Source and consumption of proton and its impacts on cation flux and soil acidification in a forested watershed of subtropical China

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Abstract

To understand the impacts of H^+ from dry and wet deposition on soil acidification, the mass balance of elements of a forested watershed in subtropical China was studied. The studied watershed is located in south Anhui Province and in which the dry and wet deposition as well as runoff were monitored from Mar. 2007 to Feb. 2009. The physical and chemical properties of soil and rock were also determined. The results show that acid deposition bring in not only a mass of H^+ directly, but also nitrogen (N) and sulphur (S) that can produce abundant H^+ by secondary transformations and specific adsorptions in soil. As the discharge of H^+ by stream is very low, a large proportion of H^+ is consumed by soil (reaction). The rate of soil acidification is *c.a.* 1144 mol/ha/yr in the forest watershed besides the consumption of H^+ by mineral weathering. By comparison of the H^+ consumption by silicate mineral weathering and caion exchange, it shows that the loss of base cation can't be complemented by mineral weathering in this study area. So soil will be subject to acidification if the acid deposition continues.

Key Words

Watershed; Acid deposition; Nitrogen deposition; Sulphur deposition; Soil acidification.

Introduction

Soil nutrient losses and acidification caused by exterior source acid is one of the global environmental problems that human being is facing with. Acid precipitation can destroy forest, reduce crop output, even harm to animal and human being. Soil, as the hub of terrestrial ecosystems plays an important role in buffering the impacts of acid precipitation on environment (Miller and Watmough 2009). Because of this buffering capacity, the change of soil pH is not easily perceptible (Jönsson *et al.* 2003) in a short time, which protects the waters and ecosystems (Miller and Watmough 2009). However, permanent acid input will inevitably cause soil acidification and irreversible damages (Stevens *et al.* 2009).The objective of this study was to ascertain (1) the acid rain intensity and sources of H^+ in the subtropical forest watershed; (2) the effects of H^+ on soil and ecosystem; (3) soil acid buffering function and soil acidification trend in the granite area under the acid precipitation, which can provide a reasonable foundation for the management of soil resource and evaluation of soil environment risk.

Methods

The study area and sampling program

The study area, Fengxingzhuang (FXZ) watershed, has an area of 359 ha and is located in the southern Anhui Province in subtropical China. It is a forested watershed with the forest age of about 30 years old. The wet and dry precipitation as well as stream water was monitored from Mar. 2007 to Feb. 2009 in the FXZ watershed. The weather station and an automated sensing wet/dry precipitation collector were installed near the outlet of the watershed. An automatic stream water collector, ISCO6712, with a sensor to measure water level was installed indoors near the flume site. The flow volume (L/s) was automatically transformed by the instrument software based on the detected flow depth and the normative flume dimensions. Water samples (1000 ml each) were collected automatically by the instrument every week and with also extra samples during the rain events. Typical soil samples were collected on the top of mountain, hillside and piedmont respectively in the watershed. The fresh granite rock samples were also sampled from the watershed.

Chemical analysis

Water samples were analyzed as soon as possible when returning to the laboratory. Water pH, NH_4^+-N, NO_3^--N, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, Si and Al were determined. Soil samples were tested with bulk density, grain size distribution, cation exchange capacity, exchangeable cations (K^+, Na^+, Ca^{2+}, Mg^{2+}), exchangeable acidity, noncrystalline Fe and Al oxides, and free Fe and Al oxides. The total contents of K, Na, Ca, Mg, Fe, Al, Si of soil and rock samples were also determined.

Results and discussion

pH of wet precipitation and stream water and H^+ flux

The pH of wet precipitation, mainly rain, varies from 3.66 to 5.80 during the monitored period (Figure 1). The frequency of acid rain (pH<5.6) is 98% of the total rainfall events. However, pH of all stream samples in the watershed is higher than that of rain, which is from 6.44 to 7.68, with a mean of 6.93.

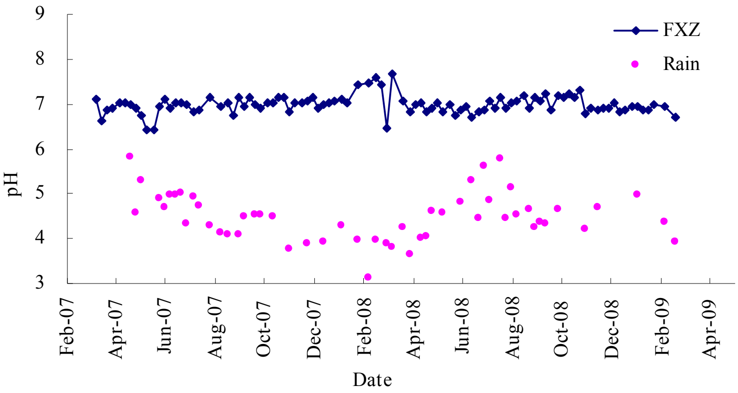


Figure 1. Dynamic changes of pH in rain and stream water from FXZ watershed during the monitored period from Mar. 2007 to Feb. 2009

The flux of H^+ by direct wet precipitation is 806 mol/ha/yr. The output of H^+ is very little, less than 1/ha/yr (Table 1). Both $SO_4^{2-}$and NO_3^- contents significantly correlates with H^+ content, which shows that the air pollution in the mountainous region of southern Anhui Province is characterized by a combination of NO_x pollution from local agricultural activities and distant SO_2 pollution transported by the atmosphere from modern industry.

