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Calculating critical loads for acidification for five forested catchments in China using an extended steady state function

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Abstract

The critical load concept has become widely accepted as an important theoretical basis for establishing effective acid deposition control strategies. In the critical load calculations, the influence of variation in base cation (BC) deposition, which plays an important role in mitigating acidification, was seldom considered. In this manner, high uncertainty and over-estimation might be caused in those areas where current BC deposition is very high and of significant anthropogenic origin since anthropogenic deposition can change due to human activity. In this study, an extended sulfur(S)–nitrogen (N)–BC function based on the Steady State Mass Balance (SSMB) method is applied to calculate the critical loads for five sampled catchments in southern China under variable S, N, and BC deposition. The ceiling of S deposition (when N deposition is zero; CL_{max}(S)) under current BC deposition varies from 4.5 to 10.8 keq ha^{-1} yr^{-1} among the five catchments, and the ceiling of N deposition (when S deposition is zero; CL_{max}(N)) varies from 23.2 to 54.5 keq ha^{-1} yr^{-1}. A 75% reduction in BC deposition is estimated to cause a 46%–86% decrease of CL_{max}(S) and 45%–81% decrease of CL_{max}(N). The critical loads for acidification are not exceeded in any of the five catchments under the current base cation deposition, despite extremely high S deposition in some places. However, if the BC deposition decreases to 25% of current while S remains unchanged, critical loads will be exceeded at all sites except one. A sensitivity analysis confirms that the long-term future BC deposition is among the most important parameters to the uncertainty of critical load, together with the dose–response relationship between ecosystem health and soil solution chemistry.

Keywords: Critical load; Base cation deposition; Acidification; Sensitivity analysis; China

1. Introduction

Acid deposition is considered a major environmental problem in China, especially in the southern and southwestern regions. Owing to large SO_2 emissions, SO_4^{2-} is the dominant anion in acid precipitation in most areas of China. However, due to large NH_3 emissions from the agriculture sector, and NO_x emissions from rapidly increasing energy production and number of vehicles, nitrogen deposition deserves attention.

To control emissions of these acidification precursors in a cost-effective way on the regional scale, the European model of critical loads can be applied to Chinese conditions. Although the critical load concept has not yet

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been directly applied in developing emission reduction policies in China, it was considered, for example, in designating the Chinese acid rain control zone (Hao et al., 2001). Several studies have been carried out to calculate the critical loads of sulfur (S) and nitrogen (N) deposition on both local and regional scale, and a map of critical loads of S and N has been derived for China using the steady state mass balance (SSMB) approach (Xie et al., 1995; Duan, 2000; Duan et al., 2001).

In most European applications, base cation (BC: Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) deposition is usually used as a constant parameter in critical load calculations, and this assumption has been applied to China (Duan et al., 2002). However BC deposition in China is commonly much higher than that in Europe (Wang and Ding, 1997), due to the higher emissions from natural and anthropogenic sources, and anthropogenic deposition will be largely reduced in the near future due to government air pollution control policies. This reduction violates the assumption of constant BC deposition, causing high uncertainty in critical load calculations. For example, the industrial emissions of calcium were estimated to be 4.0 Mt in 2000, while natural emissions of wind-blown dust from northern China were estimated to be 2.3 Mt (Zhu et al., 2004). Comparatively, the overall industrial calcium emission in Europe was approximately 0.8 Mt (Lee and Pacyna, 1999). BC deposition plays an important role in negating ecosystem acidification. Although the concentrations of SO_2 and SO_4^{2-} are extremely high in northern China (Hao et al., 2001), the pH of rain is still approximately neutral and the soil is not seriously acidified, owing to the high BC deposition fluxes (SEPA, 2006; An et al., 2001).

The influence of BC deposition on acidification in the future has been assessed in some model applications. Application of dynamic acidification models indicated that with large decreases in BC deposition, increased soil acidification can be expected in southwestern China even with considerable S emission reductions (Larssen and Carmichael, 2000; Larssen et al., 2000; An and Huang, 2000). Since the anthropogenic emissions of base cations most likely will be reduced in the future, critical loads may be misleading if not considering changes in BC deposition in the calculations.

To avoid the incorrect conclusions when the critical loads approach is applied under high BC deposition flux, an extended S–N–BC critical load function considering BC deposition as a variable has been developed (Zhao et al., 2007). This updated approach has been designed for decision making for acidification control. Before it can be applied, it is necessary to demonstrate model applications on well described monitoring catchments with real data. Therefore, in this study, acidifying critical loads of S and N are calculated with the extended approach at five intensively studied Chinese forest catchments, conducted as a part of the Sino-Norwegian Integrated Monitoring Program on Acidification of Chinese Terrestrial System (IMPACTS) project (Tang et al., 2001; Larssen et al., 2006).

2. Materials and methods

2.1. Study catchments

The five studied catchments are all located within the acid rain control zone in southern China (Fig. 1) and have been included in the IMPACTS since 1999. All the sites are forested, practically undisturbed by human land-use activities, and contain acid rain sensitive ecosystems. The geographical information for these sites is listed in Table 1. Deposition of total S and N at the sites differs from high to relatively low, while dry deposition of acid oxides, alkaline dust and especially reduced N is substantial, accounting for more than half of the total loading at some sites. Lei Gong Shan (LGS) is a pine forest situated in a remote mountain region far-east in the less developed Guizhou province. Total deposition of S, N and alkaline dust in LGS are the lowest among the studied sites. Liu Chong Guan (LCG) is a pine forest in the suburb of Guiyang city, the capital of Guizhou province. Numerous atmospheric emission sources in the proximity result in high wet and dry deposition of S as well as alkaline dust (e.g. $CaCO_3$ and CaO). Tie Shan Ping (TSP) is a pine forest located on a sandstone ridge 25 km outside the metropolitan Chongqing city. This site receives the highest total amounts of both wet and dry S and N among the monitoring sites. Cai Jia Tang (CJT) is a conifer forest situated within an agricultural region in the southwest of Hunan province. The site receives high S and N loading. Liu Xi He (LXH) is a subtropical broad-leaved evergreen forest situated 80 km inland of the coastal city Guangzhou, capital of developed Guangdong province. This site receives a relatively high deposition of oxidized and reduced N, compared to relatively low S deposition, along with a low loading of airborne alkaline dust. For further details on these catchments see Larssen et al. (2004).

