

Potential acidifying capacity of deposition Experiences from regions with high NH_4^+ and dry deposition in China

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Abstract

Acid rain may cause soil acidification possibly leading to indirect forest damage. Assessment of acidification potential of atmospheric deposition is problematic where dry and occult deposition is significant. Furthermore, uncertainty is enhanced where a substantial part of the potential acidity is represented by deposition of ammonium (NH_4^+) since the degree of assimilation and nitrification is not readily available.

Estimates of dry deposition based on deposition velocity are highly uncertain and the models need to be verified or calibrated by field measurements of total deposition. Total deposition may be monitored under the forest canopy. The main problem with this approach is the unknown influence of internal bio-cycling. Moreover, bio-cycling may neutralize much of the acidity by leaching of mainly K^+ . When the water percolates down into the rooting zone this K^+ is assimilated again and acidity is regenerated. Most monitoring stations only measure deposition. Lacking measurements of output flux of both NH_4^+ and NO_3^- from the soil one cannot assess current net N transformation rates. Assumptions regarding the fate of ammonium in the soil have strong influence on the estimated acid load. Assuming that all the NH_4^+ is nitrified may lead to an overestimation of the acidifying potential.

In parts of the world where dry deposition and ammonium are important special consideration of these factors must be made when assessing the acidification potential of total atmospheric loading. In China dry and occult deposition is considerable and often greater than wet deposition. Furthermore, the main part of the deposited N is in its reduced state (NH_4^+). The IMPACTS project has monitored the water chemistry as it moves through watersheds at 5 sites in China. This paper dwells at two important findings in this study. 1) Potassium leached from the canopy by acid rain is assimilated again upon entering the mineral soil. 2) Nitrification apparently mainly takes place in forest floor (H- and O-) horizon as NH_4^+ that escapes this horizon is efficiently assimilated in the A-horizon. This suggests that the potential acidification capacity of the deposition may be found

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in the throughfall and forest floor solution by treating K^+ and NH_4^+ , respectively, as acid cations in a base neutralization capacity (BNC) calculation.

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1. Introduction

Measuring the total atmospheric deposition is technically difficult in areas with high dry deposition. Dry and occult deposition constitutes a considerable part of the total atmospheric loading of sulphur (S), nitrogen (N) and calcium (Ca) in forested areas, especially in regions with seasonal droughts and close to large emission sources. Furthermore, deposition of reduced N is substantial in the vicinity of intensive farming and husbandry. This is a problem especially in south Asia and in eastern South America as well as NW Europe (Rodhe et al., 2002). In southern China dry deposition of S and N as well as alkaline dust is often larger than the wet deposition (Wang et al., 2004). Furthermore, deposition of N, which in most areas is found to be substantial, is mainly in its reduced form, i.e. as NH_4^+ (IMPACTS, 2004; Larssen et al., 2006).

Soil acidification due to acid rain (Reuss and Johnson, 1986) has in northern Europe been blamed for causing indirect forest damage (Matzner and Murach, 1995). Increased soil acidification by acid rain is most likely taking place in southern China (see Larssen and Carmichael, 2000). This ongoing soil acidification is a clear sign of a future threat towards forest ecosystems in this region.

Dry and occult deposition is commonly estimated by models based on air concentrations of SO_2 , NO_x , aerosols and particles using dry deposition velocities and wet scavenging coefficients. Such approximations are highly uncertain as they rely on assumptions regarding a battery of factors which vary considerably depending on land use, surface properties and climate. An alternative is to measure fluxes in throughfall (below tree canopy). However, there are practical problems with large spatial variation as well as varying chemical influence by internal bio-cycling. The optimum solution is therefore to verify and calibrate the models used to estimate regional acid deposition by means of data from plot scale monitoring of the solute flux in throughfall. This requires that we identify a way to correct for the effect of bio-cycling on the measured throughfall flux of solutes. Furthermore, in order to assess an adequate

acid rain abatement strategy there is a need for a generally applicable albeit simple measure of acidifying potential of the deposition. pH in precipitation, commonly used as such in China, is by no means a suitable proxy. This is mainly due to the reaction of ammonia with water to ammonium causing pH in precipitation to increase, though in the soil this ammonium generates acidity upon nitrification and/or assimilation by plants. In ecosystems that are nitrogen saturated Rodhe et al. (2002) suggested to calculate the potential acidity on an equivalent basis (i.e. $[pot. H^+]_{N-sat} = [H^+] + 2[NH_4^+]$) according to Eq. (1);

$$[pot.H^+]_{N-sat} =_{eqv} ([SO_4^{2-}] + [NO_3^-] + [NH_4^+] - [Ca^{2+}]). \quad (1)$$

This equation assumes that all ammonium is nitrified (i.e. NH_4^+ is converted to NO_3^- and $2H^+$) in addition to that all nitrate is leached from the soil. Actually some of the NH_4^+ is instead assimilated generating only $1H^+$. Furthermore, even in those sites that are N saturated some of the NO_3^- is assimilated releasing one OH^- . $[pot. H^+]_{N-sat}$ concentration multiplied by precipitation amount is therefore an upper limit of the effective loading (or flux) of H^+ to an ecosystem. Assumptions regarding the fate of reduced and oxidized N are not possible to come by as the amount of NH_4^+ that is nitrified and the amount of NO_3^- that is leached from the soil are not simple to measure and are therefore usually not available. Application of Eq. (1) also requires that $[Na^+] \approx [Cl^-]$ and that $[HCO_3^-]$, [organic anions, A^-], $[Mg^{2+}]$, $[K^+]$ are negligible. All these assumptions and requirements are clearly not met in many regions of the world as e.g. China. The approximations are even less satisfactory in throughfall, where the loading of most major anions and cations are substantial. Instead all major species must be considered in order to estimate total deposition loading. Potassium and ammonium pose a special challenge when attempting to establish a suitable measure for acidifying potential of the deposition below the forest canopy as the interpretation in terms of acidification potential of these parameters is not straightforward.

