

Water chemistry in forested acid sensitive sites in sub-tropical Asia receiving acid rain and alkaline dust

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Abstract

Acid rain, due to wet and dry deposition of S and N compounds, is an increasing environmental problem in China. A considerable deposition of alkaline dust serves to mitigate the acidifying effect to varying extent. Data from 3 years, a monitoring of water chemistry in 10 water compartments (i.e., two qualities of deposition, two types of throughfall, solution in five genetic soil horizons, and runoff) at five well documented sub-tropical forested catchments, have been interpreted in order to identify key processes governing the water chemistry in catchments suffering acid rain. This study of water chemistry in regions with sub-tropical climate supplements similar monitoring studies conducted in temperate regions with different types of soils and compositions of deposition. Natural organic acids as well as nutrient cycling of K^+ have strong influence on the water chemistry in throughfall and upper soil horizons at the relatively pristine sites. At sites receiving elevated S and N deposition an accelerated cycling of K^+ removes much of the mineral acidity in throughfall. The soil uptake of this K^+ results in release of H^+ . Nitrification and/or assimilation of a substantial deposition of reduced N contributes at some sites also significantly to the acidity in the soils. During the study period, Ca^{2+} in solution was exchanged for Al^{3+} in the soils with an effective base saturation less than 20%. In deeper soil horizons most of this mobilized Al is re-adsorbed along with SO_4^{2-} .

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1. Introduction

In eastern China, the deposition of S (above $10 \text{ g m}^{-2} \text{ a}^{-1}$ in several sites; Hao et al., 2001; Li and Gao, 2002; Wang et al., 2004) is similar to or even

higher than that which was deposited during the 1980s in the “Black Triangle” of Europe (Seip et al., 1999). Furthermore, deposition of reduced and oxidized N is in some areas found to be as important as S compounds in terms of acidification potential (Larssen et al., 2001; Duan et al., 2004; Vogt et al., 2006). Substantial deposition also of the alkaline dust manages to neutralize most of the acidity in the SO_2 control

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Fig. 1. Map of China with the location of IMPACTS sites marked with black circles. China's two control zones for SO₂ (black dots) and acid rain (grey) are also shown (modified from Hao et al., 2001).

zone in eastern China (Hao et al., 2001) (Fig. 1). Also in the acid rain control zone, located mainly south of the Yangtze river, alkaline dust serves to mitigate much of the acidifying potential of the anthropogenic deposition (Zhu et al., 2004; Larssen and Carmichael, 2000; Rodhe et al., 2002). Dry deposition is often similar or even greater than the wet deposition (Larssen et al., 2006; Wang et al., 2004).

Understanding which processes govern the changes in concentration of major chemical constituents in different water compartments in the catchment is a prerequisite for the adaptation and development of acid rain prediction models. The IMPACTS project ran five monitoring sites set up for truly multidisciplinary studies of these processes and the ecological impact of acid rain and alkaline

dust in China (Tang et al., 2001; Larssen et al., 2006). The sites are all forested catchments with soils ranging from moderate to strongly acidic. The total deposition of S and N, as well as alkaline dust, varies considerably between the sites (Table 1).

At each site, climate, air quality, and water chemistry in 10 water compartments (i.e., wet-only- and bulk precipitation, canopy- and ground vegetation throughfall, litterfall layer, A-, B-, BC- and C soil horizons as well as in runoff) were monitored. Chemical properties of the soils were determined at 50 plots in each site. Soil mineralogy was determined on 7–10 samples from each site. The presented data are from the years 2001 to 2003. For further details see IMPACTS (2004).

This presentation utilizes the unique data on water and soil chemistry generated by the IMPACTS monitoring programme to give an overall assessment of the key processes controlling the water chemistry as water passes through 5 sub-tropical forested watersheds receiving different loadings of acid rain and alkaline dust. This general analysis is aimed at broadening our perspective based on similar monitoring studies conducted in very different environments, especially in regards to climate (sub-tropical), morphology (e.g., older soils) and composition of the deposition. The study serves also to augment other more specific process studies based on data from these monitoring sites. (E.g., Aas et al. (2007) on atmospheric deposition, Larssen and Carmichael (2000) on alkaline dust, Vogt et al. (2006) on acidifying potential, Chen et al. (2004) and Larssen et al. (2001) on N processes, Guo

Table 1

Catchment area, annual amount of precipitation, annual inputs of S, N and Ca²⁺ in ground vegetation throughfall deposition, as well as average soil pH_{H2O}, effective base saturation (BS) and C/N ratio in soils at the five catchments, i.e., Tieshanping (TSP), Caijiatang (CJT), Luchongguan (LCG), Liuxihe (LXH) and Leigongshan (LGS)

