Contrasting pH buffering patterns in neutral-alkaline soils along a 3600-km transect in northern China

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Short title: pH buffering in neutral-alkaline soils

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Abstract

Soil pH buffering capacity (pHBC) plays a crucial role in predicting acidification rates, yet its large-scale patterns and controls are poorly understood, especially for neutral-alkaline soils. Here, we evaluated the spatial patterns and drivers of pHBC along a 3600-km long transect (1900 km sub-transect with carbonate containing soils and 1700 km sub-transect with non-carbonate containing soils) across northern China. Soil pHBC was greater in the carbonate containing soils than in the non-carbonate containing soils. Acid addition decreased soil pH in the non-carbonate containing soils more markedly than in the carbonate containing soils. Within the carbonate soil sub-transect, soil pHBC was positively correlated with cation exchange capacity (CEC), carbonate content and exchangeable sodium (Na) concentration, but negatively correlated with initial pH and clay content, and not correlated with soil organic carbon (SOC) content. Within the non-carbonate sub-transect, soil pHBC was positively related to initial pH, clay content, CEC and exchangeable Na concentration, but not related to SOC content. Carbonate content was the primary determinant of pHBC in the carbonate containing soils and CEC was the main determinant of buffering capacity in the non-carbonate containing soils. Along the transect, soil pHBC was different in regions with different aridity index. Soil pHBC was positively related to aridity index and carbonate content across the carbonate containing soil sub-transect. Our results indicated that mechanisms controlling pHBC differ among neutral-alkaline soils of northern China, especially between carbonate and non-carbonate containing soils. This understanding should be incorporated into the acidification risk assessment and landscape management in a changing world.

Keywords

Acid deposition, Acidification rates, Carbonate-containing soils, Large-scale transect, Non-carbonate containing soils, Soil and climatic variables, Soil pH

1. Introduction

Chronic acid deposition can potentially alter biogeochemistry of ecosystems, acidify soils, reduce availability of some nutrients, aggravate aluminum and manganese toxicity, and hence regulate vegetation diversity and ecosystem structure and functions in terrestrial ecosystems (Bolan et al., 2003; de Vries et al., 2014; Hoegh-Guldberg, 2007; Vet et al., 2014). The primary components of acid deposition around the world are nitrogen oxides and sulfur dioxide, largely originating from agricultural fertilizer application and fossil-fuel combustion (Barak, 1997; Dentener et al., 2006; Lu et al., 2014; Pan et al., 2013). Emerging evidence indicates that soil acidity may play a crucial role in regulating vegetation community structure and functions. For instance, soil acidity was shown to explain most of the variations in herb species richness in calcareous grasslands in the United Kingdom (van den Berg et al., 2011). Thus, it is imperative to focus our attention on the direction and rate of soil acidification processes.

Soil pHBC and acid inputs can be considered as two determinants of the soil acidification processes. Whereas acid inputs are fairly well documented, the patterns of soil pHBC across landscapes are not (Yang et al., 2012; Wong et al., 2013). Soil pHBC regulates the effect of acid deposition on terrestrial ecosystems by influencing the extent of soil pH change (Magdoff and Bartlett, 1985; Lu et al., 2015; Nelson and Su, 2010). Hence, measurement or estimation of soil pHBC is clearly beneficial for predicting the rate of soil acidification in response to predicted rates of acid deposition (Vet et al., 2014; Wong et al., 2013; Lu et al., 2015).

Three main pH buffering mechanisms in soils have been proposed, namely, buffering by carbonates in soils with high pH (>7.5), by CEC in soils with intermediate pH (4.5-7.5) and by aluminum compounds in soils with low pH (<4.5) (Bowman et al., 2008; Lieb et al., 2011). Previous studies have revealed that soil pHBC is governed mostly by acidic functional groups, dissolution/precipitation of carbonates and cation exchange capacity (CEC), in soils with pH>4.5 (Aitken, 1992; Bloom 2000; Nelson and Su, 2010). Soil organic matter is a pH buffer, mostly due to weakly acidic functional groups such as carboxyl and phenol (Aitken, 1992; Bloom 2000). Soil carbonates and non-acidic exchangeable cations can also buffer pH; carbonates consume added H^+ and exchangeable non-acid cations exchange with H^+, removing it from solution. In addition, climate can also influence pHBC and the extent and direction of soil pH change (Tan, 2011). Under regions with higher temperature and lower precipitation, in which potential evapotranspiration greatly exceeds precipitation, carbonate tends to accumulate and thereby enhance soil pHBC in the surface soil layer (Tan, 2011), whereas in regions with higher precipitation, leaching processes prevent the accumulation of carbonate and change the soil acidification rates. However, the controls of soil pHBC in neutral-alkaline soils have not received as much attention as those in acidic soils (Yang et al., 2012; Wong et al., 2013). Geographical gradients can provide an exceptional opportunity to decipher the effects of global changing environments (i.e. soil variables, climatic variables, and human disturbance) on variations of soil pHBC, which is important for understanding the underlying patterns of nutrient fluxes and the biogeochemical mechanisms of the response of terrestrial ecosystems to environment changes.

