

# Comparative Study on the Critical Loads of Acid Deposition in two major cities of India

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## ABSTRACT

A Steady State Mass Balance method (SSMB) in all different forms was used to calculate the critical load of sulphur and nitrogen for soil. The present load of sulphur (161.1 Eq ha<sup>-1</sup> yr<sup>-1</sup>), nitrogen (49.9 Eq ha<sup>-1</sup> yr<sup>-1</sup>) and ammonium (176.8 Eq ha<sup>-1</sup> yr<sup>-1</sup>) were calculated from wet and dry deposition from Agra region. Similarly, the present load of sulphur (151.1 Eq ha<sup>-1</sup> yr<sup>-1</sup>), nitrogen (244.9 Eq ha<sup>-1</sup> yr<sup>-1</sup>) and ammonium (221.8 Eq ha<sup>-1</sup> yr<sup>-1</sup>) were calculated from wet and dry deposition from Kanpur region also. The values of critical load of sulphur and nitrogen for soil with respect to Oat (*Triticum vulgare*), china orange (*Zea mays*), Eucalyptus (*Eucalyptus*), pigeon pea (*Cajanus cajan*) and lemon (*Citrus argentifolium*) were calculated. The values of actual acidity calculated for Agra were lower than the values assessed for Kanpur Region. These computed values were also lower than the values assessed by the RAINS-Asia model of these areas. But Kanpur is nearing the critical limit. It has been concluded that chloride also plays an important role in the acid deposition which changes the value of critical load significantly.

**Keywords:** Critical Load, SSMB Method, Agra Region, RAINS-Asia Model, Acid Deposition, Soil.

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## INTRODUCTION

The emission of sulphur and nitrogen compounds cause the acidification of the ecosystem. Acidification is the main environmental problem over Europe and North America and it is now spreading over Asia due to increasing industrialization<sup>1</sup>. Its effect on various ecosystems is hazardous. The documented effects of air pollution and acid deposition include the following<sup>2</sup>:

- Major contributions to forest decline, possibly in complex interactions with natural stress.
- Release of toxic metals such as aluminium that can damage soils, vegetation and surface waters.
- Damage to aquatic resources and their ecosystem.
- Direct damage to crops and vegetation by high air concentrations of pollutants or indirect damage through chemical changes in the soil.
- Increased rate of erosion of monuments, buildings and other cultural and commercial resources.
- Direct, adverse effects on human health, especially for sensitive populations with respiratory or cardiovascular problems.

The definition of critical loads adopted by the United Nations Economic Commission for Europe (UNECE) is 'a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur according to present knowledge' (NILSSON and GRENNFELT, 1988)<sup>3,4</sup>. The critical acid deposition load to an ecosystem as defined by Skokloster Critical load workshop, 1988<sup>5</sup> is 'the highest deposition of acidifying compounds that will not cause chemical changes leading to long term harmful effects on ecosystem structure and function'. The linking of the ecosystem response to deposition level is the critical principal of the critical loads approach. In order to apply the concept four elements<sup>6</sup> need to be defined are receptor, biological indicator, chemical criterion and critical limit.

A number of methods have been used to derive critical level values ranging from a formal statistical approach based on ecotoxicology to empirical field observation. Exposure-response relationships are central to the estimation of critical level values. These relationships are derived from field observation or range of experimental approaches. Special care is to be taken in the selection of an indicator organism as the experimental details are based on it.

Critical loads can be assessed by applying two methods<sup>7</sup>; relative sensitivity and mathematical models. The relative sensitivity approach provides a semi-quantitative assessment of sensitivity including geology, soil characteristics, other geophysical features of an area and plant tolerance range. Mathematical models to compute critical loads include the Steady State Mass Balance method and Water Chemistry method<sup>8</sup>.

The possibility to determine the effects of nitrogen deposition on vegetation depends on the quantity and quality<sup>9</sup> of the available data. Most of the present data come from the studies performed over different time periods, different climatic regions or receiving varying nitrogen doses through deposition and fertilization. Chronic nitrogen deposition may result in a surplus of nitrogen as related to other nutrients, the enhanced nitrogen inputs no longer stimulate plant growth but start to disrupt ecosystem structure and function. Nitrogen is mostly retained in the soil in areas with low deposition but the risk of nitrate leaching increases with higher loads. Effects on organisms probably start soon after deposition increases, being more or less detectable depending on type of organism and rate of response to altered conditions<sup>9</sup>. Empirical values based on observed changes in the structure or function of ecosystems have been used to define critical loads (CL) for terrestrial and wetland ecosystems. Apart from the acidic effect of nitrogen and sulphur, chloride also plays an important role in increasing the acidity of the ecosystem. So, chloride cannot be neglected in the determination of the critical load.