| Site | Area (ha) | Precip. amount (mm a ⁻¹) | pH | Total deposition | | | Bedrock | Soil quality | | | |
|------|-----------|--------------------------------------|-----|--|--|---|-----------------|--------------|------------------|-----------|--------|
| | | | | S (g m ⁻² a ⁻¹) | N (g m ⁻² a ⁻¹) | Ca (g m ⁻² a ⁻¹) | | Horizon | Depth limit (cm) | Soil (pH) | BS (%) |
| TSP | 16.3 | 1363 | 4.1 | 16 | 4.0 | 11 | Sandstone | A | 2/5 | 3.5 | 26 |
| | | | | | | | | B | 30/60 | 3.8 | 9 |
| LCG | 6.8 | 851 | 4.6 | 5.5 | 0.6 | 4.5 | Sandstone | A | 2/5 | 3.6 | 33 |
| | | | | | | | | B | 20/60 | 4.0 | 14 |
| CJT | 4.2 | 1404 | 4.4 | 7.6 | 4.1 | 7.3 | Sandstone/shale | A | 1/2.5 | 3.8 | 38 |
| | | | | | | | | B | 30/60 | 4.0 | 16 |
| LXH | 261 | 1437 | 4.4 | 3.5 | 1.4 | 2.6 | Granite | A | 8/12 | 4.0 | 17 |
| | | | | | | | | B | 20/50 | 4.1 | 9 |
| LGS | 6.0 | 1788 | 4.8 | 1.6 | 0.8 | 2.0 | Shale | A | 2.5/12 | 3.9 | 46 |
| | | | | | | | | B | 40/60 | 4.3 | 31 |

Total deposition values are for 2002 and 2003 and are based on ground vegetation throughfall (IMPACTS, 2004).

et al. (2004) and Larssen et al. (1999) on Al control, and Larssen et al. (2000) on acid rain models).

2. Materials and methods

2.1. Site descriptions (IMPACTS, 2004)

All IMPACTS monitoring sites are located within the acid rain control zone in south-eastern China (Fig. 1) and are acid sensitive eco-systems (i.e., forested catchments lacking limestone bedrock). Soil types in the sites are Yellow soils (Chinese classification system) or Acrisol (according to FAO classification system). The overall average effective base saturation (BS) at each site spanned from 44% in Leigongshan (LGS) to 13% in Liuxihe (LXH). BS decreased with soil depth within the top 50 cm, especially at the sites receiving high loadings of alkaline dust (i.e., Tieshanping (TSP), Caijiatang (CJT) and Luchongguan (LCG)). Parent material is sedimentary bedrock, as sandstone and shale, except for the LXH site, where there is granite (Table 1). The soils are loamy and are dominated by secondary minerals. Kaolinite constitutes between 25% (at CJT) and 81% (at LCG) of the clay minerals at the sites, followed by illite accounting for between 18% (LCG) and 69% (CJT) of the clay mass (unpublished data; IMPACTS, 2004).

The deposition of S and N at the sites differed from very high to relatively low (Table 1). Furthermore, the amount of alkaline dust (e.g., Ca^{2+}) deposited at the sites varied considerably. Reduced N (NH_4^+) showed higher concentrations than oxidized N (NO_3^-) at TSP, CJT and LXH. The TSP (104°41'E, 29°38'N) (16 ha) site is located on a sandstone ridge 25 km outside the large metropolitan Chongqing city. Soils $\text{pH}_{\text{H}_2\text{O}}$ and BS are amongst the lowest of the sites (Table 1). The B-horizon has a high content of adsorbed SO_4^{2-} ($3.7 \text{ mmol SO}_4^{2-} \text{ kg}^{-1}$) due to a presumed high anion exchange capacity facilitated by the low soil pH; i.e., below the point of zero charge (pzc) of kaolinite. The CJT (112°26'E, 27°55'N) catchment (4.2 ha) lies in an agricultural region in the SW of Hunan province. The shale bedrock at CJT probably contains some carbonates allowing for minor amounts (1–3%) of calcite to be found in the sand fraction in a few of the soil horizons at two of the four soil plots (unpublished data; IMPACTS, 2004). The LCG (106°43'E, 26°38'N) (7.0 ha) catchment is situated in the suburbs of Guiyang, the capital of the less developed Guizhou province. LXH (133°35'E,

23°33'N) is a large watershed (261 ha) positioned 80 km inland of the coastal city Guangzhou, capital of the southernmost Guangdong province. Since parent material is granite the soil mineralogy differs from the other sites. The LGS (108°11'E, 26°22'N) catchment (6 ha) is located in a rural mountain region far-east in the Guizhou province at 1630 m to 1735 m a.s.l. There is more calcite (0.6–5.7 w/w%) in the soils at this site than in CJT causing the soil $\text{pH}_{\text{H}_2\text{O}}$ and BS to be the highest among the studied sites (Table 1).

