Chapter (not refereed)

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Keynote Paper - Modification of the Simple Mass Balance Equation for Calculation of Critical Loads of Acidity

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1 Introduction

Over the last few years, the simple mass balance equation for the calculation of critical loads of acidity has been gradually modified as the underlying critical load concepts have developed and as problems with particular forms of the equation have been identified, through application in particular countries. The first major update of the equation took place following a workshop held in Vienna, Austria (Hojesky *et al.* 1993). The workshop was held to discuss problems which had been identified when the then current form of the equation was applied in countries with high rainfall. The problems had largely arisen because of simplifications and assumptions incorporated into the early formulation of the equation. The equation was reformulated to overcome the problems identified at the workshop. However, further problems were identified when the reformulated equation was applied in the UK in situations with a combination of high rainfall, large marine inputs and widespread occurrence of organic soils. A small workshop was, therefore held in Grange-over-Sands, UK in late 1993 to dicuss the problems and to further re-evaluate the equation. The problems had arisen in the UK because of simplifications and assumptions made in the formulation concerning, in particular, cation leaching and uptake. As a result, a more rigorous treatment of these variables was incorporated into the equation. The reformulation of the equation, as derived at the September 1993 workshop is described below.

2 The Basic Equation

The reformulated equation is based on the following definition of the critical load for actual acidity:

$$CL = ANCw - ANC_L \qquad (1)$$

where ANCw = alkalinity produced from weathering eq ha^{-1} yr^{-1}
CL = Critical load of acidity eq ha^{-1} yr^{-1}
ANC_L = ANC leaching eq ha^{-1} yr^{-1}

In this equation the limiting ANC leaching is determined by the maximum permitted leaching of H and Al at which damage will not occur to a sensitive biological indicator and as derived from the following simplified expression:

$$ANC_L = -H_L^{+} - Al_L^{3+} \qquad (2)$$

where Al_L^{3+} = Al^{3+} leaching eq ha^{-1} yr^{-1}
H_L^{+} = H^{+} leaching eq ha^{-1} yr^{-1}

3 Plant Response Criteria

The maximum permitted leaching of ANC is set in terms of a critical chemical limit above, or below which, damage will not occur to a selected biological indicator. The most frequently used indicator is fine roots with the critical chemical limit most commonly set in terms of the Base Cation:Aluminium ratio in soil solution. However, the Base Cation:Hydrogen ratio can be used in soils with a large organic matter content and small Aluminium contents.

The following equation gives the limiting Al flux in equation (2) when the molar Base Cation:Al ratio is used as the critical chemical limit:

$$Al_L^{3+} = \frac{BC_L}{BC/Al_{crit}} \qquad (3)$$

where BC_L = Base Cation leaching eq ha^{-1} yr^{-1}
$(BC/Al)_{crit}$ = BC/Al ratio used as the critical chemical limit

The Base Cation leaching is calculated from a mass balance:

$$BC_L = BC_{W(CaMgK)} + BC_D - BC_U \qquad (4)$$

where BC_D = Base Cation deposition eq ha^{-1} yr^{-1}
$BC_{W(CaMgK)}$ = Weathering rate of Ca+Mg+K eq ha^{-1} yr^{-1}
BC_U = Base Cation uptake eq ha^{-1} yr^{-1}

In the mass balance equation for base cations, approximately 30% of released base cations from weathering are Na, which provides no protection against Al for plants. The production of Ca, Mg and K from weathering is:

$$BC_{W(CaMgK)} = x_{BC} \cdot ANC_W \qquad (5)$$

where X_{BC} = Fraction of weathering as Ca+Mg+K = 0.7
ANC_W = Neutralisation rate due to weathering eq ha^{-1} yr^{-1}

However, two qualifications must be considered when calculating Base Cation uptake and leaching:

i base cations at very low concentrations in soil solution, <2meq m^{-3}, will be unavailable for plant uptake because of physiological limitations, and

ii the quantity of base cations leached cannot be larger than the supply from weathering plus Base Cation deposition. The minimum Base Cation leaching can be derived as follows:

$$BC_{min} = Q.[BC]_{min} \tag{6}$$

where Q is percolation, [BC] is the limiting concentration for uptake, provided sufficient base cations are available. However if:

$$BC_{min} > x_{BC} \, . \, ANC_{W} + BC_{D} \tag{7}$$

then:

$$BC_{min} = x_{BC} \, . \, ANC_{W} + BC_{D} \tag{8}$$

A further condition which must be satisfied is that plant uptake of base cations cannot exceed the quantity of bases cations available from weathering and deposition. Thus, if:

$$BC_{U} > x_{BC} \, . \, ANC_{W} + BC_{D} - BC_{min} \tag{9}$$

then:

$$BC_{U} = x_{BC} \, . \, ANC_{W} + BC_{D} - BC_{min} \tag{10}$$

The Al leaching term can then be written as:

$$AL_{L}^{3+} = 1.5 \, . \, \frac{(x_{BC} \, . \, ANC_{W} + BC_{D} - BC_{U})}{(BC/Al)_{crit}} \tag{11}$$

Operationally the H^+ concentration can be calculated using the gibbsite equation:

$$[H^{+}] = (\frac{[Al]^{3+}}{K_{gibb}})1/3 \tag{12}$$

where K_{gibb} = gibbsite coefficient 300 $m^6 eq^{-2}$ (-pK(gibb)=8.5)