The arid and semi-arid regions of northern China comprise one of the largest contiguous biomes with neutral-alkaline soils on the earth's surface (Dixon et al., 2014). In these regions, soil pH in the surface layer has declined significantly over the last two decades, with an overall decrease of 0.63 units (Yang et al., 2012).

Atmospheric nitrogen deposition (dry and wet) is expected to remain high over the next 50 years (Dentener et al., 2006; Liu et al., 2013; Yan et al., 2011; Zhao, 2009). High atmospheric sulfur deposition (dry and wet) is also predicted to continue in the short term in these regions, despite stricter regulation of sulfur dioxide emissions being implemented in recent years (Pan et al., 2013; Zhang et al., 2012; Zhao, 2009; Hijmans et al., 2005). Hence, soil acidification may continue for a long time in northern China (Guo et al., 2010; Lieb et al., 2011), posing a severe ecological threat to these ecosystems (Chen et al., 2013; Tian et al., 2015). For instance, soil scidification changed the belowground communities and soil properties, delined the plant diversity and productivity, and reduced the community stability (Chen et al., 2013). The soil scidification-induced by N addition resulted in the disruption of metal ion homeostasis in soils and hence the species loss (Tian et al., 2015). Nonetheless, there has been no comprehensive assessment of the extent, trends and mechanisms of soil pH decline in response to acid deposition across these ecosystems.

To address this knowledge gap, we established a 3600-km long terrestrial transect in China to evaluate how environment changes (i.e. variations in climatic and soil variables) will effect variations in soil pHBC of neutral-alkaline soils. We addressed the following questions: 1) to what extent does soil pHBC change along the transect? and 2) which soil and climatic variables control soil pHBC?

2. Materials and methods

2.1. *Study area and sampling*

The arid and semi-arid regions of northern China are extensive, have strong spatial climatic variability and are important for global ecological security. These regions are predominantly characterized by a dry, continental climate. Mean annual precipitation

(MAP) ranges from 34 to 436 mm, generally decreasing from east to west, and mean annual temperature (MAT) ranges from -3 to 10 °C, generally increasing from east to west. The most common soil types are chestnut soil, brown calcic soil and gray-brown desert soil (Chinese classification) (Gong, 1999), distributed in that order along a gradient from east to west. Some soils in these regions contain considerable carbonate but others do not; soil pH is significantly affected by carbonate content (Yang et al., 2012). The main vegetation types are meadow grasslands, typical grasslands and desert grasslands, distributed in that order from east to west. More details are given by Luo et al. (2013; 2015) and Wang et al. (2014).

In early August 2012, a soil survey of the region was conducted and a total of 55 sampling sites were selected along a 3600-km long transect (including a 1900-km section with carbonate containing soils and a 1700-km section with non-carbonate containing soils) extending from eastern Inner Mongolia to central-eastern Xinjiang in northern China (Figure S1). The sampling sites, which were spaced at approximately 50-100-km intervals, had minimal animal grazing and other anthropogenic disturbance, according to visual inspection of the vegetation. At each sampling site, two main plots (50-m × 50-m) were selected, 1000-m apart from each other, and five sub-plots (1-m × 1-m each) were established within each main plot (one in each corner and one in the center). A composite topsoil sample (0-10-cm) was prepared from cores taken from 10 locations in each sub-plot using a soil corer (2.5-cm diameter), after removing litter. Each soil sample was homogenized by hand mixing and was then stored in a cloth bag at room temperature for soil chemical analysis. More details are given by Luo et al. (2013; 2015) and Wang et al. (2014).

2.2. Measurements

Soil pHBC was measured by titration (Aitken and Moody, 1994). Air-dried soil was passed through 2.0-mm sieve in order to remove roots and gravel. For each titration, 2 g of air-dried soil (<2.0-mm) was weighed into each of seven polyethylene tubes, and each tube received 20 ml HNO_3 solution with a concentration of 0, 0.016, 0.032, 0.064, 0.080, 0.128 or 0.256 M. The suspensions were shaken at 25°C for 24 h, left still at 25°C for a further 6 days, re-suspended by shaking for 2 min, and then the pH was measured.

Soil pHBC was calculated from the titration data following the method described by Nelson and Su (2010). The sigmoid function

$$pH = pH_{min} + \frac{a}{1+e^{\frac{-A-A_{mid}}{b}}} \qquad \text{Equation 1}$$

where A is the amount of acid added (inserted as a negative value) and A_{mid}, a, b and pH_{min} are fitted constants, was fitted to the titration data by iteration using SigmaPlot®. In 34 cases equation 1 could not be solved because the iteration did not converge, due to the titration data covering only a small portion of the sigmoid relationship. In those cases a simpler exponential decay function was fitted to the data instead (with A as a positive value):

$$pH = pH_{min} + ae^{-bA} \qquad \text{Equation 2}$$

Buffer curves for carbonate and non-carbonate containing soil samples were obtained in this way, and six of them are presented in Figure S2.Similar relationships were observed between the amount of acid added and soil pH for the other soil samples (data not shown). The functions described fitted the curves well for all soil samples (adjusted R^2>0.88), allowing pHBC (the inverse of the slope of the curve) to be calculated for all samples.

