

# CRITICAL LOADS OF ACIDITY FOR SURFACE WATERS - Can the $ANC_{limit}$ be considered variable?

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**Abstract.** The critical load of acidity for surface waters is based on the concept that the inputs of acids to a catchment do not exceed the weathering less a given amount of ANC. The Steady State Water Chemistry (SSWC) Method is used to calculate critical loads, using present water chemistry. To ensure no damage to biological indicators such as fish species a value for  $ANC_{limit}$  of 20  $\mu\text{eq/l}$  has been used to date for calculating critical loads. The SSWC-method is sensitive to the choice of the  $ANC_{limit}$ . In areas with little acid deposition the probability of acid episodes leading to fish kills is small even if the  $ANC_{limit}$  is set to zero, while in areas with high acidic deposition fish kills may occur at this value. Thus, the  $ANC_{limit}$  can be a function of the acidifying deposition to the lake, nearing zero at low deposition and increasing to higher values at higher deposition. A formulation for such an  $ANC_{limit}$  has been worked out, and we have tested the effect of the  $ANC_{limit}$  as a linear function of the deposition, assuming  $ANC_{limit} = 0$  at zero deposition with a linear increase to 50  $\mu\text{eq/l}$  at a deposition of 200  $\text{meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ . For areas with high deposition the effect of a variable  $ANC_{limit}$  is small, while in areas with low deposition the effect is significant. For Norway the exceeded area decreases from 36 to 30% using a variable  $ANC_{limit}$  instead of a fixed value of 20  $\mu\text{eq/l}$ .

Key words: critical load, acidity, water acidification, soil acidification, fish, empirical models, sulphur deposition, acid episodes,

## 1. Introduction

In recent years large areas of Europe and eastern regions of North America have suffered from acid precipitation resulting in the acidification of surface waters, increased fish mortality and other ecological changes. The concept of critical load has come into wide use in connection with international negotiations on reducing emissions of nitrogen and sulphur compounds. It was first put into practical use in Canada in the last part of the 70's in relation to the problem of lake acidification. It was further developed by working groups established by the the Nordic Council of Ministers in 1985 and used in the Scandinavian countries as a method for quantifying the extent and spatial dimension of the acidification problem. Since then it has been developed on a European basis by a number of international cooperative programmes and activities under the United Nations Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution, signed in 1979.

## 2. The Steady State Water Chemistry Method

The critical load of acidity for surface waters can be estimated on the basis of present water chemistry by means of a simple steady-state method. The critical load of acidity is calculated as:

$$CL(Ac) = Q * ([BC^*]_0 - ANC_{limit}) \quad (1)$$

where  $Q$  ( $m \cdot yr^{-1}$ ) is the runoff,  $[BC^*]_0$  the pre-industrial seasalt corrected base cation concentration and  $ANC_{limit}$  is the selected critical ANC (Acid Neutralization Capacity) threshold (Henriksen *et al.* 1993).

The Acid Neutralization Capacity is used as the chemical criterion for sensitive indicator organisms (usually fish) in surface waters. ANC is defined as the difference between base cations and strong acid anions. Including present-day nitrate leaching the present exceedance of the critical load of acidity is defined as:

$$Ex(Ac) = S_{dep} + N_{le} - BC^*_{dep} - CL(Ac) \quad (2)$$

where  $S_{dep}$  is the total S deposition and  $BC^*_{dep}$  is the non-marine base cation deposition (Henriksen *et al.* 1993).  $N_{le}$  is present nitrate leaching from the lake and its catchment, which is estimated from yearly runoff and present lake nitrate concentration minus an estimated background concentration of nitrate in lakes not affected by acid deposition (which for Norway has been estimated as  $4 \mu eq/l$ , (Kämäri *et al.* 1992).

