The contribution of atmospheric deposition and forest harvesting to forest soil acidification in China since 1980

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HIGHLIGHTS

● The strongest acidification occurred in southwest China and/or semi-Luvisols.
● Atmospheric deposition contributed 84% to the H⁺ production causing forest soil acidification.
● H⁺ production induced by forest growth contributed 16% to the forest soil acidification.
● On average, base cation deposition neutralized 31% of the potential acid input.

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ABSTRACT

Soils below croplands and grasslands have acidified significantly in China since the 1980s in terms of pH decline in response to acid inputs caused by intensified fertilizer application and/or acid deposition. However, it is unclear what the rate is of pH decline of forest soils in China in response to enhanced acid deposition and wood production over the same period. We therefore gathered soil pH data from the Second National Soil Inventory of China and publications from the China National Knowledge Infrastructure (CNKI) database in 1981–1985 and 2006–2010, respectively, to evaluate the long-term change of pH values in forest soils. We found that soil pH decreased on average by 0.36 units in the period 1981–1985 to 2006–2010, with most serious pH decline occurring in southwest China (0.63 pH units). The soil type with the strongest pH decline was the semi-Luvisol (0.44 pH units). The decrease in pH was significantly correlated with the acid input induced by atmospheric deposition and forest harvesting. On average, the contribution of atmospheric deposition to the total acid input was estimated at 84% whereas element uptake (due to forest wood growth and harvest) contributed 16% only. Atmospheric deposition is thus the major driver for the significant forest soil acidification across China.

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1. Introduction

Since the Second Industrial Revolution, the world has got into a period of booming industrial production, with elevated emissions of acidifying compounds, notably sulphur dioxide (SO2), nitrogen oxides (NOx) and ammonia (NH3), to the atmosphere (Carmichael et al., 2002; Mylona, 1996; O’Neil et al., 2012). Subsequently, a series of environmental problems occurred (Dickerson et al., 1997; Haines et al., 1980; O’Neil et al., 2012), one of which was soil acidification (Van Breenen et al., 1984). Much research has been carried out on acidification of non-agricultural (forest) soils since the 1980s, especially in Europe (Van Breenen et al., 1984) and the US (Johnson et al., 1982) in response to deposition of SO2, NOx and NH3, recently being summarized in De Vries et al. (2015). As a consequence, international co-operation to combat the emissions of those pollutants has been carried out. Such reductions have

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occurred in Europe since 1975 for SO$_2$ (Mylona, 1996) and since 1990 for NO$_x$ (Vestreng et al., 2009) and to a lesser extent for NH$_3$ (Waldner et al., 2014; www.EMEP.int), which was accompanied by the slow soil recovery. For instance, Kirk et al. (2010) found that soil pH increased between 1978 and 2003 in Wales and England in response to decreased acid deposition.

Unlike Europe, SO$_2$ and NO$_x$ emissions have largely increased in China since 1980 (Smith et al., 2011), causing a high increase in SO$_2$ and NO$_x$ deposition (Duan, 2000; Liu et al., 2013), leading to enhanced soil acidification (Liu et al., 2010). In recent decades, China became one of the countries with the most elevated acid deposition rates due to increasing emissions of sulphur (S) and nitrogen (N) compounds (Duan, 2000; Liu et al., 2013; Pan et al., 2013; Du et al., 2014, 2015). Though S deposition is still among the highest in the world, it has decreased in China since 2005 because of the implementation of several policies to reduce SO$_2$ emission (Fang et al., 2013). However, N emissions continue to rise due to intensive cultivation and livestock production, as well as traffic and industrial development (Pan et al., 2013). This has led to a decline in ratios of sulphate (SO$_4^{2-}$) to nitrate (NO$_3^{-}$) concentrations in wet deposition (Fang et al., 2011; Wang et al., 2012). In China, reduced-N (NH$_3$ and NH$_4^+$) plays a more important role than oxidized-N (NO$_3$ and NO$_2^-$) deposition (Larsen et al., 2012; Du et al., 2014). Both the high rates and composition shifts of acid deposition may have significantly affected soil acidification in China (Liu et al., 2010; Yang et al., 2015).