Table 1. Input and output (mol/ha/yr) of some ions in wet precipitation, dry deposition and stream water

	H^+	NH_4^+	NO_3^-	S	K^+	Na^+	Ca^{2+}	Mg^{2+}	Al^{3+}	SiO_2
	mol /ha/yr									
Wet precipitation	806	670	527	628[a]	121	293	468	71	47	23
Dry deposition	ND	ND	ND	125[b]	73	45	160	63	154	ND
Stream	0.86	68	316	417	153	1510	849	262	5	1835
Net input/output	805	602	211	336	41	-1172	-221	-128	196	-1812

[a] S from wet precipitation as the form of SO_4^{2-}; [b] S from dry deposition as the form of SO_2; ND, not determined; – for net output of some elements

H^+ flux from nitrogen transformations

The content of NH_4^+ in the stream water is lower than that in wet precipitation, while the content of NO_3^- in the stream water is higher than that of wet precipitation. The total inorganic nitrogen content in the wet precipitation is higher than that in the stream water. The net input of total inorganic nitrogen is 813 mol/ha/yr in the watershed (Table 1). As for the undisturbed conifer ecosystems, the denitrification rates range from <0.01 to 0.45 g N/m^2/yr (Chen *et al.* 2000; Beier *et al.* 2001; Horvath *et al.* 2006), i.e. <7~321 mol N/ha/yr. So if taking the loss of denitrification into account, the net input of N is 492 mol/ha/yr. From this point, the forest watershed in subtropical China is still the sink of N at present.

Table 1 shows that NH_4^+ is the dominant form of inorganic nitrogen input, while NO_3^- is the dominant form of that input. The main reason is that soil colloids generally have negative charges, so easy to adsorb cations rather than anions (Zhu and Wen 1992). When NH_4^+ enters into soil, it can be adsorbed easily by soil colloids. Meanwhile the adsorbed NH_4^+ tends to be nitrified. Nitrogen transformation processes are extremely important in regulating the H^+ cycle. According to van Breemen *et al.* (1984), the actual acid-producing rate resulting from N transformations can thus be quantified by balancing the input of NH_4^+ (H^+ source) and NO_3^- (H^+ sink) verse the output on an annual basis.

$$H^+ \text{ production} = (NH_4^+{}_{(in)} - NH_4^+{}_{(out)}) - (NO_3^-{}_{(in)} - NO_3^-{}_{(out)}) \qquad (1)$$

Where $_{(in)}$ denotes the input from wet precipitation and $_{(out)}$ denotes the output by stream water. Calculated from this formula, H^+ production rate due to N transformation is 391 mol/ha/yr in the watershed (Table 2).

Table 2. Mean annual H^+ fluxes (mol/ha/yr) of key H^+ production/consumption processes at the watershed

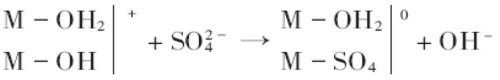
Source	H^+_{rain}	H^+_N	H^+_{SO2}	H^+_{SO4}	H^+_{BC}
H^+ production /consumption (mol/ha/yr)	805	391	250	-34	-1870

H_{rain}= net H^+ input from rainfall; H^+_N = net H^+ production/consumption due to nitrogen transformations; H^+_{SO2} = net H^+ production/consumption due to SO_2 transformations; H^+_{SO4} = net H^+ production/consumption due to SO_4^{2-} specific adsorption; BC= net H^+ production/consumption associated with base cation flux (weathering + ion exchange);– implies H^+ consumption.

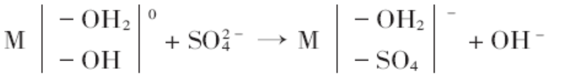
H^+ flux from sulphur transformations

The input of SO_4^{2-} through wet precipitation is 581 mol/ha/yr, while SO_2 input as the major form of sulphur (S) in dry deposition is 125 mol/ha/yr. The output of SO_4^{2-} through stream water in the FXZ watershed is 417 mol/ha/yr, less than the input of S through wet and dry deposition, showing a net sink of S in the watershed (Table 1).The adsorption and transformation of SO_2 and SO_4^{2-} in soil also involves the production and consumption of H^+. SO_2 gets rapidly oxidized into SO_4^{2-} when enters into soil system and by which double molar of H^+ is produced for every molar of SO_4^{2-}. Because the dry deposition is mainly SO_2, the production of H^+ is about 250 mol/ha/yr by SO_2 transformation (Table 2).

