C-3.3 Development of a Model for Estimation of Soil Acidification caused by Acid Deposition

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Total budget for FY1993-FY1995 19,439,000 Yen (**FY1995** 6,159,000 Yen)

Abstract The steady state mass balance model was applied to the Japanese ecosystem to estimate critical loads. Definition of an acidification criterion suitable for the ecosystem was crucially important for reliable estimation of critical loads. Weathering rates were derived from surface geology and soil types for critical loads estimation whose accuracy was examined based on the measurements of soil samples. Classification with surface geology was considered appropriate, however, the estimation had large uncertainty due to variability of measurement within a group. A dynamic model was developed to estimate soil acidification processes and was verified by applying it to soil acidification experiment using simulated acid rain.

Key Words Soil acidification, Critical loads, Steady state mass balance model, Weathering rates, dynamic model

1. Introduction

Quantitative estimation of buffering capacity of soil and its modeling are necessary for prediction of ecosystem sensitivity to acid deposition and its effects. Two approaches have been proposed. One is steady state mass balance model evaluating material budget of acidic substances and other ions. The concept of the critical load of acidic substances was proposed based on this model in the 1980s in Europe, and European scale maps of critical loads were produced by UNECE under the cooperation of many countries[1),2)]. The critical load is defined as "the highest deposition of acidifying compounds that will not cause chemical changes leading to long term harmful effects on ecosystem structure and function". This method has caused a good deal of comments, while it is now used as a ground to control the pollutant emission in Europe, and Asian scale estimation has also started (the RAINS ASIA project[3)]). We applied the steady state mass balance model to Japan. The first objective is to examine the applicability of the model to the Japanese condition where meteorology, vegetation, soil etc. are different from those in

Europe. The second objective is to evaluate the accuracy of base data needed for the CL estimation. We concentrate to the mineral weathering rate of soils.

The other approach is predicting temporal changes of soil properties with a dynamic model. A number of models were developed mainly in Europe and North America[4)-6)]. Every model has its own feature and is got a simplification according to the characteristics of an objective ecosystem for model construction. For example, variable charge property, which is an important buffering process for many Japanese soils originated from volcanic ash, is not considered in existing models. Modification of the existing model is difficult technically and also because of a copyright problem, therefore, we aimed to develop a dynamic model applicable to Japanese soils.

2. Material and method

2.1 Estimation of critical loads

The following steady state mass balance model was used for calculation of CL($eq.ha^{-1}yr^{-1}$):

$$CL = BC_{we} + H_{l(crit)} + Al_{l(crit)} = BC_{we} + [\{Al_{l(crit)}/Q\} / K_{gibb}]^{1/3} Q + Al_{l(crit)} \qquad (1)$$

where BC_{we} : base cation weathering ($eq.ha^{-1}yr^{-1}$), $H_{l(crit)}$ and $Al_{l(crit)}$: critical hydrogen and aluminum ion leaching ($eq.ha^{-1}yr^{-1}$), K_{gibb}: gibbsite equilibrium constant (m^6eq^{-2}) and Q : runoff ($m^3ha^{-1}yr^{-1}$). The maximum allowable deposition (CD: critical deposition) of acidic substances (H^++$2NH_4^+$) is estimated as follows:

$$CD = CL - acid_{biol} \qquad (2)$$

where $acid_{biol}$ denotes the net production of acidity in the ecosystem mainly by biological processes, which includes base cation uptake (BC^*_{gu}), nitrogen uptake (N_{gu}), immobilization (N_{im}), denitrification (N_{de}) etc. We took only BC^*_{gu} and N_{gu} into consideration. A criterion on an acidification limit must be defined to calculate $Al_{l(crit)}$. Three criteria have been proposed and $Al_{l(crit)}$ is formulated based on each criterion as shown in Table 1.

