

CHEMICAL CRITERIA IN THE CRITICAL LOADS CONCEPT

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Introduction

The critical loads concept has been developed in order to provide a platform for aggregation and simplification of scientific findings regarding an ecosystem's response to a given load of pollutant. The basic idea of this concept is to balance the atmospheric depositions, which a given ecosystem is exposed to with the capacity of this ecosystem to buffer the input in the system. During the last decade this concept has been at the core of quantitative policy pursued in order to provide productive interpretations of current knowledge regarding policy options for combating emissions and effects of transboundary air pollutants. The concept has been applied on the international level, within the UN/ECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) providing the scientific basis for successful negotiations of the effect-oriented protocols, i.e. the Protocol on Further Reduction of Sulfur Emission signed in Oslo in 1994 and the Protocol on the Abatement of Acidification, Eutrophication and Groundlevel Ozone adopted in Gothenburg in 2000.

Accordingly, a critical loads approach to control acidic emissions in relation to their ecological effects has been introduced. Critical load is defined as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" [NILSSON, GRENNFELT (ed.) 1988]. There are two main air pollution effects and its two basic receptors considered under the mentioned protocols, i.e. acidification and eutrophication affecting forest ecosystems and aquatic ecosystems. In central Europe, including Poland, the most widely considered receptor is the forest ecosystem.

The work under the Convention is organized and carried out by the Executive Body and its working groups and task forces – Figure 1. All these bodies are supported by the so called National Focal Centers (NFC) established by individual parties to the Convention. The responsibility of NFCs is to collect input data, derive critical loads values and to produce national maps of them. National critical load maps are then submitted to a special UN/ECE Coordination Center for Effects located in Bilthoven, Netherlands, where they are aggregated into pan-European maps. These maps form the scientific foundation for the assessment of ecological response to the negotiated sulfur and nitrogen emission scenarios.