2.2. The extended critical load function and uncertainty analysis

The extended S–N–BC critical load function, which has been explored in Zhao et al. (2007), is used in the critical load calculation for the five catchments. Based on the Steady State Mass Balance (SSMB) method (Sverdrup

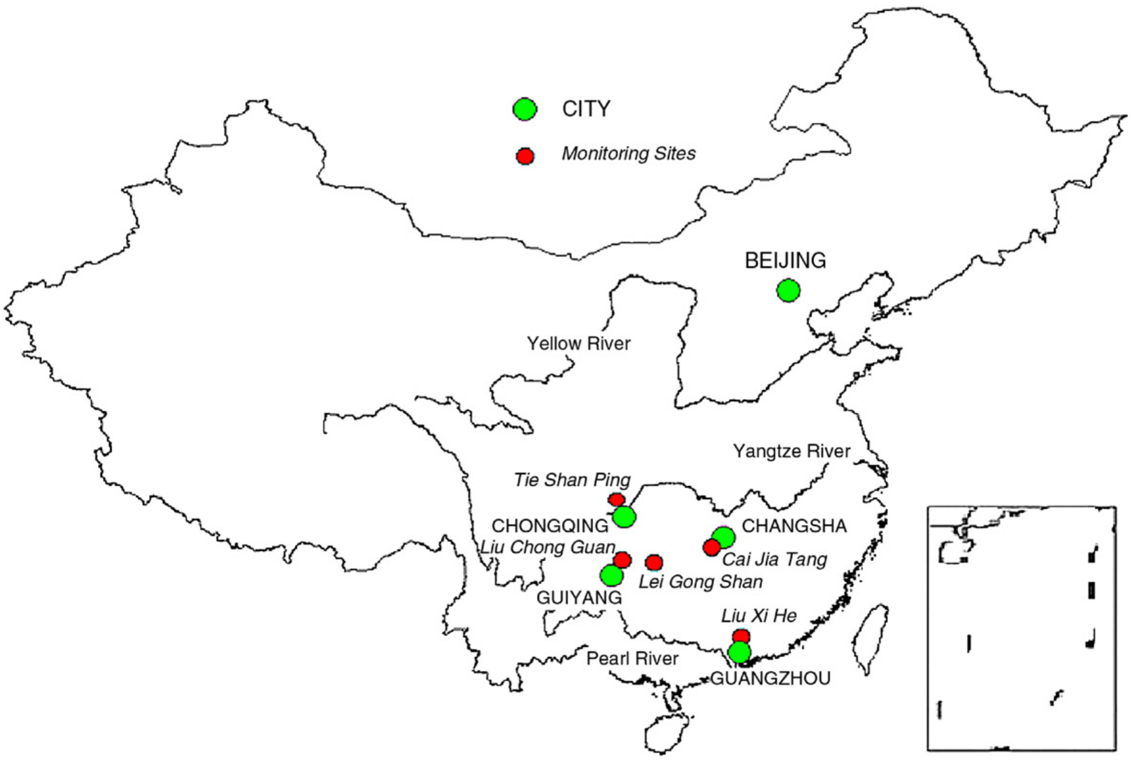

Fig. 1. Location of the five IMPACTS catchments in China.

and DeVries, 1994; UBA, 2004), the function takes the variation of BC deposition flux into account and estimates the critical load of S and N under variable BC deposition (Eq. (1)).

$$CL(S) + (1 - f_{DE})CL(N) - BC_D = BC_W - BC_U + (1 - f_{DE})(N_I + N_U) - ANC_{L,crit} \quad (1)$$

where CL(S) and CL(N) are critical load of S and N, respectively; BC_D is the deposition of base cations (Ca^{2+} Mg^{2+} Na^{+} K^{+}); BC_W is the BC weathering rate of base cations from soil minerals; BC_U is the vegetation uptake of base cations; N_I is the net N immobilization rate in the soil; N_U is the net uptake of N by vegetation; f_{DE} is the nitrate lost by denitrification; and $ANC_{L,crit}$ is the critical alkalinity leaching. Chloride deposition is of little importance for terrestrial ecosystem and thus removed from Eq. (1).

The critical molar ratio of BC to Al, at which fine root damage occur in the soil, is used as the chemical criterion for characterizing acidification. Therefore the

Table 1
Description of five IMPACTS catchments in China (Larssen et al., 2004)

Site	Longitude/latitude	Area (ha)	Elevation (m)	Precipitation (mm)	Soil	Bedrock	Vegetation
LGS	108°11′E 26°22′N	6.0	1630–1735	1367	Yellow earth	Shale	Armand pine
LCG	106°43′E 26°38′N	6.8	1320–1400	621	Yellow earth	Sandstone	Masson pine
TSP	104°41′E 29°38′N	16.3	450–500	1168	Yellow earth	Sandstone	Masson pine
CJT	112°26′E 27° 55′N	4.2	450–500	1196	Yellow earth	Sandstone/shale	Masson pine
LXH	133°35′E 23°33′N	261	500	1620	Yellow earth	Granite	Broad-leaved evergreen forest

$ANC_{L,crit}$ can be calculated as Eq. (2) (Zhao et al., 2007).

$$-ANC_{L,crit} = 1.5\frac{Bc_D + Bc_W - Bc_U}{(Bc/Al)_{crit}} + Q^{1-\frac{1}{\alpha}}\left[1.5\frac{Bc_D + Bc_W - Bc_U}{(Bc/Al)_{crit}\cdot K^*}\right]^{\frac{1}{\alpha}} \quad (2)$$

where Bc_D, Bc_W and Bc_U are respectively deposition, weathering rate and growth uptake by vegetation of Ca^{2+}, K^+ and Mg^{2+} (Na^+ has no effect on buffering the toxicity of Al to vegetation); $(Bc/Al)_{crit}$ is the critical molar ratio of the three base cations to Al in soils; Q is the water flux through the root zone of the soil profile; α and K* are the corrected coefficients of gibbsite equilibrium.

The resulting extended function can be drawn as a curvilinear surface by combining Eqs. (1) and (2). The characteristic values in the function, i.e. CL_{max}(S) (the ceiling of S deposition when N deposition flux is zero), CL_{min}(N) (the ceiling of N deposition when S deposition flux reaches CL_{max}(S)), and CL_{max}(N) (the ceiling of N deposition when S deposition flux is zero), can be calculated with Eqs. (3)–(5) (UBA, 2004).

$$CL_{max}(S) - BC_D = BC_W - BC_U - ANC_{L,crit} \quad (3)$$

$$CL_{min}(N) = N_I + N_U \quad (4)$$

$$CL_{max}(N) = N_I + N_U + \frac{CL_{max}(S)}{1 - f_{DE}} \quad (5)$$

To verify the acidification estimate from the extended function, an existing method is applied in which the variation of BC deposition is considered in the exceedance calculation (UBA, 2004).

$$Ex \quad (S) = S_D - CL(S/N) - \Delta BCL_D \quad (6)$$

$$CL(S|N) = \begin{cases} \dfrac{CL_{max}(N) - N_D}{CL_{max}(N) - CL_{min}(N)} \times CL_{max}(S) & N_D \geq CL_{min} \\ CL_{max}(S) & N_D < CL_{min}(N) \end{cases} \quad (7)$$

where Ex(S) is the exceedance of the critical load of S, CL(S|N) is the critical load of S under real N deposition, ΔBC_D is the difference between real and critical BC deposition, and S_D and N_D are the real depositions of S and N respectively.