The data used for CL and CD estimation were derived from several national data bases whose spatial resolutions are about one square kilometer. Weathering rates(BC_{we}) were estimated based on the acidity of parent material and soil texture data[7)]. Surface geology data was used to classify the parent material into acid, intermediate and basic and soil types were used to derive texture classes. Runoff (Q) was calculated as the difference between annual precipitation and evapotranspiration estimated with the Thornthwaite method. Growth uptake of base cation and nitrogen (BC^*_{gu} and N_{gu}) were calculated from net growth rates evaluated from annual average temperature and element concentration in trees for each forest type. For a natural forest net uptake was assumed zero, as the uptake by trees is in equilibrium with the release due to litter decomposition. Other parameters in the formulas were set to the same values as in European and Asian applications.

Table 1 Criteria of acidification limit and formulas to express $Al_{l(crit)}$

Criterion and critical values	Formula to express $Al_{l(crit)}$
$(BC^*/Al)_{crit}$ = 1 mol mol^{-1}	$\frac{1.5\max\{BC^*_{we}+BC^*_d-BC^*_{gu}, [BC^*_{le}]_{min}Q\}}{(BC/Al)_{crit}}$
$[Al^{3+}]_{crit}$ = 0.2 eq.m^{-3}	$[Al^{3+}]_{crit}\ Q$
$(Al_{le}/Al_{we})_{crit}$ = 1 mol mol^{-1}	$f_{Al/BC}\ (Al_{le}/Al_{we})_{crit}\ BC_w$

BC=Ca+Mg+K+Na, BC^*=CA+Mg (+K) BC^*_{dt}: Base cation deposition(eq.ha^{-1}yr^{-1}), $[BC^*_{le}]_{min}$:Minimum concentration of BC leaching(eq.m^{-3}) =0.002, $f_{Al/BC}=Al_{we}/BC_{we}$=2.0 eq.eq.$^{-1}$

2.2 Evaluation of accuracy of BC_{we} estimation

In order to evaluate the accuracy of BC_{we} estimation, a soil survey was carried out at 42 sites in the Hiroshima and Shimane Prefectures. For each site soils were collected from two layers at three sampling points that were 3 to 5 m apart each other. Particle-size distributions and total ion contents in <2 mm and >2 mm fractions were analyzed. Weathering rates indicated as BC_{we}(P), were calculated for each site with the PROFILE model[8] according to these measurements. The sites were divided into six surface geology groups (granite, rhyolite, andesite, gabbro, volcanic ash, sediment rock), and into six soil type groups (Brown forest soils(dry), Brown forest soils, Andosols, Regosols, Red soils, Yellow soils). The group average of BC_{we}(P) and variability within each group were evaluated.

2.3 Development of a dynamic model

Dependence of CEC and AEC on soil pH was measured for volcanic ash soils with the Wada/Okamura procedure, and was approximated by regression equations. Based on these equations, a sub-model was made that takes only variable charge processes into account and was verified by predicting the pH change of each step of the Wada /Okamura procedure.

A dynamic model including this sub-model and other chemical reactions was developed. We assumed an ion balance equation indicated with eq. (3) and mass balance equations for each ion exemplified with eq.(4) in the soil of 1 m^2 of area and d m of depth.

$$[H^+]+2[Ca^{2+}]+2[Mg^{2+}]+[Na^+]+[K^+]+[NH_4^+]+3[Al^{3+}]+2[AlOH^{2+}]+[Al(OH)_2^+]$$
$$= 2[SO_4^{2-}]+[NO_3^-]+[Cl^-]+[HCO_3^-]+2[CO_3^{2-}]+[R^-]+[OH^-] \quad (3)$$

$$n([X^{n+}]_t-[X^{n+}]_{t-1})Vw+(ex(X^{n+})_t-ex(X^{n+})_{t-1})Ws/100 = D(X^{n+})_t+P(X^{n+})Ws-n[X^{n+}]_tVo_t \quad (4)$$