Although S (SO$_4^{2-}$ and N (NH$_4^+$ and NO$_3^-$) deposition have received considerable attention (Bowman and Cleveland, 2008), the important role of base cation (BC, including calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), potassium (K$^+$) and sodium (Na$^+$) ions) deposition should not be neglected (Larsen and Carmichael, 2000), since the potential acid input equals the sum of S and N deposition corrected for base cation deposition. Furthermore, forest felling for timber use, leading to removal of BC from the soil, further accelerates soil acidification (Rowell and Wild, 1985). Significant site-specific soil acidification in Chinese forests has been reported previously by many researchers (e.g. Liu et al., 2010; Huang et al., 2014).

Soil acidification is mostly defined as a decrease in soil pH (e.g. Krug and Frink, 1983), but production of protons in the soil is only partially reflected in changes of the pH, being an intensity factor. For this reason, Van Breemen et al. (1983) defined soil acidification as a decrease in the acid-neutralizing capacity (ANC) of the soil, being a capacity factor. Whether changes in the ANC, which is due to net acid production in the soil, is reflected in observable changes in soil acidity (pH) depends on the buffering rate of the soil due to weathering and cation exchange (Ulrich, 1981; De Vries et al., 1989). Simultaneous information on both acid production, causing a change in ANC, and pH changes thus give information on both soil acidification and the sensitivity of the soil to acidification.

Large scale decline in soil pH has been demonstrated for both croplands (Guo et al., 2010) and natural grasslands (Yang et al., 2012) in China, during the 1980s and 2000s, in response to acid production cause by enhanced N fertilization and/or acid deposition, respectively. Nevertheless, very limited information is available on large scale pH changes in Chinese forest soils over the last two or three decades in response to acid production cause by forest management and acid deposition. Recently, a paper on regional forest acidification has been published, showing significant soil pH decrease only in broadleaved forests across China (Yang et al., 2015). However, their research was still based on a limited data set (487 samples) and no evaluation was made of the linkage between pH change and proton (acid) production by acid deposition and forest growth nor with the sensitivity of soils to acidification.

In this paper we further evaluated pH changes in forest soils over China from 1981–1985 to 2006–2010. The evaluation was based on a very large dataset (5598 samples), allocated to six regions and five soil clusters, with different sensitivities to acid inputs, respectively. The observed pH decline was evaluated for those soil clusters and regions, by calculating the acid inputs caused by SO$_2$, NO$_x$ and NH$_3$ deposition and forest uptake in different regions. Base cation deposition as well as the fate of N were accounted for to assess the net proton production and related this to the pH decrease in Chinese forests. The assessment of acid inputs by deposition and forestry growth was conducted to gain insight in the relative contribution of these drivers to soil pH decrease, which provides valuable information for predicting the future forest acidification trend.

2. Materials and methods

Soil pH datasets were collected to assess pH changes in six major sub-regions and among five major soil types in China using an unpaired t-test (2.1). To gain insight in the main sources of soil acidification in various regions, an assessment was then made to calculate the proton production (H$^+$) from deposition (2.2) and forest growth (2.3) in each region. The pH change in each region was evaluated and compared with the proton production driving these changes.

2.1. Evaluation of soil pH changes by unpaired t-tests

Approach: In assessing pH from 1981–1985 to 2006–2010, we focused on pH changes in the top 30 cm of the forest soils in six major sub-regions according to Fang et al. (2001), i.e. East, North, Northeast, Northwest, South central and Southwest (Fig. 1). We used an unpaired t-test to evaluate the significance in changes in the soil pH status between the early 1980s (1981–1985) and the late 2000s (2006–2010) across China, since pH data in the two periods are not paired but have different locations and numbers of measurements. The analysis was made after testing that the pH values in the two periods were normally distributed.

Soil groups were clustered according to their soil genetic classification (Shi et al., 2004; Zhao and Shi, 2007), as well as their sensitivity to acidification (Van Breemen et al., 1983; De Vries et al., 1989). Soil types were distinguished into 5 clusters, i.e., Ferralsols, Luvisols, Semi-Luvisols, Calcareous soils and Other Soils. 

(i) Ferralsols include highly weathered acidic red soils, yellow soils and latosols, predominantly distributed in low latitudes and humid tropical and subtropical zones (e.g. central and south part of China). These soils have mostly a low pH, a low cation exchange capacity (CEC) and a low base saturation (BS) implying that these soils are in the aluminium (Al) buffer range with a limited sensitivity to pH change.