Finally, the input parameters with corresponding statistical distribution are placed in a Monte Carlo framework, and 100 000 simulations were performed for each site to analyse the sensitivity of the calculated critical loads to the inputs. These input parameters are as follows: deposition and weathering of base cations, growth uptake of base cations and nitrogen, net immobilization rate of nitrogen, denitrification rate, water flux, critical ratio of Bc/Al, and corrected coefficients of gibbsite equilibrium, all of which are described in detail in the next section.

3. Input data

3.1. Deposition

The total deposition of air pollutants consists of both wet and dry components. Since the dry deposition fluxes are significant in the five catchments, throughfall concentrations are used to calculate the total deposition flux. Due to canopy exchange, this approach may have its limitations. However, for the main ions of concern, specifically SO_4^{2-} and Ca^{2+}, only a negligible fraction of the total flux can be attributed to canopy exchange. For NH_4^+ and K^+ canopy exchange may be important and increase the uncertainty in the estimate of the total flux (Pajuste et al., 2006; Vogt et al., 2006; Flechard et al., 1999). In this study, the fraction of wet and dry deposition for K^+ is assumed to be similar to that of Ca^{2+}, and thus total K^+ flux is calculated based on this fraction and wet deposition of K^+. In contrast, NH_4^+ may be updated when better data for estimating the total flux becomes available. The average deposition of year 2002 and 2003 are calculated based on throughfall concentrations sampled with forest throughfall collectors and are listed in Table 2 (Vogt et al., 2001; Vogt and Aas, 2001; Larssen et al., 2004). Concerning the BC deposition of the five catchments, dry deposition of calcium-rich particles is a considerable fraction of the total deposition. Calcium is highly enriched in throughfall, especially at TSP where the throughfall deposition is 8 times

Table 2
Total deposition of the five catchments (keq ha^{-1} yr^{-1}) (Larssen et al., 2004)

Catchment	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	NO_3^-	NH_4^+
LGS	0.98	0.24	0.11	0.07	0.99	0.20	0.35
LCG	2.10	0.58	0.08	0.20	3.41	0.13	0.29
TSP	5.59	1.18	0.12	1.04	9.91	0.89	1.99
CJT	3.63	0.77	0.18	0.71	4.74	1.14	1.78
LXH	1.25	0.61	0.32	0.24	2.18	0.46	0.54

higher than wet deposition (Larssen et al., 2004). In the sensitivity analysis, BC_D was assumed to have a normal distribution with Standard Error (SE) 10% of the mean value. A large part of the BC deposition is of anthropogenic origin, which will be considerably reduced in the future. Recent modeling work implied that Ca^{2+} deposition from natural source was less than 30% in eastern China (Duan et al., in press). In order to illustrate the critical load change with changing deposition of base cations, 25% of current BC deposition is assumed for the critical deposition (of natural origin). In the sensitivity analysis, natural BC deposition was set to a uniform distribution between 25% and 75% of measured the total deposition.

3.2. Growth uptake by vegetation

The long-term net uptake of N and BC by vegetation is calculated from Eq. (8) with the assumption of whole tree harvesting (Duan et al., 2004).

$$X_U = K_t X_t + K_b X_b \tag{8}$$

where X_U is the net growth uptake of element X (keq ha^{-1} yr^{-1}), K_t and K_b are the growth rates of trunk and branch (t ha^{-1} yr^{-1}), and X_t and X_b are the X element contents in trunk and branch (keq t^{-1}).

Since data for growth rates and chemical components were not available for the monitoring catchments, data from similar habitats are used (Duan et al., 2004). In the sensitivity analysis a triangular distribution was tentatively adopted, in which the estimated value is assumed as most likely, the probabilities for the interval limits are set to 0, and a linear probability distribution is assumed between the most likely and both of the interval limits. The values of growth uptake are listed in Table 3.

3.3. Critical alkalinity leaching ($ANC_{L,crit}$)

For $ANC_{L,crit}$ calculation, the chemical criterion $(Bc/Al)_{crit}$ was set to 2 for masson pine forest and 1 for broadleaf evergreen forest (Sverdrup and Warfvinge, 1993). A uniform distribution between 0.5 and 2.0 was suggested in this study. Soil water at B-, BC- and C-horizons in the five catchments was sampled with ceramic cup suction lysimeters and analysed in the lab (Vogt et al., 2001). The fraction of inorganic Al (Al_i) was determined in samples with pH below 5.5 according to the operationally defined Barnes/Driscoll procedure (Sullivan et al., 1987), and $[Al^{3+}]$ was calculated from Al_i through the computer program Alchemi (Schecher and Driscoll, 1987). The coefficients α and $\lg K^*$ and their SEs were then derived from a logarithm-linear regression, shown in Fig. 2 and listed in Table 3. However, a poor relationship between $[Al^{3+}]$ and pH was found at the catchments LGS and LCG ($R^2 < 0.40$), probably due to the heterogeneity of different layers of the soils (Guo et al., 2006). The water flux, Q, was measured from catchment monitoring and the SE was set to 20% of the mean value. Based on these parameters $ANC_{L,crit}$ were calculated from Eq. (2) for the five catchments and the result vary between −2.05 (TSP) and −0.46 (LXH) keq ha^{-1} yr^{-1} when the critical BC deposition is assumed to be 25% of the current deposition.

Table 3
Input data for calculating critical loads of the five catchments. Values in parentheses and square brackets indicate SE and range, respectively

Catchment	LGS	LCG	TSP	CJT	LXH
BC_D (keq ha^{-1} yr^{-1})	1.40(0.14)	2.96(0.30)	7.92(0.79)	5.28(0.53)	2.41(0.24)
Fraction [a]	0.25[0.25–0.75]	0.25[0.25–0.75]	0.25[0.25–0.75]	0.25[0.25–0.75]	0.25[0.25–0.75]
BC_W (keq ha^{-1} yr^{-1})	1.29(0.26)	0.65(0.13)	0.60(0.12)	1.05(0.21)	2.19(0.44)
BC_U (keq ha^{-1} yr^{-1})	0.58[0.25–1.10]	0.25[0.25–1.10]	0.25[0.25–1.10]	0.31[0.25–1.10]	2.48[2.00–3.61]
Critical Bc/Al	2.0[0.5–2.0]	2.0[0.5–2.0]	2.0[0.5–2.0]	2.0[0.5–2.0]	1.0[0.5–2.0]
Q (m^3 ha^{-1} yr^{-1})	10170(1017)	6300(630)	5220(522)	3860(386)	7810(781)
N_U (keq ha^{-1} yr^{-1})	0.59[0.21–1.17]	0.21[0.21–1.17]	0.21[0.21–1.17]	0.26[0.21–1.17]	2.00[1.46–2.88]
N_I (keq ha^{-1} yr^{-1})	0.14[0.05–0.40]	0.16[0.05–0.40]	0.17[0.05–0.40]	0.13[0.05–0.40]	0.05[0.05–0.40]
f_{DE}	0.8[0.7–0.9]	0.8[0.7–0.9]	0.8[0.7–0.9]	0.8[0.7–0.9]	0.8[0.7–0.9]
α	1.62(0.26)	1.33(0.18)	1.59(0.08)	1.42(0.22)	2.29(0.23)
$\lg K^*$	2.71(1.29)	1.49(0.79)	3.11(0.32)	2.65(1.04)	5.61(1.07)

