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Final report

# Critical Limits for Acidification and Nutrient Nitrogen

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**Abstract: Critical Limits for Acidification and Nutrient Nitrogen**

The International Cooperative Programme on Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends (ICP Modelling and Mapping) develops and uses critical loads to recommend science-based emission reductions to policy makers within the UN Air Convention (CLRTAP). A critical load defines the deposition of a pollutant below which significant harmful effects on a sensitive ecosystem element do not occur. The Simple Mass Balance (SMB) model is the most widely used steady-state model under the Air Convention to estimate critical loads of nutrient nitrogen (eutrophication) and sulphur together with nitrogen (acidification). Within the SMB model, so-called critical limits define threshold values to prevent harmful effects. In this report, we assessed the currently used critical limits for terrestrial ecosystems. The project was motivated by the Coordination Centre for Effects (CCE) to ensure continuous uptake of scientific advances in their effects work. Experts of the National Focal Centres (NFC) and beyond were invited to comment and discuss preliminary results of the project during the ICP Modelling and Mapping Task Force meetings and a workshop.

Empirical studies towards the impact of acidification on ecosystem receptors (e.g., tree growth, root damage, etc.) stagnated since the mid-nineties. Among the three available limit criteria, we suggest Bc:Al as a criterion for its direct effect on tree growth, as already applied by the NFCs. Furthermore, our sensitivity analysis using the critical load Background Database showed that a Bc:Al = 1 is probably not sufficient. Using Bc:Al > 1 is reducing indirect hydrogen criteria violation (e.g., with a Bc:Al =10 pH > 4.2 is mostly guaranteed). Moreover, using Bc:Al > 1 is also supported in order to sustain higher levels of base saturation. In case a receptor specific approach for Bc:Al is feasible, selecting the highest Bc:Al critical limit for all respective species within the mapping unit is recommended.

Regarding eutrophication, scientific advances in soil N cycling and N saturation processes are summarized in the report. As stated before, causation from either soil N concentration or N leaching towards other biotic ecosystem effects such as vegetation changes or nutrient imbalances in trees lacks empirical foundation or is based on a small number of studies. Newer literature, allowing for an improvement in the derivation of acceptable N leaching, is also not available. Based on our analyses, we recommend using only the lower end of the suggested values of soil N concentration (<0.4 mg $l^{-1}$) for ecosystem protection. This approach guarantees the consistency with the ranges of empirical critical loads and simultaneously does not exceed the onset of N leaching when an ecosystem becomes leaky (1 kg N $ha^{-1}$ $yr^{-1}$). We explored a new method that uses soil C:N ratios, a known explanatory factor contributing to the amount of N leaching, for the regionalisation of critical N leaching values. This method has its limitations and is therefore not seen as a stand-alone approach but rather as an additional information supporting the results derived from traditional critical limit values as given in the Mapping Manual.

**Zusammenfassung: Kritische Grenzwerte für Versauerung und Eutrophierung**

Das International Cooperative Programme on Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends (ICP Modelling and Mapping) entwickelt und verwendet kritische Belastungswerte, um den politischen Entscheidungsträgern im Rahmen des Genfer Luftreinhalteabkommens der Vereinten Nationen (CLRTAP) wissenschaftlich fundierte Emissionsreduzierungen zu empfehlen. Eine kritische Belastung („critical load“) definiert die Deposition eines Schadstoffs, unterhalb derer signifikante schädliche Auswirkungen auf ein empfindliches Ökosystemelement nicht auftreten. Das Simple Mass Balance (SMB)-Modell ist das im Rahmen des Genfer Luftreinhalteabkommens am häufigsten verwendete stationäre Modell zur Abschätzung der kritischen Belastung durch Stickstoff (Eutrophierung) sowie Schwefel und Stickstoff (Versauerung). Innerhalb des SMB-Modells definieren sogenannte kritische Grenzwerte („Critical Limits“) Schwellenwerte, um schädliche Effekte auf die Rezeptoren zu verhindern. In diesem Bericht haben wir die derzeit verwendeten kritischen Grenzwerte für terrestrische Ökosysteme bewertet. Das Projekt wurde vom Coordination Centre of Effects (CCE) initiiert, um die kontinuierliche Aufnahme wissenschaftlicher Fortschritte in ihre Arbeit zu gewährleisten. Expert:innen der National Focal Centres (NFC) und darüber hinaus wurden eingeladen, die vorläufigen Ergebnisse des Projekts bei den Treffen der ICP Modelling and Mapping Task Force und in einem Workshop zu kommentieren und zu diskutieren.

Empirische Studien zu den Auswirkungen der Versauerung auf Ökosystemrezeptoren (z. B. Baumwachstum, Wurzelschäden usw.) stagnieren seit Mitte der neunziger Jahre. Unter den drei verfügbaren Grenzwertkriterien schlagen wir Bc:Al als Kriterium für die direkte Auswirkung auf das Baumwachstum vor, wie es bereits von den NFCs angewendet wird. Darüber hinaus hat unsere Sensitivitätsanalyse unter Verwendung der Datenbank für die kritische Hintergrundbelastung gezeigt, dass ein Bc:Al = 1 wahrscheinlich nicht ausreicht. Die Verwendung von Bc:Al > 1 verringert zudem die indirekte Verletzung der Wasserstoffkriterien (z. B. ist bei einem Bc:Al = 10 ein pH-Wert von > 4.2 weitgehend gewährleistet). Außerdem lassen sich Bc:Al > 1 als vorteilhaft vor allem auch in Verbindung mit der Einhaltung einer akzeptablen Basensättigung bewerten. Falls ein Rezeptor-spezifischer Ansatz für Bc:Al möglich ist, wird empfohlen, den höchsten kritischen Grenzwert für Bc:Al für alle betreffenden Arten innerhalb der Kartierungseinheit zu wählen.

Im Hinblick auf die Eutrophierung werden in dem Bericht die wissenschaftlichen Fortschritte beim Stickstoffkreislauf im Boden und bei den Stickstoffsättigungsprozessen zusammengefasst. Wie bereits erwähnt, fehlt die empirische Grundlage für die Kausalität zwischen der N-Konzentration im Boden oder der N-Auswaschung und anderen biotischen Ökosystemeffekten wie Vegetationsveränderungen oder Nährstoffungleichgewichten in Bäumen, oder sie beruht auf einer kleinen Anzahl von Studien. Neuere Literatur, die eine Verbesserung der Ableitung einer akzeptablen N-Auswaschung ermöglicht, ist nicht verfügbar. Auf der Grundlage unserer Analysen empfehlen wir, nur das untere Ende der empfohlenen Werte für die N-Konzentration im Bodenwasser (<0,4 mg $l^{-1}$) für den Schutz der Ökosysteme zu verwenden. Dieser Ansatz garantiert die Übereinstimmung mit den Bereichen der empirischen kritischen Belastung und überschreitet gleichzeitig nicht den Beginn der N-Auswaschung (1 kg N $ha^{-1}$ $yr^{-1}$). Außerdem, haben wir eine neue Methode erprobt, bei der das C:N-Verhältnis des Bodens, ein bekannter Erklärungsfaktor für die Höhe der N-Auswaschung, zur Regionalisierung der kritischen N-Auswaschungswerte herangezogen wird. Diese Methode hat allerdings ihre Grenzen und ist nicht als eigenständiger Ansatz zu sehen, sondern kann lediglich als zusätzliche Information zur Unterstützung der Ergebnisse, die aus den traditionellen kritischen Grenzwerten abgeleitet werden, wie sie im Mapping Manual angegeben sind, herangezogen werden.

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## List of abbreviations

| Abbreviation | Description |
|---|---|
| **Al** | Aluminium |
| **$Al_{le,crit}$** | Critical Al leaching |
| **ANC** | Acid neutralization capacity |
| **$ANC_{le,crit}$** | Critical ANC leaching |
| **Bc** | concentration of base cations |
| **Bc:Al** | Base cation to aluminium ratio (Bc = Ca+Mg+K) in mol/mol |
| **$Bc_{dep}$** | base cation deposition |
| **$Bc_u$** | base cation uptake |
| **$Bc_w$** | base cation weathering |
| **C:N** | Carbon to nitrogen ratio |
| **Ca** | Calcium |
| **Ca:Al** | Calcium to Aluminium ratio |
| **CCE** | Coordination Centre for Effects |
| **CLempN** | Empirical critical loads of nitrogen |
| **CLmaxS** | Maximum critical load of sulphur |
| **CLnutN** | Critical load of nutrient nitrogen |
| **CLRTAP** | Convention on Long-range Transboundary Air Pollution |
| **CN EMP APR** | Approach of estimating N leaching based on forest floor CN and CLempN |
| **DIN** | Dissolved inorganic nitrogen |
| **DON** | Dissolved organic nitrogen |
| **$E_{Bc,crit}$** | Critical base saturation (i.e. without Sodium, Na) |
| **EU-DW** | soil solution N concentration European Drinking Water Directive target value |
| **$f_{de}$** | denitrification fraction |
| **H** | Hydrogen |
| **K** | Potassium |
| **$K_{gap}$** | Gapon coefficient |
| **$K_{gibb}$** | gibbsite equilibrium constant |

| Abbreviation | Description |
|---|---|
| **m.a.s.l** | Meters above sea level |
| **Na** | Sodium |
| **Mg** | Magnesium |
| **N** | Nitrogen |
| **$N_2O$** | Nitrous oxide |
| **NFC** | National Focal Centre |
| **NFC HIGH** | soil solution N concentration high NFC setting |
| **NFC MED** | soil solution N concentration medium NFC setting |
| **$NH_4$** | Ammonium |
| **$N_i$** | long-term net immobilisation of N |
| **$N_{le}$** | N leaching |
| **$N_{le(acc)}$** | Critical (acceptable) N-leaching |
| **$NO_3$** | Nitrate |
| **$N_u$** | net removal of N in harvested vegetation and animals |
| **Q** | precipitation surplus |
| **S** | Sulphur |
| **SEE** | standard error of estimate |
| **SMB** | Simple mass balance model |
| **SOC** | Soil organic carbon |
| **STD APR** | soil solution N concentration CCE standard approach |
| **UN** | United Nations |
| **UNECE** | The United Nations Economic Commission for Europe |