(ii) Luvisols include slightly acidic dark brown soils, yellow brown soils, brown soils, Albic soils and yellow-cinnamon soils. These soils mainly occur in the eastern humid monsoon climate zone (e.g. east China), and have high organic carbon contents and slightly acidic to neutral pH values, implying that these soils are in the BC exchange buffer range, being sensitive to acidification.

(iii) Semi-Luvisols include black soils, grey soils and cinnamon soils, mainly occurring in semi-humid and semi-arid zones (e.g. north China). These soils do often have carbonate (CaCO$_3$) in the subsoil, but the topsoil is mostly in the BC exchange buffer range, being sensitive to acidification.

(iv) Calcareous soils include desert soils, calcium soils, dark loessial soils and alkali-saline soils, mostly occurring in semi-arid and arid zones, for instance in Northwest and North
China. Their soil pH values are always higher than 6.5 and they are quite insensitive to acidification due to their ability to neutralize acid by carbonate.

(v) Other soils include Primarosols (including skeleton soils, loess soils, purple soils, aeolian sandy soil and alluvial soils) and the remaining soil types. Most of these soils are distributed in Northwest and Southwest China, with a big range in soil pH, mostly between 4 and 9.

Data: The soil pH datasets used in this study were derived from a combination of the Chinese Second National Soil Inventory Database (also see Guo et al., 2010) and published literature. Inventory data were derived from the published book Soil Species of China, vols. 1 to 6 (Office of National Soil Survey, 1993–1996). Literature data were collected by searching the China National Knowledge Infrastructure (CNKI) database (www.cnki.net) using two key words: “pH” and “forest”, including articles, dissertations and monographs. All of the 5598 topsoil pH data points were collected from these two datasets. In all publications, pH was measured using water as extractant (soil: water 1:2.5), further denoted as pH-H2O.

Datasets in 1980s include 1679 records of topsoil (mainly 0–30 cm) pH during 1981–1985, i.e. 1118 data points from China’s National Soil Inventory and 561 data points from CNKI publications, respectively. The data from national inventory contain information on layer thickness, soil type and soil pH values. No exact geographic locations of monitoring sites were reported, besides the names of the county and village where the samples were taken. The dataset in 2000s, which were all derived from CNKI publications, included 3919 pH-H2O records from 701 publications between 2006 and 2010. All publications used to assess the pH data are given in the Supplementary Material A.

2.2. Assessment of the proton production by atmospheric deposition

Approach: The net proton input by atmospheric deposition was calculated as:

\[
\text{Net } H^+ \text{ input: } H_{\text{dep}} = SO_4^{2-} + f_{\text{Nle}}(NH_4^+ + NO_3^-) + N_{\text{upt}} - BC^+
\]

where \(BC^+ = Ca^{2+} + Mg^{2+} + K^+ + Na^+ + Cl^-\) and where \(SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, K^+, Na^+\) denote the total deposition of these elements in kmol H\(^+\) ha\(^{-1}\). \(N_{\text{upt}}\) denotes the N accumulation by forest growth and \(f_{\text{Nle}}\) is the fraction of N leaching compared to total N deposition. Note that the net proton input can be negative when the \(BC^+\) deposition is larger than the acidifying net input of S and N compounds inducing the leaching of \(SO_4^{2-}\) and \(NO_3^-\). The calculation assumes that all NH\(_4^+\) is nitrified but that only part of it is leached as \(NO_3^-\) (causing acidification), the remaining part being taken up (\(N_{\text{upt}}\)) or emitted to the atmosphere as N\(_2\), NO\(_x\) or N\(_2\)O due to denitrification. Average field data for Europe indicate an N leaching/deposition fraction near 0.1 (De Vries et al., 2007). Other literature data indicated a fraction of N leaching (\(f_{\text{Nle}}\)) that varies between 0.01 and 1.0 of total N deposition (Larsen et al., 2011; MacDonald et al., 2002; Xi et al., 2007). Based on literature information, the value of \(f_{\text{Nle}}\) was set equal to 0.25 for Southwest, South central and East China (Larsen et al., 2011; Xi et al., 2007), 0.15 for North and Northeast China (Liu, 1992), and 0.01 for Northwest China (Xi et al., 2007), and 0.15 for the national level.