2.2. Methods

Water sampling frequency differed from weekly for deposition and runoff to 4-weekly bulked samples for throughfall and soil solution. The number of sampling stations at each site varied from 1 for precipitation (wet only and bulk), 16 for canopy throughfall, between 12 and 24 ground vegetation throughfall collectors, and between 19 and 33 soil solution collectors. Soil solution was sampled gravimetrically under the litterfall and by suction through ceramic cups (CeramTec) in the mineral soil horizons. See IMPACTS (2004) for further details. The concentrations of major cations and anions (i.e., Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , tot-F) were analyzed by means of ion chromatography (DIONEX), the amount of dissolved organic C was estimated based on UV absorbency and alkalinity was determined on samples with pH above 5 by titration to pH 4.5. The fraction of inorganic labile Al species (Al_i) was determined in samples with pH below 5.5 by means of a combined complex binder and ion exchange technique (i.e., the Barnes/Driscoll procedure; Sullivan et al., 1987). Analytical methods are described in more detail in IMPACTS (2004). Aluminium ion concentration on an equivalent basis (Al_{eqv}), as well as free (i.e., not bound to Al) SO_4^{2-} and F^- , were computed based on the inorganic labile Al fraction (Al_i) using the speciation software ALCHEMY (Schecher and Driscoll, 1987). Charge by organic anions (A^-) was calculated using Oliver's model (Oliver et al., 1983) based on DOC and pH and using $5.5 \mu\text{eq mg C}^{-1}$ as density of acidic functional groups on DOC (Henriksen and Seip, 1980). Bicarbonate concentration was calculated as the difference between the reported alkalinity and A^- that are protonated down to pH 4.5 according to Oliver's model. The water chemistry of wet-only- and bulk precipitation, canopy- and ground vegetation

throughfall and litterfall solution are all volume weighted values, while the rest are average values.

3. Results

The composition of major anions and cations in the water compartments is shown in Fig. 2. The ionic strength in the water increases through the vegetation layer, reaching exceptionally high levels in the litterfall solution in LCG, LXH and LGS (Fig. 3). Ammonium or Ca^{2+} dominated in wet-only precipitation while Ca^{2+} was ubiquitously the dominating cation in bulk precipitation. Concentrations of K^+ , Mg^{2+} and organic anions (A^-) increased and NH_4^+ decreased through the vegetation cover. Sites with heavy anthropogenic loading also showed a relative increase in concentrations of Ca^{2+} into the litterfall solution. Potassium and A^- decreased again through the rooting zone (i.e., A- and B-horizons). Likewise, NH_4^+ concentration dropped to close to detection limit levels upon entering the A-horizon (except at LXH). The relative anion charge contribution by NO_3^- increased into the litterfall solution. Hydrogen ion from the assimilation of K^+ and NH_4^+ , nitrification and formation of metal-organic complexes was mainly exchanged for Al_i at sites with BS in the mineral soil less than 20% (LXH, TSP and LCG) (see Fig. 4). The molar effect ratio ($R_{\text{CL}} = \text{Al}_i / (\text{Ca}^{2+} + \text{Mg}^{2+})$) increased therefore down through the rooting zone at these sites (cf. Fig. 4).

From the C horizon into the stream ionic strength at TSP and CJT dropped by more than 60% (Fig. 3). At LXH and LGS a less pronounced decline was found upon entering the deepest soil horizon. These declines are mainly due to loss of Al_{eqv} and SO_4^{2-} from solution. Therefore, there is also a coinciding decrease in mineral acidity and R_{CL} from the C horizon into the stream. The ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$ increased upon entering the stream (except LXH). Furthermore, the highest pH and highest relative importance of Na^+ charge were found in the streams (except at LCG).

The TSP site received large amounts of both wet and dry depositions; making the total deposition of both S and N the highest among the monitoring sites (Table 1). Water passing through the site had high ionic strengths (Fig. 3) and average pH varied only between 3.8 and 4.2, except for stream water which had a pH of 4.7. The dominant anion was free SO_4^{2-} . The major cation varied; NH_4^+ dominated in the wet-only precipitation, Ca^{2+} prevailed

in the water compartments down to the A-horizon and in deeper soil layers the Al_{eqv} charge became dominant (Fig. 2). R_{CL} well above unity was common in the C-horizon at TSP (Fig. 4).

The deposited N at CJT is mainly in its reduced form, likely due to local agricultural activity. Calcium was the major cation in all water compartments, except in the wet-only precipitation where NH_4^+ accounted for 41%. Sulphate was the dominating anion in all water compartments, except for the stream water where HCO_3^- made up half of the anionic charge. pH and Ca^{2+} concentration showed a strong increase from wet-only precipitation to ground vegetation throughfall. Between ground vegetation throughfall and A-horizon the relative anionic charge contribution by NO_3^- more than doubled (Fig. 2). At this site, with traces of calcite in the soil and probably some carbonates in the sedimentary bedrock, the amount of Al_{eqv} increased only slightly down through the soil layers and in the stream water the pH was close to neutral.

There are numerous large atmospheric emission sources in the proximity of the LCG site, likely contributing significantly to the high wet and dry deposition of S as well as of alkaline dust (e.g., CaCO_3 and CaO) (Table 1). A distinctive characteristic of the LCG site is the clear dominance of Ca^{2+} and free SO_4^{2-} in all the water compartments (Fig. 2). Relatively high NH_4^+ concentration in precipitation along with a substantial alkaline dust deposition resulted in relatively high pH values in precipitation and ground vegetation throughfall. A substantial amount of Al_{eqv} was released from the soil at this site ($266 \mu\text{eq l}^{-1}$ in the BC-horizon). Further down through the soil and into the stream the concentration of Al_{eqv} decreased though a significant amount of Al_i was still found in the acidic stream water (pH 4.4).