[a] The assumed ratio of natural BC deposition to the total BC deposition.

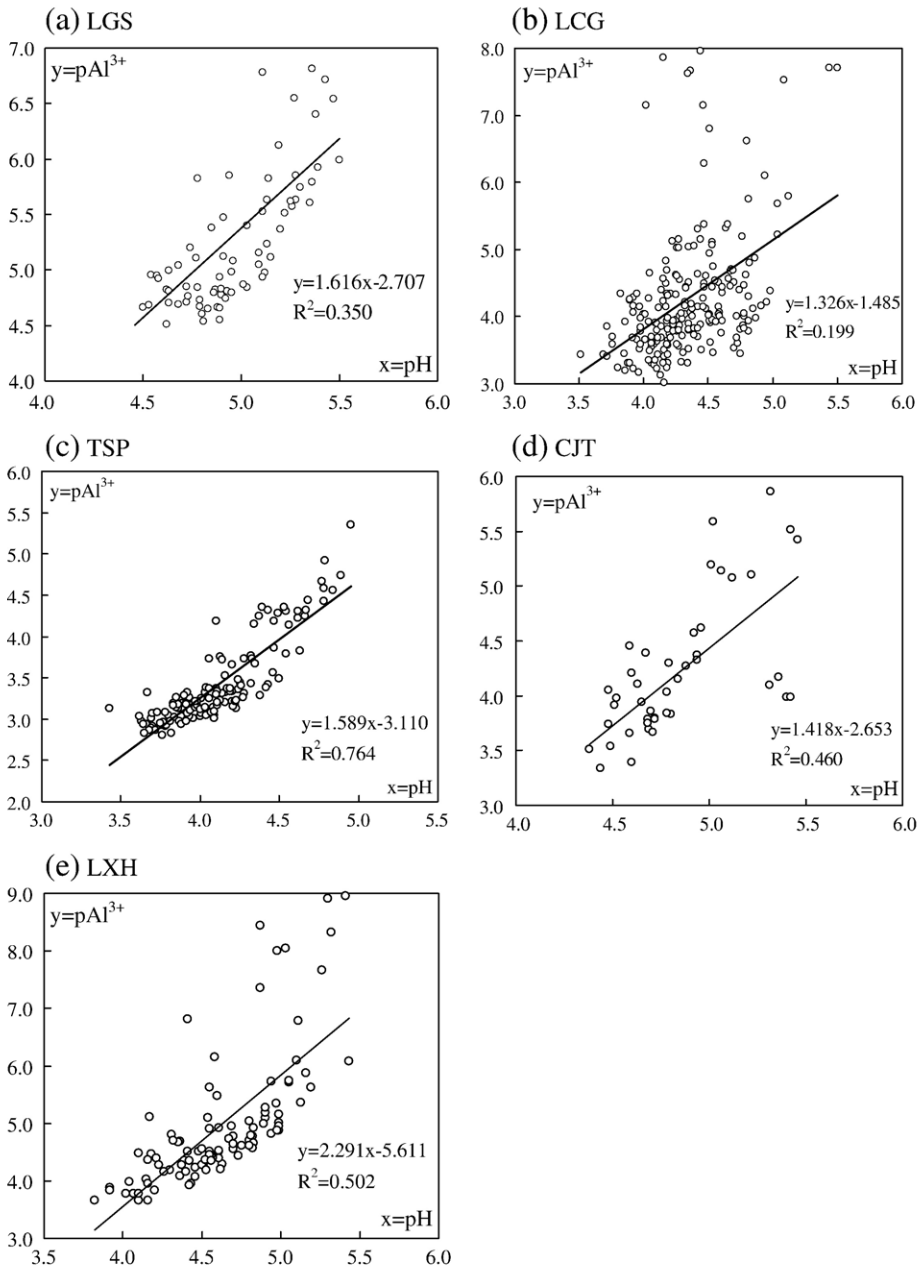

Fig. 2. The regression results of relation between pH and pAl^{3+} in the five catchments. The slope and intercept in each regression equation are α and $-\lg K^*$ for corresponding catchment, respectively.

3.4. Nitrogen inputs

The long-term net N immobilization, N_I, in stable organic N-compounds in soil was estimated from the total amount of soil N divided by the period of soil formation (De Vries, 1993; De Vries and Reinds, 1994). Data on present N amounts in the root zone of major soil types in China indicate a range of 500–4000 keq ha^{-1} (Xiong and Li, 1987) and a long-term immobilization rate of approximately 0.05–0.40 kmol ha^{-1} yr^{-1} as estimated by Hao et al. (2003). The N immobilization rates of the five catchments calculated by the same method are shown in Table 3.

Few data can be used to estimate f_{DE} for Chinese soils till now. In this study f_{DE} for the yellow earth in the five catchments was set to 0.8 with an assumed range

Table 4
Input parameters for weathering rate modeling with PROFILE

Input parameter		Soil temperature (°C)	Layer height (m)	Moisture content ($m^2\ m^{-3}$)	Soil bulk density (kg m^{-3})	Surface area ($m^2\ m^{-3}$)
LGS	Horizon1	12.6	0.08	0.49	700	3.32E+05
	Horizon2		0.25	0.50	750	3.55E+05
LCG	Horizon1	13.8	0.04	0.39	870	2.79E+06
	Horizon2		0.35	0.41	990	3.58E+06
TSP	Horizon1	16.3	0.03	0.40	1410	4.32E+06
	Horizon2		0.25	0.41	1460	4.55E+06
CJT	Horizon1	16.3	0.06	0.31	1030	3.38E+06
	Horizon2		0.28	0.32	1100	3.33E+06
LXH	Horizon1	18.0	0.09	0.40	1160	3.24E+06
	Horizon2		0.25	0.42	720	4.31E+06

between 0.7 and 0.9, slightly higher than the value suggested for clay soils in Europe (Posch et al., 1995) but closer to results reported for forest soils in northern China (Geng and Sun, 1999). Similar to the growth uptake values by vegetation, the N_I and f_{DE} were also tentatively assumed to have a triangular distribution.

