

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

3 Wentao Luo¹, Paul N. Nelson², Mai-He Li^{1,3}, Jiangping Cai^{1,4}, Yongyong Zhang^{1,4},
4 Yuge Zhang⁵, Yang Shan¹, Ruzhen Wang¹, Zhengwen Wang¹, Yunna Wu⁶, Xinguo
5 Han¹, Yong Jiang^{1*}

6 ¹State Key Laboratory of Forest and Soil Ecology, Institute of Applied Ecology,
7 Chinese Academy of Sciences, Shenyang 110164, China

8 ²College of Science, Technology and Engineering, James Cook University, Cairns,
9 Qld 4870, Australia.

10 ³Swiss Federal Research Institute WSL, Zuercherstrasse 111, CH-8903 Birmensdorf,
11 Switzerland;

12 ⁴University of Chinese Academy of Sciences, Beijing 100049, China;

13 ⁵College of Environment Science, Shenyang University, Shenyang 110044, China

14 ⁶College of Environmental and Resource Sciences, Dalian Nationalities University,
15 Dalian, China

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17 *Corresponding author at: Institute of Applied Ecology, Chinese Academy of Sciences,
18 Shenyang 110016, China. Tel.: +86 24 83970902; fax: +86 24 83970300. E-mail
19 address: jiangyong@iae.ac.cn (Y. Jiang).

20 **Abstract**

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

43 **Keywords**

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

46 **1. Introduction**

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

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

68 Three main pH buffering mechanisms in soils have been proposed, namely,
69 buffering by carbonates in soils with high pH (>7.5), by CEC in soils with

70 intermediate pH (4.5-7.5) and by aluminum compounds in soils with low pH (<4.5)
71 (Bowman et al., 2008; Lieb et al., 2011). Previous studies have revealed that soil
72 pHBC is governed mostly by acidic functional groups, dissolution/precipitation of
73 carbonates and cation exchange capacity (CEC), in soils with pH>4.5 (Aitken, 1992;
74 Bloom 2000; Nelson and Su, 2010). Soil organic matter is a pH buffer, mostly due to
75 weakly acidic functional groups such as carboxyl and phenol (Aitken, 1992; Bloom
76 2000). Soil carbonates and non-acidic exchangeable cations can also buffer pH;
77 carbonates consume added H⁺ and exchangeable non-acid cations exchange with H⁺,
78 removing it from solution. In addition, climate can also influence pHBC and the
79 extent and direction of soil pH change (Tan, 2011). Under regions with higher
80 temperature and lower precipitation, in which potential evapotranspiration greatly
81 exceeds precipitation, carbonate tends to accumulate and thereby enhance soil pHBC
82 in the surface soil layer (Tan, 2011), whereas in regions with higher precipitation,
83 leaching processes prevent the accumulation of carbonate and change the soil
84 acidification rates. However, the controls of soil pHBC in neutral-alkaline soils have
85 not received as much attention as those in acidic soils (Yang et al., 2012; Wong et al.,
86 2013). Geographical gradients can provide an exceptional opportunity to decipher the
87 effects of global changing environments (i.e. soil variables, climatic variables, and
88 human disturbance) on variations of soil pHBC, which is important for understanding
89 the underlying patterns of nutrient fluxes and the biogeochemical mechanisms of the
90 response of terrestrial ecosystems to environment changes.

91 The arid and semi-arid regions of northern China comprise one of the largest
92 contiguous biomes with neutral-alkaline soils on the earth's surface (Dixon et al.,
93 2014). In these regions, soil pH in the surface layer has declined significantly over the
94 last two decades, with an overall decrease of 0.63 units (Yang et al., 2012).