Data: In order to assess the net proton production caused by atmospheric deposition, we collected bulk deposition data on \(SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, K^+, Na^+\) and Cl\(^-\) from suburban, rural and mountain regions, where forests are mainly located. Although there is an ongoing bulk deposition monitoring programme in China (Zhong et al., 2007), we did not use these data in our study.
since locations are mainly concentrated in urban regions, where emissions and deposition of in SO₂, NOₓ and NH₃ are highly elevated (Du et al., 2014, 2015). Furthermore, this programme mainly focuses on those N and S compounds and has very limited information on BC. Therefore, key words “forest” with “precipitation chemistry composition” or “deposition” were used to gather bulk deposition including all major cations and anions from publications in the CNKI database since 1980. The deposition of each element was converted into the same unit, i.e. kmol H⁻² ha⁻¹ based on their charge and molar mass and allocated to the six regions, to allow the assessment of an average bulk deposition for each region. Trends in time and ratios for total deposition to bulk deposition were then used to calculate the total accumulated input into the forest soil in each region.

Detailed information on the calculation of the accumulated bulk and total deposition, including the used references, can be found in Supplementary Material B. Details on the number of sites, average values of bulk deposition for each element per region in the 1980s and ratios for total deposition to bulk deposition are shown in Supplementary Material B. Details on the number of sites, average forest soil in each region.

Trends in time and ratios for total deposition to bulk deposition allow the assessment of an average bulk deposition for each region. On their charge and molar mass and allocated to the six regions, to include the dominant tree species whose stock volume percentage is larger than 5% of the total stock volume, and at most 5 tree species in each sub-region. The ratio to the five (or less) dominant trees’ stock volume (Rᵢ) for each tree species was defined to assess element removal from forest growth and harvest in the region.

Data: Data of forest stock accumulation during 1981–2005 were derived from two sources, i.e. the books containing forestry statistical data of 1980–1990 (Chinese Ministry of Forestry (1990)) and 2000–2005 (State Forestry Bureau, 2005), and the summary table of annual forest felling quota during the period of 1991 and 2000 (Chinese State Council, 1990; Department of Policies Management and Resources (1996)). Both of them were based on the National Forest Resource Continuous Inventory of China (NFRIC), which was carried out by the State Forestry Bureau of China (SFB) for every five years and compiled into publications. It is also the source of volumes stock of each dominant tree species, which were used to calculate the proton (H⁺) produced by forest growth. Based on the dataset of the second to the sixth National Forest Resource Continuous Inventory of China, the total volume stock accumulation was calculated by multiplying the growth rates over every 5 years. Data that were used with respect to a real growth rate and forested area per region for the periods 1981–1990 and 1991–2005 are given in Table 1.

Used data for wood density, ratios of branch wood to stem wood, and element contents (N, K, Ca, Mg) in stem wood and branches of certain tree species are shown in Table 2. They were summarized from 22 published articles, dissertations and monographs from the CNKI database (for references: see Ref. 2 Vegetation data references in Supplementary Material B).

3. Results

3.1. Changes in forest soil pH over China

The broad-scale dataset exhibits a widespread acidification in forest soil, showing a decline of about 0.36 pH units at national level between the 1980s and 2000s (Table 3). The Southwest region suffers from the most serious soil acidification, with 0.63 pH units decrease, closely followed by Northeast region with 0.55 pH units decrease and South Central with 0.50 pH units decrease, then followed by North (0.44 pH units) and East (0.25 pH units), respectively. The unpaired t-test indicated significant pH change in all sub-regions except the Northwest (P > 0.05).

To evaluate the soil acidification in dominant forest soils, we also present pH changes per soil cluster in Table 4. The strongest increase in soil acidity occurred in Semi-Luwisols, Ferralsols and Luvisols, with an average pH decrease of 0.44, 0.36 and 0.33 units, respectively. These soils are all non-calcareous and sensitive to acidification. As expected, the Calcareous soils did not show significant acidification in the past 25 years, as the same was true for the cluster of all other soils.