3.5. Weathering rate

The weathering rate is one of the key parameters for the critical load calculation. In this paper, the PROFILE model (Sverdrup and Warfvinge, 1993), a geochemical steady state model based on soil properties, was applied to calculate the weathering rate, with a double-layer assumption for the five catchments.

Exposed mineral surface area, soil temperature, and moisture content are considered the most sensitive input parameters in PROFILE (Hodson et al., 1996). Values of the exposed mineral surface area were taken from Duan et al. (2000). The rest of the aforementioned parameters, as well as soil thickness and soil density, were obtained from monitoring data (Larssen et al., 2004), and are listed in Table 4. Other required parameters in the PROFILE, including element deposition and growth uptake, are described in Sections 3.1 and 3.2.

The calculated BC weathering rates for the five catchments are listed in Table 3. Jonsson et al. (1995) concluded that simultaneous variation of input parameters of PROFILE model in the 10–100% range led to a maximum of 40% variation in weathering rates. In the sensitivity analysis the BC_W was assumed to have a normal distribution and the SE was set to 20% of the modeling results, which indicate that 95% confidential intervals vary from −40% to +40% of the mean value.

Table 3 summarizes the input data with uncertainty assumptions for the critical load calculation in the five catchments.

4. Results and discussion

4.1. S–N–BC critical load function for the five catchments

The critical loads were first calculated using Eqs. (3)–(5) under both current and assumed stable BC deposition (Table 5). When current BC deposition is applied in the calculation, the $CL_{max}(S)$ for the TSP and CJT sites, where the largest BC deposition flux was found, are the highest (above 10 keq $ha^{-1}\ yr^{-1}$) among all the five catchments. The site with the lowest deposition, LGS, has the lowest $CL_{max}(S)$, despite a relatively large BC weathering rate. The southernmost site, LXH, where the BC_W is the highest, also has a relatively low $CL_{max}(S)$, owing to the high vegetation

Table 5
Critical loads with its exceedance for the five catchments (keq $ha^{-1}\ yr^{-1}$)

Catchment	$CL_{max}(S)$	$CL_{max}(S)$ [a]	$CL_{min}(N)$	$CL_{max}(N)$	$CL_{max}(N)$ [a]	CL(S|N) [a]	Ex(S)	Ex(S) [a]
LGS	4.50	2.42	0.73	23.22	12.81	2.42	−2.47	−1.43
LCG	7.06	2.51	0.37	35.65	12.90	2.49	−1.30	0.92
TSP	10.62	4.38	0.38	53.48	22.27	3.88	−0.01	6.03
CJT	10.82	3.76	0.39	54.49	19.18	3.25	−2.48	1.48
LXH	5.50	0.78	2.05	29.52	5.93	0.78	−0.41	1.40

[a] Results under the 25% of current BC deposition.

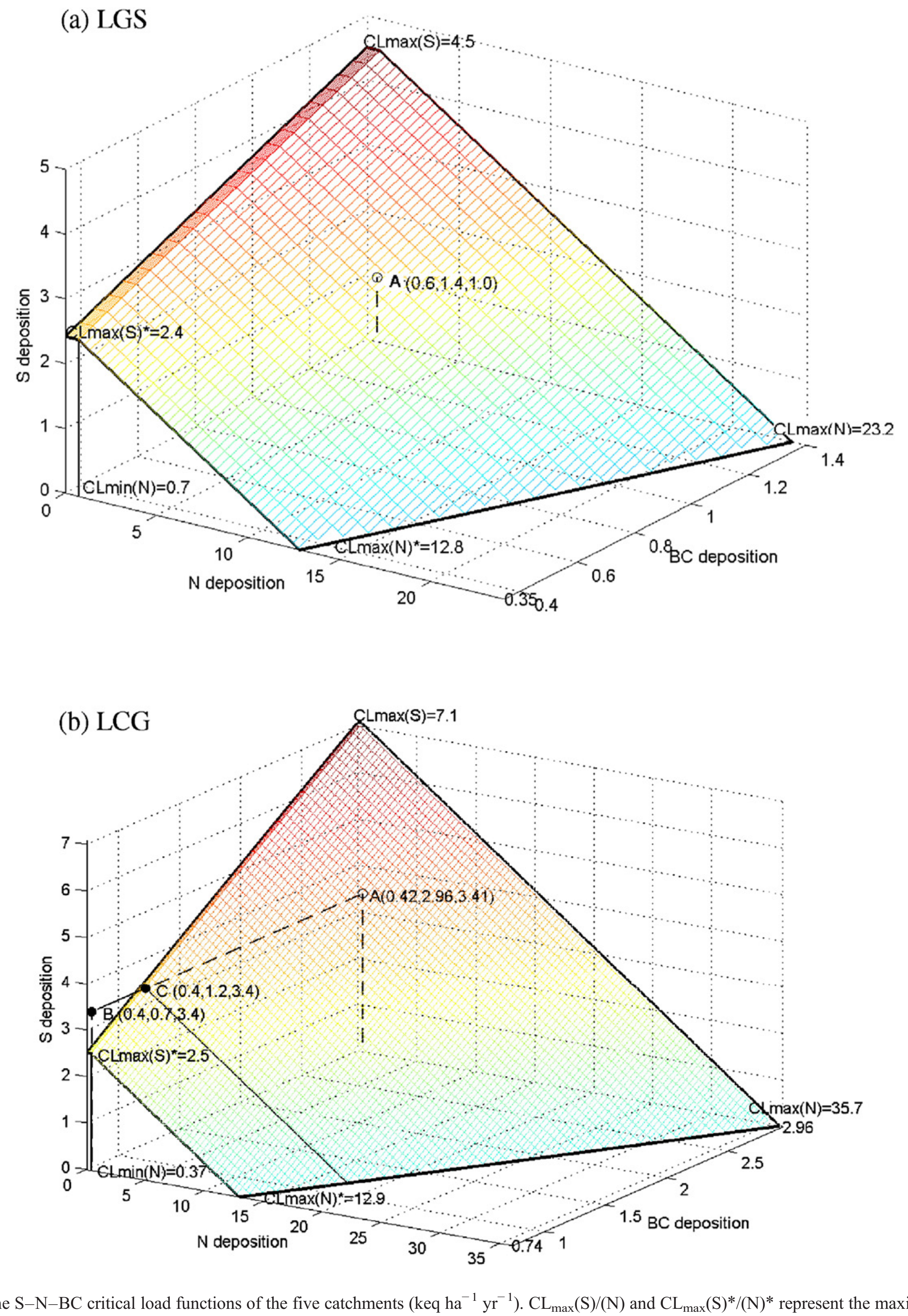

Fig. 3. The S–N–BC critical load functions of the five catchments (keq ha^{-1} yr^{-1}). CL_{max}(S)/(N) and CL_{max}(S)*/(N)* represent the maximum S/N critical load under current and natural background BC deposition (25% of current deposition assumed), respectively. Each point with coordinates of (N_D, BC_D, S_D) represents current deposition level of N, BC and S.