95 Atmospheric nitrogen deposition (dry and wet) is expected to remain high over the
96 next 50 years (Dentener et al., 2006; Liu et al., 2013; Yan et al., 2011; Zhao, 2009).
97 High atmospheric sulfur deposition (dry and wet) is also predicted to continue in the
98 short term in these regions, despite stricter regulation of sulfur dioxide emissions
99 being implemented in recent years (Pan et al., 2013; Zhang et al., 2012; Zhao, 2009;
100 Hijmans et al., 2005). Hence, soil acidification may continue for a long time in
101 northern China (Guo et al., 2010; Lieb et al., 2011), posing a severe ecological threat
102 to these ecosystems (Chen et al., 2013; Tian et al., 2015). For instance, soil
103 acidification changed the belowground communities and soil properties, delined the
104 plant diversity and productivity, and reduced the community stability (Chen et al.,
105 2013). The soil acidification-induced by N addition resulted in the disruption of metal
106 ion homeostasis in soils and hence the species loss (Tian et al., 2015). Nonetheless,
107 there has been no comprehensive assessment of the extent, trends and mechanisms of
108 soil pH decline in response to acid deposition across these ecosystems.

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

114 **2. Materials and methods**

115 *2.1. Study area and sampling*

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

119 (MAP) ranges from 34 to 436 mm, generally decreasing from east to west, and mean
120 annual temperature (MAT) ranges from -3 to 10 °C, generally increasing from east to
121 west. The most common soil types are chestnut soil, brown calcic soil and gray-brown
122 desert soil (Chinese classification) (Gong, 1999), distributed in that order along a
123 gradient from east to west. Some soils in these regions contain considerable carbonate
124 but others do not; soil pH is significantly affected by carbonate content (Yang et al.,
125 2012). The main vegetation types are meadow grasslands, typical grasslands and
126 desert grasslands, distributed in that order from east to west. More details are given by
127 Luo et al. (2013; 2015) and Wang et al. (2014).

128 In early August 2012, a soil survey of the region was conducted and a total of 55
129 sampling sites were selected along a 3600-km long transect (including a 1900-km
130 section with carbonate containing soils and a 1700-km section with non-carbonate
131 containing soils) extending from eastern Inner Mongolia to central-eastern Xinjiang in
132 northern China (Figure S1). From west to east, there is a gradient of increasing MAP
133 and decreasing MAT (Figure S2). The sampling sites, which were spaced at
134 approximately 50-100-km intervals, had minimal animal grazing and other
135 anthropogenic disturbance, according to visual inspection of the vegetation. At each
136 sampling site, two main plots (50-m × 50-m) were selected, 1000-m apart from each
137 other, and five sub-plots (1-m × 1-m each) were established within each main plot (one
138 in each corner and one in the center). A composite topsoil sample (0-10-cm) was
139 prepared from cores taken from 10 locations in each sub-plot using a soil corer (2.5-cm
140 diameter), after removing litter. Each soil sample was homogenized by hand mixing
141 and was then stored in a cloth bag at room temperature for soil chemical analysis.
142 More details are given by Luo et al. (2013; 2015) and Wang et al. (2014).

143 *2.2. Measurements*

144 Soil pHBC was measured by titration using HNO₃ because the nitrate anion is widely
145 thought to interact with soil materials to a lesser extent than other acid anions
146 (Aitken and Moody, 1994). Air-dried soil was passed through 2.0-mm sieve in order
147 to remove roots and gravel. For each titration, 2 g of air-dried soil (<2.0-mm) was
148 weighed into each of seven polyethylene tubes, and each tube received 20 ml HNO₃
149 solution with a concentration of 0, 0.016, 0.032, 0.064, 0.080, 0.128 or 0.256 M. The
150 suspensions were shaken at 25°C for 24 h, left still at 25°C for a further 6 days,
151 re-suspended by shaking for 2 min, and then the pH was measured by a pH meter
152 (S210 SevenCompact™, Mettler, Germany).