To calculate pHBC for soils fitted with the sigmoid function, equation 1 was rearranged to obtain A as a function of pH, and then differentiated to obtain

$$pHBC = \frac{ab}{(a+pH_{min}-pH)(pH-pH_{min})} \qquad \text{Equation 3}$$

To calculate pHBC for soils fitted with the exponential function, equation 2 was rearranged and differentiated to obtain

$$pHBC = \frac{1}{b(pH-pH_{min})} \qquad \text{Equation 4}$$

As soil pHBC changes with pH, an appropriate value had to be chosen to examine the relationships between pHBC and possible explanatory variables. Following Nelson and Su (2010), we used pHBC_{mid} as the dependent parameter in the statistical analyses. The pHBC_{mid} is the pHBC at the inflection point of the titration curve (i.e. A_{mid}). However, the inflection point could not be estimated where an exponential function was used. In those cases, we used the value of pHBC at the initial pH of the soils, which is a reasonable approximation of the value pHBC_{mid} would have if the buffer curve had been extended to higher values of pH using additions of alkali. We also calculated the value of pHBC at a particular pH obtained in all titrations, that is pH=7.5 for the carbonate containing soils, and pH=6 and 5 for the non-carbonate containing soils.

To simulate the effects of acid deposition on pH dynamics, the effects of the 0.016 M HNO_3 treatment (comparable to the average cumulative amount of acid deposited over 10 years) on the soils were examined. Soil inorganic carbon (SIC) content was determined by measuring the volume of CO_2 released from 10 g of air-dried soil (<2.0-mm) following addition of 8 ml HCl (2 M) at room temperature. The pressure of CO_2 changes with variation in the atmospheric pressure, hence, to avoid such measurement error we made a standard curve graph using standard matter calcium (Ca) carbonate before soil SIC measurement. The content of SIC was taken as carbonate content. Soil clay content (<2.0-µm) was measured using the pipette method, after dispersing the soils with an ultrasonic probe (Roscoe, 2000). Exchangeable sodium (Na),potassium(K), calcium and magnesium (Mg) concentrations were determined by extracting air-dried soil (2.5 g, <2.0-mm) with 50 ml NH_4OAc (1 M, pH=7.0), and measuring concentrations in the extracts using atomic absorption spectrophotometer (AA6800, Japan). Cation exchange capacity (CEC) was calculated as the sum of charge equivalents of exchangeable K, Na, Ca and Mg (Aprile and Lorandi, 2012). The ratio of CEC to clay content (CCR) was calculated to obtain an index of clay mineralogy (Shaw et al. 1998).

Soil organic carbon (SOC) content was measured using an elemental analyzer (2400II CHN elemental analyzer, Perkin-Elmer, USA) with a combustion temperature of 950°C and a reduction temperature of 640°C, at the Stable Isotope Facility of the University of California, Davis, after removing carbonate using 0.5 M HCl according to the approach of Harris et al. (2001).

Relationships between climate and soil pHBC were analyzed using the indices MAP, MAT and aridity index (AI). We used ArcGIS® software v. 9.2 (ESRI, Redlands, CA, 2006) to extract the MAP, MAT and potential evaporation (PET) from a global climate dataset (http://www.worldclim.org/; resolution of ~1 km at the equator), which was based on interpolated values of climatic data (1950-2000) provided by weather stations throughout the territory and adjusted to the topography (Hijmans et al., 2005). Then, AI was calculated as the inverse of the ratio of MAP to PET according to methods in Delgado-Baquerizo et al. (2013).

2.3. Statistical analysis

The non-carbonate containing soils were defined as those from which we were unable to detect the CO_2 release (lower than the detection limit), and other soil samples were defined as carbonate containing soils. Before numerical and statistical analysis, all variables were averaged at the site level. An independent sample t-test was used to test for differences between the carbonate and non-carbonate containing parts of the transect. Ordinary least squares linear regression was used to determine the relationships between soil pHBC and other soil variables (SIC, SOC, CEC, clay, pH, exchangeable Na) and climatic variables (AI, MAP and MAT) in the carbonate soil and non-carbonate soil subsets, separately. In order to further illuminate the impacts of climate on the patterns of soil pHBC, we divided the transect into an arid part (AI>0.8) and a semi-arid part (AI<0.8), according to the criterion of Arora (2002).

Thereafter, stepwise multiple regressions were applied to identify the most influential variables among the soil and climatic variables. In these analyses, a *P*-value of 0.05 was used to determine whether each variable should be added to or removed from the model.

Soil $pHBC_{mid}$ (or its estimate for the buffer curves that did not fit a sigmoid function) was significantly correlated with the values of pHBC at pH=7.5 (carbonate containing soils) or at pH=6 and 5 (non-carbonate containing soils) (Figure S3). Therefore, we show only the results for $pHBC_{mid}$, which we refer to hereafter simply as pHBC. All statistical analyses were conducted using the statistical package SPSS 17.0 (SPSS Inc., Chicago, IL, USA, 2004).