### SITE DESCRIPTION

Agra ( 27°10' N, 78°05' E ) lies in a semi-arid zone adjacent to the Thar desert of Rajasthan. The soil of the district is alluvial except for residual soils occurring in a narrow strip in the south and south-west lower horizons of the region is having sandy loam soil. The pH and conductivity of soil varies between 7.5 and 8.4 and 0.07 to 2.6 mScm<sup>-1</sup> respectively. The weathering rate of the soil is 1430 Eq ha<sup>-1</sup> yr<sup>-1</sup> as calculated from the observed correlation between observed weathering rates and whole soil total content of magnesium and calcium<sup>10</sup> ( Olsson and Melkerud, 1990 ). Table 1 depicts the mean values of wet and dry deposition of sulphate, nitrate, chloride and ammonium. The annual rainfall at Agra is 766 mm<sup>11</sup>.

Kanpur ( 18°09' N, 82°05' E ) lies in a Gangetic plain. The soil of the district is alluvial. The pH and conductivity of soil varies between 6.6 and 7.4 and 0.09 to 1.4 mScm<sup>-1</sup> respectively. The weathering rate of the soil is 1240 Eq ha<sup>-1</sup> yr<sup>-1</sup> as calculated from the observed correlation between observed weathering rates and whole soil total content of magnesium and calcium<sup>10</sup> ( Olsson and Melkerud, 1990 ). Table 1 depicts the mean values of wet and dry deposition of sulphate, nitrate, chloride and ammonium. The annual rainfall at Agra is 850 mm<sup>11</sup>.

### MATERIALS AND METHODS

The Steady State Mass Balance method (SSMB) is being applied to determine the critical load in the present study. It is the most commonly used method. The basic principle<sup>3</sup> of the method is to identify the long term average sources of acidity and alkalinity in the system and to determine the maximum acid input that will balance the system at a bio-geochemical safe-limit.

#### Method for calculating critical load

The critical load of actual acidity<sup>12,13</sup> CL(Ac<sub>act</sub>) was first of all computed by the method given by Hettelingh et al which is as follows:

$$CL(Ac_{act}) = BC_w + [H]_{crit} \cdot Q + [Al]_{crit} \cdot Q \quad (i)$$

Where

- BC<sub>w</sub> = Weathering of the base cation (Eq ha<sup>-1</sup> yr<sup>-1</sup>)
- Q = Runoff (Eq ha<sup>-1</sup> yr<sup>-1</sup>)
- [H]<sub>crit</sub> = Critical hydrogen leaching (Eq m<sup>-3</sup>)
- [Al]<sub>crit</sub> = Critical aluminium leaching (Eq m<sup>-3</sup>)

After substituting the values from table 2 in the equation (i), the value of actual acidity was found to be **432.4 Eq ha<sup>-1</sup> yr<sup>-1</sup>** for Agra region and **782.4 Eq ha<sup>-1</sup> yr<sup>-1</sup>** for Kanpur region.

The sulphur fraction is designed to compute the net contribution of sulphur (S) and nitrogen (N) to the critical load of actual acidity. The sulphur fraction ( $S_f$ ) is defined as follows when

$$PL(NO_x) + PL(NH_4) > N_u + N_i$$

$$S_f = \frac{PL(SO_x)}{PL(SO_x) + PL(NO_x) + PL(NH_x) - N_u - N_i} \quad (ii)$$

otherwise  $S_f$  is equal to unity.

Where

$$\begin{aligned} PL(SO_x) &= \text{Present load of Sulphur (Eq ha}^{-1}\text{ yr}^{-1}\text{)} \\ PL(NO_x) &= \text{Present load of Nitrogen (Eq ha}^{-1}\text{ yr}^{-1}\text{)} \\ PL(NH_x) &= \text{Present load of Ammonium (Eq ha}^{-1}\text{ yr}^{-1}\text{)} \\ N_u &= \text{Nitrogen uptake for managed crops (Eq ha}^{-1}\text{ yr}^{-1}\text{)} \\ N_i &= \text{Nitrogen immobilization (Eq ha}^{-1}\text{ yr}^{-1}\text{)} \end{aligned}$$

Critical loads of S and N were calculated using the following formulae:

$$CL(S) = S_f \times CL(Ac_{act}) \quad (iii)$$

$$CL(N) = N_u - (1 - S_f) \times CL(Ac_{act}) \quad (iv)$$

Based on this model, several formulae have been proposed to calculate critical loads depending on the different definition of critical aluminium leaching<sup>16</sup>. We have applied four formulae shown in Table 3 to obtain values for obtaining critical loads. The values obtained are shown in Table 4.