The deposition of alkaline dust at LXH was low compared to the deposition of strong mineral acid anions. Deposition of both oxidized and reduced N is somewhat high relative to comparably low S deposition (Table 1). A high Cl^- concentration at LXH is due to its close proximity to the ocean. The dominant anion and cation differed between the various water compartments (Fig. 2). Potassium accounted for 62% of cation charge in the canopy throughfall and significant amount of both K^+ and NH_4^+ were leached out into the stream. R_{CL} was comparable to the high values found at TSP (Fig. 4), receiving considerably more S and N deposition, though far less alkaline dust (Table 1).

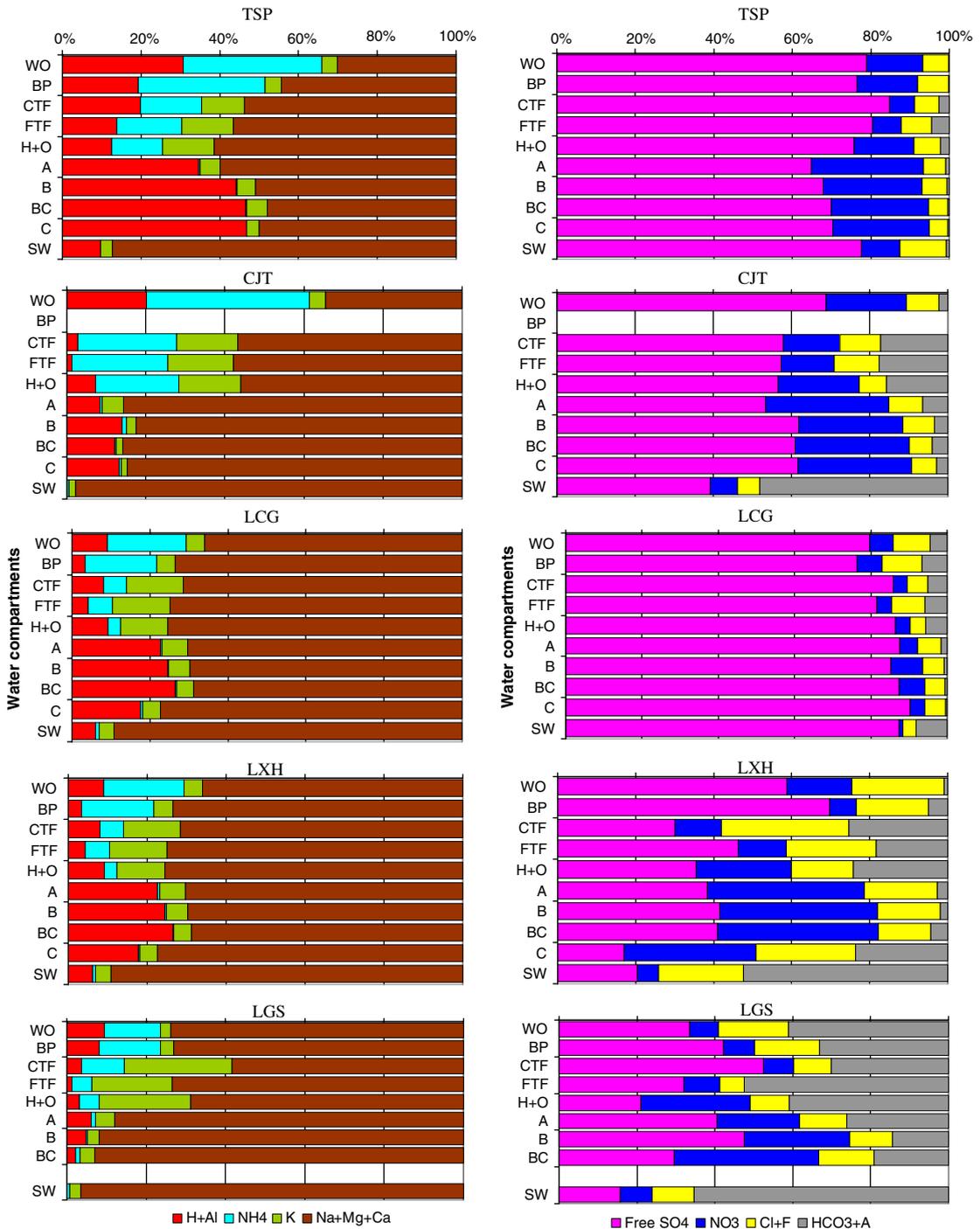


Fig. 2. Composition of major cations and anions in the 10 water compartments at the five IMPACTS sites for 2001–2003. Left graphs show cations, right graphs show anions. Wet-only precipitation (WO), bulk precipitation (BP), canopy throughfall (CTF), ground vegetation throughfall (FTF), volume weighted litterfall (H + O) solutions, and stream water (SW).

