a threat to plant productivity in agroecosystems.

1. Introduction

Pyrogenic organic matter (PyOM), also called biochar or black carbon derives from incomplete combustion of organic materials including plant biomass and fossil fuels (Gibson et al., 2016). Incorporation of PyOM into soil can alter soil physicochemical properties and carbon (C) from PyOM makes up ~5–45% of soil organic C (SOC) (Glaser et al., 1998; Skjemstad et al., 2002). The PyOM is highly condensed aromatic substance with high hydrophobicity and low microbial accessibility (Gray et al., 2014; Gibson et al., 2016). After adding to soils, PyOM could be eventually oxidized through abiotic and biotic processes to be hydrophilic as incorporation of oxygen-containing functional groups and accessible to soil microorganisms (Gul et al., 2015; Zimmerman, 2010). Being more hydrophilic, aged PyOM (after addition for one year or more) plays a more important role in providing favorable habitat (ample aeration, water and nutrients) for soil microorganisms and retaining soil nutrients (Cheng et al., 2006; Mukherjee et al., 2014). Pyrogenic organic matter improves soil properties but also the environment (Paz-Ferreiro et al., 2014). The PyOM is used for agricultural soils (Hüppi et al., 2015) affected by salinization (Wu et al., 2014; Drake et al., 2016), under intense agriculture land (De Melo Carvalho et al., 2014; Weyers and Spokas, 2014) but also on shifting agriculture as charcoal (Coomes and Miltner, 2016) and to restore mine soils and quarries (Muñoz et al., 2016).

PyOM addition could increase soil pH and reduce the loss of base cations (Laird et al., 2010). The PyOM could bind H^+ in soil solutions by the negatively charged functional groups (i.e. phenolic, carboxyl, and

* Corresponding author.
E-mail address: ylzhang@iae.ac.cn (Y. Zhang).

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hydroxyl groups) on its surface (Gul et al., 2015). Also, PyOM produced from corn stalk is commonly alkaline due to the formation of alkalis during pyrolysis (Yuan et al., 2011). Additionally, surface area of PyOM would offer cation exchange capacity (CEC) provision to soils, and it was more evident after abiotic or microbial oxidation of PyOM with negatively-charged groups on its surface (Liang et al., 2006; Zimmerman, 2010). In line with this, Cheng et al. (2006) found a rapid formation of CEC during a four-month incubation experiment of PyOM surface oxidation. Soil exchangeable Ca and Mg were found to increase with PyOM amendment (Uzoma et al., 2011; Yuan and Xu, 2011). Soil physical properties, such as soil aggregation, soil aeration and water holding capacity could also be ameliorated by PyOM addition (Du et al., 2016; Zong et al., 2016). In this case, PyOM amendment was asserted to benefit the international crop production due to the improvement of soil physicochemical properties (Yamato et al., 2006; Kauffman et al., 2014). Micronutrients, such as Fe, Mn, Cu, and Zn could be incorporated into soils through PyOM application as they would not turn into volatile substances during pyrolysis (Laird et al., 2010; Chintala et al., 2014). However, current studies rarely considered the responses of plant available micronutrients to PyOM addition.

In agroecosystems, soil acidification is common as caused by heavy fertilization and atmospheric N deposition (Liu et al., 2013). Soil pH buffering capacity (pHBC) plays an essential role in counteracting decrease of soil pH during soil acidification (Bowman et al., 2008). Amendment of PyOM is deemed to alleviate soil acidification and enhance soil fertility (Ge et al., 2010; Du et al., 2016). The PyOM addition would enhance soil pHBC through its alkalization effect and increase of soil organic matter (SOM) and CEC (Yamato et al., 2006; Xu et al., 2012). Previous studies reported that PyOM addition increase soil pHBC by up to 73.6%, 92.0%, and 123.2% for different soil types of Ultisol (SOM concentration of 5.1 g kg soil^{-1}), Oxisol, and Ultisol (SOM concentration of 17.3 g kg soil^{-1}) after 40-day incubation (Xu et al., 2012). However, soil pHBC was also reported to remain unchanged for some soils after PyOM addition (Xu et al., 2012). The direction of soil pHBC change after PyOM addition would be driven various factors, such as edaphic properties, soil types, change of CEC, and PyOM properties.