As the resulted critical loads were different in magnitude and spatial distribution according to the formulae, we need some criteria to decide which formula should be employed for estimation?

Recently Posch et al (1995, 1997)<sup>12,13</sup> has redefined the calculation of critical loads of S and N. The deposition of chloride ( $Cl_{dep}$ ) is a new term added in the equation because one cannot neglect the contribution of chloride in the acidity. Although the contribution of chloride is negligible and is assumed to be a tracer<sup>12,13</sup>, it is being taken into account. As there are no sources or sinks of chloride within the soil compartment, so

$$Cl_{le} = Cl_{dep} \quad (x)$$

Where

$$Cl_{le} = \text{Chloride leaching (Eq m}^{-3}\text{)}.$$

The formulae given by Posch et al are as under:

$$CL_{max}(S) = BC_{dep} - Cl_{dep} + BC_w - BC_u - Alk_{le(crit)} \quad (v)$$

$$CL_{max}(N) = CL(S+N) = CL_{min}(N) + CL_{max}(S) \quad (vi)$$

or  $CL_{max}(N) = N_i + N_u + CL_{max}(S) \quad (vii)$

where

$$\begin{aligned} BC_{dep} &= \text{Base Cation Deposition (Eq ha}^{-1}\text{ yr}^{-1}\text{)} \\ Cl_{dep} &= \text{Chloride Deposition (Eq ha}^{-1}\text{ yr}^{-1}\text{)} \\ BC_w &= \text{Weathering of the base cation (Eq ha}^{-1}\text{ yr}^{-1}\text{)} \\ BC_u &= \text{Base Cation uptake for managed crops (Eq ha}^{-1}\text{ yr}^{-1}\text{)} \\ Alk_{le(crit)} &= \text{Critical Alkalinity Leaching (Eq m}^{-3}\text{)} \\ Alk_{le(crit)} &= Al_{le(crit)} - H_{le(crit)} \\ &= -Q ([Al]_{crit} - [H]_{crit}) \end{aligned} \quad (viii)$$

Therefore the modified formula for the critical load of actual acidity is

$$CL(Ac_{act}) = BC_w + [H]_{crit} \cdot Q + [Al]_{crit} \cdot Q - Cl_{dep} \quad (ix)$$

So the actual acidity calculated is **377.08 Eqha<sup>-1</sup>yr<sup>-1</sup>** for Agra and **477.08 Eq ha<sup>-1</sup>yr<sup>-1</sup>** for Kanpur.

### (b) Input Data

The data required are as under:

- (1) **Weathering rate** : Weathering rate of soil was calculated from the observed correlation between the observed weathering rates<sup>10</sup> and whole soil total content of magnesium and calcium (Olsson and Melkerud, 1990).
- (2) **Runoff** : Runoff was calculated as the difference between the annual precipitation and the annual evapotranspiration.

$$\text{Runoff} = \text{Precipitation} - \text{Evapotranspiration} - \text{Surface runoff}$$

- (3) **Base Cation Deposition** : Base cation deposition was calculated from the wet and dry deposition. The values are taken from the local available data<sup>15</sup>.
- (4) **Base Cation Uptake** : The values are taken from ICAR handbook<sup>16</sup>.
- (5) **Nitrogen uptake for managed crops** : The values are taken from the records<sup>16</sup>.
- (6) **Nitrogen Deposition** : The values are taken from the local data<sup>15</sup> available.
- (7) **Ammonium Deposition** : The values are taken from the local data<sup>17</sup> available.

### CONCLUSION

The values of actual acidity calculated for Agra by equation (i) and equation (ix) are 432.4 Eq ha<sup>-1</sup> yr<sup>-1</sup> and 377.08 Eq ha<sup>-1</sup> yr<sup>-1</sup>. The values of actual acidity calculated for Kanpur by equation (i) and equation (ix) are 782.4 Eq ha<sup>-1</sup> yr<sup>-1</sup> and 477.08 Eq ha<sup>-1</sup> yr<sup>-1</sup>. These obtained values are lower than the values assessed by the RAINS-Asia model of this area which is in the range of 500-1000 Eq ha<sup>-1</sup> yr<sup>-1</sup>. When the values of equation (v) and equation (vii) are compared with rest of the equations, it is seen that due to chloride deposition the critical load of sulphur and nitrogen changes significantly. It is also seen that deposition of chloride cannot be neglected in the calculation of critical loads of acidity. It has also been assessed by different methods that present load is still lower than the critical load values calculated.