Due to an absence of local emission sources at LGS this site received the lowest total deposition of S and N among the sites. However, the loading is nevertheless similar to the deposition encountered

in southernmost Norway (Aas et al., 2004), which has caused detrimental effects on freshwater ecosystems (Overrein et al., 1980). Weak acids and base nutrients were important driving forces at this still

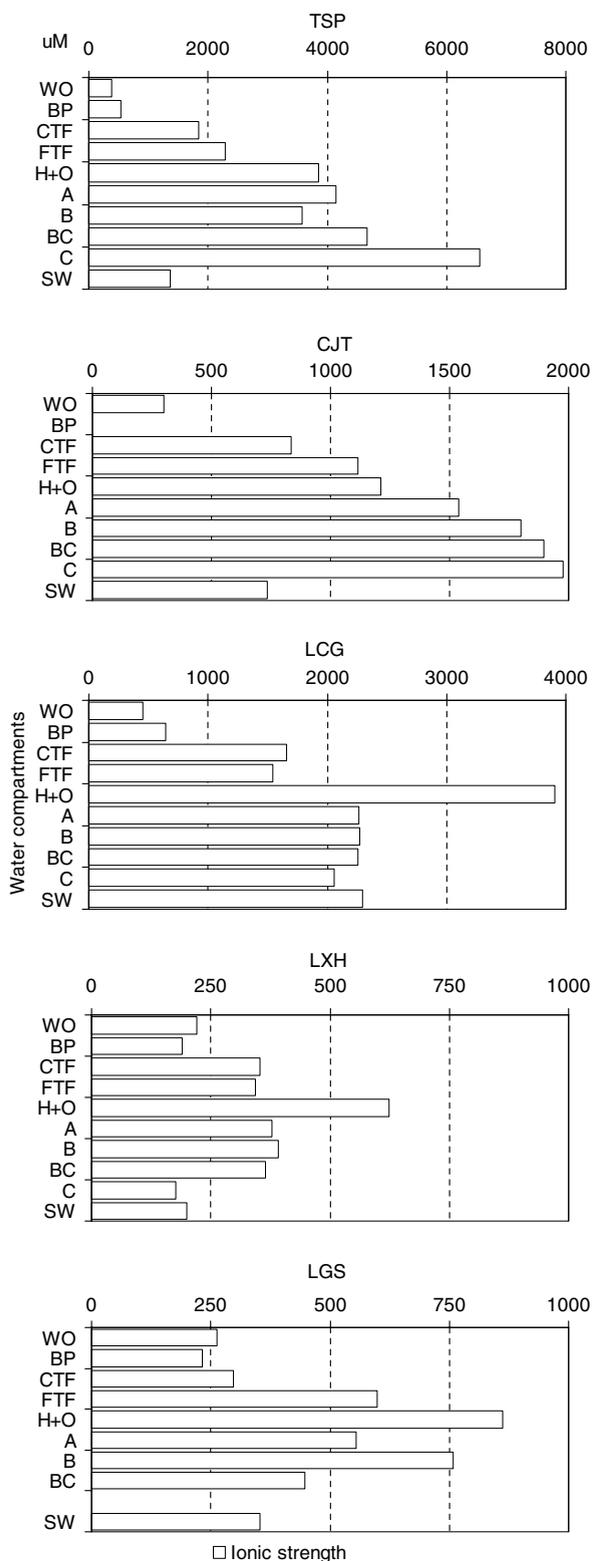


Fig. 3. Ionic strength (I) in the 10 water compartments at the five IMPACTS sites for 2001–2003.

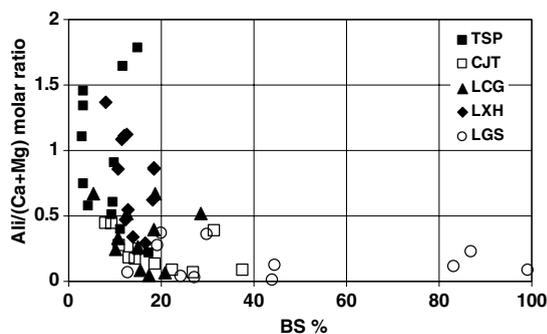


Fig. 4. Median molar effect ratio ($Al_i/(Ca + Mg)$) as a function of base saturation ($BS = (\text{exchangeable } Ca + Mg + Na + K) / CEC_E$) of the soil. Note that only effect ratios in samples collected from soils with known BS are used in this graph.

relatively pristine site; HCO_3^- dominated the anionic charge in wet-only precipitation, ground vegetation throughfall, and stream water, while A^- accounted for 25% of the anionic charge in the litterfall solution. The major cation in all the water compartments was Ca^{2+} , followed by K^+ in throughfall and litterfall. pH at LGS remained above 4.8 in all the water compartments of the watershed. Only a small amount of Al_{eqv} was able to be mobilized in A- and B-horizon, where soil solution pH was close to 5.

4. Discussion

4.1. Chemistry changes in deposition through the vegetation cover

Increase in ionic strength through the vegetation cover and into the litterfall solution (Fig. 3) was mainly due to dry deposition and evaporation as well as mineralization of organic matter in the litterfall. Evaporation in the litterfall compartments at LCG, LXH and LGS were likely somewhat enhanced by the sampling procedure. The cause for this is believed to be that some water is retained in the sampling equipment, thereby enhancing evaporation.

The difference between H^+ and the sum of SO_4^{2-} and NO_3^- in deposition varied greatly among the sites. For example in wet-only precipitation this difference ranged from 206 to $51 \mu\text{eq l}^{-1}$ in the following site sequence: $LCG > TSP > CJT \gg LXH > LGS$. This was mainly due to the acid neutralizing effect of the alkaline (basic) dust and NH_3 (Larsen and Carmichael, 2000). The importance of alkaline dust was also demonstrated by the high Ca^{2+}

loading at the TSP, LCG and CJT sites (Table 1). Furthermore, the considerable N deposition in China is mainly in the form of reduced N (Galloway et al., 1987; Chen et al., 2004) due to the omnipresence of intensive agriculture.