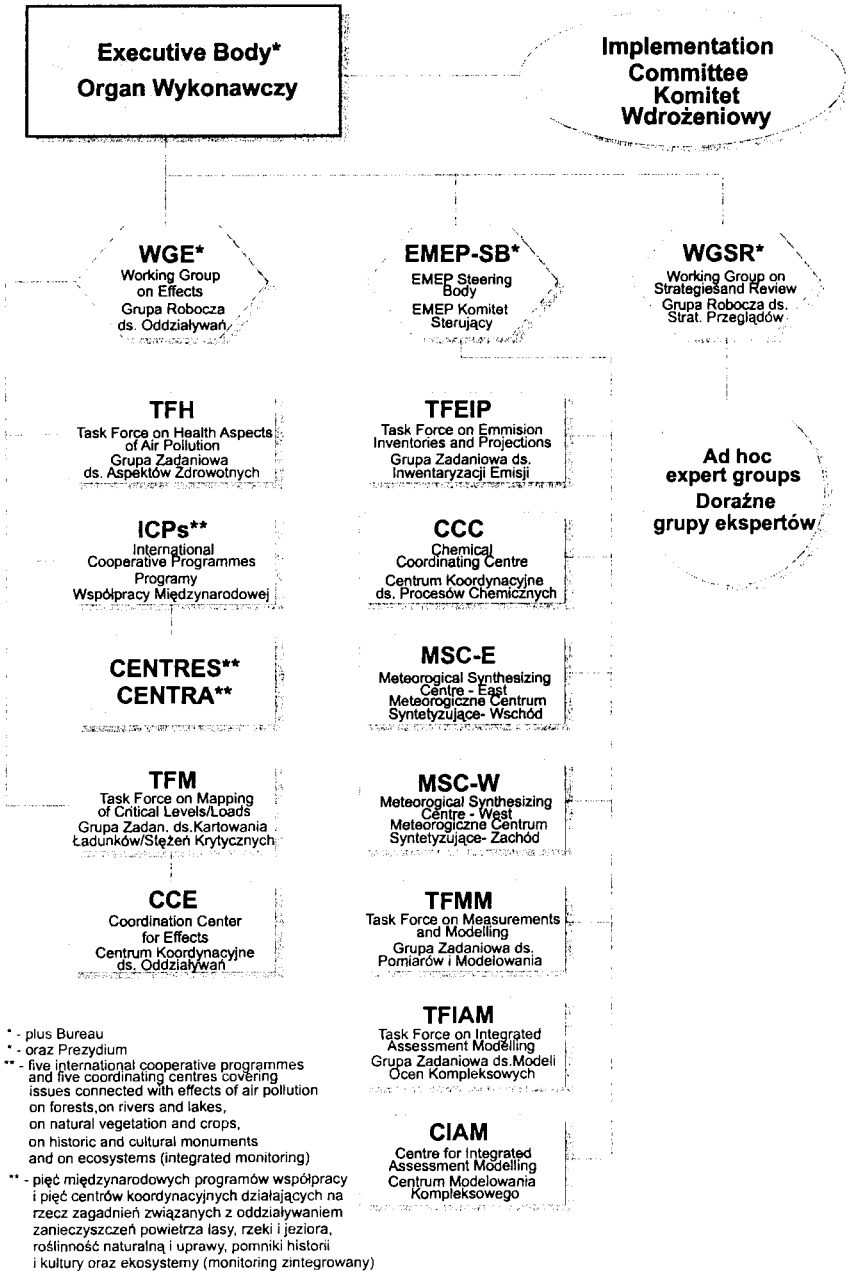


Fig. 1. Organizational structure of the Convention on Long-range Transboundary Air Pollution

Rys. 1. Struktura organizacyjna Konwencji w sprawie Transgranicznego Zanieczyszczenia Powietrza na Dłgie Odległości

The Polish National Focal Center located at the Institute of Environmental Protection has been established in 1990, actively contributing to not only the generation of European critical load maps by producing national maps, but also the development of the methodology for critical loads calculation. In this way the Polish NFC contributed to successful negotiations of the above mentioned Protocols [MILL, RZYCHOŃ 1991; MILL et al. 1993, 1995; MILL 1997, 2001; MILL, SCHLAMA 1999].

Calculating and mapping of critical loads

Under the UN/ECE Working Group on Effects and particularly its Task Force on Mapping Critical Loads, a Steady State Mass Balance model has been developed by an international group of experts. The mass balance approach calculates critical loads assuming steady state equilibrium. It is based on an equation which balances all the main inputs of sulfur and nitrogen – the main acidity precursors – to the system and outputs from the system. A simplified acidity balance between sources and sinks of sulfur and nitrogen in a given forest soil compartment is given by the following equation [UBA 1996]:

$$S_{dep} + N_{dep} - BC_{dep} + BC_w - BC_u + N_u + N_i + N_{de} - Alk_{le} \quad (1)$$

where:

- S_{dep} – sulfur deposition
- N_{dep} – nitrogen deposition
- BC_{dep} – base cation deposition
- BC_w – net input of base cations from weathering
- BC_u – net uptake of base cations by vegetation
- N_u – net uptake of nitrogen by vegetation
- N_i – nitrogen immobilization rate
- N_{de} – nitrogen denitrification rate
- Alk_{le} – alkalinity leaching, which represents the sum of base cations minus strong acid anions in the soil leachate. Alk_{le} is a measure for the acidification status of forest soils.

The units used in the above equation are eq/ha/yr. The above balance equation holds for every deposition of S and N. Specifying a critical alkalinity leaching, i.e. a criterion linking chemical changes to a harmful effect on structure or functioning of forest ecosystem, yields the maximum sum of S and N deposition allowed, i. e. the critical load for sulfur $CL(S)$ and nitrogen $CL(N)$:

$$CL(S) + CL(N) = BC_{dep} + BC_w - BC_u + N_i + N_u + N_{de} - Alk_{le(crit)} \quad (2)$$

where $Alk_{le(crit)}$ is the alkalinity flux leaving the system at the critical level.

By subtracting the deposition of base cations from the critical loads of S and N, the critical load for acidity is defined:

$$CL(Ac_{pot}) = BC_w - BC_u + N_i + N_u + N_{de} - Alk_{le(crit)} \quad (3)$$

Every acid deposition exceeding the critical load of acidity should be aba-

ted completely or to a target value by the corresponding emission reduction of sulfur and nitrogen. This is what the above mentioned protocols are to control. Because sulfur and nitrogen produce acidity simultaneously, it is impossible to define their separate critical loads, therefore for a given ecosystem a pair of sulfur and nitrogen deposition is considered. Although, under extreme conditions only sulfur is deposited or nitrogen and consequently in case of sulfur the expression for critical load $CL_{max}(S)$ is as follows:

$$CL_{max}(S) + BC_{dep} + BC_w - BC_u - Alk_{le(crit)} \quad (4)$$

In case of nitrogen the critical load formulation depends on the amount of deposited N and there are two possible situations:

$$\text{if } N_{dep} \leq N_i + N_u + N_{de} \text{ then } CL_{min}(N) = N_i + N_u + N_{de} \quad (5)$$

otherwise

$$CL_{max}(N) = CL_{min}(N) + CL_{max}(S) = BC_{dep} + BC_w - BC_u + N_i + N_u + N_{de} - Alk_{le(crit)} \quad (6)$$

what refers to the maximum amount of nitrogen deposition in case of zero S deposition. Figure 2 shows the relationship between S and N deposition and the critical loads defined by equations (4) to (6).