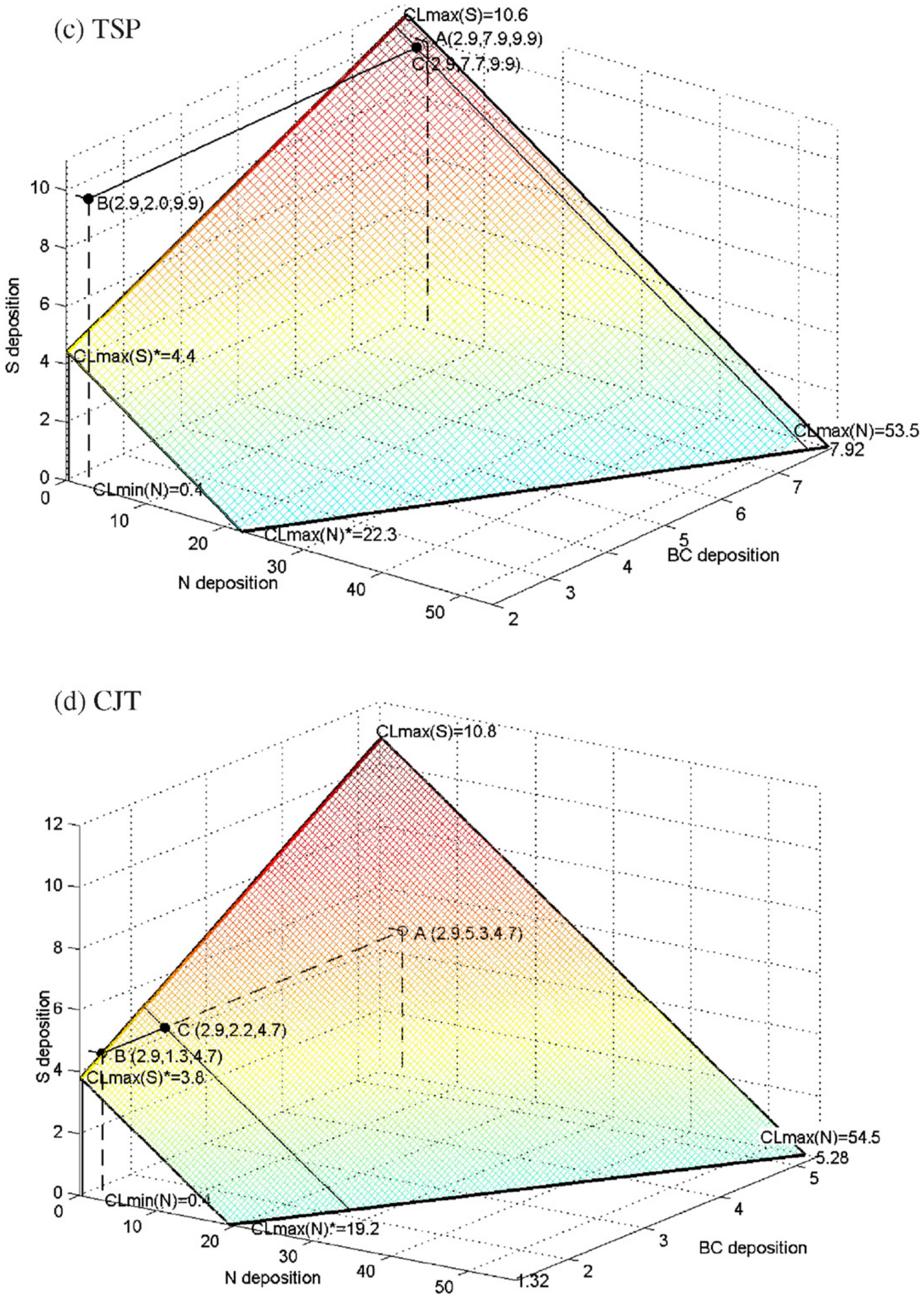

Fig. 3 (*continued*).

uptake and relatively low BC deposition. Since the $CL_{min}(N)$ for all the catchments are low and f_{DE} are uniformly set to 0.8 in the calculations, the performance of $CL_{max}(N)$ in these sites are very similar to $CL_{max}(S)$. These results imply that BC deposition could have great impact on the critical load estimates for Chinese

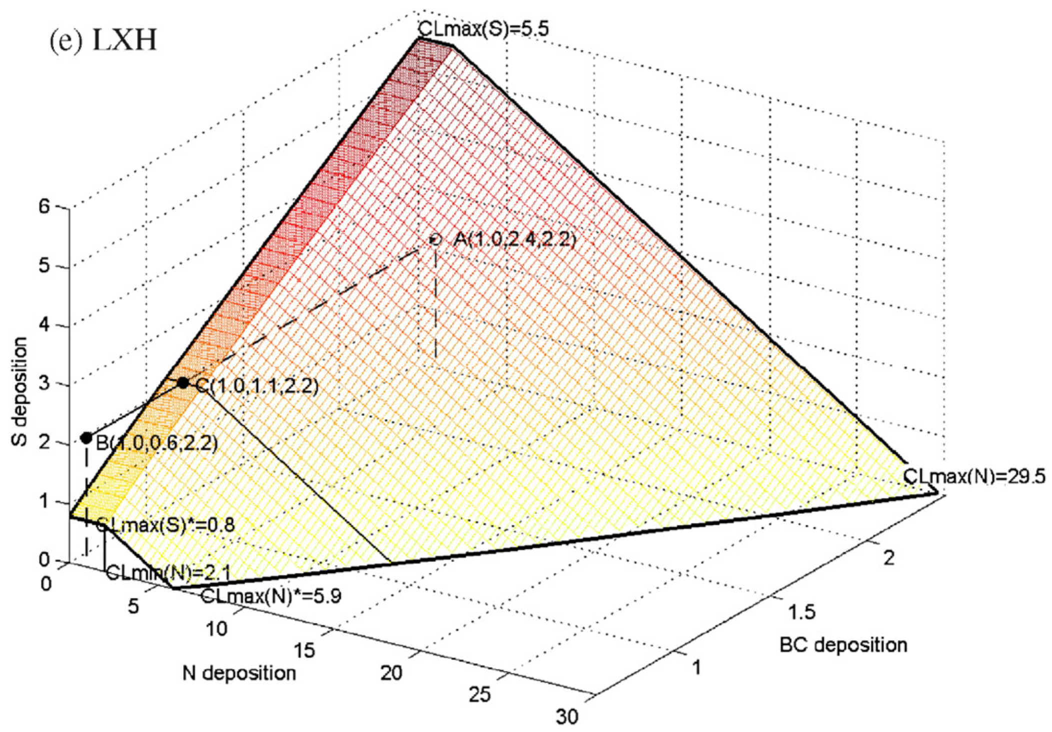

Fig. 3 (*continued*).

ecosystems. When BC deposition is cut by 75%, the critical loads decline considerably, with the largest decrease (86%) in LXH and the smallest (46%) in LGS for $CL_{max}(S)$, and the largest (80%) in LXH and the smallest (45%) in LGS for $CL_{max}(N)$. Under assumed stable BC deposition (i.e. 25% of current), some other parameters, such as BC_W and BC_U, could play a more important role in the critical load estimate, especially at LGS and LXH.