Water chemistry changes as it passes through the different water compartments in a watershed (e.g. precipitation, throughfall, soil solution and runoff). These changes are due to biogeochemical processes between vegetation or soil and the water (Vogt et al., *in press*). Understanding these processes is a prerequisite for the selection of a sound monitoring strategy and interpretation of deposition data. In 2001 a comprehensive acid rain monitoring network, including both deposition and effects, was established in China by the Sino-Norwegian multidisciplinary IMPACTS project (www.impacts.net.cn; Tang et al., 2001). The 5 monitoring sites are all forested catchments with soils ranging from moderately to strongly acidic. The deposition of S and N, as well as alkaline dust, varies considerably between the sites. Water chemistry as it passed through 10 water compartments in the watersheds was monitored on a daily to monthly basis for two or three years. We here utilize these unique data to give an assessment of key processes controlling the acidification potential as water passes through the vegetation cover and genetic soil profile horizons.

2. Materials and methods

2.1. Sampling sites

The IMPACTS monitoring sites were all located within the acid rain control zone (Hao et al., 2001) in southern China (Fig. 1). Only acid rain sensitive

ecosystems were studied; all monitoring sites are forested and with no limestone bedrock, see Table 1. Trees were planted in the 1960s, since a large part of the forest in China was logged during *The Great Leap Forward* between 1958 and 1962. The *Haplic Acrisols* (i.e. Yellow soils in the Chinese classification system) are highly weathered. Overall average base saturation (BS) at each site (incl. all soil plots and horizons) spanned from 44% to 13% (IMPACTS, 2004). These soils are representative for this part of China. Parent material is sedimentary bedrock, as sandstone and shale, except for the southernmost site (Lixihe; LXH), where there is granite. Deposition of S and N at the sites differed from high to relatively low, comprising sites with high S, though low N loading and low S, though high N loading. Dry deposition of acid oxides, alkaline dust and especially reduced N were substantial, accounting for more than half of the total loading at some sites.

TieShanPing (TSP) is a pine forest located on a sandstone ridge 25 km outside the metropolitan Chongqing city (Fig. 1). This site received highest total amounts of both wet and dry S and N among the monitoring sites (Table 1). *CaiJiaTang* (CJT) is a mixed conifer-broadleaf forest situated within an agricultural region in the southwest of Hunan province. The site receives high S and N loading. The shale bedrock at CJT hold relatively high amounts of carbonates. *LiuChongGuan* (LCG) is a pine forest in the suburb of Guiyang city, the capital of less

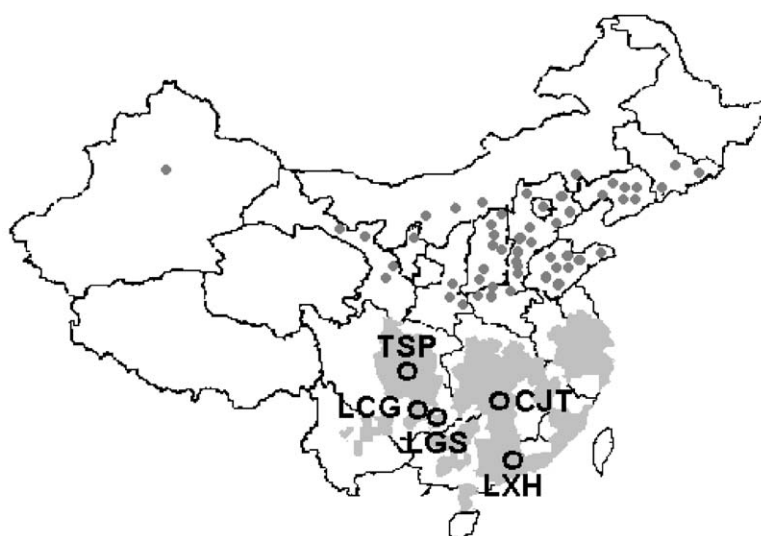


Fig. 1. Map of China with China's two control zones for SO₂ (dark dots) and acid rain (grey) (modified from Hao et al., 2001). The locations of IMPACTS sites are marked with blue circles.

Table 1

Catchment area, annual amount of precipitation, volume weighted pH, annual inputs of sulphur (S), nitrogen (N) and calcium (Ca) in ground vegetation throughfall deposition, soil pH and base saturation (BS) as well as potential acidity (PAc) in the forest floor solution and base neutralization capacity of mineral soil water at the five catchments, i.e. TieShanPing (TSP), CaiJiaTang (CJT), LuChongGuan (LCG), LiuXiHe (LXH) and LeiGongShan (LGS)

Site	Size ha	Prec mm yr ⁻¹	pH	Total deposition					Bedrock	Soil quality			BNC μeq L ⁻¹
				S	N	Ca	PAc	Dry		Horizon	pH H ₂ O	BS %	
TSP	16.3	1363	4.1	16	4.0	11	787	88	Sandstone	A	3.6	26	764
										BC	3.8	10	976
LCG	6.8	851	4.6	5.5	0.6	4.5	443	65	Sandstone	A	3.6	36	353
										BC	4.0	14	414
CJT	4.2	1404	4.4	7.6	4.1	7.3	341	82	Sandstone/shale	A	4.0	41	59
										BC	4.1	22	172
LXH	261	1437	4.4	3.5	1.4	2.6	31	48	Granite	A	4.1	17	8
										BC	4.0	9	5
LGS	6.0	1788	4.8	1.6	0.8	2.0	-51	29	Shale	A	4.0	52	-73
										BC	4.3	42	9

(IMPACTS, 2004). Estimated contribution of dry deposition to the total deposition is based on differences in Ca fluxes between ground vegetation throughfall and wet only precipitation.

developed Guizhou province. Numerous atmospheric emission sources in the proximity likely result in high wet and dry deposition of S as well as alkaline dust (e.g. CaCO₃ and CaO). *LiuXiHe* (LXH) is a subtropical broadleaved evergreen forest situated 80 km inland of coastal city Guangzhou, capitol of developed Guangdong province. This site receives a relatively high deposition of oxidized and reduced N, compared to comparably low S deposition, along with a low loading of airborne alkaline dust. Parent material is igneous plutonic granite, as apposed to sedimentary rock at the other sites. *LeiGongShan* (LGS) is a pine forest situated in a remote mountain region far-east in the Guizhou province limit at 1735 m a.s.l. Total deposition of S, N and alkaline dust in LGS are the lowest among the studied sites, but similar to the deposition of S and N encountered in southernmost Norway (Aas et al., 2004), where serious freshwater acidification with accompanying fish loss occurred. For further details see IMPACTS (2004).