3.2. Contribution of atmospheric deposition and forest growth to soil acidification

In the period 1981–1985 to 2006–2010, S deposition contributed 31.9–92.8 kmol H⁺ ha⁻¹, depending on the region, which is
between the early 1980s and the late 2000s.

Supplementary Material B(41.2 to 66.7 kmol H\(^+\)) comparable or greater than total N deposition, which varied from 1981–1985 to 2006–2010 was 39.3 kmol H\(^+\) ha\(^{-1}\), being equal to a net proton input into soil by deposition of 1.58 kmol H\(^+\) ha\(^{-1}\) yr\(^{-1}\) (Table 5).

Table 1

<table>
<thead>
<tr>
<th>Sub-region</th>
<th>Total volume stock Accumulation (10^8 m(^3))</th>
<th>Area (10^6 ha)</th>
<th>Areal stock accumulation (m(^3) ha(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>North</td>
<td>922</td>
<td>1342</td>
<td>25.8</td>
</tr>
<tr>
<td>North West</td>
<td>494</td>
<td>623</td>
<td>17.1</td>
</tr>
<tr>
<td>South Central</td>
<td>266</td>
<td>460</td>
<td>8.6</td>
</tr>
<tr>
<td>South West</td>
<td>796</td>
<td>1718</td>
<td>23.1</td>
</tr>
<tr>
<td>East</td>
<td>1202</td>
<td>1797</td>
<td>28.7</td>
</tr>
<tr>
<td>Total China</td>
<td>4282</td>
<td>7474</td>
<td>125</td>
</tr>
</tbody>
</table>

\(^a\) Data based on the third National Forest Continuous Inventory between 1984 and 1988.\(^b\) Data based on the fifth National Forest Continuous Inventory between 1994 and 1998.

Table 2

<table>
<thead>
<tr>
<th>Tree species</th>
<th>Wood density(^a) g cm(^{-3})</th>
<th>Branch to stem ratio ((^b))</th>
<th>Element concentrations in stem wood (%)</th>
<th>Element concentrations in branch wood (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>N K Ca Mg</td>
<td>N K Ca Mg</td>
</tr>
<tr>
<td>Dahurian larch</td>
<td>490</td>
<td>0.13</td>
<td>0.11 0.05 0.72 0.07 0.63 0.57 0.36 0.45</td>
<td>0.11 0.05 0.72 0.07 0.63 0.57 0.36 0.45</td>
</tr>
<tr>
<td>Chinese fir</td>
<td>307</td>
<td>0.10</td>
<td>0.07 0.06 0.35 0.11 0.57 0.36 0.45 0.38</td>
<td>0.07 0.06 0.35 0.11 0.57 0.36 0.45 0.38</td>
</tr>
<tr>
<td>Pinus yunnanensis</td>
<td>483</td>
<td>0.25</td>
<td>0.09 0.02 0.12 0.02 0.40 0.29 0.25 0.09</td>
<td>0.09 0.02 0.12 0.02 0.40 0.29 0.25 0.09</td>
</tr>
<tr>
<td>Birch</td>
<td>541</td>
<td>0.47</td>
<td>0.26 0.17 0.50 0.04 0.61 0.14 0.25 0.05</td>
<td>0.26 0.17 0.50 0.04 0.61 0.14 0.25 0.05</td>
</tr>
<tr>
<td>Poplars</td>
<td>396</td>
<td>0.22</td>
<td>0.18 0.18 0.20 0.04 0.42 0.70 0.58 0.15</td>
<td>0.18 0.18 0.20 0.04 0.42 0.70 0.58 0.15</td>
</tr>
<tr>
<td>Korean pine</td>
<td>393</td>
<td>0.20</td>
<td>0.08 0.06 0.07 0.01 0.45 0.12 0.61 0.06</td>
<td>0.08 0.06 0.07 0.01 0.45 0.12 0.61 0.06</td>
</tr>
<tr>
<td>Spruce</td>
<td>342</td>
<td>0.23</td>
<td>0.08 0.03 0.18 0.07 0.30 0.15 0.32 0.18</td>
<td>0.08 0.03 0.18 0.07 0.30 0.15 0.32 0.18</td>
</tr>
<tr>
<td>Fir</td>
<td>366</td>
<td>0.17</td>
<td>0.42 0.19 0.80 0.14 0.74 0.44 0.47 0.18</td>
<td>0.42 0.19 0.80 0.14 0.74 0.44 0.47 0.18</td>
</tr>
<tr>
<td>Pinus densata</td>
<td>413</td>
<td>0.13</td>
<td>0.07 0.07 0.02 0.20 0.14 0.27 0.05 0.05</td>
<td>0.07 0.07 0.02 0.20 0.14 0.27 0.05 0.05</td>
</tr>
<tr>
<td>Mason pine</td>
<td>431</td>
<td>0.23</td>
<td>0.07 0.05 0.08 0.03 0.15 0.10 0.14 0.05</td>
<td>0.07 0.05 0.08 0.03 0.15 0.10 0.14 0.05</td>
</tr>
<tr>
<td>Quercus</td>
<td>676</td>
<td>0.22</td>
<td>0.30 0.18 0.68 0.04 0.58 0.24 1.61 0.09</td>
<td>0.30 0.18 0.68 0.04 0.58 0.24 1.61 0.09</td>
</tr>
</tbody>
</table>