where Vw: water volume (m^3), Ws: soil weight (kg), Vo_t: leachate volume (m^3), $[X^{n+}]$: concentration in soil solution (mol/m^3), $ex(X^{n+})$: exchangeable concentration (eq/100g), D(X): deposition rate (eq/m^2). P(X) denotes consumption or supply in the system(eq/kg) due to mineral weathering, uptake, nitrification etc. Under these conditions, concentrations of elements at each time step are calculated according to the equilibrium or quasi-equilibrium reactions such as cation exchange, sulfate adsorption, precipitation and dissolution of $Al(OH)_3$, dissociation of organic acids etc. The model was applied to experiments of soil acidification using simulated acid rain for the model validation. In the experiment, dilute H_2SO_4 solution was poured into 10 kg soils periodically for several years and soil properties before and after the treatment were measured every year. Some input parameters to the model, selectivity coefficients of cation exchange, nitrification rate etc were estimated from the result of the experiment.

3. Result and Discussion

3.1 Estimation of the Critical loads

Table 2 shows the spatial average, minimum and maximum values of CLs and CDs based on each acidification criterion shown in Table 1. CDs were generally lower than CLs because of the higher BC^*_{gu} than N_{gu}. Values based of BC/Al ratio were much smaller than those by other criteria. For the first and third criteria, the major factor to determine spatial distribution of CL and CD was BC_{we}, and sensitive areas were located in the north coast of the Inland Sea covered by Regosols originated from acidic rocks, and mountainous area around the center of the Main Island covered with Lithosols (Fig. 1). The spatial distribution based on the second criterion was extremely different from Fig. 1. We conclude that it is crucially important to determine the most realistic criterion for the objective area.

3.2 Evaluation of accuracy of BC_{we} estimate

Variances of ion contents due to particle size, layers were very small and that due to sampling points within a several square meters was relatively small that was less than 15% of total

Table 2 Spatial mean, minimum and maximum values of estimate CL and CD(eq $ha^{-1}yr^{-1}$)

Acidification criteria	Critical load (CL)			Critical deposition (CD)		
	mean	minimum	maximum	mean	minimum	maximum
$(BC^*/Al)_{crit}$=1 mol/mol	2269	240	9265	1930	0	9265
$[Al^{3+}]_{crit}$=0.2eq.m^{-3}	5164	5	12893	4683	0	12417
$(Al_{le}/Al_{we})_{crit}$=1	5118	5	12721	4636	0	12721

variance. Fig. 2 shows average $BC_{we}(P)$ for each surface geology group. The classificat-ion by acidity was considered appropriate qualitatively because average rates were signifi-cantly low for acidic rocks (granite and rhyolite) compared to other geology types. The BC_{we} for gabbro, volcanic ash and sediment rock have large uncertainties due to spatial variability within the same geology group as shown by bars indicating standard deviation in Fig. 2.

3.3 Application of the dynamic model for validation

As the sub-model of variable charge could predict the change of soil pH to a certain extent, it was introduced to the dynamic model. In Fig.3 predicted values by the model were compared with the measurements of soil acidification experiments using sand dune soil for four years. B and A in Fig 3(1) and (3) indicate the before and after treatment with acid rain, respectively, and ①and ② in Fig.3(2) and (4) denote the first and the second half of percolated water of each year, respectively. The model could predicted the trend of change of soil chemistry in Fig. 3(1), (2) and (3), especially well for pH of percolated water and ex-Al. Al concentration in percolated water, however, could not predicted by the model at all because mechanism of Al release at high pH was not included in the model. Accurate data on the nitrification rate and capacity of sulfur adsorption were required for estimation in real ecosystems, because these data had a great influence on the prediction results.