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**Table 1**

*Computed values of wet and dry deposition (Eq ha<sup>-1</sup>yr<sup>-1</sup> of sulphate, nitrate, ammonium and chloride)*

Sulphate	as S	Nitrate	as N	Ammonium	Chloride
<b>Agra Region</b>					

<b>Dry</b>	212.2	70.8	111.3	25.1	77.4	19.32
<b>Wet</b>	271.0	90.3	109.8	24.8	99.4	36.00
<b>Total</b>	483.2	161.1	221.1	49.9	176.8	55.32
<b>Kanpur Region</b>						
<b>Dry</b>	222.4	65.4	171.2	30.2	79.4	29.32
<b>Wet</b>	279.4	88.2	111.4	28.2	109.4	35.28
<b>Total</b>	501.8	153.6	282.6	58.4	188.8	64.50

**TABLE 2**

Values used for  $[H]_{crit}$ ,  $[Al]_{crit}$ , Aluminium Weathering ( $Al_w$ ) Runoff ( $Q$ ) and Base cation weathering rate ( $BC_w$ ) for soil

$Al_w$ Eq ha <sup>-1</sup> yr <sup>-1</sup>	$[H]_{crit}$ Eq m <sup>-3</sup>	$[Al]_{crit}$ Eq m <sup>-3</sup>	Runoff (Q) Eq ha <sup>-1</sup> yr <sup>-1</sup>	$BC_w$ Eq ha <sup>-1</sup> yr <sup>-1</sup>	$BC_d$ Eq ha <sup>-1</sup> yr <sup>-1</sup>	$N_i$ Eq ha <sup>-1</sup> yr <sup>-1</sup>
<b>Agra Region</b>						
2860	0.09 <sup>a</sup>	0.2 <sup>a</sup>	-3440	1430	473 <sup>17</sup>	0.009
<b>Kanpur Region</b>						
2560	0.06 <sup>a</sup>	0.2 <sup>a</sup>	-3100	1240	588 <sup>17</sup>	0.007

<sup>a</sup>Hettelingh et al (1991)

**TABLE 3**

Criterion & Critical Values	Formula	Equation No.
$\frac{((Ca+Mg+K+Na) / Al_{crit})}{= 1 \text{ mol mol}^{-1}}$	$\frac{1.5(BC_w + BC_d - BC_u)}{((Ca+Mg+K+Na) / Al_{crit})}$	xii
$\frac{((Ca+Mg) / Al_{crit})}{= 1 \text{ mol mol}^{-1}}$	$\frac{1.5 \max\{f_{BC1}(BC_w+BC_d-BC_u-[BC]_{lmin} \cdot Q)\}}{((Ca+Mg) / Al_{crit})}$	xiii
$(Al_w / BC_w) = 1 \text{ mol mol}^{-1}$	$f_{Al/BC} (Al_l / Al_w)_{crit} BC_w$	xiv
$\frac{((Ca+Mg+K) / Al_{crit})}{= 1 \text{ mol mol}^{-1}}$	$\frac{1.5\{f_{BC2}(BC_w+BC_d-BC_u-[BC]_{l(min)} \cdot Q)\}}{((Ca+Mg+K) / Al_{crit})}$	xv

$BC_{l(min)}$  = Minimum concentration of BC leaching (Eqm<sup>-3</sup>) = 0.002

$f_{BC1} = (Ca_w + Mg_w) / BC_w = 0.7 \text{ eq eq}^{-1}$

$f_{BC2} = (Ca_w + Mg_w + K_w) / BC_w = 0.8 \text{ eq eq}^{-1}$

$f_{Al/BC} = Al_w / BC_w = 2.0 \text{ eq eq}^{-1}$

**TABLE 4**

Comm on Name	Botanical Name	Nitro gen uptake	Base Cation uptake	Calculated Critical Loads using various equations							
				Equatio n iii	Equatio n iv	Equation v	Equation vii	Equation xii	Equation xiii	Equat ion xiv	Equation xv
Wheat	Triticum vulgaris	2000	195.2	432.4	2000	5779.48	7780.39	2561.70	1928.52	2860	2143.02
Maize	Zea mays	1997	190.1	432.4	1997	5784.58	7782.50	2569.35	1936.17	2860	2150.67
Rye	Triticale	1250	157.3	432.4	1250	5817.38	7067.39	2618.56	1985.37	2860	2199.87
Potato	Solanum tuberosum	3125	200.0	432.4	3125	5774.68	8899.69	2594.45	1921.32	2860	2135.82
Lemon	Citrus argentifolium	1555	99.6	432.4	1555	5875.08	7430.09	2705.10	2071.92	2860	2286.42
Anjan Grass	Cenchrus ciliaris	46.2	30.3	250.3	135.95	5944.38	5990.59	2809.05	2175.87	2860	2390.37
Bajra	Pennisetum typhoides	2571.43	100.7	432.4	2571.43	5873.98	8445.42	2703.45	2070.27	2860	2284.77