Accordingly, the limiting H^+-concentration corresponding to a certain Al concentration in the soil is calculated from the Al^{3+}-flux calculated as above (equation 11), divided by the flow and the gibbsite coefficient:

$$[H^{3}]_{limit} = (\frac{Al_L^{3+}}{Q \cdot K_{gibb}})1/3 \qquad (13)$$

By inserting the expression for the Al-limiting flux in the expression and multiplying by flow Q to get from H$^+$-concentration to flow, we get:

$$H_L^{+} = (1.5 \cdot \frac{x_{BC} \cdot ANC_W + BC_D - BC_U}{(BC/Al)_{crit} \cdot Q \cdot K_{gibb}})1/3 \cdot Q \qquad (14)$$

The modified SMB equation for critical load of acidity in eq ha^{-1} yr^{-1} thus becomes:

$$CL = ANC_W + (1.5 \cdot \frac{(x_{BC} \cdot ANC_W + BC_D - BC_U)}{(BC/Al)_{crit} \cdot K_{gibb}})1/3 \cdot Q^{2/3}$$

$$+1.5 \cdot (\frac{x_{BC} \cdot ANC_W + BC_D - BC_U}{(BC/Al)^{crit}}) \qquad (15)$$

4 Plant Response based on Base Cation:Hydrogen Ion Ratio

The use of the Base Cation: Aluminium ratio is inappropriate for highly organic, peat soils which have very small contents of aluminium. In these soils, the critical chemical limit may be more appropriately expressed in terms of the Base Cation: Hydrogen ion ratio at which root damage occurs. The limiting H$^+$ flux can then be determined as follows:

$$H_L^{+} = \frac{BC_L}{(BC/H)_{crit}} \qquad (16)$$

The Base Cation leaching is calculated from a mass balance:

$$BC_L = BC_{W(CaMgK)} + BC_D - BC_U \qquad (17)$$

Al is normally set to zero in pure peat:

$$[Al^{3+}] = 0 \qquad (18)$$

We can now fill in the equation:

$$CL = ANC_W + H_L^{\cdot} \tag{19}$$

$$CL = ANC_W + \frac{0.5 \,.\, (x_{BC} \,.\, ANC_W + BC_D - BC_U}{(BC/H)_{crit}} \tag{20}$$

The factor 0.5 arises from the use of a molar BC/H$^+$ ratio in an expression based on equivalents. The critical load is then given by:

$$CL = ANC_W + \frac{0.5 \,.\, (x_{BC} \,.\, ANC_W + BC_D - BC_U}{(BC/H)_{crit}}$$

$$+1.5 \,.\, \frac{(x_{BC} \,.\, ANC_W + BC_D - BC_U)}{(BC/Al)_{crit}} \tag{21}$$

The equation should be applied to peat, mosses, shallow rooted grasslands, organic alpine soils, raised bogs, black earth soils.

5 Soil Stability Criteria

In high precipitation areas, net soil Aluminium depletion may cause structural changes in soils. For many soils, secondary Aluminium phases and complexes are important structure bearers in the soil. Stability of these soils depend on the stability of the reservoir of these substances. In high precipitation areas, acid deposition may potentially lead to Aluminium leaching in excess of Aluminium produced in weathering:

$$Al_l = Al_w \tag{22}$$

where Al_w = Production of Al from weathering in eq ha^{-1} yr^{-1}

The production of Al from weathering of minerals is related to the production of base cations from weathering through the stoichiometry of the minerals. An approximation, using typical mineralogy of North European soils would imply:

$$Al_W = RAL \,.\, BC_W \tag{23}$$

where RAL is the Aluminium to Base Cation release rate ratio in the weathering raction. RAL vary in the range from 1 in volcanic soils to 3 in soil mainly composed of aluminium-rich clays such as in the topical areas. A good average for RAL would be to use the value 2.

$$H_l = (\frac{RAL\ .\ BC_W}{K_{gibb}})^{1/3}\ .\ Q^{2/3} \qquad (24)$$

The Aluminium criterium (leaching not greater than weathering of aluminium) leads to the equation for critical load of acidity:

$$CL^{*} = ANC_W + RAL\ .\ BC_W + (\frac{RAL\ .\ BC_W}{K_{Gibb}})^{1/3}\ .\ Q^{2/3} \qquad (25)$$

where
CL* = Critical load for soil stability eq ha^{-1} yr^{-1}
ANC_W = BC_W neutralization from weathering eq ha^{-1} yr^{-1}

$$CL^{*} = (1 + RAL)\ .\ ANC_W + (\frac{RAL\ .\ BC_W}{K_{Gibb}})^{1/3}\ .\ Q^{2/3} \qquad (26)$$

The effective critical load will be the minimum of critical load of activity calculated from plant tolerance of Aluminium (BC:Al-ratio) and critical load of acidity calculated from soil stability criteria.

6 Basic Assumptions

The factor 1.5 derives from the conversion of critical loads and Base Cation concentrations in equivalents to molar ratio.

The equation is based on the following assumptions:

- The soil profile is assumed to be one stirred tank
- The same gibbsite coefficient is assumed to apply through the soil profile
- The weathering rate is evenly distributed over the soil profile
- Uptake is evenly distributed over the soil profile
- The weathering rate is independent of chemical conditions
- The BC/Al ratio is assumed to have a value such that the value of ANC_L always is negative.

The calculation does not distinguish between marine and non-marine ions of any sort. This implies that the full Base Cation deposition is used in the calculation. It also implies that the full sulphur deposition is used for calculation of sulphur exceedance and the full ion balance for the calculation of acidity exceedances. This implies that all Cl and Na also enter the calculation. Na is still excluded from being bioactive.