# 1 Introduction

Over the last decades, human activities have led to vast emissions of sulphur (S) and nitrogen (N), resulting in acidification and eutrophication of ecosystems. Already in 1979, totally 32 countries in the pan-European region signed the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP, UN Air Convention) to deal with air pollution on a broad regional basis (Maas and Grennfelt 2016). Among the bodies addressing ecosystem effects of air pollution, the International Cooperative Programme on Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends (ICP Modelling and Mapping) develops and uses critical loads and exceedance maps to recommend science-based emission reduction targets to policy makers. Around 30 countries represented by their respective National Focal Centres (NFC) participate in the programme activities and contribute data to be integrated into European critical load maps in collaboration with the Coordination Centre for Effects (CCE).

The critical load concept has been postulated in the mid-1980s. Within the context of elevated sulphur depositions, Nilsson and Grennfelt (1988) defined a critical load 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 line with the current ICP Modelling and Mapping Manual (CLRTAP 2017), stated as Mapping Manual in this work, critical loads can be derived from empirical studies (Bobbink et al. 2022), steady-state mass balance models (Posch et al. 2015b) or via dynamic models (Bonten et al. 2015). The Simple Mass Balance (SMB) model as described by Posch et al. (2015b) is the most widely used steady-state model under the Air Convention to estimate critical loads of nutrient nitrogen (eutrophication) and acidification.

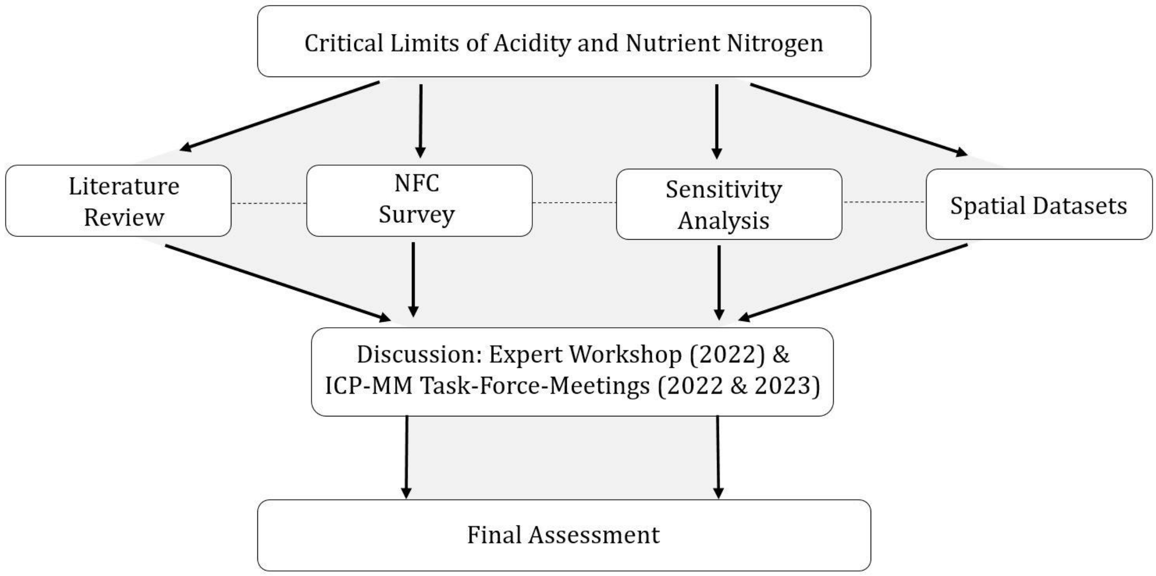
The SMB model assumes undisturbed long term steady state of an ecosystem. For the detailed equations we refer to the Mapping Manual (CLRTAP 2017). Within the SMB model, so-called critical limits define threshold values to prevent adverse effects on specific parts of an ecosystem. Linkages between critical limits and "harmful effects" account for a large fraction of uncertainty as stated by Reinds et al. (2008), besides the structural uncertainty of the SMB model. Moreover, decisions have to been made defining the level of protection from a political and societal point of view. In this report, we focus on the technical uncertainties of the critical limits used to calculate critical loads of acidification and nutrient nitrogen applying SMB modelling. We assessed the current assumptions within the SMB model and its applications and reviewed critical limits used in the SMB model for critical load calculations of nutrient nitrogen and acidification within the Pan-European region. We restricted our assessment to terrestrial ecosystems. For critical limits of acidification, we focused on the three geochemical criteria, namely: aluminium criteria, hydrogen ion criteria and critical base saturation. For critical limits for nutrient nitrogen (eutrophication), we focused on critical concentration of nitrogen in soil solution and critical nitrogen leaching.

This project was motivated by the CCE to ensure continuous uptake of scientific advances in their effects work. The results and conclusion of this report aim at improving the knowledge base of SMB modelling to be used for technical discussions within the CCE and the ICP Modelling and Mapping Task Force. Furthermore, the report may be used for any review of the Mapping Manual in the future. Experts of the NFCs and beyond were invited to comment and discuss preliminary results of the project during the ICP Modelling and Mapping Task Force meetings in 2022 and 2023 and a specific project workshop in autumn 2022.

# 2 Methods

Overall, this project includes 1) a literature review, 2) a survey regarding the applied methods and critical limits by NFCs, 3) an in-depth discussion and sensitivity analysis of selected critical limits using the critical load Background Database as well as 4) an assessment of available spatial data sources for mapping of critical limits. Throughout the report, critical limits for acidification and nutrient nitrogen (eutrophication) are mostly treated separately. The project structure is summarized in Figure 1 below.

**Figure 1: Structure of the project.**




Source: own illustration, Environment Agency Austria

## 2.1 Literature review

The aim of the literature review was to gain a detailed overview of the latest scientific knowledge in relation to critical limits for acidification and nutrient nitrogen. We started by capturing the applied methodology as stated in the Mapping Manual (CLRTAP 2017), the CCE Status Reports and the PINETI II report (Schlutow et al. 2017). The gained information served as a baseline for a more recent literature search. For this, we screened scientific libraries Scopus (Elsevier, Amsterdam, Netherlands) and Google Scholar (Google Inc., Mountain View, CA, USA) for the latest literature using different combinations of relevant keywords. The literature has been compiled in a literature database, categorized by acidification and nutrient nitrogen and has been annotated with keywords applicable for the different critical limit criteria. The literature review for critical limits of acidification focused on the three relevant geochemical criteria namely the aluminum-, hydrogen- and base saturation criteria. In total, we identified 47 papers on the aluminum criteria, 28 on the hydrogen ion criteria and 28 on the base saturation critical limit. For the critical limits of nutrient nitrogen, we identified quite a huge number of potentially relevant papers. However, many studies do not make explicit assessment of soil N concentration or leaching together with other impacts and rather directly link N deposition with impacts. This makes it difficult to pinpoint the key papers. The focus of the literature review for critical limits of eutrophication relied upon the three relevant geo-chemical criteria namely the critical C:N ratio, nitrate concentration in the soil solution, and critical nutrient ratios across diverse semi-natural ecosystems. We identify 13 peer-reviewed publications for critical C:N ratio, 25 on critical nitrate concentration, and 53 on critical nutrient ratios mostly for forest ecosystems.

## 2.2 Spatial datasets for critical limits

Regionalization of input parameters in SMB modelling enables an enhanced receptor specific computation of critical loads. Apart from a few exceptions, critical limits are mostly applied as constant values, currently. However, depending on the critical limit criteria applied, critical limits do vary spatially. Hence, applying critical limits spatially distinct, would lead to an overall improvement in the computation of critical loads, because critical loads are derived on receptors specific critical limits. Therefore, we screened the latest available land cover and soil datasets available at a European level, seeking ways to link critical limits spatially in the best possible way. Further, based on the CCE status reports from the years 2011 – 2022, we assessed whether NFCs use national or European vegetation datasets, to compute critical loads.