In order to calculate the critical load of acidity to surface waters a value for the  $ANC_{limit}$  is needed. This value has been derived from the information on water chemistry and fish status obtained from the 1000 lake survey carried out in Norway in 1986 (Henriksen *et al.* 1988, Lien *et al.* 1992). The Scandinavian countries have so far used  $ANC_{limit} = 20 \mu eq/l$  as the critical chemical value for fish in surface waters (Henriksen *et al.* 1990). The natural ANC in lakes can, however, be equal or less than  $20 \mu eq/l$  in areas with granitic and gneissic bedrock with thin soil cover. For such lakes the  $ANC_{limit}$  has so far been set to the original ANC-value of the lake. The critical load for acidity will thus be zero for such lakes. For Norway 163 (16%) of the lakes included in the 1000-lake survey in 1986 have "negative" critical loads using  $ANC_{limit} = 20 \mu eq/l$ . The corresponding figures for Sweden and Finland are 18 (0.4%) out of 4015 and 4 (0.3%) out of 1450, respectively (Henriksen *et al.* 1993). The much higher percentage of lakes with negative critical loads in Norway is due to the larger number of lakes with low base cation concentrations. These Norwegian lakes are all located in areas where the bedrock consist of granites and gneisses and the soil covers are thin, as is also the case for the Swedish and Finnish lakes.

The critical load is thus sensitive to the choice of the  $ANC_{limit}$ . For Norway, a value of  $ANC_{limit} = 0 \mu eq/l$  will give a critical load exceedance in 25% of the area of Norway, whereas an  $ANC_{limit} = 20 \mu eq/l$  will result in an exceeded area of 36%. In this paper we suggest a variable  $ANC_{limit}$  that adresses some of the shortcomings of a fixed value.

### 3. Fish and ANC

The value of  $20 \mu eq/l$  for  $ANC_{limit}$  was chosen to ensure no toxic episodes during the year. In areas with little acid deposition, however, the probability of acid episodes leading to

fish kills is small even if ANC is close to zero, while in areas with high acidic deposition fish kills may occur at this value. Thus, the  $ANC_{\text{limit}}$  could be considered variable, e.g. a function of the deposition to the lake, nearing zero at low critical loads and increasing to an upper limit at higher critical loads. There are good biological arguments for considering  $ANC_{\text{limit}}$  as a variable: The pH-range 5.5 to 6.0 is regarded as safe under natural conditions for most fish species. One of the first attempts on setting a critical level for effects of acidification on aquatic systems was made in a Swedish case study (1971). The study used a critical limit of  $pH = 5.5$  for salmon fish species. The toxicity of inorganic Al was unknown at this time (Schofield 1977). The toxicity of Al in the pH range 5.5 to 6.0 depends on the concentration and chemical form of Al, the concentration of Ca as well as temperature (Brown 1982; Rosseland and Hindar 1991). In areas with higher critical loads, deposition of sulphur to acidified forest soils causes leaching of Al. This will result in the presence of inorganic Al-forms in lakes and streams also at deposition levels of sulphur at the critical load as long as the soils remain dominated by Al and  $H^+$  (Hultberg 1988). Inorganic Al causes toxic effects on young life stages and to adults of many fish species and other aquatic animals also at low concentrations (salmonid fishes  $\geq 30$  to  $50 \mu\text{g/l}$ ; lake plankton  $100 \mu\text{g/l}$ ) in the pH-range 5.5 to 6.0 (Fivelstad and Leivestad 1984; Henriksen *et al.* 1984; Hultberg 1988).

In lakes roach (*Leuciscus rutilus*) and Arctic char (*Salvelinus alpinus*) are two of the most sensitive fish species. Crayfish species in lakes (*Astacus astacus* and *Pacifastacus leniusculus*), glacial relicts of crustaceans as well as molluscs (*Margaritana margaritifera*) and mayfly species (*Ephemera sp.*) among the insects are very sensitive to acid episodes and inorganic Al (Hultberg 1977; Nyberg *et al.* 1986). In streams with sea-running brown trout (*Salmo trutta*) and rivers with Atlantic salmon (*Salmo salar*) draining of upstream acid lakes or soils, later running into areas with non-acid soils with resulting high pH (5.5 to  $> 6.0$ ) in the water are still affected by low survival of overwintering young year classes as well as fish kills of adult fish (Rosseland *et al.* 1986; Degerman *et al.* 1986). This is caused by inflow of water with inorganic Al into water with higher pH and ANC of 20 to  $\geq 50 \mu\text{eq/l}$  at periods with high waterflow and low temperatures. Liming of such upstream acid areas results in decreased transport of inorganic Al which in turn has caused dramatic increases in survival of overwintering young year classes of sensitive fish populations as well as invertebrates in the non-acid downstream parts of the water system (Nyberg *et al.* 1986). Decreased concentrations of inorganic Al was caused by precipitation of Al in lakes, wetlands and headwater streams in upstream limed parts of the catchment. Inflow of inorganic Al from acid catchments into limed lakes and streams may result in toxicity to fish at high pH in the mixing zone (Dickson 1978, 1983; Skogheim *et al.* 1984; Rosseland *et al.* 1992; Poleo *et al.* 1994).