2.2. Sampling and analyses

Water chemistry in 9 compartments (wet- and bulk precipitation, canopy- and ground vegetation throughfall, forest floor (H+O) layer, A-, B-, BC- and C-horizons) in the 5 watersheds are applied in this presentation. Water monitoring frequency differed from weekly for deposition and runoff to 4-weekly bulked samples for soil solution. Number of sampling stations at each site varied from 1 for precipitation (wet

only and bulk), 16 canopy throughfall, between 12 and 24 ground vegetation throughfall collectors, and between 19 and 33 soil solution collectors. See Vogt et al. (2001) for further details.

The following chemical parameters were measured: major anions and cations (i.e. Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, SO₄²⁻, NO₃⁻, Cl⁻, tot-F) by means of ion chromatography, UV absorbency and alkalinity (Vogt and Aas, 2001). In addition the fraction of inorganic labile aluminium species (Al_i) was determined in samples with pH below 5.5 according to the operationally defined Barnes/Driscoll procedure (Sullivan et al., 1987). Alkalinity was only analyzed on samples with pH higher than 5.0. The chemical laboratories participate in the EMEP intercomparison programme (Uggerud et al., 2003) and all data have passed a quality control by means of satisfactory agreement between measured and calculated conductivity as well as acceptable ion balance (Hovind, 2002). Average base saturation (BS) of the effective cation exchange capacity (CEC_E; Vogt and Mulder, 2001) of five composite soil samples was determined at three depths (A, B and BC) in twenty 100 m² plots around the soil solutions sampling spots. Prior to analysis laboratory quality was controlled in a soil analysis intercalibration study (Austnes et al., 2002). For further details confer IMPACTS (2004).

2.3. Data calculation and computational methods

Aluminium concentration on an equivalent basis (i.e. average Al charge · Al concentration = Al_{eqv}), as well as

free SO_4^{2-} and -fluoride (F^-) (i.e. not bound to Al), were computed based on Al_i using the computer speciation programme Alchemy (Schecher and Driscoll, 1987). Total organic carbon (TOC) values were derived from UV 254 nm absorbencies, using a general conversion factor established for Chinese conditions (Guo and Vogt, 2004). Charge by organic anions were calculated using the model by Oliver et al. (1983) with $5.5 \mu\text{eq mg C}^{-1}$ as density of acidic functional groups on DOC (Henriksen and Seip, 1980). The reported value for alkalinity is based on the titrated value subtracted for the amount of H^+ added in order to lower the pH to the end-point value of 4.5. The reported bicarbonate (HCO_3^-) concentration was set as the difference between the measured alkalinity and the sum of calculated organic anions (A^-) that are protonated at pH 4.5. The raw data are presented in IMPACTS (2004).

Acid Neutralizing Capacity (ANC) was calculated based on charge balance as the equivalent sum of major base cations minus the equivalent sum of major strong acid anions;

$$\text{ANC} = \sum_{\text{eqv}} (\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+, \text{NH}_4^+) - \sum_{\text{eqv}} (\text{free SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{free F}^-). \quad (2)$$

Base Neutralizing Capacity (BNC), or mineral acidity, is assessed as the negative ANC (Stumm and Morgan, 1981; Reuss and Johnson, 1986; Cosby et al., 1985). In the samples with pH above 5 the ANC is mainly accounted for by the weak acids HCO_3^- and A^- and is similar to the titrated alkalinity. In samples with pH less than 5 the acidity (BNC) is mainly constituted by $\text{Al}_{\text{eqv}} + \text{H}^+ - \text{A}^-$.

Ionic strength (I) of all the chemical constituents with concentration (C in mol L^{-1}) and with charge n is calculated as $I = 1/2 \sum (C \cdot n^2)$. Molar effect ratio is calculated as $[\text{Al}_i]/[\text{Ca} + \text{Mg}]$. Base saturation (BS) is the percentage fraction of base cations on the cation exchanger and is calculated as $(\text{Ca} + \text{Mg} + \text{Na} + \text{K})/\text{CEC}_E$.

The presented chemistry of the deposition compartments (i.e. wet only- and bulk precipitation, canopy- and ground vegetation throughfall as well as forest floor solution) are volume weighted values, while the chemistry in the remaining compartments are described by average values. Relative amount of dry deposition fluxes for K^+ and Mg^{2+} are assumed to be equal to the relative amount of dry deposition of Ca^{2+} .