## 2.3 European Background Database for critical loads

For most calculations throughout this work, we used the critical load Background Database for Europe (version 2017). This Background Database contains geo-referenced information used to compute critical loads and is the basis for the CCE to derive Pan-European data and maps in the absence of national data. It is a combination (overlay) of the following basic maps:

a) *Land cover*: The harmonised LRTA land cover map (Cinderby et al. 2007; Slootweg et al. 2009) is used, on which land cover is classified according to EUNIS codes (Davies et al. 2004).

b) *Soils*: The European Soil Database v2 map (ESDB 2004) at a scale 1:1 M was used, which includes Belarus, Ukraine, and the Russian territory.

c) *Forest growth regions*: Forest growth regions for Europe were taken from the EFI database (Schelhaas et al. 2006) that provides data for about 250 regions in (most of) Europe for various species and age classes. For Russia the forest regions from Alexeyev et al. (2004) were used.

d) *Distance to coast:* The distance to coast is needed for deriving base cation deposition; it was taken from a NASA dataset (see https://oceancolor.gsfc.nasa.gov/docs/distfromcoast/).

e) *Nature 2000 (N2k) areas:* Critical loads are of particular interest for nature protection areas and thus N2k areas were integrated into the EU-DB (Tamis et al. 2008). The borders of the Natura 2000 areas can be found at ec.europa.eu/environment/nature/natura2000/data.

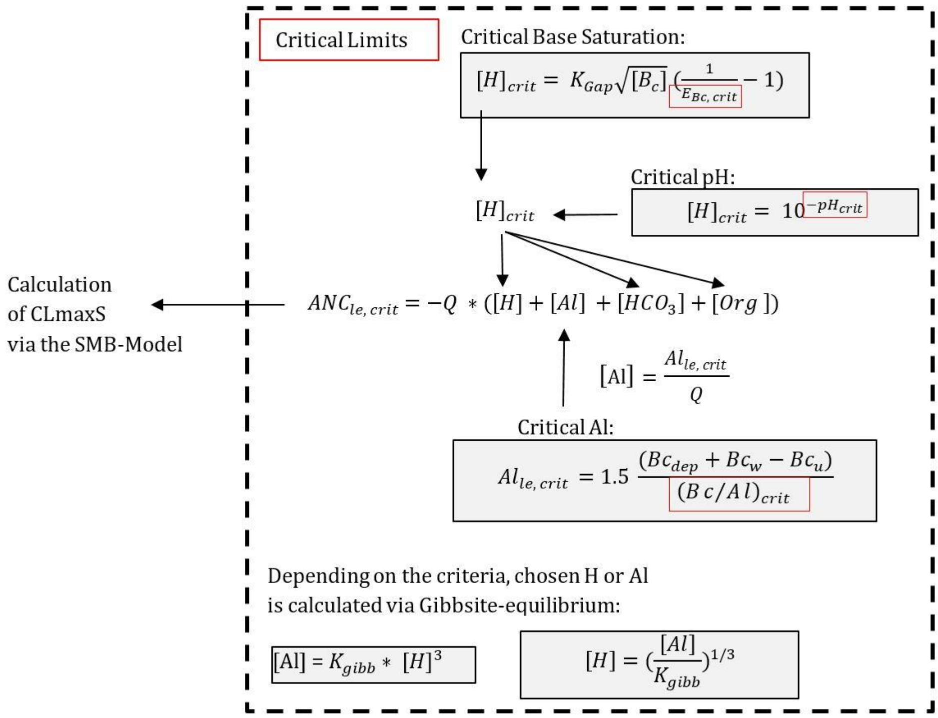
f) *Altitude:* Altitude was obtained from a global map of detailed elevation data (on a 30"×30" grid) from NOAA/NGDC (Hastings and Dunbar 1998).

Overlaying these maps and European country borders and merging polygons with common soil, vegetation, and region characteristics within blocks of 0.10° × 0.05° resulted – after neglecting non-N2k areas below 0.2 km$^2$ – in about 4.94 million computational units with EUNIS classes D-G, with a total area of 3.33 million km$^2$ for Europe west of 42°E. In addition, other data (bases) were used, e.g., on (long-term) meteorology and base cation deposition. Further details can be found in Posch and Reinds (2017). Note that this data base is now maintained and further developed by the CCE at UBA Germany (Reinds et al. 2021).

## 2.4 Critical limits for acidification

Critical loads for acidification are calculated via the SMB model from given input parameters such as base cation deposition, base cation weathering and uptake. Within the SMB model a so-called critical leaching of acid neutralization capacity ($ANC_{le,crit}$), is determined based on critical limits, linking biological effects (CLRTAP 2017) in relation to acidification. The $ANC_{le,crit}$ needs to be defined in accordance with the present knowledge - preventing ecosystems from harmful effects in relation to acidification. An in depth derivation of the SMB model for acidification can be found in the Mapping Manual (CLRTAP 2017). In this work, we mainly focus on $ANC_{le,crit}$ and the different ways it can be defined. The Mapping Manual (CLRTAP 2017) recommends that $ANC_{le,crit}$ is derived using the critical limit of one of following geochemical criteria, i.e. *aluminium criteria (e.g., Bc:Al), hydrogen criteria (e.g., critical pH) and critical base saturation criteria.* By definition, $ANC_{le,crit}$ provides an estimate of the maximum leachate allowed below which "harmful effects" are not expected according to the "present knowledge" (Posch et al. 2015b; Nilsson and Grennfelt 1988). Most critical limits used today were derived from empirical studies investigating the impact of acidification on, for example, tree growth (Cronan and Grigal 1995; Sverdrup and Warfvinge 1993). The SMB model pathways for the computation of CLmaxS based on critical ANC leaching ($ANC_{le, crit}$) are illustrated in Figure 2, where the system boundaries of the Figure is the calculation of $ANC_{le,crit}$. Note that the gibbsite-equilibrium plays a key role in calculating the hydrogen ion concentration [H] from the aluminium concentration [Al] and vice versa.

**Figure 2: SMB model equations visualizing how CLmaxS is calculated based on the leaching of acid neutralization capacity ANCle,crit via the different critical limit pathways. [H]crit = critical concentration of hydrogen ions; [Bc] = concentration of base cations; EBc,crit = critical base saturation; Kgap = Gapon coefficient; Kgibb = gibbsite equilibrium constant; Alle,crit = critical aluminium leaching; Bcdep = base cation deposition; Bcw = base cation weathering; Bcu = base cation uptake; Bc:Al = critical base cation to aluminium ratio; Q = precipitation surplus.**




Source: own illustration, Environment Agency Austria

### 2.4.1 Sensitivity of CLmaxS in the Background Database due to variation of critical Bc:Al and pH

With the knowledge gained from the literature review and from the NFC survey, we assessed how and to which extent changes in critical limits affect the maximum critical load of sulphur (CLmaxS). We focused on the aluminium criteria and hydrogen criteria i.e. Bc:Al and pH respectively. For this, we chose three different critical pH values and three different Bc:Al ratios and performed six SMB model runs for every computational unit in the critical load Background Database. For Bc:Al we ran the Background Database with values of Bc:Al = 1 (standard value), Bc:Al = 7 (used by Switzerland), and Bc:Al = 10 (used in Canada). Following the German approach for critical pH, we ran three different models, with pH = 4.2 (cation exchange buffer); pH = 5.0 (silicate buffer), and pH = 6.2 (carbonate buffer). The different pH-limits were chosen based on the different soil buffer systems as described by Schlutow et al. (2017). In all model runs pH and Bc:Al limits were applied as constants irrespective of the receptor.

### 2.4.2 Interrelation between Bc:Al and pH

In accordance with the SMB model structure, setting a limit value, by choosing one of the outlined criteria, automatically implies the indirect definition of the critical limits of the other criteria via the gibbsite equilibrium. For example setting Bc:Al, the pH value and base saturation will be set indirectly. Hence, by definition, the aluminium criterion is interrelated with critical pH via the gibbsite equilibrium. Consequently, the question of indirect critical limit violation arises from an empirical and a modelling point of view. Therefore, we assessed how critical pH and the Bc:Al are interrelated via the gibbsite equilibrium within the Background Database.

## 2.5 Critical limits for nutrient nitrogen

The SMB model derives critical loads using a mass balance of N immobilization, removal of N (harvest), denitrification, and leaching (Equation 1). The latter term describes the acceptable N leaching below which no harmful effects on an ecosystem are expected in the long-term. Critical limits of $N_{le(acc)}$ for a variety of effects (e.g., root damages, nutrient imbalances in trees, changes in plant species) are either set directly (N leaching) or via water percolation rates and the soil N concentration below the root zone.

### 2.5.1 Assessing changes in critical soil solution N concentrations and N leaching

Overall, we aimed at elaborating how different critical (or ‘acceptable’) concentration parameter settings 1) affect critical loads of nutrient nitrogen across the Pan-European region, 2) render N leaching values and 3) how the N leaching values compare with the newest empirical critical limits (Bobbink et al. 2022). As for the analyses of critical limits for acidification, the SMB model as defined in the Mapping Manual was the basis. The SMB model for nutrient nitrogen and its equations is shown in Equation 1.