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

$$155 \quad pH = pH_{min} + \frac{a}{1 + e^{\frac{-A - A_{mid}}{b}}} \quad \text{Equation 1}$$

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

$$162 \quad pH = pH_{min} + ae^{-bA} \quad \text{Equation 2}$$

163 Buffer curves for carbonate and non-carbonate containing soil samples were
164 obtained in this way, and six of them are presented in Figure S3. Similar relationships
165 were observed between the amount of acid added and soil pH for the other soil
166 samples (data not shown). The functions described fitted the curves well for all soil

167 samples (adjusted $R^2 > 0.88$), allowing pHBC (the inverse of the slope of the curve) to
168 be calculated for all samples.

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

$$171 \quad pHBC = \frac{ab}{(a+pH_{min}-pH)(pH-pH_{min})} \quad \text{Equation 3}$$

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

$$174 \quad pHBC = \frac{1}{b(pH-pH_{min})} \quad \text{Equation 4}$$

175 As soil pHBC changes with pH, an appropriate value had to be chosen to examine
176 the relationships between pHBC and possible explanatory variables. Following
177 Nelson and Su (2010), we used $pHBC_{mid}$ as the dependent parameter in the statistical
178 analyses. The $pHBC_{mid}$ is the pHBC at the inflection point of the titration curve (i.e.
179 A_{mid}). However, the inflection point could not be estimated where an exponential
180 function was used. In those cases, we used the value of pHBC at the initial pH of the
181 soils, which is a reasonable approximation of the value $pHBC_{mid}$ would have if the
182 buffer curve had been extended to higher values of pH using additions of alkali. We
183 also calculated the value of pHBC at a particular pH obtained in all titrations, that is
184 $pH=7.5$ for the carbonate containing soils, and $pH=6$ and 5 for the non-carbonate
185 containing soils.

186 To simulate the effects of acid deposition on pH dynamics, the effects of the 0.016 M
187 HNO_3 treatment (comparable to the average cumulative amount of acid deposited over
188 10 years) on the soils were examined. Soil inorganic carbon (SIC) content was

189 measured by gasometric method (Page, 1982). Briefly, 10 g air-dried soils (<1-mm)
190 were mixed with 8 ml HCl (2 M) in a 50-ml sealed flask at room temperature. Then
191 the CO₂ pressure was recorded by barometers and was converted into soil carbonate
192 content based on the standard curve. The content of SIC was used to represent the
193 carbonate content in our study. Soil clay content (<2.0-μm) was measured using the
194 pipette method, after dispersing the soils with an ultrasonic probe (Roscoe, 2000).
195 Exchangeable sodium (Na), potassium(K), calcium and magnesium (Mg)
196 concentrations were determined by extracting air-dried soil (2.5 g, <2.0-mm) with 50
197 ml NH₄OAc (1 M, pH=7.0), and measuring concentrations in the extracts using atomic
198 absorption spectrophotometer (AA6800, Japan). Cation exchange capacity (CEC) was
199 calculated as the sum of charge equivalents of exchangeable K, Na, Ca and Mg
200 (Aprile and Lorandi, 2012). The ratio of CEC to clay content (CCR) was calculated to
201 obtain an index of clay mineralogy (Shaw et al. 1998).

202 Soil organic carbon (SOC) content was measured using an elemental analyzer
203 (2400II CHN elemental analyzer, Perkin-Elmer, USA) with a combustion temperature
204 of 950°C and a reduction temperature of 640°C, at the Stable Isotope Facility of the
205 University of California, Davis, after removing carbonate using 0.5 M HCl according
206 to the approach of Harris et al. (2001).

207 Relationships between climate and soil pHBC were analyzed using the indices MAP,
208 MAT and aridity index (AI). We used ArcGIS[®] software v. 9.2 (ESRI, Redlands, CA,
209 2006) to extract the MAP, MAT and potential evaporation (PET) from a global climate
210 dataset (<http://www.worldclim.org/>; resolution of ~1 km at the equator), which was
211 based on interpolated values of climatic data (1950-2000) provided by weather

212 stations throughout the territory and adjusted to the topography (Hijmans et al., 2005).
213 Then, AI was calculated as the inverse of the ratio of MAP to PET according to
214 methods in Delgado-Baquerizo et al. (2013).