Field experiments usually apply PyOM into soils once (low frequency) (Major et al., 2010) or yearly for several times (high frequency) (Du et al., 2016), but few study compared the effect of these two different PyOM application ways on soil properties. Even being hydrophobic and highly aromatic at the initial stage of soil application, PyOM amendments could still supply labile components into soil which is hydrophilic and easily washed out by soil water (Gibson et al., 2016; Zimmerman, 2010). Higher frequency of PyOM amendment would continuously supply labile organic materials and complement the nutrients for plants through fresh PyOM amendment (Gibson et al., 2016). Incorporation of fresh PyOM into soil would increase soil nutrient status and stimulate microbial activities as the release of dissolved organic matter from PyOM after addition (Cheng et al., 2006; Jenerette and Chatterjee, 2012). Thus, higher frequency of PyOM amendment might result in higher levels of available nutrients, such as base cations and micronutrients as compared to lower frequency at the same amount of total PyOM addition. Under lower frequency of PyOM addition regime, the amended PyOM would be oxidized in the first weeks and months coincided with altered properties (Zimmerman, 2010; Gul et al., 2015; Heitkötter and Marschner, 2015). The surface area of aged PyOM (with hypothetically higher hydrophilicity) was found to be ~2 times lower than that of fresh PyOM (Zhao et al., 2015) which might influence the nutrient adsorption efficiency of PyOM. In this context, the nutrient absorption by PyOM would be basically determined by two distinct properties of its hydrophilicity and surface area. Yet, less is known about the effects of different PyOM amendment frequencies (purportedly different aging degrees) on soil base cations, soil pHBC, and available micronutrients.

In April of 2013, a field manipulation of PyOM amendment was initiated to improve the soil properties in the lower Liaohe River Plain which serves as one of the main food production area in Northeast China. Located near an old industrial city of Shenyang, the agricultural ecosystem in this area is intensively managed to support large population density and high level of economic development. Previous studies suggested that this area suffered from relatively high N deposition as caused by fossil fuel consumption and heavy fertilization (Yu et al., 2011; Jiang et al., 2013). The soil in this area has degraded and featured by soil acidification and decrease in thickness of top soil layer (Ge et al., 2010). We hypothesized that 1) PyOM addition would increase soil base cations of exchangeable Ca and Mg and available micronutrients with stronger effect caused by higher frequency of PyOM amendment; 2) PyOM amendment would enhance soil pHBC as increase of soil pH, SOM, and base cations.

2. Materials and methods

2.1. Study area

The study was conducted at the National Field Research Station of Shenyang Agroecosystems, Chinese Academy of Sciences (CAS). The experimental site (41°31′N, 123°24′E, elevation 31 m a.s.l.) was located in the central part of Liaohe River Plain and embraced by typical heavy industry cities of Northeast China, about 35 km south of Shenyang and Fushun, and 40 km north of Liaoyang, Benxi and Anshan (Jiang et al., 2013). The mean annual temperature is 7.5 °C and mean annual precipitation is about 520 mm, which defines the area as warm-temperate continental monsoon climate. The frost-free period lasts 147–164 days. Soil texture of the experimental site is silty loam with 21.4% sand, 46.5% silt, and 32.1% clay at 0–20 cm depth (Liang et al., 2005). The soil is developed from alluvial deposits of the Liaohe River. The soil type is classified as an aquic brown soil according to the USDA classification and a Hapli-Udic Cambosols in Chinese Soil Taxonomy (CRGCST, 2001). Monoculture maize crop (*Zea mays* L.) is planted in the experimental plots.

2.2. Production of PyOM and experimental design

The PyOM was purchased from Liaoning Gold and Bliss Agricultural Company. Feedstock of PyOM was maize straw of cultivar Fuyou No. 9 which was commonly planted in Liaoning Province. Maize straw was pyrolized at constant 350 °C for 3 h under N_2 environment. The PyOM was ground to pass through 250 μm sieve prior to field application.

In April 2013, a complete randomized block design was applied to the site. Five treatments were established with different PyOM intensities and frequencies: 0 (CK), 22.5 Mg hm^{-2} (1% of 0–20 cm soil mass, applied once), 67.5 Mg hm^{-2} (3% of 0–20 cm soil mass, applied once), 112.5 Mg hm^{-2} (5% of 0–20 cm soil mass, applied once), and 67.5 Mg hm^{-2} (3% of 0–20 cm soil mass, applied yearly from 2013 to 2015 and 22.5 Mg hm^{-2} for each time). Each treatment was replicated three times and each experimental plot was 2.55 m^2. For maize plantation, the inter-row space is 60 cm and intra-row of 30 cm. The treatment of higher PyOM addition frequency was denoted as '+1%' as the PyOM (equivalent amount of 1% soil mass) was applied each year for three years. With equivalent amount, lower frequency of PyOM addition was the treatment of 3% soil mass of PyOM which was applied once in 2013. In the sampling year of 2015, the effect of PyOM addition frequency could be determined by comparing solely PyOM addition (3% of soil mass) and annual PyOM addition (1% of soil mass annually for 3 years) to CK treatment. The PyOM application rates of 1%, 3%, 5%, and +1% were approximately 5, 15, 25, and 15 folds of total PyOM mass produced from maize stalk of year 2013. For each plots, the surface soil of 0–20 cm was mixed evenly with PyOM; then the mixture were filled back to the respective plots. The chemical characteristics of 0–20 cm soil and PyOM were listed in Table 1.