3. Results

The magnitude of soil pHBC varied widely, ranging from 27.2 to 188.5 mmol H^+ kg^{-1}

pH unit^{-1} for the carbonate containing soils and from 10.4 to 58.4 mmol H$^+$ kg^{-1} pH unit^{-1} for the non-carbonate containing soils (Table 1). Mean pHBC was much greater in the carbonate containing soils (87.7 mmol H$^+$ kg^{-1} pH unit^{-1}) than in the non-carbonate containing soils (25.7 mmol H$^+$ kg^{-1} pH unit^{-1}) (Table 1). When 0.016 M HNO_3 (comparable to the average cumulative amount of acid deposited over 10 years) was added to the soils, the average decrease in pH was 0.21 units for the carbonate containing soils and 0.44 units for the non-carbonate containing soils (Figure 1).

Soil pHBC was significantly correlated with carbonate content in the carbonate containing soils, accounting for 48% of the variation (Table 2, Figure 2). Soil pHBC of both carbonate and non-carbonate containing soils was positively correlated with CEC (P<0.01 for both) and exchangeable Na concentration (P<0.01 for both) but was not related to SOC content (P>0.05) (Table 2, Figure 2). Soil pHBC was negatively correlated with clay content and initial pH in the carbonate containing soils (P<0.05 for both) but was positively correlated with those two parameters in the non-carbonate containing soils (P<0.05 for both) (Table 2, Figure 2).

Soil pHBC was significantly related to AI in the carbonate containing soils (P<0.01) but not in the non-carbonate containing soils (P>0.05) (Table 2, Figure 3). The pHBC of soils in the arid regions (AI>0.8) was higher than that of soils in the semi-arid regions (AI<0.8) along the whole transect (Figure 3).

When all soil variables were entered into a stepwise multiple linear regression, with soil pHBC as the dependent variable, carbonate content was the only significant explanatory variable for the carbonate containing soils and CEC was the only significant explanatory variable for the non-carbonate containing soils. None of the other soil or climatic variables provided significant extra explanatory power (i.e. those variables were removed from multiple stepwise regression using a cutoff value of $P=0.05$) (Table 2).

The carbonate containing soils and the non-carbonate containing soils had similar clay contents but the former had higher pH than the latter (Table 1). In the non-carbonate containing soils, CEC was closely related to clay content ($R^2=0.83$, $P<0.001$) (Figure S4), with a narrow range of CCR (0.18-0.46 cmol (+) kg^{-1} clay) (Table 1). In the carbonate containing soils, CEC was unrelated to clay content; CCR covered a much wider range and was inversely related to clay content, ranging from 0.26 cmol (+) kg^{-1} clay at the highest clay content (21.1%) to 5.26 cmol (+) kg^{-1} clay at the lowest clay content (1.4%) (Table1, Figure S4). The initial pH of soils was negatively correlated with carbonate content in the carbonate containing soils, accounting for 16% of the variation ($P<0.05$) (Figure S6). The soil pH significantly increased with increasing aridity along the transect (Figure S7)

4. Discussion

4.1. Soil pHBC and potential consequences of soil acidification

Our results demonstrated substantially greater pHBC in the carbonate containing soils than in the non-carbonate containing soils (Table 1). Stepwise regression of the relationships between soil pHBC and other variables identified carbonate and CEC (both positive influence) as the most significant explanatory variables for pHBC, in the carbonate and non-carbonate containing soils, respectively (Table 2). These results may be attributed to the differences in their acid buffering systems (Bowman et al., 2008;Van Breemen, 1983). In the carbonate containing soils, the primary buffering process is acid neutralization, i.e. $CO_3^{2-}+2H^+ \leftrightarrow HCO_3^-+H^+$ and $HCO_3^-+H^+ \leftrightarrow H_2O+CO_2\uparrow$. If sufficient carbonate is present, the added acid may be consumed with little or no decrease in pH (Van Breemen, 1983). In contrast, cation exchange reactions were the primary buffering process in non-carbonate containing soils. In this process, non-acidic cations such as Ca^{2+}, Mg^{2+}, K^+ and Na^+ held on soil surfaces exchange with added H^+, limiting the change in soil pH (Bowman et al., 2008;Van Breemen, 1983).

Our acid-addition experiment found that soil pH declined in the carbonate containing and non-carbonate containing soils but the magnitude of pH change was smaller in the former group (0.21 vs. 0.44 units) (Figure 1). In the carbonate containing soils, acid addition will have little effect on soil pH until all the carbonate has been dissolved. However, net addition of acid always reduces the acid neutralizing capacity of soil. In line with our results, soil pH in Russian forest soils derived from carbonate parent has significantly declined from 1893 to 2004 (Lapenis et al., 2004).