Elevated concentrations of K^+ in throughfall and litterfall solution due to leaching from vegetation by anthropogenic H^+ (Hosobuchi and Hatano, 1999; Johnson et al., 1985; Horntvedt et al., 1980) was evident at all sites. This increased bio cycling is likely to consume energy and induce stress on the plants. One may hypothesize that this contributes to the weakening of the trees and thereby is a contributing factor to the observed severe defoliation at TSP and LCG (Wang et al., 2007). A minor leaching also of Mg^{2+} was seen as a slight increase in the ratio of Mg^{2+} over Ca^{2+} from bulk precipitation down to the litterfall horizon at all sites, despite the large dust source of Ca^{2+} . This leaching of base cations in exchange for H^+ contributed significantly to an increase in pH through the vegetation cover at the more pristine sites (i.e., LGS and LXH). At TSP and LCG the overall effect of high deposition of alkaline dust and increased leaching especially of K^+ was overshadowed by the acidifying impact of dry deposited S and oxidized N (i.e., producing mineral acidity) along with NH_4^+ assimilation, causing a decrease in pH through the vegetation cover. Apparently NH_4^+ assimilation is especially important at LCG, since the pH drops from precipitation into the canopy throughfall despite considerable deposition of alkaline dust. At CJT the neutralizing effect of an overall more pronounced deposition of alkaline dust than of total S- and N deposition, causes the volume weighted pH to continue to increase through the canopy and into the ground vegetation throughfall solution. The LXH site appears to be N saturated (see below) allowing the relative cationic charge by NH_4^+ to be the same in the wet-only precipitation as in the ground vegetation throughfall and litterfall solution.

Weak natural organic acids (HA) had an acidifying effect, especially in the litterfall solution at the rather pristine LGS site. This was clearly demonstrated by the relatively low pH in litterfall solution at LGS, along with a high concentration of A^- . At sites receiving a high load of acid rain and alkaline dust, the anions of the weak organic acids are however protonated by strong mineral acids and/or bound to polyvalent cations. The contribution of A^- to the anionic charge in litterfall was therefore less than 7% at TSP and LCG, while at the more

pristine LGS and LXH sites the A^- accounted for as much as 33 and 25% of the anionic charge, respectively.

4.2. Chemistry changes in soil solution through the soil profile

Nitrification, which is believed to mainly take place in the litterfall solution (Vogt et al., 2006), caused the relative charge contribution by NO_3^- to increase (Fig. 2) in this horizon. The lack of a corresponding loss in NH_4^+ may be explained by the addition of NH_4^+ from mineralization of organic matter. Ammonium that escaped nitrification became assimilated as the water moved into the A-horizon. Concentrations of nutrient base cations are strongly linked to the internal bio-cycle of elements. At these sites it was mainly K^+ that was leached out (see above) and assimilated again when the water percolated into the rooting system. This assimilation caused the K^+ concentration to drop sharply upon entering the A-horizon. K-fixation, by non -1:1 type clay minerals, is not believed to make a noteworthy contribution to this decrease in the A-horizon. While a slight decrease in the K^+ concentration deeper in the soil profile (Fig. 2) may be due to K fixation by illite and smectite (Khaliquzzaman et al., 2004) as well as some additional K assimilation. At more pristine sites the significant contribution of A^- to the anionic charge in the litterfall solution decreased down through the soil profile (Fig. 2) as the organic matter became saturated with metal cations and precipitated.

Al_{eqv} is mobilized when acid soils (i.e., BS < 20%) are exposed to acid rain increasing the concentration of mobile anions (Seip, 1980). The observed increase in Al_{eqv} below the A-horizon was generated by Ca^{2+} in the solution exchanging with Al in the soil (see Guo et al., 2004) causing short-term soil alkalization. This process can be provoked by fluctuations in the water chemistry due to high deposition of Ca^{2+} and/or variation in precipitation amount. Variation in the R_{CL} ratio may be conceptually and empirically explained by the differences in BS of the soil (Fig. 4). Elevated ratios are, as generally found, limited to soils with BS less than about 20% (Reuss and Johnson, 1986); High R_{CL} at LXH, despite considerably lower deposition of acid rain than at LGC and CJT (Table 1), is probably due to the low BS caused by the igneous bedrock and less deposition of the alkaline dust.