**Equation 1 Equation to calculate critical load for nutrient nitrogen (CLnutN) with: $N_i$ = long-term net immobilisation of N, $N_u$ = net removal of N in harvested vegetation and animals, $[N]_{acc}$ = acceptable/critical N concertation in soil solution, $N_{le(acc)}$ = acceptable leaching of N below the root zone, $f_{de}$ = denitrification fraction, Q = precipitation surplus. N-leaching is set directly or derived via critical N-concentration and precipitation surplus.**

$\boxed{\text{critical N-concentration}}$

$$N_{le(acc)} = Q\boxed{[N]_{acc}}$$

$$CL_{nut}(N) = N_i + N_u + \frac{N_{le(acc)}}{1 - f_{de}}$$

Source: own illustration, Environment Agency Austria

For the assessment of critical limits for nutrient nitrogen, we conducted various SMB model runs using receptor specific critical soil solution N concentrations via the critical load Background Database. In accordance with Hettelingh et al. (2017), we distinguished four different types of receptors, i.e., coniferous, deciduous, and mixed forests as well as non-forests.

In total, we ran four different parameter sets which are listed in Table 1. For the first model run (STD APR) we used the same limit values as the CCE in their final report as stated in Hettelingh et al. (2017). This setting considers the lower limits (0.2 -0.3 mgN $l^{-1}$) of soil solution N concentrations of vegetation changes and of nutrient imbalances in forests (CLRTAP 2017), some of the NFCs use very similar values. The next higher setting (NFC MED) was based on limit values used by countries like Belgium (Wallonia) and was ranging up to 2 mgN $l^{-1}$. The third parameter set (NFC HIGH) represents the highest limit values used by NFCs (e.g., Belgium/Wallonia) and was ranging up to 3.5 mgN $l^{-1}$. Finally, the EU-DW parameter set was an upper bound scenario, using the recommended target value of $NO_3^-$ of 25 mg $l^{-1}$ (Drinking Water Directive 98/83/EC) corresponding to 5.6 mgN $l^{-1}$.

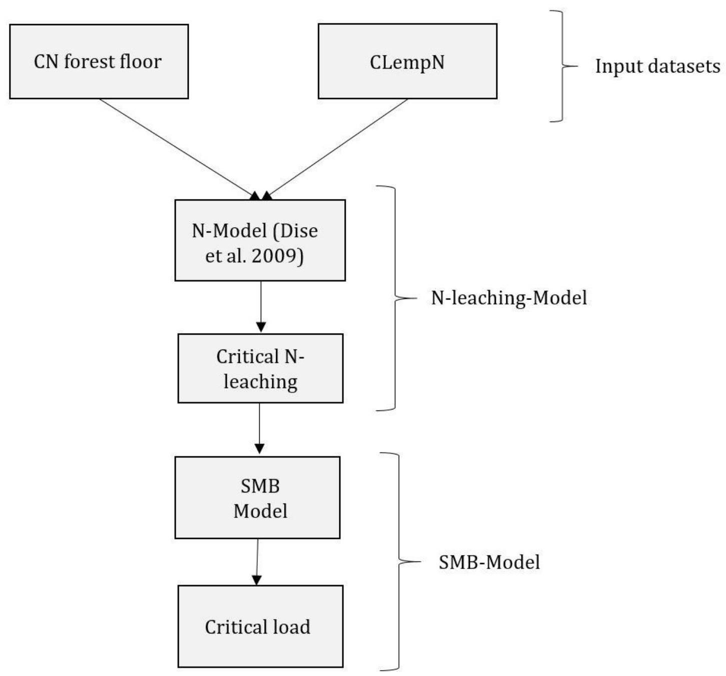
**Table 1. Model runs to evaluate critical limits for nutrient N (soil solution N concentration in mg $l^{-1}$). STD APR: CCE standard approach; NFC MED: medium NFC setting; NFC HIGH: high NFC setting; EU-DW: European Drinking Water Directive target value.**

| Model Run | Non-Forest | Deciduous | Mixed | Coniferous |
|---|---|---|---|---|
| STD APR | 0.3 | 0.3 | 0.25 | 0.2 |
| NFC MED | 2 | 2 | 1.5 | 1 |
| NFC HIGH | 3.5 | 3.5 | 3 | 2.5 |
| EU-DW | 5.6 | 5.6 | 5.6 | 5.6 |

### 2.5.2 Constraining critical N leaching based on soil C:N and empirical critical loads

Critical N concentrations (N in mg $l^{-1}$) as suggested in the Mapping Manual (chapter 5, page 24) are partly derived via inverse modelling using empirical knowledge of impacts of N deposition to derive critical N leaching ($N_{le(acc)}$). Examples are being described in detail in De Vries et al. 2007 in Annex 9. For this study, we also applied an inverse approach estimating $N_{le(acc)}$ using validated empirical relationships, based on European forest data, between N deposition, soil C:N ratios (forest floor) and N leaching (Dise et al. 2009). This approach (henceforth referred as CN EMP APR) is circular because critical loads for nutrient nitrogen (CLnutN) are essentially calculated based on empirical critical loads, which are insert as N deposition values into the empirical relationships provided by Dise et al. 2009. Nonetheless, our approach enables a receptor-specific spatial derivation of critical N-leaching based on the spatial variation of forest floor C:N, which we consider an ecosystem-specific indicator of N saturation and allows for regionalization. The general procedure of CN EMP APR is outlined in Figure 3.

**Figure 3: Workflow of the derivation of regionalized critical N leaching using forest floor C:N ratios via the CN EMP APR.**




Source: own illustration, Environment Agency Austria

#### 2.5.2.1 Input datasets for the CN EMP APR

We used two input datasets to derive N-leaching on a spatial basis, namely soil C:N ratio (forest floor) as well as empirical critical loads for forest ecosystems (CLempN).

The principle empirical relationships we used, were the well-known functions linking N-leaching and forest floor C:N ratios, published by Dise et al. (2009). By means of the topsoil C:N map of the European LUCAS database available for EU countries (Ballabio et al. 2019), we approximated forest floor soil C:N ratios based on average forest floor to topsoil C:N factors per ecoregion, which we derived from Cools et al. (2014). The data published by Cools et al. (2014) is based on ICP Forests data from more than 4000 plots and is available for 17 ecoregions (EEA 2004) shown in Table 2, providing mean forest floor C:N and topsoil C:N ratios per ecoregion. Following Table 2 and naming two examples here: in the ecoregion “Italy and Corsica” forest floor C:N is on average 64% higher compared to top soil C:N, within the “Western highlands” forest floor C:N is on average 37% higher than in the topsoil. Since, we were only interested in topsoil C:N ratios relevant for forest ecosystems we intersected the latest CORINE Land Cover dataset for coniferous, deciduous and mixed forest with the LUCAS database. Eventually, we transformed LUCAS C:N topsoil data to approximate forest floor C:N values by multiplication with the factors presented in Table 2. We are aware that this approach is rather simplistic. Nonetheless, we were unable to find a spatial resource providing C:N ratios for forest floor directly. If available, more accurate national datasets could be used to increase accuracy.

Within the critical load Background Database from 2017, we allocated the recent empirical critical loads for the forest ecosystems via the EUNIS classification system for the respective ecosystems. Therefore, we first mapped the old EUNIS habitat types as listed in the critical load Background Database, with current EUNIS habitat types 2021, using the EUNIS crosswalks and expert judgement. Next, we linked the EUNIS codes with the best possible empirical critical loads available from Bobbink et al. (2022). We then calculated the mean empirical critical load from the given range as the final input for the N-leaching formulas (Equation 2) provided by Dise et al. (2009). Exemplary, for some of the forest ecosystems listed in the critical load Background Database we present the latest empirical critical loads in Table 3 below.