In the carbonate containing soils, sustained long-term acid deposition releases a large amount of carbon dioxide into the atmosphere, altering the carbon balance of these globally important drylands (Yang et al., 2012). On the other hand, lowering the pH of carbonate containing soils would, to some degree, improve their quality and thus increase the vegetation cover and biological productivity (Lieb et al., 2011; Yang et al., 2012). In the non-carbonate containing soils, an increase in soil acidity may reduce availability of some nutrient cations, such as Ca and Mg, and enhance availability of some toxic cations, such as aluminum (Al) and manganese (Mn), which might limit plant growth and increase susceptibility to low temperature, drought and herbivory stress in these ecosystems (Blake et al., 1999; Lieb et al., 2011; Chen et al., 2013).

Although this is the most comprehensive assessment of soil pHBC in northern China, uncertainties about future acidification rates still exist. Firstly, the amount of acid deposition is known to vary across northern China (Zhao et al., 2009), but the pattern of deposition at the scale of our measurements is unknown. Secondly, our study did not assess the biological activity, nutrient uptake by plants, and leaching or accumulation of solutes that occur in the field and influence soil pH and response to acid addition (Aitken and Moody, 1994). Nevertheless, the knowledge about pHBC acquired in this study is fundamental for predicting acidification rates in soils of the region (Aitken and Moody, 1994).

4.2. Effects of soil properties on soil pHBC

Linear regression showed that the soil pHBC was positively correlated with CEC for both carbonate containing and non-carbonate containing soils (Table 2, Figure 2). This is consistent with the findings of Aitken (1992) demonstrating that CEC accounted for up to 76% of the variations in pHBC of acidic soils in eastern Queensland, Australia. Likewise, Xu et al. (2012) also showed a strong positive relationship between soil pHBC and CEC across 18 acidic soils from tropical to sub-tropical regions in China (R^2=0.71, P<0.001).

Linear regression did not demonstrate a clear relationship between soil pHBC and SOC content in either carbonate or non-carbonate containing soils (Table 2, Figure 2).

These results were inconsistent with previous studies, which have shown that SOC content played an important role in soil pHBC (Aitken, 1992; Magdoff and Bartlett, 1985; Nelson and Su, 2010; Geissen et al., 2013). The discrepancy is probably caused by different types of organic matter involved (Nelson and Su, 2010). In the carbonate containing soils, the low SOC content and the small range of SOC content (due to aridity and low net primary production) can help explain the lack of significant relationship between pHBC and SOC content (Nelson and Su, 2010; Geissen et al., 2013). Moreover, those soils had a wide range of clay mineralogy, and the effect of this variability on CEC and hence pHBC may have masked any effect of SOC. However, in the non-carbonate containing soils, the lack of relationship between SOC content and pHBC is more difficult to understand. It is possible that the organic matter in those soils (with high SOC content) may have been mostly material with low charge.

Over recent decades it has become clear that soil particle size distribution, particularly clay content, plays a crucial role in determining soil pHBC (Aitken et al. 1990; Weaver et al. 2004). For instance, Aitken et al. (1990) demonstrated that soil pHBC is primarily determined by clay content; it explained approximately 32% of the variance in the pHBC of acidic topsoils in Australia. In our study we found that pHBC was positively correlated with clay content for the non-carbonate containing soils but that the relationship was negative for the carbonate containing soils (Table 1, Figure 2). The difference between the behavior of the two soil subsets was apparently due to differences in their clay mineralogy. The close relationship between CEC and clay content of the non-carbonate containing soils meant that both parameters were similarly related to pHBC (Figure S4). The CCR values of those soils indicated that clay mineralogy was dominated by kaolin and illite (Shaw et al. 1998). On the other hand, in the carbonate containing soils there was a negative relationship between CCR and clay content, and a negative relationship between pHBC and clay content (Figure S4). The soils with higher clay content had lower CCR values, reflecting clay mineralogy dominated by kaolin, whereas the soils with lower clay content had higher CCR values, indicating dominantly smectitic clay mineralogy (Shaw et al. 1998). Kaolin is a 1:1 clay mineral with low CEC whereas smectite is an expanding 2:1 clay mineral with high CEC. Previous work has shown higher soil pHBC in the presence of clay minerals having high surface area and CEC, such as chlorite and smectite (Aitken and Moody, 1994). Similarly, Xu et al.(2012) oberserved that soils rich in smectite usually have a large capacity to absorb H^+ and contribute to higher soil pHBC than soils rich in kaolinite. Thus clay content is not a good predictor of pHBC across the neutral-alkaline soils in northern China. It is a reasonable predictor of pHBC only if it is closely related to CEC, i.e. where clay mineralogy is fairly uniform.