\(^a\) We assumed the wood density was same in branch and stem; \(^b\) and \(^c\) The references of element concentration and the ratio of branch to stem were presented in Supplementary Material B (Ref. 2 Vegetation data references).

Table 3

<table>
<thead>
<tr>
<th>Sub-region</th>
<th>Number of samples</th>
<th>pH value Early 1980s</th>
<th>pH value Late 2000s</th>
<th>Decrease</th>
<th>1980s–2000s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Southwest</td>
<td>485</td>
<td>1016</td>
<td>6.10</td>
<td>5.47</td>
<td>0.63 (^\ast)</td>
</tr>
<tr>
<td>Northeast</td>
<td>259</td>
<td>478</td>
<td>6.15</td>
<td>5.60</td>
<td>0.55 (^\ast)</td>
</tr>
<tr>
<td>South Central</td>
<td>268</td>
<td>618</td>
<td>5.46</td>
<td>4.96</td>
<td>0.50 (^\ast)</td>
</tr>
<tr>
<td>North</td>
<td>97</td>
<td>348</td>
<td>7.10</td>
<td>6.66</td>
<td>0.44 (^\ast)</td>
</tr>
<tr>
<td>East</td>
<td>367</td>
<td>954</td>
<td>5.60</td>
<td>5.35</td>
<td>0.25 (^\ast)</td>
</tr>
<tr>
<td>Northwest</td>
<td>203</td>
<td>505</td>
<td>7.37</td>
<td>7.51</td>
<td>0.14 (^\ast)</td>
</tr>
<tr>
<td>China</td>
<td>1679</td>
<td>3919</td>
<td>6.10</td>
<td>5.74</td>
<td>0.36 (^\ast)</td>
</tr>
</tbody>
</table>

\(^\ast\) means the highly significant difference (P < 0.01) on pH value between the early 1980s and the late 2000s; \(^\ast\) means no significant difference (P > 0.05) on pH value between the early 1980s and the late 2000s.

Table 4

<table>
<thead>
<tr>
<th>Soil cluster</th>
<th>Number of samples Early 1980s</th>
<th>pH value Early 1980s</th>
<th>pH value Late 2000s</th>
<th>pH decrease 1980s–2000s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferralsols</td>
<td>530</td>
<td>5.01</td>
<td>4.65</td>
<td>0.36 (^\ast)</td>
</tr>
<tr>
<td>Luvisols</td>
<td>346</td>
<td>5.77</td>
<td>5.44</td>
<td>0.33 (^\ast)</td>
</tr>
<tr>
<td>Semi-Luvisols</td>
<td>184</td>
<td>7.00</td>
<td>6.56</td>
<td>0.44 (^\ast)</td>
</tr>
<tr>
<td>Calcareous soils</td>
<td>74</td>
<td>7.79</td>
<td>7.81</td>
<td>-0.02 (^\ast)</td>
</tr>
<tr>
<td>Others</td>
<td>545</td>
<td>6.85</td>
<td>6.97</td>
<td>-0.12 (^\ast)</td>
</tr>
<tr>
<td>China</td>
<td>1679</td>
<td>6.10</td>
<td>5.74</td>
<td>0.36 (^\ast)</td>
</tr>
</tbody>
</table>