215 *2.3. Statistical analysis*

216 The non-carbonate containing soils were defined as those from which we were unable
217 to detect the CO₂ release (lower than 1 ppm), and other soil samples were defined as
218 carbonate containing soils. Before numerical and statistical analysis, all variables
219 were averaged at the site level. An independent sample t-test was used to test for
220 differences between the carbonate and non-carbonate containing parts of the transect.
221 Ordinary least squares linear regression was used to determine the relationships
222 between soil pHBC and other soil variables (SIC, SOC, CEC, clay, pH, exchangeable
223 Na) and climatic variables (AI, MAP and MAT) in the carbonate soil and
224 non-carbonate soil subsets, separately. In order to further illuminate the impacts of
225 climate on the patterns of soil pHBC, we divided the transect into an arid part (AI>0.8)
226 and a semi-arid part (AI<0.8), according to the criterion of Arora (2002).

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

231 Soil pHBC_{mid} (or its estimate for the buffer curves that did not fit a sigmoid
232 function) was significantly correlated with the values of pHBC at pH=7.5 (carbonate
233 containing soils) or at pH=6 and 5 (non-carbonate containing soils) (Figure S4).
234 Therefore, we show only the results for pHBC_{mid}, which we refer to hereafter simply
235 as pHBC. All statistical analyses were conducted using the statistical package SPSS

236 17.0 (SPSS Inc., Chicago, IL, USA, 2004).

237 **3. Results**

238 The magnitude of soil pHBC varied widely, ranging from 27.2 to 188.5 mmol H⁺ kg⁻¹
239 pH unit⁻¹ for the carbonate containing soils and from 10.4 to 58.4 mmol H⁺ kg⁻¹ pH
240 unit⁻¹ for the non-carbonate containing soils (Table 1). Mean pHBC was much greater
241 in the carbonate containing soils (87.7 mmol H⁺ kg⁻¹ pH unit⁻¹) than in the
242 non-carbonate containing soils (25.7 mmol H⁺ kg⁻¹ pH unit⁻¹) (Table 1). When 0.016
243 M HNO₃ (comparable to the average cumulative amount of acid deposited over 10
244 years) was added to the soils, the average decrease in pH was 0.21 units for the
245 carbonate containing soils and 0.44 units for the non-carbonate containing soils
246 (Figure 1).

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

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

259 When all soil variables were entered into a stepwise multiple linear regression, with
260 soil pHBC as the dependent variable, carbonate content was the only significant
261 explanatory variable for the carbonate containing soils and CEC was the only
262 significant explanatory variable for the non-carbonate containing soils. None of the
263 other soil or climatic variables provided significant extra explanatory power (i.e. those
264 variables were removed from multiple stepwise regression using a cutoff value of
265 $P=0.05$) (Table 2).

266 The carbonate containing soils and the non-carbonate containing soils had similar
267 clay contents but the former had higher pH than the latter (Table 1). In the
268 non-carbonate containing soils, CEC was closely related to clay content ($R^2=0.83$,
269 $P<0.001$) (Figure S5), with a narrow range of CCR (0.18-0.46 cmol (+) kg⁻¹ clay)
270 (Table 1). In the carbonate containing soils, CEC was unrelated to clay content; CCR
271 covered a much wider range and was inversely related to clay content, ranging from
272 0.26 cmol (+) kg⁻¹ clay at the highest clay content (21.1%) to 5.26 cmol (+) kg⁻¹ clay
273 at the lowest clay content (1.4%) (Table1, Figure S6). The initial pH of soils was
274 negatively correlated with carbonate content in the carbonate containing soils,
275 accounting for 16% of the variation ($P<0.05$) (Figure S7). The soil pH significantly
276 increased with increasing aridity along the transect (Figure S8)