4.3. Changes in chemistry from soil solution to surface runoff

The pH increased and the concentrations of Al_{eqv} and SO_4^{2-} decreased substantially upon entering the stream at TSP and CJT or already upon entering the deepest soil horizon at LXH and LGS (Fig. 2). A coinciding large drop in ionic strength (Fig. 3) below the rooting zone implies that precipitation or adsorption processes are important. There was a substantial net loss of SO_4^{2-} and Ca^{2+} within the TSP catchment. Most likely the main cause of this is the exchange of Ca^{2+} with Al_{eqv} in the B- and BC horizon (see above), followed by co-sorption of Al_{eqv} and SO_4^{2-} in deeper soil layers. Anion exchange capacity is high in these soils with low pH and a high content of Al oxides. A similar co-sorption was found by Vogt et al. (2001) in Polish sites with high SO_4^{2-} concentration. This sorption is stoichiometrically equivalent to formation of basic sulphates such as jurbanite (AlOHSO_4 ; avg. $\text{SI}_{\text{Jurbanite}} = 0,2 \pm 0,5$ in pH range 2.6 to 7.5) (van Breemen et al., 1983). Neutralization occurred also through weathering in the bedrock as evident from increased Na^+ (especially at TSP, LGS and LXH) and Mg^{2+} concentrations from soil- to stream water (except LXH). This increased the pH of the percolating water allowing for precipitation of gibbsite.

5. Conclusions

The main responses to acid deposition in sub-tropical forests are found to be similar to the key processes controlling the water chemistry in temperate regions. In sub-tropical forests receiving a high loading of S and N the weak organic acids are replaced by strong mineral acidity and elevated levels of mobile anions leached cations out of the soil profile. Leaching of K^+ and some Mg^{2+} from the vegetation and subsequent assimilation by the roots causes a significant reduction of the acidity in throughfall solution and a similar increase of mineral acidity in the soil solution. Ammonium nitrification, especially in the litterfall horizon, and assimilation in the rooting zone are important processes producing additional acidity in the soil solution at these catchments.

During the monitoring period ion exchange of Ca^{2+} in solution with Al in the soil appears also to contribute to soil solution acidity at these sites. A net loss of Ca^{2+} and SO_4^{2-} through the catchments is partly due to this cation exchange followed by co-sorption of Al^{3+} and SO_4^{2-} in deeper soil layers.

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References

- Aas, W., Shao, M., Jin, L., Larssen, T., Zhao, D., Xiang, R., Zhang, J., Xiao, J., Duan, L., 2007. Air concentrations and wet deposition of major inorganic ions at five non-urban sites in China, 2001–2003. *Atmos. Environ.* 41, 1706–1716.
- Aas, W., Solberg, S., Berg, T., Manø, S., Yttri, K.E., 2004. Surveillance of long-range transported air and rain. *Atmosfærisk tilførsel*, 2003. Statlig program for forurensningsovervåking. Rapport 903/2004. TA-2033/2043. OR 47/2004. ISBN: 82-425-1594-8. Available at <<http://www.nilu.no/>> (In Norwegian).
- Chen, X.Y., Mulder, J., Wang, Y.H., Zhao, D.W., Xiang, R.J., 2004. Atmospheric deposition, mineralization and leaching of nitrogen in subtropical forested catchments, south China. *Environ. Geochem. Health* 26, 179–186.
- Duan, L., Huang, Y., Hao, J., Xie, S., Hou, M., 2004. Vegetation uptake of nitrogen and base cations in China and its role in soil acidification. *Sci. Total Environ.* 330, 187–198.
- Galloway, J.N., Zhao, D., Xiong, J., Likens, G.E., 1987. Acid rain: China, United States, and a remote area. *Science* 236, 1559–1562.
- Guo, J., Vogt, R.D., Zhang, X., Zhang, Y., Seip, H.M., Tang, H., 2004. Ca–Al exchanges and aluminium mobilization in two Chinese acidic forest soils. *Environ. Geol.* 45, 1148–1153.
- Hao, J., Duan, L., Zhou, X., Fu, L., 2001. Application of a LRT model to acid rain control in China. *Environ. Sci. Technol.* 35, 3407–3415.
- Henriksen, A., Seip, H.M., 1980. Strong and weak acids in surface waters of southern Norway and southwestern Scotland. *Water Res.* 14, 809–813.
- Hornvedt, R., Dollard, G.J., Joranger, E., 1980. Atmosphere–vegetation interactions. In: Drabløs, D., Tolland, A. (Eds.), *Ecological Impacts of Acid Deposition*. SNSF Project. Johs. Grefslie Trykkeri, Mysen, Norway. 192–193.
- Hosobuchi, Y., Hatano, R., 1999. The influence of acidic deposition on the forest ecosystem and base cation cycling in the deciduous broad-leaved forest of andic regosol. *Nippon Dojo Hiriyogaku Zasshi* 70, 505–513.
- IMPACTS, 2004. Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems, Annual Report, results 2003. In: Larssen, T., Tang, D. (Eds.), NIVA Report No. 4905-2004, ISBN 82-577-4594-4.
- Johnson, D.W., Richter, D.D., Lovett, G.M., Lindberg, S.E., 1985. The effects of atmospheric deposition on potassium, calcium, and magnesium cycling in two deciduous forests. *Can. J. Forest Res.* 15, 773–782.