For example;

$$\text{Dry dep. Mg}^{2+} = \text{Mg}^{2+} \text{ flux}_{\text{precip}} \cdot (\text{Ca}^{2+} \text{ flux}_{\text{throughfall}} - \text{Ca}^{2+} \text{ flux}_{\text{precip}}) / \text{Ca}^{2+} \text{ flux}_{\text{precip}}. \quad (3)$$

3. Results

The relative contribution of dry deposition to the total solute flux in throughfall was high at all sites and varied from 88% at TSP to 29% at LGS (Table 1). Relative and absolute ion compositions in the water compartments are shown in Fig. 2. Absolute amount of all ions, except H^+ , increased from wet only, through the forest canopy and ground vegetation layer to the forest floor solution. As often found either NH_4^+ or Ca^{2+} dominated among the cations in wet only precipitation while Ca^{2+} was ubiquitously the dominating cation in bulk precipitation. Relative amounts of K^+ and A^- increased and NH_4^+ decreased through the vegetation cover. Similarly there was an increase in the ratio of Mg^{2+} over Ca^{2+} from bulk precipitation down to the forest floor horizon at all the sites. Estimated contribution by bio-cycling to the total flux in ground vegetation throughfall of magnesium (i.e. total flux — Eq. (3)) varied considerably from 4% at CJT to 68% at LGS. For potassium estimated contribution by bio-cycling increased clearly from 15% and 51% at the heavily polluted TSP and LCG sites to 93% and 95% of the total flux in the more pristine LXH and LGS sites. The solute concentration reaches an intermittent maximum value in the O+H-horizon. Differences in BNC in precipitation and throughfall between sites were minor compared to the large dissimilarity in actual mineral acidity in the soils (Fig. 3). Relative concentrations of K^+ and A^- decreased again through the rooting zone of the mineral soil. NH_4^+ concentration dropped to close to detection limit levels in the A-horizon. The relative amount of NO_3^- decreased significantly from precipitation into the vegetation cover at TSP and CJT. In the forest floor and somewhat down through the soil profile the relative amount of nitrate generally increased to substantially higher values than what was initially found in the precipitation. Upon entering the mineral soil the mineral acidity (i.e. BNC) increased (Fig. 3). An important exception is CJT. Rather surprisingly BNC increased also down through the rooting zone (i.e. from A- to BC-horizons) (except at LXH) (Fig. 3).

Water passing through the TSP site was very acidic ($\text{pH} = 3.8\text{--}4.2$) with high ionic strengths ($I = 380\text{--}3719$). NH_4^+ was the dominant cation in the wet only precipitation, accounting for 35% of the volume weighted cationic charge (Fig. 2). Ca^{2+} dominated the

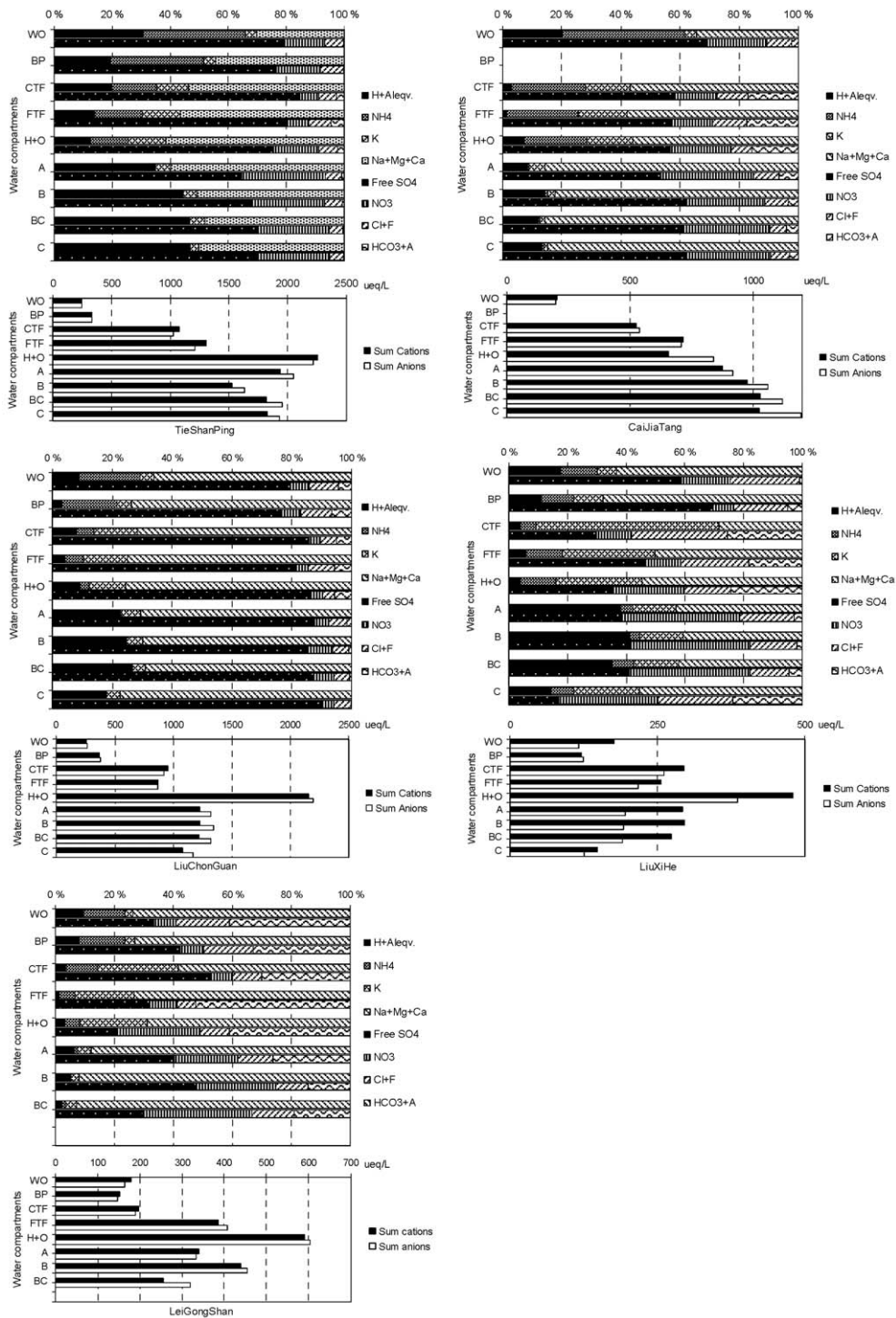


Fig. 2. Annual average concentrations at the five IMPACTS sites for 2011–2003. Upper bar shows cations, lower bar shows anions. Wet only precipitation (WO), Bulk precipitation (BP), Canopy throughfall (CTF) and Ground vegetation throughfall (FTF) are volume weighted.