277 **4. Discussion**

278 4.1. Soil pHBC and potential consequences of soil acidification

279 Our results demonstrated substantially greater pHBC in the carbonate containing soils
280 than in the non-carbonate containing soils (Table 1). Stepwise regression of the

281 relationships between soil pHBC and other variables identified carbonate and CEC
282 (both positive influence) as the most significant explanatory variables for pHBC, in
283 the carbonate and non-carbonate containing soils, respectively (Table 2). These results
284 may be attributed to the differences in their acid buffering systems (Bowman et al.,
285 2008; Van Breemen, 1983). In the carbonate containing soils, the primary buffering
286 process is acid neutralization, i.e. $\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{HCO}_3^- + \text{H}^+$ and
287 $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$. If sufficient carbonate is present, the added acid may be
288 consumed with little or no decrease in pH (Van Breemen, 1983). In contrast, cation
289 exchange reactions were the primary buffering process in non-carbonate containing
290 soils. In this process, non-acidic cations such as Ca^{2+} , Mg^{2+} , K^+ and Na^+ held on soil
291 surfaces exchange with added H^+ , limiting the change in soil pH (Bowman et al.,
292 2008; Van Breemen, 1983).

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

301 In the carbonate containing soils, sustained long-term acid deposition releases a
302 large amount of carbon dioxide into the atmosphere, altering the carbon balance of
303 these globally important drylands (Yang et al., 2012). On the other hand, lowering the
304 pH of carbonate containing soils would, to some degree, improve their quality and

305 thus increase the vegetation cover and biological productivity (Lieb et al., 2011; Yang
306 et al., 2012). In the non-carbonate containing soils, an increase in soil acidity may
307 reduce availability of some nutrient cations, such as Ca and Mg, and enhance
308 availability of some toxic cations, such as aluminum (Al) and manganese (Mn), which
309 might limit plant growth and increase susceptibility to low temperature, drought and
310 herbivory stress in these ecosystems (Blake et al., 1999; Lieb et al., 2011; Chen et al.,
311 2013).

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

321 4.2. Effects of soil properties on soil pHBC

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

328 ($R^2=0.71$, $P<0.001$).

329 Linear regression did not demonstrate a clear relationship between soil pHBC and
330 SOC content in either carbonate or non-carbonate containing soils (Table 2, Figure 2).
331 These results were inconsistent with previous studies, which have shown that SOC
332 content played an important role in soil pHBC (Aitken, 1992; Magdoff and Bartlett,
333 1985; Nelson and Su, 2010; Geissen et al., 2013). The discrepancy is probably caused
334 by different types of organic matter involved (Nelson and Su, 2010). In the carbonate
335 containing soils, the low SOC content and the small range of SOC content (due to
336 aridity and low net primary production) can help explain the lack of significant
337 relationship between pHBC and SOC content (Nelson and Su, 2010; Geissen et al.,
338 2013). Moreover, those soils had a wide range of clay mineralogy, and the effect of
339 this variability on CEC and hence pHBC may have masked any effect of SOC.
340 However, in the non-carbonate containing soils, the lack of relationship between SOC
341 content and pHBC is more difficult to understand. It is possible that the organic matter
342 in those soils (with high SOC content) may have been mostly material with low
343 charge.

344 Over recent decades it has become clear that soil particle size distribution,
345 particularly clay content, plays a crucial role in determining soil pHBC (Aitken et al.
346 1990; Weaver et al. 2004). For instance, Aitken et al. (1990) demonstrated that soil
347 pHBC is primarily determined by clay content; it explained approximately 32% of the
348 variance in the pHBC of acidic topsoils in Australia. In our study we found that pHBC
349 was positively correlated with clay content for the non-carbonate containing soils but