**Table 2: Factors used to transform topsoil C:N ratios to forest floor C:N factors (TF Factor) for the specified ecoregions derived from Cools et al. 2014.**

| Ecoregion | TF_Factor |
|---|---|
| Italy and Corsica | 1.65 |
| Hungarian lowlands | 1.53 |
| Western highlands | 1.37 |
| The Carpathians | 1.56 |
| Eastern plains | 1.38 |
| England | 1.51 |
| Pyrenees | 1.49 |
| Central highlands | 1.36 |
| Alps | 1.50 |
| Central plains | 1.24 |
| Western plains | 1.34 |
| Dinaric western Balkan | 1.61 |
| Baltic province | 1.66 |
| Ireland and Northern Ireland | 1.66 |
| Fennoscandian shield | 1.45 |
| Ibero-Macaronesian region | 1.88 |
| Borealic uplands | 1.80 |

**Table 3: EUNIS code of some selected forest ecosystems listed in the critical load Background Database and ranges of empirical critical loads (kg N ha$^{-1}$ yr$^{-1}$). We updated the EUNIS habitat types 2004 with the EUNIS habitat types present in the critical load Background Database, which we then linked with the best matching empirical critical loads based on Bobbink et al. (2022).**

| EUNIS Code | EUNIS description | CLempN, Low | CLempN, High |
|---|---|---|---|
| T11 | Riparian Salix, Alnus and Betula woodland | 10 | 20 |
| T17 | Fagus woodland | 10 | 15 |
| T2 | Broadleaved evergreen woodland | 10 | 15 |
| T21 | Mediterranean evergreeen [Quercus] woodland | 10 | 15 |
| T3 | Coniferous woodland | 3 | 15 |
| T31 | Abies and Picea woodland | 10 | 15 |
| T34 | Alpine Larix - Pinus cembra woodland | 10 | 20 |
| T35 | Pinus sylvestris woodland south of the taiga | 5 | 15 |
| T39 | Subalpine Mediterranean Pinus woodland | 10 | 15 |

#### 2.5.2.2 N-leaching model

The equations (Equation 2) provided by Dise et al. (2009) require N-deposition and the forest floor C:N ratio as inputs. We substituted N deposition by CLempN. In general, the critical N leaching can be calculated for CLempN < 8 kg ha$^{-1}$ yr$^{-1}$ using the upper part of Equation 2 and for CLempN >= 8 kg ha$^{-1}$ yr$^{-1}$ critical N leaching is calculated using the bottom part of Equation 2. For both, we subtracted the standard error of estimate (SEE) to ensure getting the lower bound of N-leaching values. Furthermore, whenever the results of the equations were negative, we set these values to zero.

**Equation 2: Calculation of critical N-leaching via empirical relationships between N deposition and N leaching taken from Dise et al. 2009.**

$$N_{le(acc)} - \begin{cases} 0.13\, CLempN;\, CLempN < \ 8\, kg\ ha^{-1}yr^{-1}, SEE = 0.63 \\ 0.56\, CLempN - 0.43(C\!:\!N) + 7.2;\, CLempN \geq 8\, kg\ ha^{-1}yr^{-1}, SEE\ = 5.75 \end{cases}$$

ClempN = empirical critical loads of nitrogen; C:N = carbon to nitrogen ratio; SEE = standard error of estimate

We then inserted the output of Equation 2, i.e. $N_{le(acc)}$, into the SMB-Model as already described in Equation 1 above to derive critical loads for nutrient nitrogen via the Background Database.

## 2.6 Integration of external expertise

Throughout our project, we included the expertise available in the ICP Modelling and Mapping community. Project aims, approaches, and preliminary results were discussed during a workshop in December 2022, and the Task Force Meetings of ICP Modelling and Mapping in 2022 (online) and 2023 (in Prague). Furthermore, a survey regarding critical limits was distributed to national experts to get more detailed information from NFCs.

### 2.6.1 National Focal Centre survey

In order to gain a better overview regarding the geochemical criteria and respective critical limits applied by different countries, we conducted an NFC survey via the Coordination Centre for Effects (CCE), which was sent out as a fillable pdf form. We contacted NFCs also directly in order to clarify open questions and to increase the number of responses. The survey was structured in two parts, separating critical limits for acidification and nutrient nitrogen.

The survey part for critical limits for acidification aimed at addressing the following questions:

- Which geochemical criteria (i.e. aluminium criteria, hydrogen criteria and critical base saturation) are used to compute critical loads for acidity?
- Are critical limit values applied receptor/habitat specific?
- What kind of harmful effects are aimed to be avoided with the applied critical limits?
- On which reference/source is the specific method/critical limit value based?

The survey part for critical limits for nutrient nitrogen addressed the following questions:

- Do you use critical N-concentration or critical N-leaching values to compute critical loads for eutrophication?
- Do you apply spatially distinct critical limits for eutrophication?
- What kind of harmful effects did you consider?
- On which reference/source of information are your critical limits based?

### 2.6.2 Expert workshop

An expert workshop was organized in order to gather feedback from NFCs and to discuss further analyses and assessment procedures among experts in the field. The workshop was hold on 5.-6. Dec. 2022, in total 29 participants attended the workshop. The overall goal of the workshop was to present primary results of this project, complementing it with presentations and arguments scientifically relevant for the projects, and to provide a platform to discussion and critically review.

Specifically, the workshop raised the following questions for acidification and nutrient nitrogen:

Critical limits for acidification:

- Does scientific literature suggest an update of critical limits for acidification (e.g., aluminium and hydrogen criteria)?
- How would an alteration in Bc:Al or critical pH affect critical loads (i.e. CLmaxS) on a European scale?

Critical limits for nutrient nitrogen:

- Are the SMB derived critical loads for nutrient nitrogen reasonable in the face of new scientific knowledge?
- Can we derive $N_{le(acc)}$ from the relationship between the soil C:N ratio and N leaching without inflating the SMB steady state assumption?
- Novel insights during the last two decades have reshaped our knowledge about the N cycle in ecosystems. Do these insights influence the way we define impacts related to critical soil N concentration and leaching?

The expert workshop was crucial for improving our work. We summarize the workshop agenda in Table 4 on the next page.

**Table 4 Agenda of the expert workshop in brief. The workshop was structured in two days. Day 1 was focusing on critical limits for nutrient nitrogen and day 2 for critical limits of acidification.**

| Day 1 – Nutrient nitrogen (eutrophication) and partly acidification | Day 2 – Acidification |
|---|---|
| Welcome and introduction to the workshop | Wrap up Day 1 |
| Critical limits for nutrient nitrogen – presentation of preliminary results at the time Simple Mass Balance Model (SMB) for modelling nutrient nitrogen critical loads | Critical limits for acidification – presentation of the primary results of this work at the time |
| | Simple Mass Balance Model (SMB) for modelling critical loads of acidity |
| The new CCE receptor map | German method for acidification: soil buffer system specific pH criteria |
| Critical limits for acidity and nitrogen: comments on the draft report and results from forest monitoring | Discussion and wrap up of Day 2 |
| Can we link nitrogen and acidity indicators to plant responses? | |
| Some aspects of N-retention and loss of NO3, NH4 and DON | |
| Critical limits seen from the angle of N2O losses | |
| Evaluating Simple Mass Balance regarding climate dependences and impacts | |
| Discussion of Day 1 | |

# 3 Results

We present the results regarding critical limits for acidification in chapter 3.1, followed by the critical limits for nutrient nitrogen in chapter 3.2. Next, spatial datasets relevant for critical limits both acidification and nutrient nitrogen are presented in chapter 3.3. Finally, we close the chapter by reflecting on the expert workshop discussions in section 3.4.

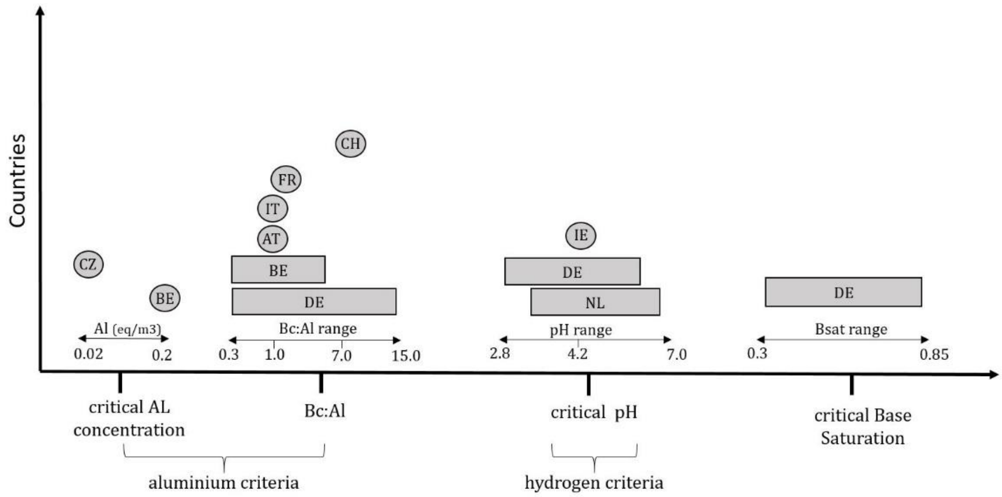
## 3.1 Critical limits for acidification

In the following section, we present the current state of knowledge of the different geochemical criteria and respective critical limits, starting by an overview, which geochemical criteria and critical limits NFCs are applying.