For every pair of deposition (S_{dep} , N_{dep}) lying on the thick line or below it, in the gray shaded area, there is no-exceedance of the critical load of acidity.

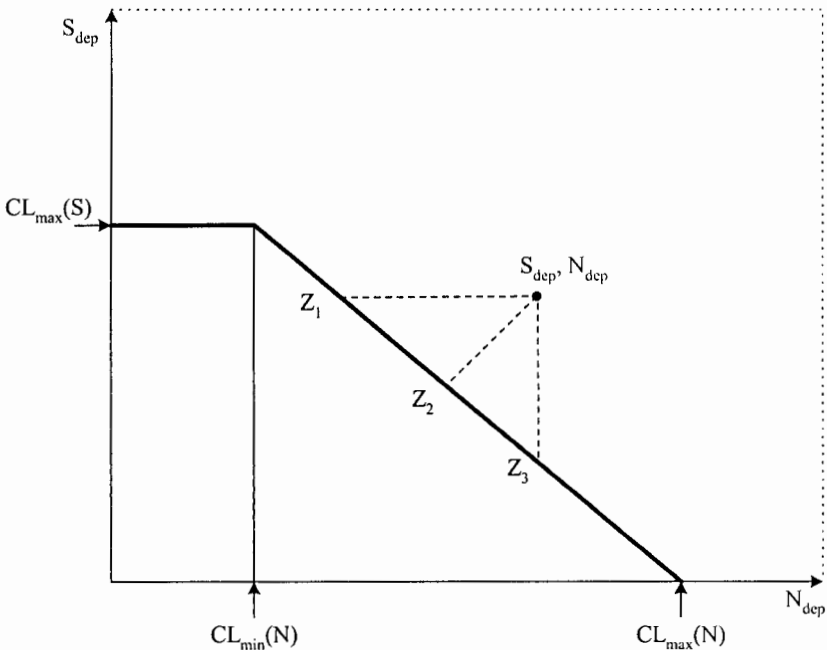


Fig. 2. Critical load function for acidity
Rys. 2. Funkcja ładunków krytycznych kwasowości

Critical alkalinity leaching

Alkalinity leaching is one of the key parameters of the Steady State Mass Balance model. It reflects the net output of all biochemical processes occurring in a soil compartment. Alkalinity leaching, according to DE VRIES [1991], is defined as a charge balance of ions in the soil leachate flux:

$$Alk_{le} = HC_{0.3,le} + RCOO_{le} - H_{le} - Al_{le} \quad (7)$$

flux:

where the subscript *le* stands for leaching, *RCOO* is the sum of organic anions and *Al* stands for all aluminum species. For acid forest soils $HC_{0.3,le}$ and *RCOO* can be neglected and the critical alkalinity leaching is calculated as:

$$Alk_{le(crit)} = -Al_{le(crit)} - H_{le(crit)} = -Q \cdot ([Al]_{crit} + [H]_{crit}) \quad (8)$$

where *Q* is the precipitation surplus, i.e., the amount of water leaving the root zone and the square brackets denote concentrations.

The relationship between *Al* and *H* is described by a gibbsite equilibrium:

$$[Al] = K_{gbb} \cdot [H]^3 \quad \text{or} \quad [H] = ([Al]/K_{gbb})^{1/3} \quad (9)$$

where K_{gbb} is the gibbsite equilibrium constant dependent on soil properties.

To obtain a critical alkalinity leaching a critical *Al* concentration or critical pH should be specified what is the crucial point of the methodology of calculating critical loads of acidity.

For the purpose of protocol negotiations two methods for calculating critical alkalinity leaching for mineral soils have been basically applied.

Alkalinity leaching determined by a critical base cation to Al ratio

Most widely used is the connection between soil chemical status and plant response via a critical molar base cation to aluminum ratio $(BC/Al)_{crit}$, where *BC* stands for the sum of Ca, Mg and K. The critical Al_{crit} leaching is then calculated from the leaching of base cations and the critical *BC/Al* ratio:

$$Al_{le(crit)} = 1.5 \cdot \frac{BC_{le}}{(BC/Al)_{crit}} \quad (10)$$

The factor 1.5 arises from the conversion of mols to equivalents. The base cation leaching BC_{le} is calculated from the following mass balance:

$$BC_{le} = BC_{dep} + BC_w \cdot BC_u \quad (11)$$

Combining equations (8) to (11) the critical alkalinity leaching formula is determined:

$$Alk_{le(crit)} = - \left(1.5 \cdot \frac{BC_w + BC_{dep} - BC_u - 0.015 \cdot Q}{(BC/Al)_{crit} \cdot K_{gibb}} \right)^{1/3} \cdot Q^{2/3} - \quad (12)$$

$$- 1.5 \cdot \frac{BC_w + BC_{dep} - BC_u - 0.015 \cdot Q}{(BC/Al)_{crit}}$$

$$CL_{max}(S) = BC_{dep} + BC_w - BC_u + 1.5 \cdot \frac{BC_w + BC_{dep} - BC_u - 0.015 \cdot Q}{(BC/Al)_{crit}} + \quad (13)$$

$$+ Q^{2/3} \cdot \left(1.5 \cdot \frac{BC_w + BC_{dep} - BC_u - 0.015 \cdot Q}{(BC/Al)_{crit} \cdot K_{gibb}} \right)^{1/3}$$

Inserting equation (12) into equation (4) one obtains the expression for $CL_{max}(S)$ as determined by BC/Al ratio:

The default value for the critical BC/Al ratio has been internationally accepted as 1 mol/mol what holds for coniferous forests, although values for a large number of plant species can be found in SVERDRUP and WARFVINGE [1993]. Based on their findings, the critical loads for Polish forest ecosystem have been calculated using the following BC/Al ratios [MILL 2001]:

Tree stand; Drzewostan	BC_{le}/Al_{le}
Beech; Buk pospolity (<i>Fagus sylvatica</i> L.)	0.6
Oak; Dąb szypułkowy (<i>Quercus robur</i> L.)	0.6
Birch; Brzoza brodawkowata (<i>Betula pendula</i> ROTH.)	0.8
Spruce; Świerk pospolity (<i>Picea abies</i> (L.)H. KARST.)	1.2
Pine; Sosna pospolita (<i>Pinus sylvestris</i> L.)	1.2
Fir; Jodła pospolita (<i>Abies alba</i> MILL.)	1.4

Alkalinity leaching determined by a critical Al mobilization rate

Another criterion that can be used to calculate a critical alkalinity leaching is that depletion of secondary aluminum phases and complexes is not allowed as it may cause structural changes in soils. Secondary Al compounds are important structure elements, and the stability of soils depends on the stability of the reservoirs of these substances. Furthermore, Al depletion may cause a further pH decline. Aluminum depletion occurs when acid deposition leads to its leaching in excess to Al produced by weathering of primary minerals. The equation for critical Al leaching is thus derived from the requirement that it must not exceed net Al weathering from primary minerals Al_w :

$$Al_{le(crit)} = Al_w \quad (14)$$

The production of Al from weathering is related to the weathering of base cations via the stoichiometry of the minerals involved according to the following expression:

$$Al_w = r \cdot BC_w \quad (15)$$

where r is the stoichiometric ratio of Al to base cation weathering in primary minerals. The maximum critical load of sulfur, based on soil stability, is then given by:

$$CL_{\max}(S) = BC_{dep} - BC_u + (1+r) \cdot BC_w + Q^{2/3} \cdot \left(\frac{r \cdot BC_w}{K_{gibb}} \right)^{1/3} \quad (16)$$

The r ratio values range from 1.5 to 3 [UBA 1996] and the default value used in the Polish critical load calculations was $r=2$, what corresponds to the typical Central European mineralogy of soils.

Summary of current status and need for further work

The current status of chemical criteria and critical limits has been discussed and summarized within an expert workshop organized by the United Kingdom National Focal Center in March 2001. The key aims of the workshop were to:

- Examine the chemical criteria and critical limits currently used for acidification critical loads models;
- Consider new or alternative chemical criteria and critical limits;
- Consider what guidance is needed in their application.

The workshop concluded with the following statements and recommendations:

- There is a need and time to update the experimental data relating the BC : Al ratio to observed damage to forest ecosystems;
- The BC : Al ratio is in general a high confidence criterion for inhibition of root growth and its all relevant consequences;
- In particular there is a need for a further development of ecosystem-specific BC : Al ratio values, i.e. for individual tree species;
- The critical Al mobilization rate related to Al weathering flux was accepted with no need for further research;
- The percentage base saturation was introduced as a potential new criterion. Its importance is determined by the fact that it may be considered as a linking criterion between the steady state and dynamic approaches. A recommendation has been made to elaborate on the international level appropriate critical limits for this new criterion.