350 that the relationship was negative for the carbonate containing soils (Table 1, Figure
351 2). The difference between the behavior of the two soil subsets was apparently due to
352 differences in their clay mineralogy. The close relationship between CEC and clay
353 content of the non-carbonate containing soils meant that both parameters were
354 similarly related to pHBC (Figure S5). The CCR values of those soils indicated that
355 clay mineralogy was dominated by kaolin and illite (Shaw et al. 1998). On the other
356 hand, in the carbonate containing soils there was a negative relationship between CCR
357 and clay content, and a negative relationship between pHBC and clay content (Figure
358 S5). The soils with higher clay content had lower CCR values, reflecting clay
359 mineralogy dominated by kaolin, whereas the soils with lower clay content had higher
360 CCR values, indicating dominantly smectitic clay mineralogy (Shaw et al. 1998).
361 Kaolin is a 1:1 clay mineral with low CEC whereas smectite is an expanding 2:1 clay
362 mineral with high CEC. Previous work has shown higher soil pHBC in the presence
363 of clay minerals having high surface area and CEC, such as chlorite and smectite
364 (Aitken and Moody, 1994). Similarly, Xu et al.(2012) observed that soils rich in
365 smectite usually have a large capacity to absorb H^+ and contribute to higher soil
366 pHBC than soils rich in kaolinite. Thus clay content is not a good predictor of pHBC
367 across the neutral-alkaline soils in northern China. It is a reasonable predictor of
368 pHBC only if it is closely related to CEC, i.e. where clay mineralogy is fairly
369 uniform.

370 Soil pH was an important explanatory variable for soil pHBC, according to
371 theoretical predictions and previous observations (Nelson and Su, 2010). During the

372 laboratory acidification process the pHBC of each soil tended to increase with
373 decreasing soil pH (Figure S6). Initial soil pH also influenced pHBC. In the
374 non-carbonate containing subset there was a positive relationship between pHBC and
375 initial pH (Table 2, Figure 2). The carbonate containing soils had high pH and high
376 pHBC, presumably due to the carbonate and high saturation with non-acidic
377 exchangeable cations. However, for the carbonate containing soils, the relationship
378 between initial soil pH and pHBC was negative (Table 2, Figure 2). This negative
379 relationship appeared to be directly associated with the negative relationship between
380 carbonate content and initial pH in the carbonate containing soil subset (Figure S7). In
381 carbonate containing soils, pH is largely determined by the carbonate equilibrium,
382 which is influenced by the suite of exchangeable and dissolved cations and anions
383 present (Bloom, 2000). In our study, there was a significantly positive relationship
384 between soil pHBC and soil exchangeable Na concentration among the carbonate
385 containing soils (Table 2, Figure 2). Therefore, in soils containing significant amounts
386 of carbonate, exchangeable Na content appears to have more of an influence on pHBC
387 than carbonate content.

388 4.3. Effects of climatic variables on soil pHBC

389 Linear regression showed that soil pHBC increased with increasing aridity; the buffer
390 strength of soils in the arid region ($AI > 0.8$), which were the carbonate containing soils,
391 was significantly greater than that of soils in the semi-arid region ($AI < 0.8$) (Figure 3).
392 Under arid conditions, in which potential evapotranspiration greatly exceeds
393 precipitation, carbonate tends to accumulate in the topsoil (Cross and Schlesinger,
394 2001; Wang et al., 2012). In less arid regions, leaching processes prevent the
395 accumulation of carbonate. Thus, soil carbonate content decreased to zero with
396 increasing precipitation from west to east along the climatic gradient. In the east,

397 where the soils do not contain carbonate, soil CEC was the most significant
398 explanatory variable for soil pHBC. Climate can also affect soil pHBC through its
399 effect on biological processes, and water availability is the most limiting factor for
400 plant growth in our study area (Luo et al., 2013; 2015). Primary productivity and
401 nitrogen fixation greatly increase with increasing precipitation, and this change in
402 biological activity influences soil properties, including pHBC (Magdoff and Bartlett,
403 1985; Delgado-Baquerizo et al., 2013). Overall, climatic regimes can exert large
404 effects on soil pHBC because of their direct and biologically mediated influence on
405 soil variables such as carbonate content and CEC.