The calculated critical loads are generally close to, or somewhat higher than other results in China and abroad. European results with similar SSMB methods concluded 0.5–5.0 keq ha^{-1} yr^{-1} for $CL_{max}(S)$ (Hettelingh et al., 2004). Considering that all of the five catchments in this study are located at subtropical areas with higher temperatures and humidity than Europe, the differences are thus acceptable. Kuylenstierna et al. (2001) applied a method of acid-sensitivity classification of soils and indicated that the preliminary critical load of acidity in southern China was 0.5–2.0 keq ha^{-1} yr^{-1}. Xu et al. (2000) calculated the critical load of S for seven provinces in eastern China with the MAGIC model, concluding 1.6–3.3 keq ha^{-1} yr^{-1}. Similar results were also found by Tao and Feng (2000), who combined the ecosystem sensitivity with site-specific studies conducted by the MAGIC model, and estimated the critical load of S for southern China as 1.4–3.3 keq ha^{-1} yr^{-1}. These Chinese studies also conclude similar or slightly lower critical load estimates compared with the results in this study, partly because of the large amounts of BC deposition in the sampled catchments.

As shown in Fig. 3, the extended S–N–BC critical load functions are determined for the five catchments based on Eq. (1), and the real deposition fluxes in these catchments are labeled as N_D, BC_D, and S_D (point A in Fig. 3(a)–(e)). The critical loads are not exceeded in any of the five catchments using the current BC deposition. At the TSP catchment, the current S deposition is particularly high and very close to the calculated CL_{max} (S). In a subset of the sites, the monitored molar ratio of Bc to Al_i in the soil is less than or equal to 2 in deep layers, implying possible harmful effects to the vegetation for parts of the area (Larssen et al., 2004). In a long-term perspective, however, the acidifying deposition ceiling at TSP will be reached when BC_D decreases to 7.72 keq ha^{-1} yr^{-1}, i.e. 97.5% of current value, if S or N deposition is unchanged (point C in Fig. 3(c)). This result indicates a serious potential risk of soil acidification at TSP. Similar trends, though not as urgent, are also found at three of the other catchments. The critical load for acidity at LCG, CJT and LXH will be reached when BC_D decreases to 1.18, 2.15 and

1.10 keq ha^{-1} yr^{-1}, i.e. 40%, 41% and 46% respectively, of current values given constant S and N deposition (point C in Fig. 3(b), (d) and (e)). If the BC_D were to be decreased by 75% in these 4 catchments, the critical loads for acidity would be clearly exceeded without reducing S or N deposition (point B in Fig. 3(b), (c), (d) and (e)). As an exception, the least polluted catchment LGS will not have its critical load exceeded even if BC_D is reduced by 75% (Fig. 3(a)).

As a comparison, the exceedance estimate of S critical load was also calculated using the "traditional" exceedance method (Eqs. (6) and (7)) and then listed in Table 5. The result indicates that current exceedance of S (Ex(S) in Table 5) for all the sites are negative implying current acid deposition is allowable for ecosystem protection. When BC deposition is reduced to the critical level, all sites except LGS would have their critical load of S exceeded, particularly TSP, the site with the largest exceedance (Ex(S)* in Table 5). This result agrees with that estimated from extended critical load function. However, the extended critical load function could illustrate more clearly the quantitative relation between ecosystem acidification and inconstant base cation deposition thus indicating the importance of base cation emission control in the acid deposition assessment for policy makers. Therefore it would be of great use in environmental decision making in China.

Particulate matter (PM), which contains considerable amounts of base cations, is considered the most important atmospheric pollutant in Chinese cities. In 2005, the annual average PM level exceeded Class II of the Chinese National Ambient Air Quality Standard (NAAQS) in 41% of the monitored cities (200 μg/m^3 for total suspended particulates and 100 μg/m^3 for PM_{10}) (SEPA, 2006). High BC deposition, as opposed to weathering, is the most important source of alkalinity in Chinese soils. To reduce the serious negative health effects from PM, much attention has been focused on the issue and the anthropogenic sources of base cations should be gradually controlled. Emissions from natural sources may also decrease, for instance from ecological restoration, afforestation and paving roads. On the other hand, the SO_2 and NO_x emissions continue to increase due to the rise in energy consumption, and thus ecosystem acidification is becoming more and more serious (SEPA, 2006). Therefore China is now facing the challenge of reducing the emissions of S, N, and PM (as well as BC) simultaneously. To face this challenge, the extended critical load function can be applied to provide more reasonable estimates of critical load and support emission control planning for both acid compounds and particulates.

4.2. Sensitivity analysis

The results of sensitivity analysis using the Monte Carlo method are shown in Fig. 4. As opposed to the situation in Europe where BC weathering is commonly considered to be the main source of uncertainty in critical load estimate (Hettelingh and Jansen, 1993; Skeffington et al., 2006), contribution to the overall uncertainty from BC_W among our five catchments is only found to be important at LXH. The BC_W contribution at this site are 39.7% and 38.7% for $CL_{max}(S)^*$ and $CL_{max}(N)^*$ respectively, and less than 9.0% at other four sites. The variation of the critical BC deposition fraction contributes most to the uncertainty of critical loads at TSP and CJT, 61.1% and 39.2% for $CL_{max}(S)^*$, and 48.0% and 31.1% for $CL_{max}(N)^*$ respectively. At LCG and LXH, where relatively lower current BC depositions are found, the critical load results are most sensitive to the gibbsite parameters (indicated by α and $\lg K^*$) and BC weathering respectively. However, the fraction of the critical BC deposition still plays an important role with an uncertainty contribution higher than 20% for both $CL_{max}(S)^*$ and $CL_{max}(N)^*$. At the most pristine site LGS gibbsite parameters contribute over 50% to the uncertainty. The results of sensitivity analysis imply that the anthropogenic and natural BC deposition need to be studied further in order to get more accurate results for critical loads in China. Since it is quite difficult to evaluate the current status and future trend of anthropogenic BC deposition without enough data, it is suggested that long-term measurements, monitoring and modeling work should be carried out to make clear the base cation emission and its contribution to deposition.