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Key words: atmospheric pollution, acid deposition, critical loads, ecosystems protection

Abstract

The critical loads concept has been developed under the Convention on Long-Range Transboundary Air Pollution as a scientific basis for the negotiations of its environmentally effect-oriented protocols. The basic idea of this concept is to balance the atmospheric depositions which a given ecosystem is exposed to with the capacity of this ecosystem to buffer the input in the system. Accordingly, a critical loads approach to control acidic emissions in relation to

their ecological effects has been introduced. Critical load is defined as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge". In this study, the critical loads approach has been applied to the problem of forest ecosystem acidification resulting from sulfur and nitrogen emission.

There are several criteria that may be used as critical chemical limits in forest soil solution. These are critical pH, critical Al concentration, critical BC/Al ratio and Al depletion criterion.

The reliability of the calculated critical loads is strongly influenced by the quality of the chemical criteria applied. For abiotic aspects like soil chemistry or ground water quality the critical limits are clear because the dose-effect relations are quite well understood. For biotic indicators like root damage it is more difficult to find critical limits which can be used as threshold levels below which effects are negligible. The process of root damage is quite a complex one and a combination of side factors like droughts and adverse soil chemical condition may contribute to it. So, when a single critical limit such as the BC/Al ratio is used, this will inherently lead to a considerable uncertainty in the value of this critical limit. Critical limits are based on laboratory experiments during a limited period of time in which sample roots are subject to constantly elevated BC/Al ratios. One of major problems in applying this kind of criteria is the interpretation of the laboratory bioassay results in relation to field conditions.

The aim of this paper is to summarize the current knowledge and to formulate the major questions that should be answered to abate the existing uncertainty in relating the anthropogenically modified soil chemistry and the reaction of forest ecosystems.

KRYTERIA CHEMICZNE W KONCEPCJI ŁADUNKÓW KRYTYCZNYCH

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Słowa kluczowe: zanieczyszczenie powietrza, depozycja kwaśna, ładunki krytyczne, ochrona ekosystemów

Streszczenie

Koncepcja ładunków krytycznych powstała w ramach Konwencji w Sprawie Transgranicznego Zanieczyszczenia Powietrza na Długości, jako naukowa podstawa dla negocjowania jej protokołów zorientowanych na oddziaływania ekologiczne. Podstawowym założeniem tej koncepcji jest bilansowanie atmosferycznej depozycji kwaśnej ze zdolnością ekosystemów naturalnych do jej buforowania. Jako ilościową miarę wrażliwości ekosystemów lądowych i wodnych na depozycję kwaśną wprowadzono pojęcie ładunku krytycznego. Ładunek krytyczny definiowany jest jako: „największą depozycję związków kwaśnych, niewywołującą zmian chemicznych, prowadzących do długotrwałych, szkodliwych skutków dla

struktury i funkcjonowania ekosystemów, zgodnie z najnowszym stanem wiedzy”. W niniejszych badaniach koncepcję ładunków krytycznych wdrożono do oceny problemu zakwaszania ekosystemów leśnych, w wyniku emisji związków siarki i azotu.

Istnieje szereg kryteriów mających zastosowanie w określaniu progowego składu chemicznego przesącza gleb leśnych, takich jak: odczyn, krytyczne stężenie glinu aktywnego, krytyczny stosunek BC : Al i krytyczne stężenie glinu wymiennego.

Wiarygodność wielkości wyznaczanych ładunków krytycznych jest silnie powiązana z rodzajem wybranego kryterium chemicznego w układach abiotycznych, takich jak: struktura chemiczna gleb lub wód gruntowych. Wartości progowe są jednoznaczne, bowiem w tego typu układach zależności dawka-odpowiedź są dobrze wyjaśnione. W przypadku takich wskaźników biotycznych jak np. uszkodzenie systemu korzeniowego wskazanie wartości krytycznych, poniżej których to uszkodzenie nie wystąpi, jest trudniejsze. Proces uszkodzania systemów korzeniowych jest bardzo złożony i oprócz czynników chemicznych uczestniczą w nim takie czynniki uboczne jak: susze, mrozy, choroby grzybowe itp. Wartości progowe ustanawiane są w oparciu o badania laboratoryjne o określonym czasie trwania w trakcie, którego próbki korzeni poddawane są ciągłemu oddziaływaniu np. dobieranych wartości stosunku BC : Al. Jednym z podstawowych problemów w stosowaniu tak wyprowadzonych kryteriów jest wiarygodność przeniesienia wyników laboratoryjnych na warunki polowe.

W artykule tym podsumowano aktualny stan wiedzy i sformułowano zagadnienia wymagające dalszych badań celem zmniejszenia niepewności w opisie zależności pomiędzy antropogenicznie modyfikowanym statusem chemicznym gleb, a reakcją ekosystemów leśnych.

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