The acidification recovery process at critical load will be slower for soils than for surface waters. Fish populations and other aquatic biota in lakes and rivers may therefore be exposed to toxic Al-forms also at very low sulphur load. In areas with higher critical loads ANC-values up to  $50 \mu\text{eq/l}$  are necessary to avoid negative effects on fish and other aquatic fauna. The  $ANC_{\text{limit}}$  of  $20 \mu\text{eq/l}$  was set to the reaction of brown trout, the most abundant fish species in Norway. In other countries other species are more abundant and thus a variable  $ANC_{\text{limit}}$  seems to be required to protect most aquatic organisms.

#### 4. Method

In order to develop an equation for a variable  $ANC_{limit}$  we can rewrite the critical load equation (equation 1) in the following way:

$$[BC^*]_0 - CL(Ac)/Q = ANC_{limit} \quad (3)$$

which can be visualized by intersecting the line  $y = [BC^*]_0 - x/Q$  with the horizontal line  $y = ANC_{limit}$ , where  $y$  is the concentration-axis and the  $x$ -axis is the deposition axis. The  $x$ -coordinate of the point of intersection of these two straight lines is the critical load.

This way of deriving the critical load can be generalized for an  $ANC_{limit}$  which depends on the deposition, i.e.  $x$ . Then  $y = ANC_{limit}$  is no longer a horizontal line, but a function of the deposition. The critical load is then computed by intersecting the line  $y = [BC^*]_0 - x/Q$  with the curve  $y = ANC_{limit}(x)$  (see Figure 1). As argued above, the  $ANC_{limit}$  can be low in areas with low deposition (background areas) and should be higher in areas with high deposition. The simplest way to express this is to assume a constant  $ANC_{limit}$  below and above given deposition values and a linear dependence between those limits:

$$ANC_{limit} = \begin{cases} A_1 & \text{for } Ac_{dep} \leq Ac_1 \\ k * Ac_{dep} + d & \text{for } Ac_1 < Ac_{dep} < Ac_2 \\ A_2 & \text{for } Ac_{dep} \geq Ac_2 \end{cases} \quad (4)$$

where  $k = (A_2 - A_1)/(Ac_2 - Ac_1)$  and  $d = A_1 - k * Ac_1$ . If  $A_1 > 0$ , it must be ensured that  $[BC^*]_0 > A_1$ . Depending on  $[BC^*]_0$  and  $Q$  we have three cases, and for each of them we can derive explicit formulae for the critical load and the  $ANC_{limit}$  (see Figure 1):

(a)  $Q * ([BC^*]_0 - A_1) \leq Ac_1$ :  
Then we simply have:  $CL(Ac) = Q * ([BC^*]_0 - A_1)$  and  $ANC_{limit} = A_1$  (5a)

(b)  $Q * ([BC^*]_0 - A_1) > Ac_1$  and  $Q * ([BC^*]_0 - A_2) < Ac_2$ :  
In this case we obtain after a few calculations:  
 $CL(Ac) = Q * ([BC^*]_0 - d) / (1 + k * Q)$   
and  $ANC_{limit} = (k * Q * [BC^*]_0 + d) / (1 + k * Q)$  (5b)

(c)  $Q * ([BC^*]_0 - A_2) \geq Ac_2$ :  
Again, one simply gets:  $CL(Ac) = Q * ([BC^*]_0 - A_2)$  and  $ANC_{limit} = A_2$  (5c)

The critical load, i.e. the deposition obtained by solving equation 3 after inserting the  $ANC_{limit}$  given by equation 4, depends on the parameters of the ANC-function ( $Ac_1$ ,  $A_1$ ,  $Ac_2$  and  $A_2$ , see equations 5a-c), which have to be derived from biological criteria, i.e. the (fish) species to be protected. The expression for the  $ANC_{limit}$  is not restricted to the broken linear function as defined in equation 4, but any monotonously increasing function, e.g., a S-shaped curve, could be chosen. However, in such a case equation 3

would become non-linear, and the critical load would have to be computed by an iterative method.