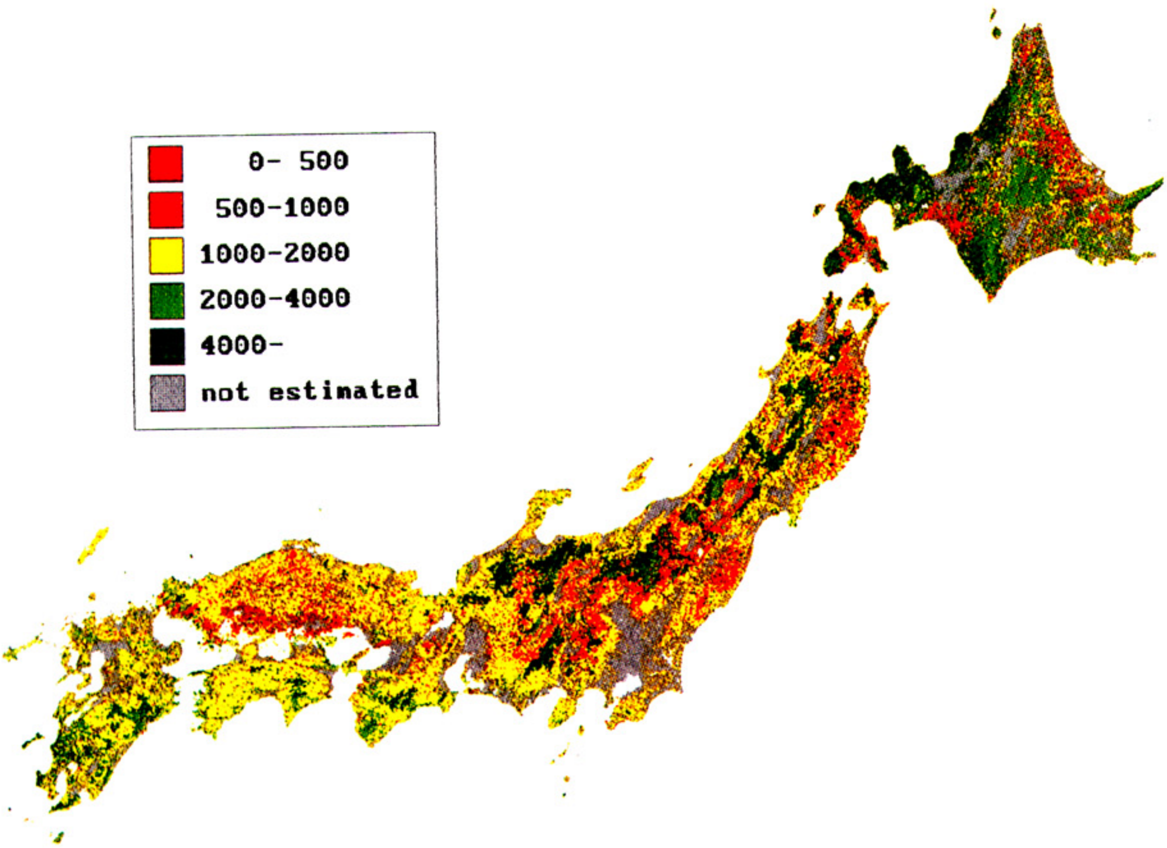

Fig.1 Spatial distribution of CD estimates ($eq.ha^{-1}yr^{-1}$)

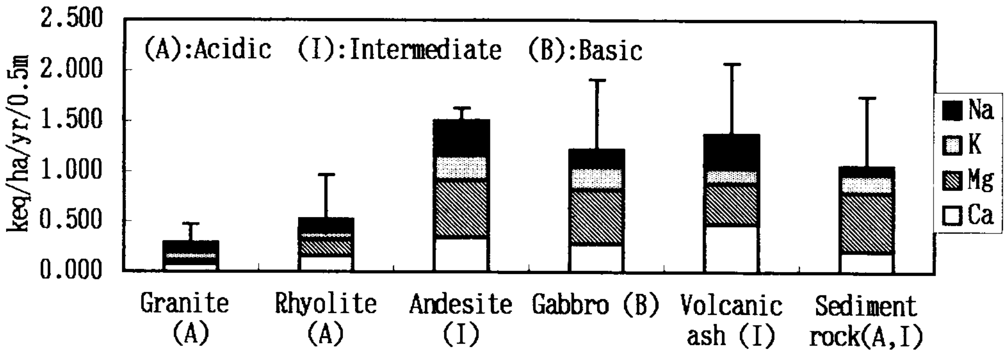

Fig.2 Average and standard deviation of $BC_{we}(P)$ for each surface geology group