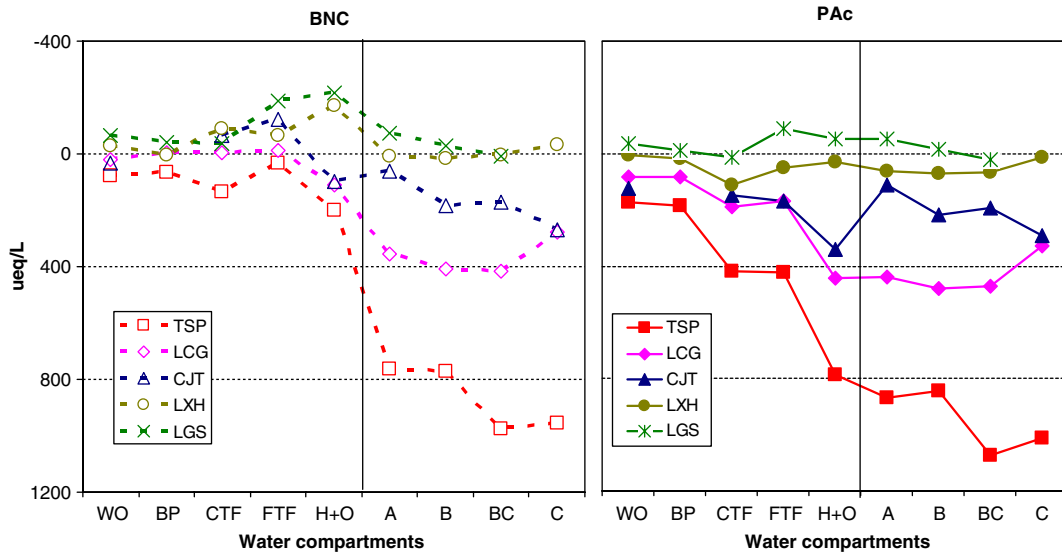


Fig. 3. Changes in BNC (left) and PAC (right) through the watersheds.

cationic charge down to the A-horizon. In deeper soil layers Al_{eqv} became dominant. BNC increased strongly from only $34 \mu\text{eq L}^{-1}$ in the ground vegetation throughfall to $764 \mu\text{eq L}^{-1}$ in the A-horizon. In the deeper soil horizon (BC) the BNC became record high ($976 \mu\text{eq L}^{-1}$) (Fig. 3). The relative importance of NH_4^+ decreased to 13% of the cation charge in forest floor. In the A-horizon ammonium was negligible. There was a substantial increase in potassium concentration through the vegetation cover into the forest floor solution ($295 \mu\text{eq L}^{-1}$). In the A-horizon the relative concentration of K^+ decreased again so that it accounted for the same fraction of the cation charge as found in precipitation ($\sim 4\%$).

At LCG the highest pH values (4.6–4.9) were found in precipitation and ground vegetation throughfall. Ca^{2+} and free SO_4^{2-} were by far the dominating ions in all the water compartments. NH_4^+ concentration was relatively high in precipitation (e.g. $68 \mu\text{mol L}^{-1}$ in bulk precipitation), while the NO_3^- concentration was low. Practically all of the NH_4^+ was consumed through the vegetation cover and rooting zone. The relative amount of K^+ increased through the vegetation cover (15%) and decreased again to initial values (4–5%) in the rooting zone.

CJT is a relatively acid tolerant site. Ca^{2+} was generally the major cation, accounting for around half (41–69%) of the cationic charge, except in the wet only precipitation where instead NH_4^+ accounted for 41% of the cationic charge. Mineral acidity ($32 \mu\text{eq L}^{-1}$) was neutralized and ANC increased to $123 \mu\text{eq L}^{-1}$ from wet

only precipitation to ground vegetation throughfall, despite a substantial S and N loading (Table 1). The relative anion charge contribution by NO_3^- increased from 14% to 31% between ground vegetation throughfall and A-horizon (Fig. 2). pH in soil solutions continued to decrease with depth, contrary to other sites, approaching 4.8 in the C-horizon. The amount of Al_{eqv} increased gradually down through the soil layers, reaching $118 \mu\text{eq L}^{-1}$ in the C-horizon. The highest BNC was found in the C-horizon ($271 \mu\text{eq L}^{-1}$).

LXH is an acid sensitive site with a relatively dilute water system ($I=98\text{--}624$). The dominant anions and cations in the water compartments varied. Absolute and relative amounts of NO_3^- increased down through the vegetation cover into the A-horizon. In fact NO_3^- was similar or even greater than SO_4^{2-} in the mineral soil horizons accounting for 34–41% of the anionic charge. The Cl^- concentration at LXH is relatively high due to its proximity to the ocean. K^+ concentration increased substantially in throughfall and accounted for 62% of cation charge in the canopy throughfall. Absolute and relative amounts of K^+ as well as NH_4^+ decreased down through the rooting zone (Fig. 2), though significant amounts are still found below the rooting zone. ANC increased (BNC decreased) down through the vegetation cover ($170 \mu\text{eq L}^{-1}$ in forest floor solution) for then to decrease again into the A-horizon (Fig. 3). The significant anion deficiency especially in the soil solution, apparent in Fig. 3, is an expression of uncertainty in the data from this site as the chemical analysis is conducted at the respective provincial laboratories.

Weak acids and bases were important at the relatively pristine LGS site. HCO_3^- contributed with most of the anionic charge in wet only precipitation and ground vegetation throughfall, while A^- accounted for 25% of the anionic charge in the forest floor solution. Ionic strength of the water was, similarly to LXH, relatively low (198–913). The major cation in all the water compartments was Ca^{2+} (42–77%), followed by K^+ in throughfall and forest floor (20–27%) (Fig. 2). Volume weighted or average pH at LGS remained above 4.8 in all water compartments. An already elevated ANC in wet only precipitation ($65 \mu\text{eq L}^{-1}$) increased further into forest floor solution ($216 \mu\text{eq L}^{-1}$) (Fig. 3), despite a drop in pH.