- Khaliqzaman, M., Moslehuddin, A.Z., Haque, Q., Egashira, K., 2004. Impact of mineralogy on fixation and release of potassium in soils from three agroecological regions of Bangladesh. *Clay Sci.* 12, 205–212.
- Larssen, T., Carmichael, G.R., 2000. Acid rain and acidification in China: The importance of base cation deposition. *Environ. Poll.* 110, 89–102.
- Larssen, T., Lydersen, E., Tang, D., He, Y., Gao, J., Liu, H., Duan, L., Seip, H.M., Vogt, R.D., Mulder, J., Shao, M., Wang, Y., Shang, H., Zhang, X., Solberg, S., Aas, W., Økland, T., Eilertsen, O., Angell, V., Liu, O., Zhao, D., Xiang, R., Xiao, J., Luo, J., 2006. Acid rain in China. *Environ. Sci. Technol.* 39, 418–425.
- Larssen, T., Mulder, J., Wang, Y., Chen, X., Xiao, J., Zhao, D., 2001. Nitrogen deposition and leaching from two forested catchments in southwest China – Preliminary data and research needs. *TheScientificWorld* [online computer file] 1.
- Larssen, T., Schnoor, J.L., Seip, H.M., Dawei, Z., 2000. Evaluation of different approaches for modeling effects of acid rain on soils in China. *Sci. Total Environ.* 246, 175–193.
- Larssen, T., Vogt, R.D., Seip, H.M., Furuberg, G., Liao, B., Xiao, J., Xiong, J., 1999. Mechanisms for aluminum release in Chinese acid forest soils. *Geoderma* 91, 65–86.
- Li, W., Gao, J., 2002. Acid deposition and integrated zoning control in China. *Environ. Manag.* 30, 169–182.
- Oliver, B.G., Thurman, E.M., Malcolm, R.L., 1983. The contribution of humic substances to the acidity of coloured natural waters. *Geochim. Cosmochim. Acta* 47, 2031–2035.
- Overrein, L., Tollan, A., Seip, H.M., 1980. Acid precipitation – Effects on forest and fish, Final report of the SNSF-project 1972–1980. Ås, Norway, SNSF project.
- Reuss, J.O., Johnson, D.W., 1986. Acid deposition and the acidification of soils and waters, *Ecological Studies* 59, Springer-Verlag.
- Rodhe, H., Dentener, F., Schulz, M., 2002. The global distribution of acidifying wet deposition. *Environ. Sci. Technol.* 36, 4382–4388.
- Schecher, W., Driscoll, C.T., 1987. An evaluation of uncertainty associated with aluminum equilibrium calculations. *Water Resour. Res.* 23, 525–535.
- Seip, H.M., 1980. Acidification of freshwaters – sources and mechanisms. In: Drabløs, D., Tolland, A. (Eds.), *Ecological Impacts of Acid Deposition*. SNSF project. Johs. Grefslie Trykkeri, Mysen, Norway, 358–365.
- Seip, H.M., Aagard, P., Angell, V., Eilertsen, O., Larssen, T., Lydersen, E., Mulder, J., Muniz, L.P., Semb, A., Tang, D.G., Vogt, R.D., Xiao, J., Xiong, J., Zhao, D., Kong, G., 1999. Acidification in China: Assessment based on studies at forested sites from Chongqing to Guangzhou. *Ambio* 28, 522–528.
- Sullivan, T.J., Christophersen, N., Hooper, R.P., Seip, H.M., Muniz, I.P., Sullivan, P.D., Vogt, R.D., 1987. Episodic variation in streamwater chemistry at Birkenes southernmost Norway: Evidence for importance of flow pathways. *Acidification and Water Pathways*, Proc. Vol. I. Norwegian National Com. for Hydrology, Box 5091 Majorstua 0301, Oslo 3 Norway, 269–279.
- Tang, D., Lydersen, E., Seip, H.M., Angell, V., Eilertsen, O., Larssen, T., Liu, X., Kong, G., Mulder, J., Semb, A., Solberg, S., Torseth, K., Vogt, R.D., Xiao, J., Zhao, D., 2001. Integrated monitoring program on acidification of Chinese terrestrial systems (IMPACTS) – A Chinese–Norwegian cooperation project. *Water Air Soil Poll.* 130, 1073–1078.
- van Breemen, N., Mulder, J., Driscoll, C.T., 1983. Acidification and alkalization of soils. *Plant Soil* 75, 283–308.
- Vogt, R.D., Seip, H.M., Larssen, T., Zhao, D., Xiang, R., Xiao, J., Luo, J., Zhao, Y., 2006. Potential acidifying capacity of deposition – experiences from regions with high NH_4^+ and dry deposition in China. *Sci. Total Environ.* 367, 394–404.
- Vogt, R.D., Seip, H.M., Orefellen, H., Skotte, G., Irgens, C., Tyszka, J., 2001. Aluminium mobility at an acid sensitive site with high S-deposition. *Water Air Soil Poll.* 130, 745–750.
- Wang, T.J., Hu, Z.Y., Xie, M., Zhang, Y., Xu, C.K., Chao, Z.H., 2004. Atmospheric sulfur deposition onto different ecosystems over China. *Environ. Geochem. Health* 26, 169–177.
- Wang, Y., Solberg, S., Yu, P., Myking, T., Vogt, R.D., Du, S., 2007. Assessments of the health of two Masson pine forests in the acid rain region in south China. *Forest Ecol. Manag.* (accepted for publication).
- Zhu, X., Duan, L., Tang, G., Hao, J., Dong, G., 2004. Estimation of atmospheric emissions of alkaline cations in China. *Qinghua Daxue Xuebao, Ziran Kexueban* 44, 1176–1179.