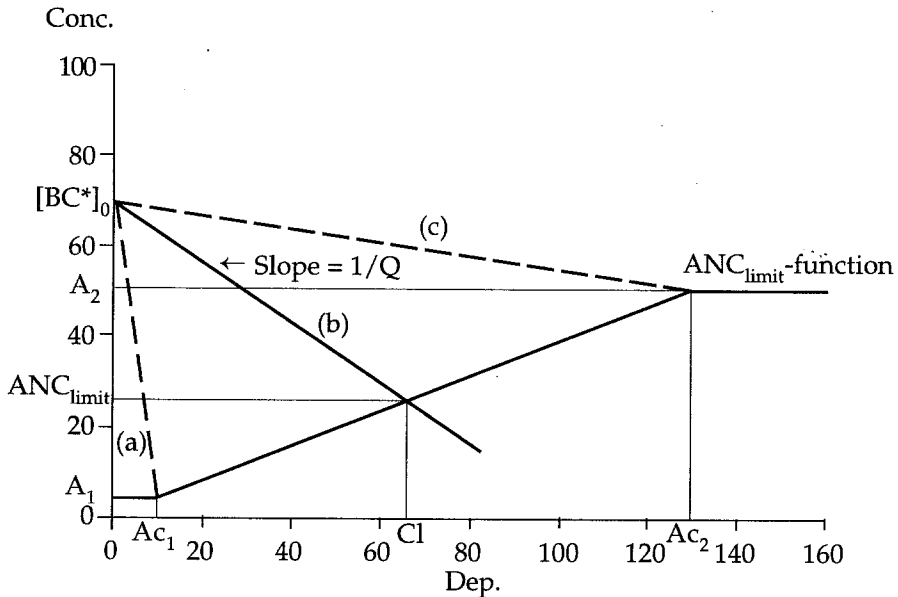


Figure 1. Determination of the critical load for a deposition dependent  $ANC_{limit}$  (equation 4). Three cases are possible, depending on the parameters of the function ( $Ac_1$ ,  $A_1$  and  $Ac_2$ ,  $A_2$ ),  $[BC^*]_0$  and the runoff  $Q$  (see text).

It should be noted that, although now  $ANC_{limit}$  is not a fixed value for all lakes, each lake will have its own value for all depositions, given by the characteristics of the lake ( $[BC^*]_0$  and  $Q$ ).

## 5. Results

To test the consequences of a variable  $ANC_{limit}$  for the critical loads in Norway, Sweden and Finland we used  $A_1 = 0$  for  $Ac_1 \leq 0$ , and  $A_2 = 50$  for  $Ac_2 = 200$ . Using the critical load databases for Finland, Norway and Sweden (Henriksen et al 1990), we have calculated the critical loads and their exceedances (Table 1).

Table 1. Percent of area (Norway) and percentage of lakes (Finland and Sweden) for which critical loads of acidity is exceeded for a variable  $ANC_{limit}$  and a fixed  $ANC_{limit}$  ( $20 \mu eq/l$ ).

Country	Fixed $ANC_{limit}$	Variable $ANC_{limit}$	Difference
Sweden	30,2	28,6	1,6
Finland	17,2	14,3	2,9
Norway	36,0	30,0	6,0

The effect of a deposition dependent  $ANC_{limit}$  is larger in Norway than in Sweden and Finland, because the number of sensitive lakes are highest here, as pointed out above.

Using a fixed  $ANC_{limit} = 20 \mu\text{eq/l}$ , the critical load of present acidity for surface waters is exceeded in 36% of the area of Norway. The variable  $ANC_{limit}$  (0-50 $\mu\text{eq/l}$ ) reduces the exceeded area to 30%, and most of these areas receive little acidific deposition (central and northern Norway). The distribution of areas where the critical load of acidity is presently exceeded using the variable  $ANC_{limit}$  corresponds better to those where fish populations are damaged than using the fixed  $ANC_{limit}$  (Henriksen and Hesthagen, in prep.).

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