Soil pH was an important explanatory variable for soil pHBC, according to theoretical predictions and previous observations (Nelson and Su, 2010). During the laboratory acidification process the pHBC of each soil tended to increase with decreasing soil pH (Figure S5). Initial soil pH also influenced pHBC. In the non-carbonate containing subset there was a positive relationship between pHBC and initial pH (Table 2, Figure 2). The carbonate containing soils had high pH and high pHBC, presumably due to the carbonate and high saturation with non-acidic exchangeable cations. However, for the carbonate containing soils, the relationship between initial soil pH and pHBC was negative (Table 2, Figure 2). This negative relationship appeared to be directly associated with the negative relationship between carbonate content and initial pH in the carbonate containing soil subset (Figure S6). In carbonate containing soils, pH is largely determined by the carbonate equilibrium, which is influenced by the suite of exchangeable and dissolved cations and anions present (Bloom, 2000). In our study, there was a significantly positive relationship between soil pHBC and soil exchangeable Na concentration among the carbonate containing soils (Table 2, Figure 2). Therefore, in soils containing significant amounts of carbonate, exchangeable Na content appears to have more of an influence on pHBC than carbonate content.

4.3. Effects of climatic variables on soil pHBC

Linear regression showed that soil pHBC increased with increasing aridity; the buffer strength of soils in the arid region (AI>0.8), which were the carbonate containing soils, was significantly greater than that of soils in the semi-arid region (AI<0.8) (Figure 3). Under arid conditions, in which potential evapotranspiration greatly exceeds precipitation, carbonate tends to accumulate in the topsoil (Cross and Schlesinger, 2001; Wang et al., 2012). In less arid regions, leaching processes prevent the accumulation of carbonate. Thus, soil carbonate content decreased to zero with increasing precipitation from west to east along the climatic gradient. In the east, where the soils do not contain carbonate, soil CEC was the most significant explanatory variable for soil pHBC. Climate can also affect soil pHBC through its effect on biological processes, and water availability is the most limiting factor for plant growth in our study area (Luo et al., 2013; 2015). Primary productivity and nitrogen fixation greatly increase with increasing precipitation, and this change in biological activity influences soil properties, including pHBC (Magdoff and Bartlett, 1985; Delgado-Baquerizo et al., 2013). Overall, climatic regimes can exert large effects on soil pHBC because of their direct and biologically mediated influence on soil variables such as carbonate content and CEC.

Atmospheric wet nitrogen and sulfur depositions in rainfall and snowfall play a crucial role in soil acidification (Dentener et al., 2006), and the amounts deposited will be greater in semi-arid regions than arid regions because of the greater precipitation. Precipitation has important effects on acid addition not just because of the solutes deposited, but also because of the leaching of water through the profile. In areas with sufficient precipitation to leach the topsoil, the main alkali material in soil (carbonate) is removed downwards (Jenny, 1941). In addition, once pH reaches 6 or less, the leaching of non-acidic cations becomes important, because it leads to an accumulation of the less mobile and acidic Al^{3+} as an exchangeable cation(Jenny, 1941). Finally, in wetter soils weathering occurs more rapidly, which tends to result in a lowering of CEC. Therefore, lower soil pHBC in soils of semi-arid regions compared to arid regions, in combination with greater acid inputs, indicates that semi-arid regions would be much more sensitive to global changes such as elevated nitrogen deposition and altered precipitation regimes.

5. Conclusions

We found that soil pHBC was primarily associated with carbonate, being higher in the carbonate containing soils than non-carbonate containing soils. In the carbonate containing soils pHBC was primarily related to carbonate content and in the non-carbonate containing soils it was primarily related to CEC. There was little or no relationship between pHBC and SOC content in either carbonate or non-carbonate containing soils. Effects of clay content and initial pH on soil pHBC differed between the two soil groups. Lower soil pHBC and higher acid inputs in the semi-arid regions (AI<0.8) than in the arid regions (AI>0.8) make soils much more sensitive to future acid deposition in the former than in the latter. Overall, this study generally document the spatial patterns of soil pHBC and their controlling factors in neutral-alkaline soils at landscape scales. Our findings are the beginning of a data compilation and analysis exercise that will focus on soil pHBC as an effective parameter to assess acidification risks, acidification rates, and potential management interventions. Models for realistically predicting acidification risks and rates and in this environment should incorporate the different mechanisms controlling pHBC in carbonate and non-carbonate-containing soils.

Acknowledgements

We thank all members of the Field Expedition Team from the Institute of Applied Ecology, Chinese Academy of Sciences for field assistance. The algebraic help provided by Carolyn R. Scherzer Diedricks is gratefully acknowledged. This work was financially supported by the National Science Foundation of China (41371251) and by the National Basic Research Program of China (2011CB403204).

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Table 1 Physicochemical properties of the carbonate containing soils and the non-carbonate containing soils along the transect across northern China.

	pH	SIC ($g\ kg^{-1}$)	SOC ($g\ kg^{-1}$)	CEC ($cmol(+)\ kg^{-1}$)	Clay (%)	pHBC ($mmol\ H^{+}\ kg^{-1}\ pH\ unit^{-1}$)	CCR ($cmol(+)\ kg^{-1}$ clay)
Carbonate soils							
Range	7.7-9.2	1.4-12.7	0.5-4.0	2.8-17.6	1.4-21.1	27.2-188.5	0.3-5.3
Mean	8.3	5.8	1.5	7.9	8.3	87.7	1.3
Non-carbonate soils							
Range	6.4-8.4		2.1-44.6	1.5-6.1	3.8-33.7	10.4-58.4	0.2-0.5
Mean	7.4		14.7	3.1	11.0	25.7	0.3

Soil pH was measured in a 1:2.5 soil:water mixture. SIC, soil inorganic carbon; SOC, soil organic carbon; CEC, cation exchange capacity; pHBC, pH buffering capacity; CCR, ratio of CEC to clay content

Table 2 Summary of regression models (linear and stepwise) for the effects of soil, climatic and all environmental variables on soil pH buffering capacity in the carbonate containing soils and the non-carbonate containing soils.