\(^\ast\) means the highly significant difference (P < 0.01) on pH value between 1980s and 2000s; \(^\ast\) means no significant difference (P > 0.05) on pH value between 1980s and 2000s.
Another reason for speeding up the process of soil acidification was base cation uptake due to forest growth and harvesting. Because of the differences on a real stock accumulation (Table 1) and element concentrations of each dominant tree species (Table 2), H⁺ production showed a significant variation between 4.5 and 10.8 kmol H⁺ ha⁻¹ for the different regions in the period 1981–1985 to 2006–2010, with an average of 7.5 kmol H⁺ ha⁻¹ for the whole of China (Table 6). The Northeast region ranked the first in H⁺ production by forest uptake across China, as 10.8 kmol H⁺ ha⁻¹; while the lowest H⁺ production by forest uptake (only 4.5 kmol H⁺ ha⁻¹) was observed in the East and Northwest regions of China.

A regression analysis was carried out between the pH decrease in each region and the proton production induced by the sum of forest growth and atmospheric deposition (H-sum), respectively (Fig. 2). Results show a significant correlation between soil pH decrease and H-sum (r² = 0.72) in Chinese forest (P < 0.05).

Deposition induced proton production accounted for 84% of the total proton production while forest uptake was responsible for only 16%. This indicates that acid deposition is the main driver for forest soil acidification in China, with accumulated S and N deposition being the dominant cause.

4. Discussions

4.1. Unpaired versus paired datasets

It should be realized that our results were based on pH data in 1981–1985 and 2006–2010 that differ in location and record numbers (unpaired data). Despite this limitation, significant changes in soil pH are likely to have occurred in view of the large dataset. However, paired datasets of pH, especially in combination with data on soil properties that determine the buffer capacity of soils, i.e. calcium carbonate (CaCO₃) content (in calcareous soils), cation exchange capacity (CEC) and base saturation, would largely improve the evaluation. Some paired long-term observation data provide additional strong evidence of forest soil acidification. For instance, soil pH decrease of about 0.56–0.73 units occurred from 1980s to 2005 in the Dinghushan Biosphere Reserve (Liu et al., 2010), located in South Central of China. Acidification also occurred in the Northeast China, in the period 1980–2009, with an observed soil pH decrease at 0.26–0.51 units in Laoshan, Heilongjiang province (Wang et al., 2011). Similar results were presented by Zhang and Li (2010), with the soil pH in Mountain Tai declining by 0.46–0.61 units from 1983 to 2009 in the East of China. In general, our results were consistent with these trends at site level, confirming significant acidification in forest soils of China.

4.2. Variations in soil acidification by region and soil type

Forest soil acidification across China was indicated by a widespread pH decrease (average of 0.36 units) between 1981 and 1985 vs 2006–2010. The most serious acidification occurred in South (Southwest and South central) and Northeast China (Table 1), where the acid sensitive Luvisols, semi-Luvisols and Ferralsols are mainly distributed (Zhao and Shi, 2007) and where acid deposition is elevated. In these soils, pH values were between 7 and 4, and the acid load needs to be buffered by exchange with base cation adsorbed to clay and organic matter (De Vries and Breeuwsma, 1987) with a limited buffering capacity (De Vries et al., 1989). Calcareous soils and Primarsols were the dominant soil types in Northwest China, with CaCO₃ contents between 5 and 10% in most of the soils (Zhao and Shi, 2007). The strong buffering capacity of CaCO₃ hardly caused any soil acidification in terms of pH change, which is in accordance with long term model simulations (De Vries et al., 1989). The low precipitation and high evaporation can also be one of the reasons that prevent the soil from being acidified (Duan et al., 2013; Zhao and Shi, 2007).

4.3. Relative contribution of acid deposition and forest growth to acidification of forest soils

Deposition has been recognized as an important pathway of H⁺ input to soil acidification in China. However, most research only focuses on the N and S deposition, with the neutralizing impact of base cation (BC) deposition being largely neglected (Cui et al., 2014; Liu et al., 2013). Actually, BC deposition must be taken into account when evaluating possible effects of atmospheric deposition on soils.
China where the accumulated BC deposition was estimated at deposition can be very high in some parts of China, such as North China where the accumulated BC deposition was estimated at 51.7 kmol H⁻¹ ha⁻¹ for the period from 1981–1985 to 2006–2010 (Table 5).