4. Discussion

Changes in pH and ANC or BNC through the vegetation cover are the result of the varying importance of several processes. Main factors generating acidity are dry deposition of S and oxidized N, assimilation of NH_4^+ and production of weak natural organic acids (HA). ANC is generated by deposition of alkaline dust and assimilation of NO_3^- . Strong increase in the relative amount of K^+ in throughfall and forest floor solution at all sites (Fig. 2) is due to leaching in exchange for H^+ and NH_4^+ assimilation. This was also found by Shibata et al. (1995) studying chemical changes of acid deposition through the canopy in Japanese sites. This leaching contributed therefore significantly to an increase in pH and ANC through the vegetation cover at the more pristine sites (i.e. LGS and LXH) and to stabilize the pH and BNC at TSP, LCG and CJT. At CJT the neutralizing effect of an overall larger deposition of alkaline dust than of total acidifying S- and N deposition causes the volume weighted ANC to continue to increase slightly through the canopy and into the ground vegetation throughfall solution. A leaching of also Mg^{2+} , albeit less than for K^+ , was seen as a increase in the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio from bulk precipitation down to the forest floor horizon at all the sites. A strong increase in ionic strength through the vegetation cover and into the forest floor solution (Fig. 2) was mainly due to evaporation (deduced by decreased water flux) but also partly due to mineralization of organic matter. Significant nitrification does apparently not occur before the solutions enter the forest floor compartment possibly due to lack of decomposable organic matter for the microbial mineralization in preceding water compartments. Since NH_4^+ consumed by nitrification may be replaced by mineralization, an increase in the relative amounts of nitrate, as seen at all sites except at LCG, is not necessarily

accompanied by decreasing ammonium. The higher solute concentration in the forest floor horizon than in the A-horizon, especially at LCG, LXH and LGS, can be attributed to enhanced evaporation from the collection trap. This should not have significant effect on relative ion composition. NH_4^+ that was not nitrified in the forest floor was mainly assimilated as the water moved into the A-horizon, causing the relative charge contribution by NH_4^+ to decrease to detection limit levels (except at LXH).

Concentrations of nutrient base cations (in particular K^+ , but also some Mg^{2+}) are linked to the internal biological cycle of elements. K^+ leached out from the vegetation cover was in general assimilated again when the water percolated into the rooting system of the A-horizon. This caused the relative amounts of K^+ to drop sharply in the A-horizon. This was not seen for Mg^{2+} , which is likely due to that loss by assimilation is compensated by input from weathering.

BNC increased down to the A-horizon at all sites except CJT. This increase in water acidity was mainly due to assimilation of NH_4^+ and K^+ and co-sorption of organically complexed base cations. An illustrative measure of the potential acidifying effect of deposition on soil or soil solution may be obtained by $\text{PAC} = \text{H}^+ + \text{NH}_4^+ + \text{K}^+ + \text{Al}_{\text{eqv}} - \text{A}^- - \text{HCO}_3^-$, since ammonium is nitrified and/or assimilated by vegetation and potassium is generally assimilated by vegetation. Based on charge balance it may be calculated as;

$$\text{PAC} = \sum_{\text{eqv}} ([\text{free SO}_4^{2-}], [\text{NO}_3^-], [\text{Cl}^-], [\text{free F}^-]) - \sum_{\text{eqv}} ([\text{Ca}^{2+}], [\text{Mg}^{2+}], [\text{Na}^+]). \quad (4)$$

The PAC, i.e. not including the NH_4^+ and K^+ in a BNC calculation, differs from BNC mainly in the O+H horizon (Fig. 3), but reaches similar levels as BNC in the A-horizon. This illustrates that the main cause for the increase in BNC upon entering the A-horizon is assimilation of NH_4^+ and K^+ . At CJT the high BS (41%) in the A-horizon is able to decrease the BNC, despite acidity generated by assimilation of K^+ and NH_4^+ upon entering the rooting zone.

PAC differs from $[\text{pot. H}^+]_{\text{N-sat}}$ (Eq. (1)) in how it treats NH_4^+ and potassium. The conceptual difference in regards to reactive N lies in whether reduced N is considered to be assimilated (PAC) or nitrified and leached ($[\text{pot. H}^+]_{\text{N-sat}}$). Used generally the PAC may therefore give an underestimation of the acidifying potential since some of the NH_4^+ may be nitrified to NO_3^- and 2H^+ . This is avoided by using the N chemistry in the

forest floor water compartment when calculating the PAC since most of this nitrification occurs in the forest floor solution. Note that K^+ is considered as a potential acidifying component. Calculated for throughfall solution, PAC includes dry deposition but also a considerable contribution from internal cycling, particularly K^+ . As discussed above this K^+ , released from the canopy in exchange for H^+ , is an acidifying component as it is converted back again into acidity once it gets in contact with roots. NH_4^+ (and some K^+) produced in the throughfall and forest floor solution by mineralization of litter is not believed to affect PAC significantly since an equivalent amount of organic anions (A^-) is also generally produced. In addition to the measured organic charge (A^-) found in solution a substantial amount of these organic anions becomes protonated or complexed by aluminium, thereby reducing the PAC equivalently.