406 Atmospheric wet nitrogen and sulfur depositions in rainfall and snowfall play a
407 crucial role in soil acidification (Dentener et al., 2006), and the amounts deposited
408 will be greater in semi-arid regions than arid regions because of the greater
409 precipitation. Precipitation has important effects on acid addition not just because of
410 the solutes deposited, but also because of the leaching of water through the profile. In
411 areas with sufficient precipitation to leach the topsoil, the main alkali material in soil
412 (carbonate) is removed downwards (Jenny, 1941). In addition, once pH reaches 6 or
413 less, the leaching of non-acidic cations becomes important, because it leads to an
414 accumulation of the less mobile and acidic Al^{3+} as an exchangeable cation(Jenny,
415 1941). Finally, in wetter soils weathering occurs more rapidly, which tends to result in
416 a lowering of CEC. Therefore, lower soil pHBC in soils of semi-arid regions
417 compared to arid regions, in combination with greater acid inputs, indicates that
418 semi-arid regions would be much more sensitive to global changes such as elevated
419 nitrogen deposition and altered precipitation regimes.

420 **5. Conclusions**

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

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443

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582

583 **Table 1** Physicochemical properties of the carbonate containing soils and the
 584 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 |

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

588 **Table 2** Summary of regression models (linear and stepwise) for the effects of soil,
589 climatic and all environmental variables on soil pH buffering capacity in the
590 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 |

591 SIC, soil inorganic carbon; SOC, soil organic carbon; CEC, cation exchange capacity;

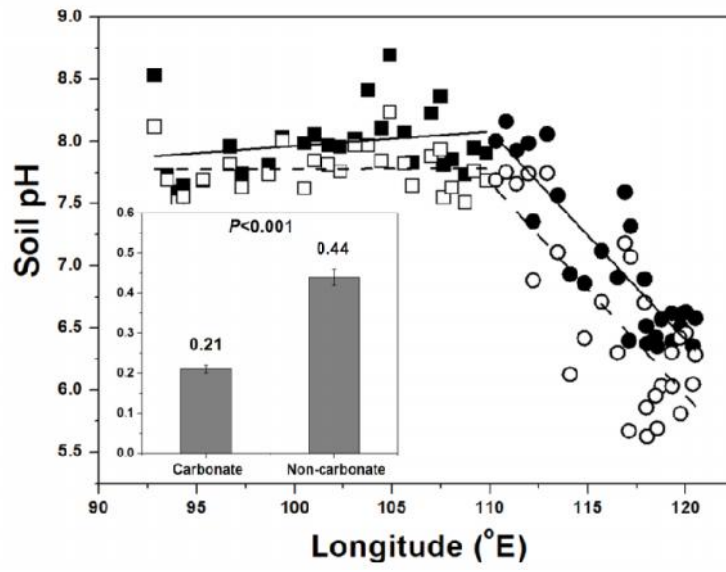
592 AI, aridity index; MAP, mean annual precipitation; MAT, mean annual temperature

593 **Figure Legends**

594 **Figure 1** Acidification of grassland soils upon acid addition ($16 \text{ mmol H}^+ \text{ kg}^{-1}$ soil
595 added) to carbonate containing soils (squares) and the non-carbonate containing soils
596 (circles) collected from the 3600 km-long transect. The empty symbol denotes
597 background soil pH as control, while the filled symbol represents soil pH value after
598 acidification. Mean changes in pH values for both carbonate-containing and
599 non-carbonate containing soils are shown in the inset. The solid line and dashed line
600 represent the mean pH values of controls and acid-treated soils across the transect,
601 respectively.