	Equation	R^2	P	Equation	R^2	P
	Carbonate soils			Non-carbonate soils		
Soil variable						
Linear regression						
SIC	$y=29.477+9.988x$	0.482	<0.001			
SOC	$y=104.46-11.53x$	0.073	0.183	$y=24.243+0.1x$	0.01	0.603
CEC	$y=44.322+5.52x$	0.290	0.005	$y=8.924+5.46x$	0.281	0.003
pH	$y=475.26-46.845x$	0.154	0.047	$y=-27.624+7.243x$	0.146	0.041
Clay	$y=133.755-5.56x$	0.319	0.003	$y=16.09+0.873x$	0.208	0.013
Stepwise regression						
	SIC	0.482	<0.001	CEC	0.281	0.003
Climatic variable						
Linear regression						
AI	$y=-277.923+400.266x$	0.269	0.007	$y=15.613+15.651x$	0.027	0.393
MAP	$y=129.363-0.486x$	0.272	0.006	$y=32.96-0.026x$	0.032	0.351
MAT	$y=11.931+10.625x$	0.222	0.015	$y=24.361+1.453x$	0.073	0.155
Stepwise regression						
	MAP	0.272	0.006	Non-convergence		
Environmental variable						
Stepwise regression						
	SIC	0.482	<0.001	CEC	0.281	0.003

SIC, soil inorganic carbon; SOC, soil organic carbon; CEC, cation exchange capacity; AI, aridity index; MAP, mean annual precipitation; MAT, mean annual temperature

Figure Legends

Figure 1 Effects of acid addition (16 mmol H^+ kg^{-1} soil added) on soil pH in the carbonate containing soils (squares) and the non-carbonate containing soils (circles) collected from the 3600 km-long transect. Mean changes in pH values for both carbonate-containing and non-carbonate containing soils are shown in the inset. The solid line and dashed line represent the mean pH values of controls and acid-treated soils, respectively. The mean pH values are represented by a solid line (controls) and a dashed line (acid-added soils) across the transect.

Figure 2 Relationships between soil pH buffering capacity (pHBC) and soil variables (cation exchange capacity (CEC), soil organic carbon (SOC), soil clay content, soil pH, soil inorganic carbon (SIC), and soil exchangeable sodium (Na)) in the carbonate containing soils and non-carbonate containing soils. All the regression results are referred to Table 2.

Figure 3 Relationships between soil pH buffering capacity (pHBC) and aridity index in the carbonate containing soils (solid circles) and the non-carbonate containing soils (empty circles). Dashed line represents the boundary between the arid regions (aridity index>0.8) and the semi-arid regions (aridity index<0.8). All the regression results are referred to Table 2.

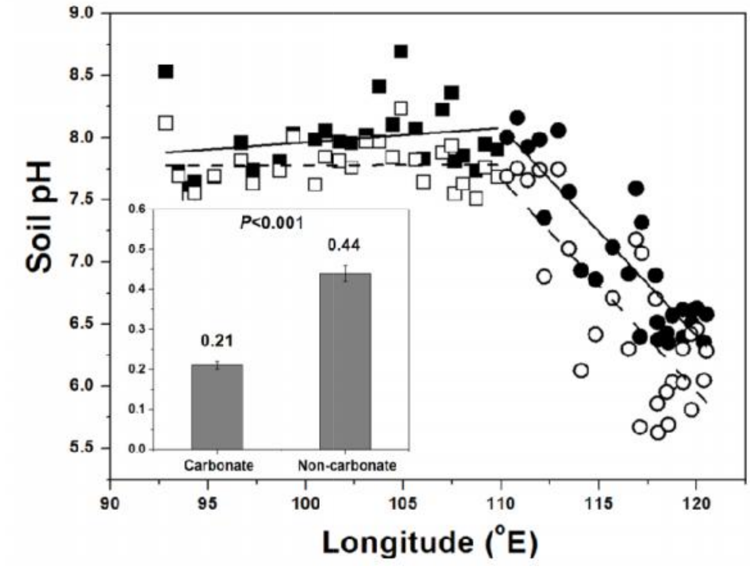
Soil pH
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
90
95
100
105
110
115
120
Longitude (°E)
P<0.001
0.44
0.21
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Carbonate
Non-carbonate