Although BNC remained slightly higher (due to small remains of K^+ and NH_4^+ in solution) no significant divergence between BNC and PAC was observed in the mineral soil horizons (A–C) (Fig. 3). The fact that also PAC increases shows that assimilation and nitrification are not the cause for the increased BNC (i.e. water acidification). Note that with the exception of CJT the PAC in the forest floor horizon resembles the actual mineral acidity (BNC) found in the solution in the A-horizon (Fig. 3 and Table 1). H^+ was to a large extent exchanged for Al_i instead of base cations at sites with BS in the mineral soil less than 30% (LXH, TSP and LCG). This caused the molar effect ratio to increase (Fig. 4). Both BNC and PAC increased therefore down below the rooting zone (i.e. from A- to BC-horizons) (except at LXH) (Fig. 3). This water acidification may indicate soil alkalinization (i.e. reverse acidification) in these soil horizons during the study period. Short term

soil alkalinization may be caused by elevated levels of Ca^{2+} in solution exchanging with H^+ and Al_{eqv} on the soil (Guo et al., 2004). This process can be provoked by short term fluctuations in the water chemistry due to high deposition of Ca^{2+} and drop in precipitation amount (i.e. salt effect). Weathering is not an important process on the time scale considered in these old and already highly weathered soil profiles. Van Breemen et al. (1984) commented that where the supply of solutes exceed the leaching of solutes a reverse weathering occurs resulting in alkalinization. The reduction in ionic strength in the BC-horizon compared to the A-horizon (Fig. 2; except for the CJT site) imply such an effect if we assume a constant flux of water below the A-horizon. Anion exchange capacity is known to be high in soils with low pH and high content of Al oxides. Sulphate adsorption is a concentration-dependent process and it was found to be relatively low at concentrations corresponding to ambient sulphate levels at LCG (Liao et al., 1994). The amount of adsorbed sulphate did not differ much between the sites though increased significantly with depth, reaching an overall average of 2.6 mmol kg^{-1} in the BC horizon (IMPACTS, 2004). The concentrations of SO_4^{2-} decreased upon entering the deepest soil horizon at the rather pristine LXH and LGS sites. It is likely that sulphate is not in equilibrium and that sulphate is therefore being adsorbed in these two horizons.

The opposite effect (i.e. soil acidification) causing a decrease in PAC upon entering the A-horizon was only observed where the BS in this horizon is above 30% (i.e. CJT). Since soil alkalinization generally implies water acidification this indicates that water acidification occurs in these soils already when BS is less than 30%, and not 20% as stated by Reuss and Johnson

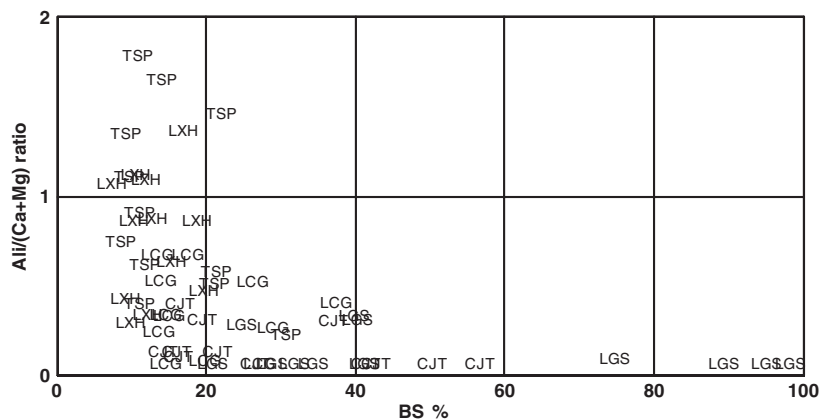


Fig. 4. Molar effect ratio ($Al_i / Ca+Mg$) in soil solution as a function of base saturation ($(\text{exchangeable } Ca+Mg+Na+K) / CEC_E$) of the soil. The markings are the site acronyms. Note that only effect ratios in samples collected from soils with known BS are used in this graph.

(1986). Decreased PAC was observed deeper into the soils (i.e. C-horizon at TSP, LCG and LXH) where the BS is less than 30%.

5. Conclusions

In Chinese atmospheric deposition there is a substantial effect on the acidity by reduced and oxidized N as well as a considerable dry and occult deposition of especially S, reduced N and alkaline dust. Monitoring throughfall deposition, including all major acid anions and base cations (i.e. H^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- and F^-), is necessary in order to estimate ecological effects. However, throughfall monitoring introduces new challenges in interpreting the data since enhanced leaching of base cation nutrients (esp. K^+) from plant surfaces through accelerated bio-cycling compensates temporarily for much of the added acidity. Another problem is that a part of the NH_4^+ in throughfall is nitrified. Monitoring of the forest floor solution may provide a good indication of the importance of nitrification since this nitrification mainly takes place in this compartment.

The true mineral acidity of the deposition was revealed in the A-horizon, where K^+ and NH_4^+ were assimilated in exchange for H^+ . An important exception is made for the CJT site where BS in the A-horizon is above 30%. Neutralization of acidity by release of base cations from the ion exchanger caused instead both the BNC and PAC to decrease upon entering the mineral soil horizon at this site. Increase in soil solution acidity caused a substantial increase in molar effect ratio in soils with BS less than about 30%.

Base Neutralizing Capacity is clearly a better measure for acidification potential than pH in deposition. However, a parameter giving an even better expression for the acidification potential in throughfall is obtained if K^+ is not reckoned as base cation as it is largely converted to mineral acidity upon entering the soil. The fate of NH_4^+ cannot be solved completely without detailed monitoring in all soil layers, but our data show that the nitrification primarily occurs in the forest floor. The PAC found in the forest floor solution corresponds therefore well with the BNC in the mineral soil.