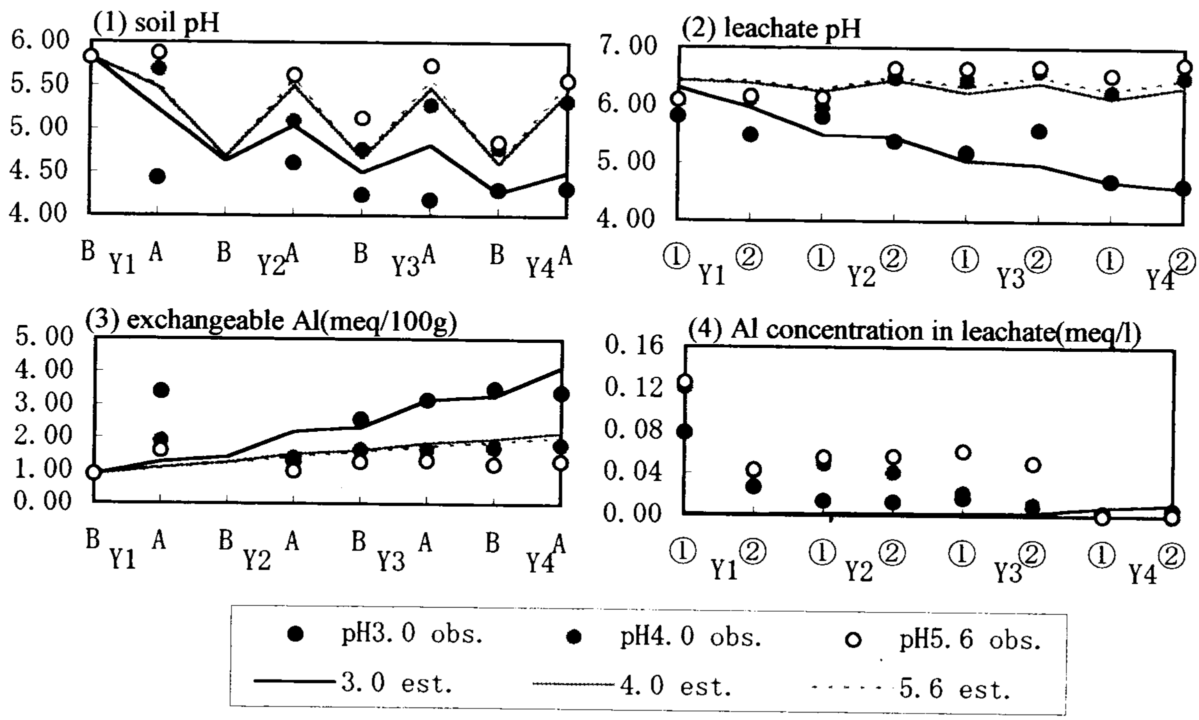

Fig.3 Comparison of predicted valued to measurements of the soil acidification experiment

4. Conclusion

The existing method for critical load estimation simplifies both acidification effects on ecosystems and the neutralization/acidification mechanisms. Regarding the effects, aluminum concentration is considered to determine the ecosystem damage in the method. It was shown that the different acidification criteria on Al produced extremely different CL values, and definition of suitable criterion for the objective ecosystem was fundamentally important. Moreover, the effect of acidification has been recognized as the complex effects of multi factors, therefore other criterion than Al would be possible[10)]

Mechanisms that should be considered depend on spatio-temporal scale of estimation . For long term and global scale estimation, evaluating material budget was considered important. On the other hand short term and smaller scale estimation requires specific mechanism too. Extraction and modeling of importantmechanisms will be necessary for each objective area.

Evaluation of accuracy of CL esitmation is inevitable according to the accuracy and uncertainty of base data. Analysis of accurccy for weathering rates suggested the necessity of improvement of the estimation method. For other processes, similar evaluation should be done.

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