### 3.1.1 National Focal Centre survey

In total, elven NFCs responded to our survey. Norway, Sweden and Finland responded that they compute critical loads for aquatic ecosystems only, using models such as MAGIC or FAB, and were thus not included in this assessment. Spain does not compute critical loads for acidification. The aluminum criterion as the most commonly used chemical criterion followed by the hydrogen criterion and the critical base saturation. The Czech Republic and Belgium (Wallonia) implemented the critical Al concentration. The Czech Republic used the Drinking Water Directive 98/83/EC with a limit of Al = 0.2 mg $l^{-1}$ (i.e. 0.02 eq $m^{-3}$) as their critical limit. The Bc:Al ratio was implemented by Germany, Belgium (Flanders), Austria, Italy, France, and Switzerland aiming the prevention of tree growth reduction. All NFCs, except Switzerland and France, used Bc:Al = 1 according to Sverdrup and Warfvinge (1993). France used a Bc:Al of 1.2. and Switzerland of 7. Germany was the only country computing critical loads of acidity based on all three available geochemical criteria. Furthermore, the Netherlands and Germany were the only NFCs applying receptor specific critical limits. Ireland, Germany and the Netherlands implemented the hydrogen criteria i.e. a critical pH value. Ireland used a constant default pH of 4.2 aiming to avoid the acidification of soils. Germany and the Netherlands used receptor-specific pH values ranging from 2.8 – 6.2 and 3.7 – 7, respectively. Germany was the only NFC using the critical base saturation concept with values ranging from 0.3 – 0.85. Their approach is based on the BERN-Database (Schlutow et al. in prep) providing information on the ecological niche of species in relation to soil base saturation. Figure 4 summarizes the results by showing the criteria and respective limit values applied by the NFCs.

**Figure 4: Countries (two-letter ISO codes) and applied geochemical criteria (i.e., critical aluminium concentration, critical pH, and critical base saturation). The bars show countries who used a receptor specific approach, the circles the countries who used a single critical limit value. Note that Belgium appears two times since we got answers from Belgium Wallonia and Flanders.**




Source: own illustration, Environment Agency Austria

### 3.1.2 Aluminium criteria

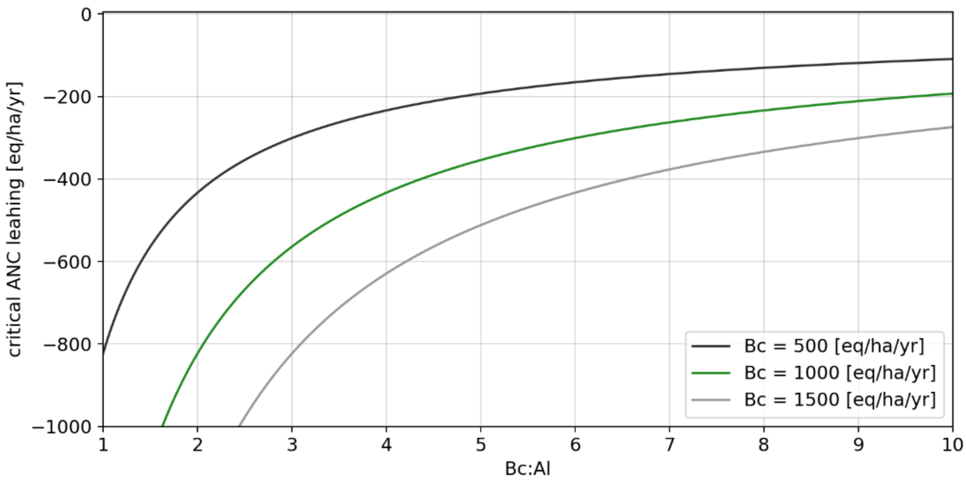
The critical Al leaching ($Al_{le,crit}$) from the soil can be derived via direct definition of a critical Al concentration or via a critical base cation to aluminium ratio (Posch et al. 2015b) or via a critical aluminium mobilisation rate (CLRTAP 2017). The threshold of 200 µg $l^{-1}$ ([Al] = 0.02 eq $m^{-3}$) in accordance with the EU drinking water guideline (EC 2020) as well as an inorganic Al threshold of 2 mg $l^{-1}$ (0.2 eq $m^{-3}$; De Vries et al. 2015) in relation to biomass reduction of trees are used for setting a critical Al concentration directly. Deriving ANC leaching via the calculation of a critical aluminium mobilisation rate, aims to protect the soil structure (CLRTAP 2017) but is rarely used. The current version of the Mapping Manual suggests restricting the Al criterion to soils with low soil organic carbon (SOC). For soils with high SOC, e.g., peatlands, the hydrogen criteria is recommended (CLRTAP 2017). With respect to NFC responses, critical Al leaching is almost exclusively estimated from critical Bc:Al ratios (Equation 3). Hence, our analyses focused mainly on the Bc:Al ratio. The link between Bc:Al and ANC leaching is exemplary visualized in Figure 5 for three different levels of Bc = $Bc_{dep}$ + $Bc_w$ – $Bc_u$, showing how higher Bc:Al levels generally correspond with lower critical $Al_{le,crit}$ leading to overall lower critical load for acidification, Bc levels were selected to cover a wide European range.

**Equation 3 Critical Al leaching derived from critical Bc:Al ratio.**

$$Al_{le,crit} = 1.5 \frac{Bc_{dep} + Bc_w - Bc_u}{(Bc:Al)_{crit}}$$

$Al_{le,crit}$ = critical aluminium leaching; $Bc_{dep}$ = base cation deposition; $Bc_w$ = base cation weathering; $Bc_u$ = base cation uptake; Bc:Al = critical base cation to aluminium ratio

**Figure 5 ANC leaching as a function of Bc:Al for different levels of Bc ($Bc = Bc_{dep} + Bc_w - Bc_u$) with $K_{gibb}$ = 600 $m^6$ / $eq^2$.**




Source: own illustration, Environment Agency Austria

In an extensive literature review Sverdrup and Warfvinge (1993) integrated the results of about 200 pot experiments on impacts of Al on different plant seedlings and suggested critical Bc:Al ratios for various plant species and different levels of protection, allowing for a maximum growth reduction ranging from 5% - 20% compared to control conditions (see the exemplary selection in Table 5). The Bc:Al ratios derived from this study are the basis for critical load calculations via the aluminium criteria within the SMB model (CLRTAP 2017). In an literature review based on 300 articles by Cronan and Grigal (1995), the Ca:Al ratios of 1, 0.5 and 0.2 were indicated as an appropriate indicator for predicting adversely impacts of Al on tree growth (50%, 75%, and 100% risks of harmful effects) or nutrient imbalances, with an overall uncertainty of ± 50%. The significance of Ca:Al indicator increases through supplementary indicators such as critical base saturation or Ca:Al ratios in fine root tissue. Overall, critical load estimates for acidification are mostly conducted using either the tree-specific Bc:Al limits based on Sverdrup and Warfvinge (1993), e.g., ranging from 0.3 – 5 (Iost et al. 2012; Lorenz et al. 2008; Waldner et al. 2015; Meesenburg et al. 2016) or by using a uniform limit of Bc:Al = 1 (Graf Pannatier et al. 2004; Reinds et al. 2008). In Canada a Bc:Al ratio of 10 has been proposed as a safety measure (Arp et al. 1996), considering soil heterogeneity, to ensure the protection of the receptor under study (NEG/ECP Forest Mapping Group 2001). Ouimet et al. (2006) emphasised the usage of Bc:Al = 10 as an appropriate critical limit for forests in Eastern Canada. Consequently, McDonnell et al. 2010; Duarte et al. 2013 used Bc:Al = 1 for conifers forests (UNECE 2001) and Bc:Al = 10 for deciduous forests. Nonetheless, Watmough and Dillon (2003) stated that, even when setting Bc:Al = 10, a critical base saturation level > 20% is not ensured. In Switzerland a Bc:Al = 7 was selected to ensure higher level of base saturation (Braun et al. 2020). According to the literature we studied, no additional data is available allowing for a more stringent definition of critical Bc:Al or Ca:Al ratios.

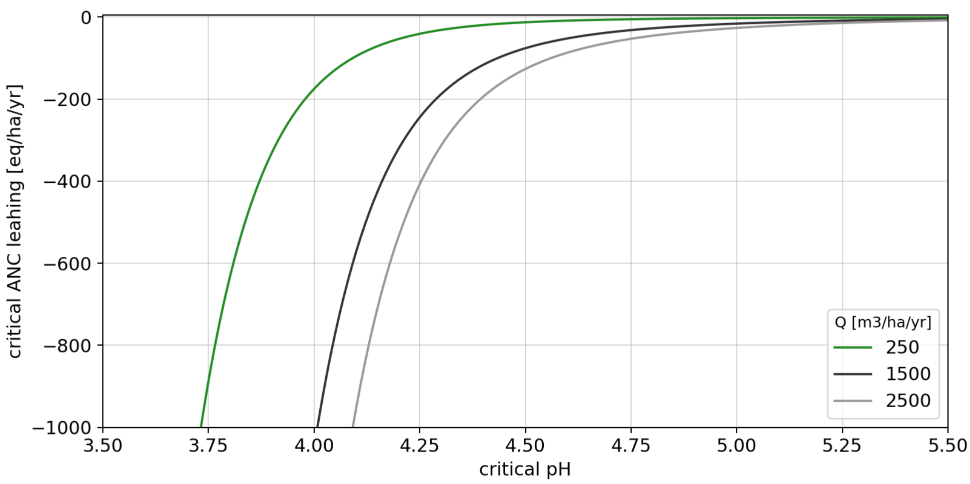
**Table 5 Bc:Al ratios for different tree species and different levels of growth reduction (20%, 10% and 5%) as well the forest type (C = Coniferous, D = Deciduous) according to Sverdrup and Warfvinge (1993).**