Furthermore, the contribution of N deposition to soil acidification is limited due to N uptake, soil N accumulation and denitrification. Consequently, only part of the N deposition (about 0.01–0.25 of total N deposition) was assumed to be leached out in our calculation, depending on the region. It should be realized however that with further N saturation, the N accumulation will decline and in extreme cases also forest growth will not respond any more to additional N deposition (Hoeegberg et al., 2006). In the worst case situation that all N deposition is leached out (neither vegetation uptake nor N accumulation or denitrification), the potential H²⁺ production (81.2 kmol H⁻¹ ha⁻¹) will be 2.1 times the actual H²⁺ production (H-dep, 39.3 kmol H⁻¹ ha⁻¹) in the period from 1981–1985 to 2006–2010, as shown in Table 5.

The contribution of forest growth and removal by harvesting to the proton (H⁺) input was only 7.5 kmol H⁻¹ ha⁻¹ (equal to 0.3 kmol H⁻¹ ha⁻¹ yr⁻¹), with a range from 4.5 to 10.8 kmol H⁻¹ ha⁻¹ (or 0.18–0.43 kmol H⁻¹ ha⁻¹ yr⁻¹) during the period 1981–2005, responsible for 16.0% of the total H⁺ input (the sum of forest uptake and deposition) at national level. We should note that the calculation was based on the area-averaged forest growth in each region, implying that H⁺ production might be much higher in some major timber production areas or dense forests areas (i.e. the artificial forest). For example, the H⁺ production by forest growth can be up to 1.54 kmol H⁻¹ ha⁻¹ yr⁻¹ in subtropical evergreen sclerophyllous forests ecosystem (Duan et al., 2004).

On the other hand, we allocated N uptake-induced neutralization to forest growth. Other authors (e.g. De Vries and Breeuwsma, 1987) did not allocate N uptake to forest growth since the accumulated N by forest comes mainly from N deposition rather than from soil. If we would reallocate N-uptake-induced proton consumption to deposition, the proton production caused by forest uptake would be recalculated as:

$$H_{\text{dep}} = BC_{\text{upt}}$$ (6)

And hence the deposition-induced H⁺ production would be:

$$H_{\text{dep}} = SO_4^{2-} + f_{\text{flue}} (NH_4 + NO_3) - BC^-$$ (7)

Even when using in this option, atmospheric deposition contributed most to the proton input to the forest soil, i.e. about 33.7 kmol H⁻¹ ha⁻¹ (with a range from -9.7 to 46.8 kmol H⁻¹ ha⁻¹), while forest BC uptake induced H⁺ input was 13.1 kmol H⁻¹ ha⁻¹ (with a range from 7.9 to 19.8 kmol H⁻¹ ha⁻¹) during the early 1980s and the late 2000s. This implies an annual average contribution of deposition and forest growth of 1.35 and 0.52 kmol H⁻¹ ha⁻¹ yr⁻¹, respectively. Both allocation methods thus revealed that atmospheric deposition is the dominant factor causing significant acidification in major Chinese forest soils.

Our analysis indicates that except for Northwest China, forest soils have significantly acidified in China between the 1981–1985 and 2006–2010. Enhanced soil acidification might have resulted in negative effects on timber production (Hoeegberg et al., 2006) and led to loss of biodiversity and reduction of ecosystem stability (Chen et al., 2012; Azevedo et al., 2013; Ceulemans et al., 2013). In order to maintain forest productivity and its ecological functions, we should pay much more attention to the occurring forest soil acidification and its negative impacts on Chinese forests.

5. Conclusions

In our study, we found China’s forest soils have significant acidified, as indicated by an average decline of 0.36 pH units from 1981–1985 to 2006–2010. The largest pH decline occurred in southwest China (0.63 pH units) and in semi-Luvisolos (0.44 pH units). The acid production causing these pH changes was mainly due to atmospheric deposition, i.e. 84%, whereas the remaining 16% was due to element removal by forest wood growth and harvest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.04.023.

References