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

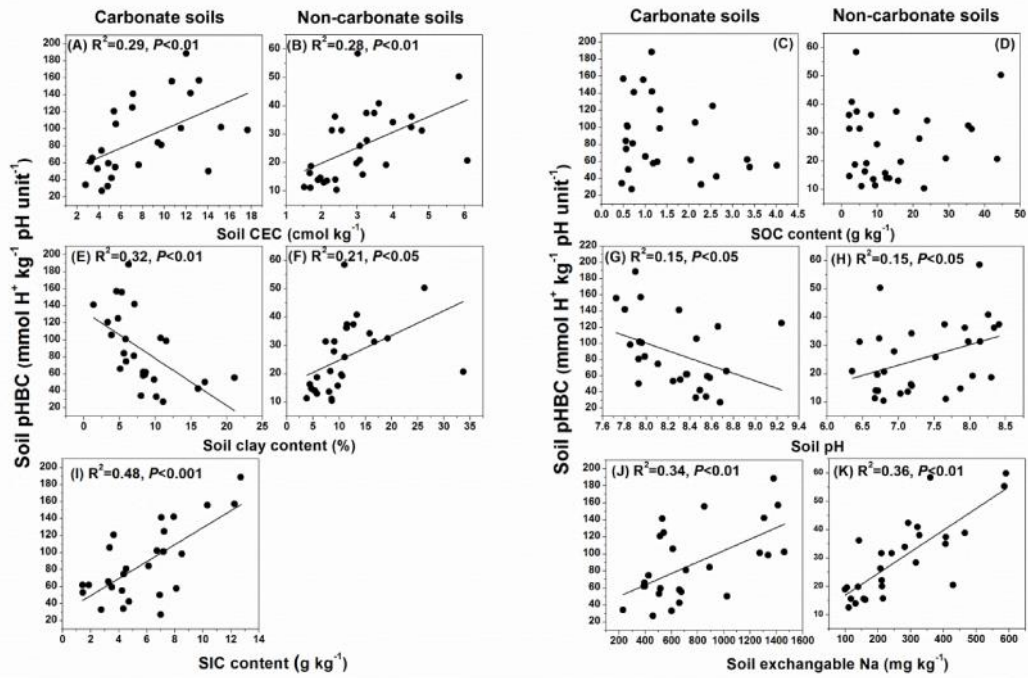
607 **Figure 3** Relationships between soil pH buffering capacity (pHBC) and aridity index
608 in the carbonate containing soils (solid circles) and the non-carbonate containing soils
609 (empty circles). Dashed line represents the boundary between the arid regions (aridity
610 index > 0.8) and the semi-arid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



612

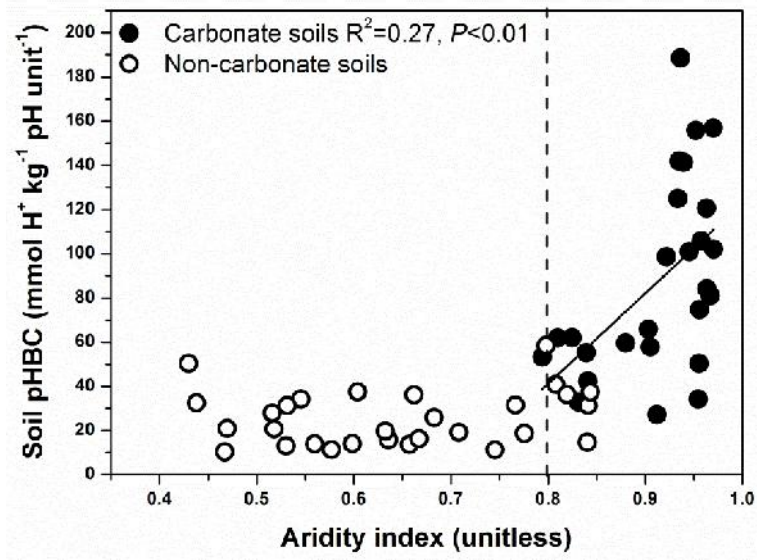
613 **Figure 1**

614



615

616 **Figure 2**



617

618 **Figure 3**

619