Figure 1

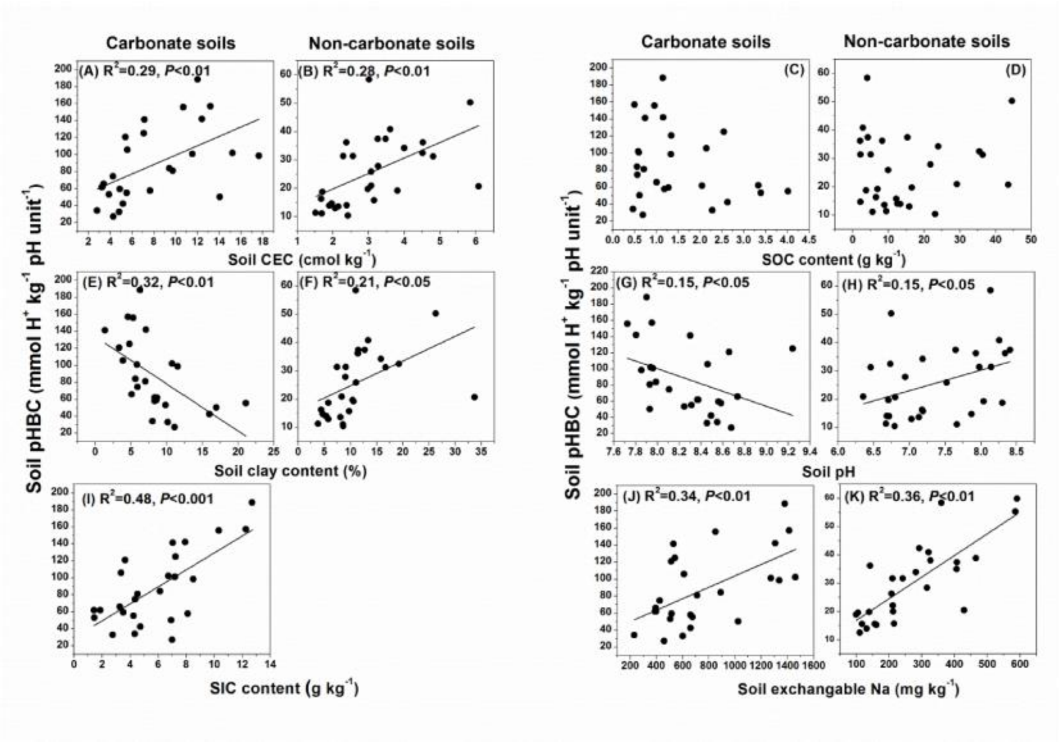
Carbonate soils
Non-carbonate soils
Carbonate soils
Non-carbonate soils
(A) R²=0.29, P<0.01
(B) R²=0.28, P<0.01
(C)
(D)
Soil CEC (cmol kg⁻¹)
SOC content (g kg⁻¹)
(E) R²=0.32, P<0.01
(F) R²=0.21, P<0.05
(G) R²=0.15, P<0.05
(H) R²=0.15, P<0.05
Soil clay content (%)
Soil pH
(I) R²=0.48, P<0.001
(J) R²=0.34, P<0.01
(K) R²=0.36, P<0.01
SIC content (g kg⁻¹)
Soil exchangable Na (mg kg⁻¹)
Soil pHBC (mmol H⁺ kg⁻¹ pH unit⁻¹)
Soil pHBC (mmol H⁺ kg⁻¹ pH unit⁻¹)

Figure 2

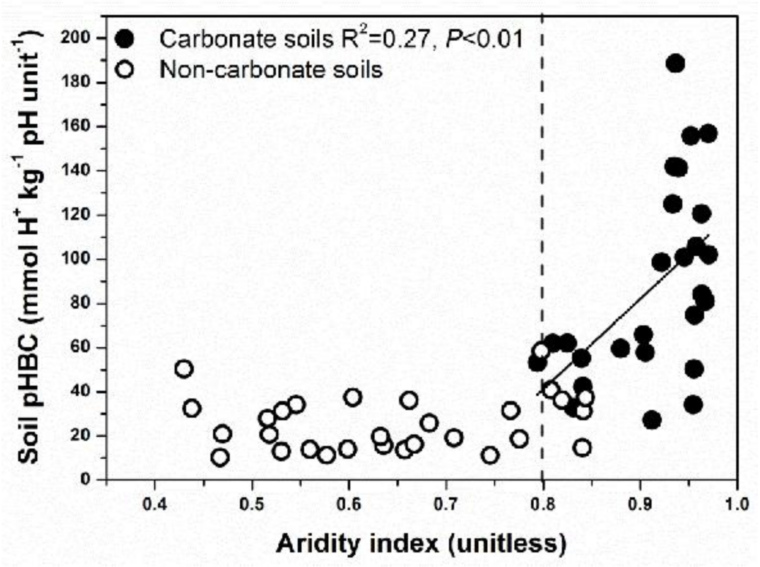
Carbonate soils R^2=0.27, P<0.01
Non-carbonate soils
Soil pHBC (mmol H^+ kg^{-1} pH $unit^{-1}$)
Aridity index (unitless)
0
20
40
60
80
100
120
140
160
180
200
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Figure 3