The choice of the chemical criterion is also a source of uncertainty to the critical load (An et al., 2001). Other indicators besides $(Bc/Al)_{crit}$ can also be applied as the chemical criterion for $ANC_{L,crit}$ calculation, such as the critical aluminum concentration $[Al]_{crit}$, critical pH $[H]_{crit}$, and the critical aluminum mobilization rate Al_w (UBA, 2004). However, $[Al]_{crit}$ and $[H]_{crit}$ are usually used for drinking water (ground water) and organic soil (e.g. peatland and bogs) protection, respectively. With regard to Al_w, the necessary parameter p, the stoichiometric ratio of Al to BC weathering in primary minerals, is not established in China. In European mapping of critical loads of acid deposition, the value of $(Bc/Al)_{crit}$, has commonly been set to 1.0, although the use of this value has raised questions (Mulder et al., 1989; Hogberg and Jensen, 1994; Løkke et al., 1996). In China the value for the main vegetation type in subtropical areas is

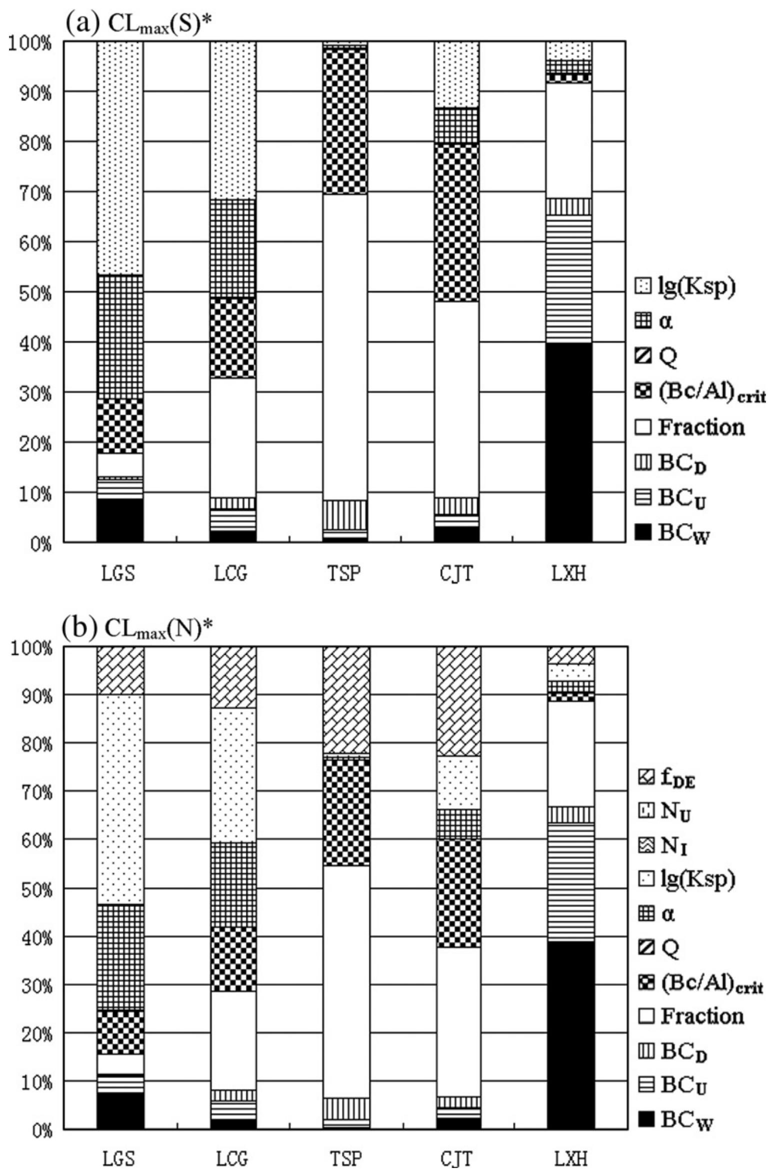

Fig. 4. The contributions of different input parameters to the uncertainty of $CL_{max}(S)$* and $CL_{max}(N)$* for the five catchments.

suggested to lie in the range between 1.0 and 2.0, but few field tests confirm this (Duan et al., 2001). According to the sensitivity analysis, the contribution of $(Bc/Al)_{crit}$ is 1.7% (LXH) to 31.3% (CJT) and 1.6% (LXH) to 22.3% (CJT) to the uncertainty of $CL_{max}(S)$* and $CL_{max}(N)$* respectively, implying that the value of $(Bc/Al)_{crit}$ should be selected carefully for accurate conclusions.

The variation of f_{DE} contributes significantly to the uncertainty of $CL_{max}(N)$*. The transformation of N in ecosystems is controlled by several biochemical processes, and the physical and chemical processes of N in soils are thus more complex than for S. Until now, very few studies have been carried out to determine the long-term denitrification rates in China. Based on the flux differences between nitrate in soils and surface water in the five catchments, considerable N disappears between the root zone and the stream, which might imply a high value of f_{DE}. However, it is difficult to determine the contribution of denitrification, which might cause a high variation in f_{DE}. The N immobilization and vegetation uptake, despite high uncertainty, have very little effect on $CL_{max}(N)$*. However, they could greatly affect $CL_{min}(N)$, which is much smaller than $CL_{max}(N)$* in this study.

The uncertainty of other parameters, such as vegetation uptake of base cations (BC_U) and runoff rate (Q), have little influence on the results.

When a Monte Carlo approach is applied for sensitivity analysis, the result is inevitably affected by the input uncertainty. According to the so called pedigree developed by Barkman and Alveteg (2001) and Skeffington (2006), the distribution of most parameters in this study are not from ideal site-specific monitoring but instead based on general theory, previous relevant studies, or even worse, expert judgment. Thus field work on more accurate statistic distribution of these parameters is still needed to improve the sensitivity analysis of critical load in China.

5. Conclusions

High deposition flux of base cations counteracts the acidifying effect of high S and N deposition, and its variation should be taken into account in critical load estimate in China. From the estimate using an extended S–N–BC critical load function, none of the five monitoring forested catchments has their critical load exceeded under current deposition but four will with a 75% reduction of the BC deposition. BC deposition, as well as chemistry criterion, is one of the main sources of uncertainty in critical load calculation and hence the assessment of the future acidification status in China. Based on the special catchment application, the extended critical load model can be further generalized for mapping critical loads in regional scale and developing acid rain mitigation policies in the future.

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