| Species | Latin name | Type | 20% | 10% | 5% |
|---|---|---|---|---|---|
| Balsam Fir | *Abies balsamea* | C | 1.1 | 3 | 6 |
| Black Spruce | *Picea marina* | C | 0.8 | 1.2 | 2.5 |
| White Pine | *Pinus strobus* | C | 0.5 | 0.9 | 1.5 |
| Jack Pine | *Pinus banksiana* | C | 1.5 | 2 | 3 |
| Sitka Spruce | *Picea sitchensis* | C | 0.4 | 1.2 | 2.5 |
| Tamarack (Larch) | *Larix laricina* | C | 2 | 3 | 4 |
| Larch | *Larix decidua* | C | 2 | 3 | 4 |
| Western Hemlock | *Tsuga heterophylla* | C | 0.2 | 0.4 | 1 |
| Western Red Cedar | *Thuja plicata* | C | 0.1 | 0.4 | 1 |
| White Spruce | *Picea glauca* | C | 0.5 | 1.2 | 2.5 |
| Norway Spruce | *Picea abies* | C | 1.2 | 3 | 6 |
| Scots Pine | *Pinus sylvestris* | C | 1.2 | 2 | 3 |
| Beech | *Fagus grandifolia* | D | 0.6 | 0.9 | 1.3 |
| Maple | *Acer saccarum* | D | 0.6 | 0.9 | 1.3 |
| Oak | *Quercus robur* | D | 0.6 | 0.9 | 1.3 |
| Trembling Aspen | *Populus tremuta* | D | 4 | 6 | 8 |
| Alder | *Alnus glutinosa* | D | 2 | 3 | 4 |
| White Birch (Paper Birch) | *Betula papyrifera* | D | 2 | 3 | 4 |
| Yellow Birch | *Betula alleghaniensis* | D | 2 | 3 | 4 |
| Grey Birch | *Betula populifolia* | D | 2 | 3 | 4 |
| Silver Birch | *Betula pendula* | D | 0.8 | 1.2 | 2 |

### 3.1.3 Hydrogen ion criteria

For soils with a high SOC content it is recommended to calculate critical loads based on the hydrogen ion criterion (CLRTAP 2017; Posch et al. 2015b). The critical limit of the hydrogen criterion is set directly by defining a critical pH (i.e. $-\log_{10}[H^+]$) or via a critical Bc:H ratio (Posch et al. 2015b) as described in the Mapping Manual (CLRTAP 2017). As for the aluminium criteria, ANC leaching is derived from critical pH (Figure 2). In all studies we examined, critical loads for acidification were estimated directly by setting a critical pH limit instead of using Bc:H ratios. Furthermore, the data availability of Bc:H ratios appears to be limited and Bc:H ratios we found seemed to be derived from Bc:Al ratios. Hence, we focus on critical pH in the following analyses. The relationship between critical pH and ANC leaching is illustrated in Figure 6 below and shows the high sensitivity of critical ANC within the pH range of 3.5 – 4.5.

**Figure 6 ANC leaching as a function of critical pH, for different levels of precipitation surplus (Q) and $K_{gibb}$ = 600 $m^6/eq^2$.**




Source: own illustration, Environment Agency Austria

Critical pH limits used for terrestrial ecosystems range from 4.0 – 4.5 (Hettelingh et al. 1991; Veerhoff et al. 1996; Sverdrup et al. 1990). A critical pH limit of 4.2, as recommended in the Mapping Manual (CLRTAP 2017), is based on the work of Ulrich (1981, 1987) and is most frequently applied (e.g., Hall et al. 2001; Skeffington 2006; Pardo et al. 2018). Nonetheless, critical pH limits also deviate from the recommended value of 4.2. Posch et al. (2015a) for example set the critical pH to 4.4 for non-calcareous soils; Langan et al. (2004) implemented a critical pH = 4.0 for woodlands and a pH = 4.4 for deep peat soils. Although species (receptor) specific pH limits and dose response curves are mentioned in the UNECE (2001) workshop paper, we could not find applicable thresholds for critical load of acidification calculations. Most of the studies used a default critical pH value irrespective of the receptor. A receptor(soil)-specific approach was developed by Schlutow et al. (2017) using reference soil profiles to set pH limits referring to the various soil buffer system (Table 6). In summary, we identified critical pH values but no critical Bc:H ratios. Species-specific Bc:H ratios were only listed in a report of Schlutow et al. (2017) and appear to be calculated from Bc:Al ratios provided by Sverdrup and Warfvinge (1993).

**Table 6 Critical soil pH values based on the pH range of the various soil buffer systems (Schlutow et al. 2017)**

| Soil buffer system | pH range | Lowest acceptable pH, i.e. critical pH |
|---|---|---|
| Carbonate buffer | 8.6-6.2 | 6.2 |
| Silicate buffer | 6.2-5.0 | 5.0 |
| Exchange buffer | 5.0-4.2 | 4.2 |
| Aluminium buffer | 4.2-3.8 | 3.8 |
| Aluminium-Iron-buffer | 3.8-3.2 | 3.2 |
| Iron-buffer | < 3.2 | 2.8 |

### 3.1.4 Critical base saturation

The critical ANC leaching can be also derived via the definition of a critical base saturation ($E_{Bc,crit}$), where $E_{Bc,crit}$ is defined as *"the fraction of base cation at the cation exchange complex"* (CLRTAP 2017). Subsequently, for the calculation of the critical ANC, the critical $H^+$ concentration is computed from the critical base saturation following Equation 4 as shown below (Posch et al. 2015b), were Equation 4 is mainly limited by an appropriate determination of the parameters required to derive the Gapon coefficient ($K_{gap}$). For three different $K_{gap}$ values, the relationship between critical ANC leaching and critical base saturation is visualized in Figure 7, showing the general trend of higher critical ANC leaching in relation to an increase in critical base saturation.

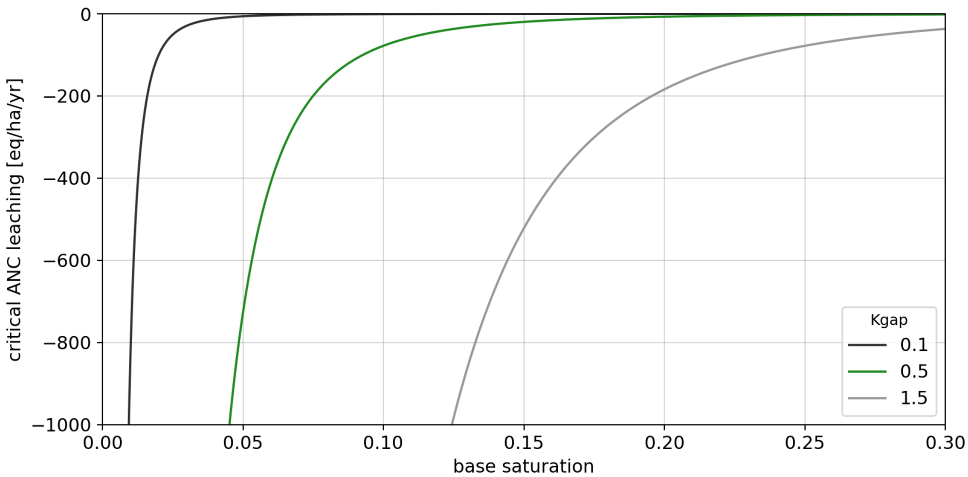
**Equation 4 Critical hydrogen ion concentration as derived from critical base saturation ($E_{Bc,crit}$) and the Gapon model**

$$[H]_{crit} = K_{Gap}\sqrt{[B_c]}\left(\frac{1}{E_{Bc,crit}} - 1\right) \quad \text{with} \quad K_{Gap} = \frac{1}{k_{HBc} + k_{AlBc} + K_{gibb}^{1/3}}$$

$[H]_{crit}$ = critical concentration of hydrogen ions; [Bc] = concentration of base cations; $E_{Bc,crit}$ = critical base saturation; $K_{gab}$ = Gapon exchange with site specific selectivity coefficients ($K_{HBc}$ and $K_{AlBc}$); $K_{gibb}$ = gibbsite equilibrium constant

Based on our literature review, critical base saturation ranged between 15% and 30%. Several studies have used the critical base saturation criteria, e.g., Augustin et al. (2005) used $E_{Bc,crit}$ = 15%; Holmberg et al. (2001) used $E_{Bc,crit}$ = 15% for the soil mineral layer and 30% for the organic layer; Reinds et al. (2008) used a critical base saturation of 15%. As stated by Wellbrock and Bolte (2019), vegetation-specific critical base saturation critical limits were provided by Balla et al. (2013) derived via the BERN Model (Schlutow et al. in prep).