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References

- Aas W, Solberg S, Berg T, Manø S, Yttri KE. Surveillance of long-range transported air and rain (in Norwegian). *Atmosfærisk tilførsel*, 2003. Statlig program for forensningsovervåking. Rapport 903/2004. TA-2033/2043. OR 47/2004. ISBN: 82-425-1594-8; 2004. Available at <<http://www.nilu.no/>>, 168 pp.
- Austnes K, Liu Z, Vogt RD. Intercalibration report. CRAES, Beijing. IMPACTS project, integrated monitoring program on acidification of Chinese terrestrial systems; 2002. Available at www.IMPACTS.net.cn, 35 pp.
- Cosby BJ, Wright RF, Hornberger GM, Galloway JN. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Water Resour Res* 1985;21(11):1591–601.
- Guo J, Vogt RD. Quantity and quality of nom in 5 acid sites in mid- and southern China. Humic substances and soil and water environment. In: Martin-Neto L, et al, editors. Proceedings 12th international meeting of IHSS, São Pedro, Brasil, July 25–30. International Humic Substance Society. São Pedro–São Paulo: Embrapa Instrumentação Agropecuária; 2004. p. 30–3.
- Guo J, Vogt RD, Zhang X, Zhang Y, Seip HM, Tang H. Ca–H–Al exchanges and aluminium mobilization in two Chinese acidic forest soils. *Environ Geol* 2004;45(8):1148–53.
- Hao J, Wang S, Liu B, He K. Designation of sulfur dioxide and acid rain pollution control zones and its impacts on energy industry in China. *J Chem Eng Jpn* 2001;34(9):1108–13.
- Henriksen A, Seip HM. Strong and weak acids in surface waters of southern Norway and southwestern Scotland. *Water Res* 1980;14:809–13.
- Hovind H. Internal quality control. Handbook for chemical analytical laboratories; 2002. Available at NIVA, POB 173, Kjelsås, NO-0411, Norway, 31 pp.
- IMPACTS. Integrated monitoring program on acidification of Chinese terrestrial systems, annual report, results 2003. In: Larssen T, Tang D, He Y, editors. Norwegian Institute for Water Research, Oslo, Norway. NIVA report SNO 4905-2004. ISBN: 82-577-4594-4; 2004. 94 pp.
- Larssen T, Carmichael GR. Acid rain and acidification in China: the importance of base cation deposition. *Environ Pollut (Oxford, United Kingdom)* 2000;110(1):89-102.
- Larssen T, Lydersen E, Tang D, He Y, Gao J, Liu H, et al. Acid rain in China. *Environ Sci Technol* 2006;39(2):418–25.
- Liao B, Larssen T, Seip HM, Vogt RD. Anion adsorption and aluminium release from Chinese soils treated with different concentrations of $(NH_4)_2SO_4$ and NH_4NO_3 . In: Pawłowski L, Seip HM, Sullivan TJ, editors. Aluminum in the environment, vol. 3. Special issue of *J. Ecol. Chem*; 1994. p. 281–301.
- Matzner E, Murach D. Soil changes induced by air pollutant deposition and their implication for forests in central Europe. *Water Air Soil Pollut* 1995;85(1):63–76.

- Oliver BG, Thurman EM, Malcolm RL. The contribution of humic substances to the acidity of coloured natural waters. *Geochim Cosmochim Acta* 1983;47:2031–5.
- Reuss JO, Johnson DW. Acid deposition and the acidification of soils and waters VIII. Ecological studies, vol. 59. Springer-Verlag; 1986. 120 pp.
- Rodhe H, Dentener F, Schultz M. The global distribution of acidifying wet deposition. *Environ Sci Technol* 2002;36:4382–8.
- Schecher W, Driscoll CT. An evaluation of uncertainty associated with aluminium equilibrium calculations. *Water Resour Res* 1987;23:525–35.
- Shibata H, Satoh F, Tanaka Y, Sakuma T. The role of organic horizon and the canopy to modify the chemistry of acidic deposition in some forested ecosystems. *Water Air Soil Pollut* 1995; 85:119–1124.
- Stumm JH, Morgan JJ. *Aquatic chemistry*. New York: Wiley Interscience; 1981. 780 pp.
- Sullivan TJ, Christophersen N, Hooper RP, Seip HM, Muniz IP, Sullivan PD, et al. 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; 1987. p. 269–79.
- Tang D, Lydersen E, Seip HM, Angell V, Eilertsen O, Larssen T, et al. Integrated monitoring program on acidification of Chinese terrestrial systems (IMPACTS) — a Chinese–Norwegian cooperation project. *Water Air Soil Pollut* 2001;130:1073–8.
- Uggerud HT, Hanssen JE, Schaugh J, Skjelmoen JE. The twentieth intercomparison of analytical methods within EMEP, EMEP/CCC-Report 8/2003, O-7729. NILU, POB 100, NO-2027 Kjeller, Norway; 2003. 81 pp.
- Van Breemen N, Driscoll CT, Mulder J. Acid deposition and internal proton sources in acidification of soils and waters. *Nature* 1984;307:599–604.
- Vogt RD, Aas W. Local laboratory manual for the TieShanPing (TSP) monitoring site, ChongQing Institute of Environmental Sciences and Monitoring (CIESM), ChongQing, China. IMPACTS project: integrated monitoring program on acidification of Chinese terrestrial systems. Postboks 173, Kjelsås 0411 Oslo, Norway: NIVA; 2001. Available at <<http://www.impact.net.cn/>>, 35 pp.
- Vogt RD, Mulder J. Central laboratory manual. Chinese Research Academy of Environmental Sciences (CRAES) Beijing, IMPACTS project: integrated monitoring program on acidification of Chinese terrestrial systems. Postboks 173, Kjelsås 0411 Oslo, Norway: NIVA; 2001. Available at <<http://www.impact.net.cn/>>, 22 pp.
- Vogt RD, Mortensen T, Mulder J, Solberg S, Aas W. TieShanPing (TSP) monitoring site, ChongQing municipality. Catchment manual, IMPACTS project: integrated monitoring program on acidification of Chinese terrestrial systems. Postboks 173, Kjelsås 0411 Oslo, Norway: NIVA; 2001. Available at <<http://www.impact.net.cn/>>, 33 pp.
- Vogt RD, Guo J, Luo J, Peng X, Xiang R, Xiao J, et al. Water chemistry in forested acid sensitive sites in sub-tropic Asia receiving acid rain and alkaline dust. Proceedings of the acid rain 2005 conference in Prague. 2000, *Appl Geochem*; in press.
- Wang TJ, Hu ZY, Xie M, Zhang Y, Xu CK, Chao ZH. Atmospheric sulfur deposition onto different ecosystems over China. *Environ Geochem Health* 2004;26(2–3):169–77.