The adsorption and transformation of SO_4^{2-} in soil is rather complex and involves a so-called specific adsorption mechanism by positively charged oxides colloids. The complexation and exchange of SO_4^{2-} on the surface of oxides has the following general ways (Parfitt 1980):



$$\left.\begin{matrix} M-OH_2 \\ M-OH \end{matrix}\right|^{+} + SO_4^{2-} \rightarrow \left.\begin{matrix} M-OH_2 \\ M-SO_4 \end{matrix}\right|^{0} + OH^-$$



$$M\left|\begin{matrix} -OH_2 \\ -OH \end{matrix}\right|^{0} + SO_4^{2-} \rightarrow M\left|\begin{matrix} -OH_2 \\ -SO_4 \end{matrix}\right|^{-} + OH^-$$

Therefore, when the input of hydrogen ion is relatively low, the complexation exchange of SO_4^{2-} with surface hydroxyl group leads to the release of hydroxyl which can buffer soil acidity by the reaction with H^+. Many studies showed that the apparent ratio of the OH^- release and the SO_4^{2-} adsorption is about 0.10~0.22 (Yu *et al.* 1996), not exactly following the 1:1 ratio. Taking the reality of the low soil oxide content of the area, the current study uses the OH^-/ SO_4^{2-} ratio of 0.10 for further calculation. It is estimated that the production of OH^- by the specific adsorption of SO_4^{2-} is about 34 mol/ha/yr, which in turn can consume 34 mol/ha/yr of H^+ in the watershed.

Flux of base cation and H^+ consumption

The content of K^+, Na^+, Ca^{2+}, Mg^{2+} in the stream water from the watershed are generally higher than that in wet precipitation, respectively. The net output of base cations are 1870 mol (p+)/ha/yr in the watershed (Table 1), which come from mineral weathering and cation exchange. Data in Table 2 shows there is a slight imbalance of H^+ with more consumption in soil than input, as dry deposition N is not measured currently. Generally dry deposition of N accounts for 25% to 30% that of wet deposition (Zeller *et al.* 2000). Of course, acid organic exudates in soil contribute a small amount of H^+ too (Forsius *et al.* 2005).

The molar ratio of total base elements (K, Na, Ca, Mg) to that of Si in the parent rock is averaged 0.204 in the watershed. If the rock is weathered completely, one can have such a hypothesis that release of base cations and the release of Si are proportional (1:5). As the hydrolysis of silicates is the predominant SiO_2 source, the release of base cations by silicates weathering can be estimated then. In the study, the net output of Si is 1812 mol/ha/yr (Table 2), so the base cation release in this way should be 362 mol/ha/yr (Table 3) that is about 19% of the net output of base cations. According to this proportion (19%), the H^+ consumption from weathering is about 268 mol/ha/yr to the total net input of H^+ is 1412 mol/ha/yr, while cation exchange is estimated about 1144 mol/ha/yr, accounting for 81% of total net input H^+. Weathering of primary minerals consumes directly H^+ and should not lead to soil acidification, while cation exchange would lead to soil acidification by exporting base cations. H^+ exchange will eventually lower the base cation saturation degree and the buffering capacity to acid addition. Accordingly, the soil acidification rate caused by direct and secondary H^+ addition is calculated as 1144 mol/ha/yr.

Table 3. SiO$_2$, base cation net output and H$^+$ consumption (mol (p+)/ha/yr) and the percentage (%) from rock weathering and cation exchange

SiO$_2$ net output	Base cation net output 1870		H$^+$ net consumption 1412	
1812	Contribution from silicate weathering	Contribution from cation exchange	Contribution from silicate weathering	Contribution from cation exchange
	362 (19 %)	1508 (81 %)	268 (19%)	1144 (81%)

Conclusion

Although the studied forested watershed is far from urban environment, acid precipitation is frequent and has a strong acidity, as affected equally by long distance source of SO$_2$ and the local agricultural NO$_x$ contribution. The watershed, as a typical forest ecosystem in subtropical China, is a net sink for both N and S. Atmospheric deposition adds H$^+$ to the forest ecosystem directly and through the transformation of the deposited ammonium and SO$_2$ indirectly. The transformation of ammonium contributes 27% of the total H$^+$ input, and the dry deposition of SO$_2$ contributes about 17%. The input of SO$_4^{2-}$ is supposed to consume H$^+$ by its specific adsorption but the contribution is only 2.4%. The total net input of H$^+$ to the watershed by dry and wet deposition is 1412 mol/ha/yr. If the weathering of soil minerals is taken into consideration, the acidification rate of the soils would be about 1144 mol/ha/yr.

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