**Figure 7 ANC leaching as a function of critical base saturation for three different Kgap (eq/m3)1/2 values.**

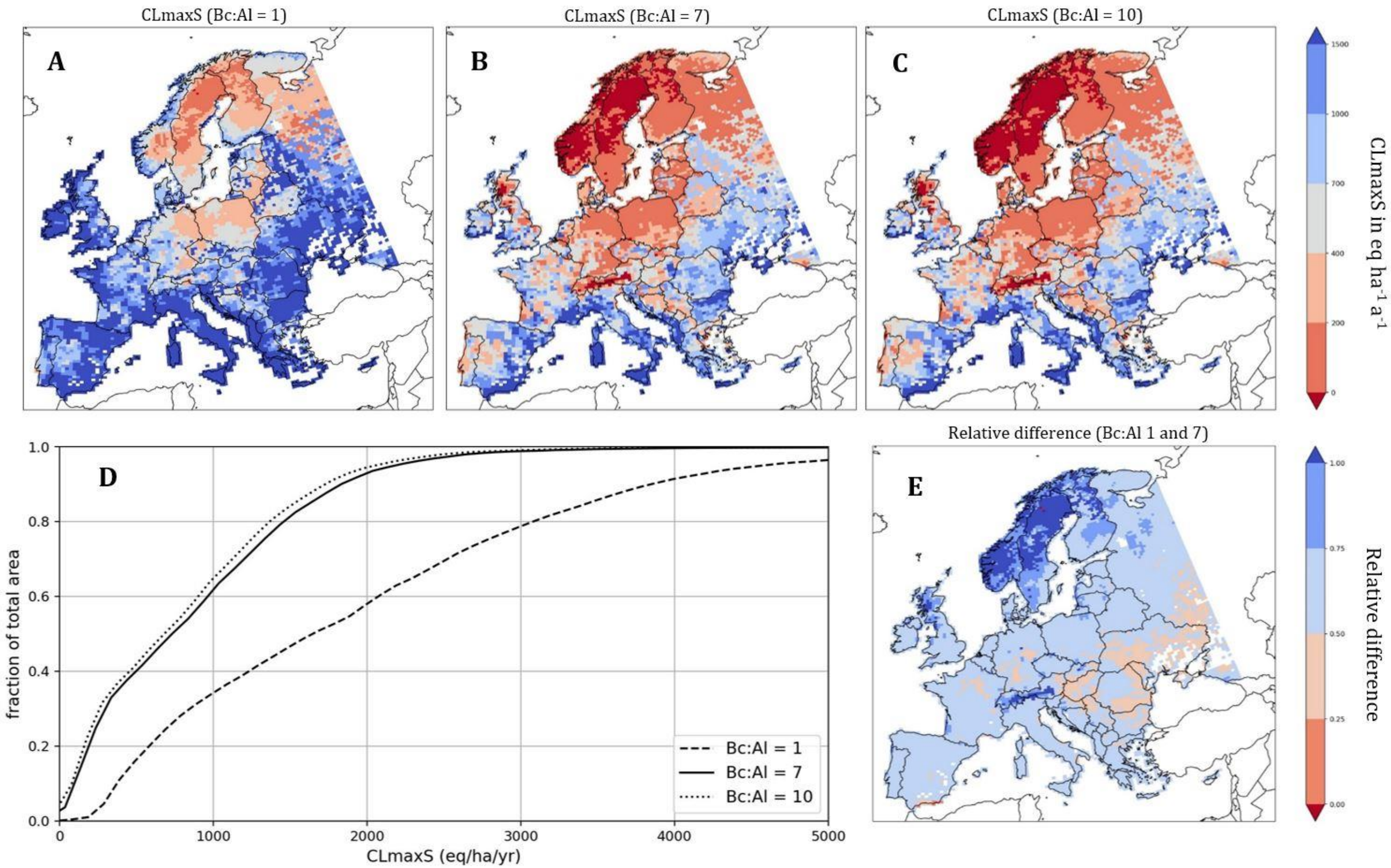



Source: own illustration, Environment Agency Austria

### 3.1.5 Sensitivity of CLmaxS in the Background Database due to variation of critical Bc:Al and pH

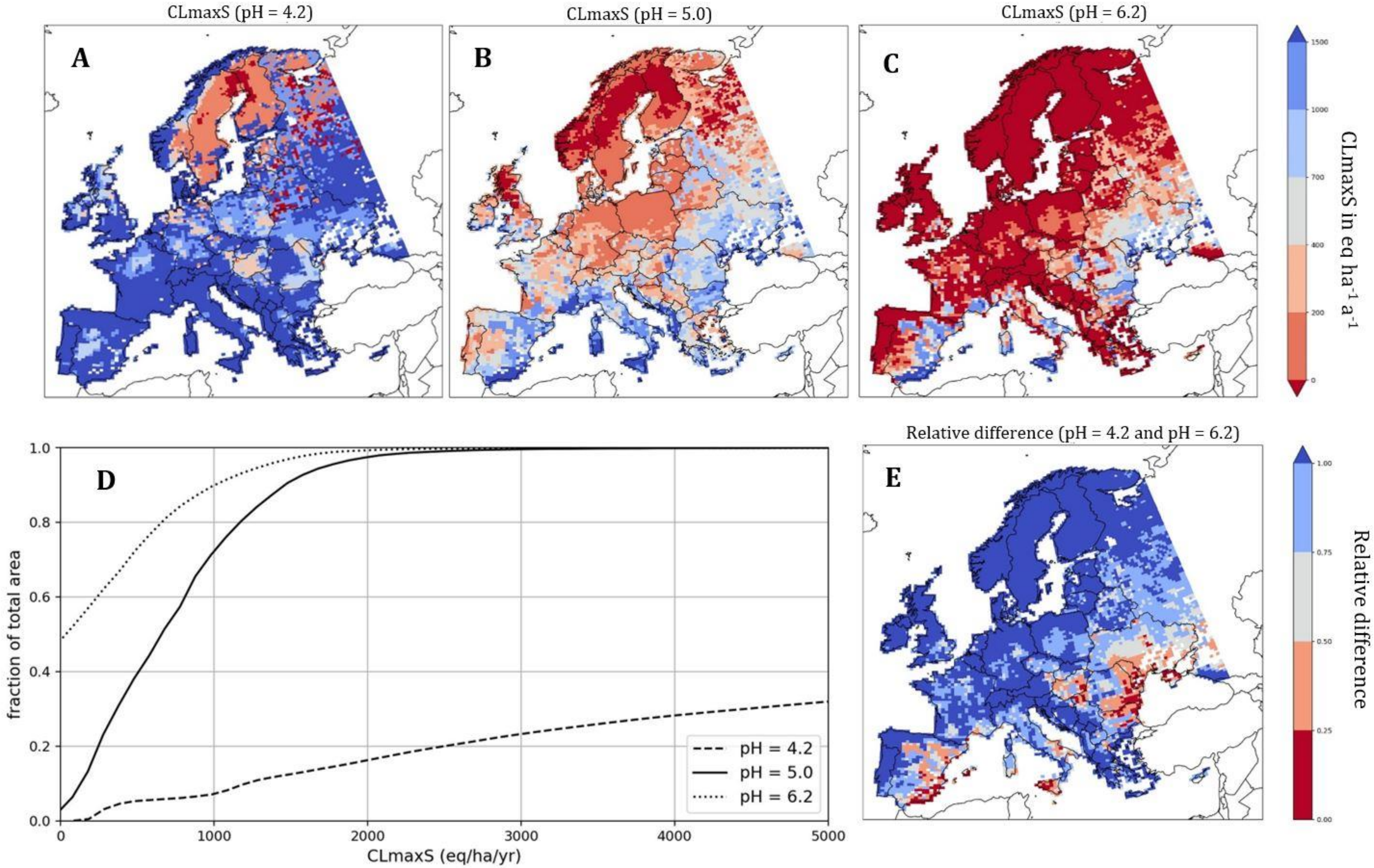
An increasing Bc:Al defines an increase of base cations in comparison to aluminium in soil solution. While Bc:Al = 1 allows for equal concentration (in mol) of base cations and aluminium, ratios of 7 or 10 define the concentration of base cations in soil solution to be 7 or 10 times higher compared to aluminium. Thus, increasing Bc:Al results in decreasing critical loads of acidity. Applying Bc:Al = 1, resulted in an median critical load of CLmaxS = 1687 eq $ha^{-1}$ $yr^{-1}$ (27 kg $ha^{-1}$ $yr^{-1}$) protecting 50% of the total area of all ecosystems. Increasing Bc:Al from 1 to 7 and 10 led to decreasing median critical loads of 735 eq $ha^{-1}$ $yr^{-1}$ (11.76 kg $ha^{-1}$ $yr^{-1}$) and 677 eq $ha^{-1}$ $yr^{-1}$ (i.e. a reduction by 56% and 60%) in comparison to a Bc:Al = 1. The difference in CLmaxS between Bc:Al = 7 and Bc:Al = 10 were marginal. Spatially, we summarised the results of the different simulations in Figure 8, presenting the area weighted 5$^{th}$ percentile of CLmaxS, i.e. protecting 95% of ecosystems within the respective grid cell. Furthermore, we calculated the relative difference between the 5th percentile maps, visualizing the change when increasing Bc:Al from 1 to 7 (Figure 8). The analysis revealed an average decrease of 5$^{th}$ percentile critical loads by 68% considering all grid cells. Noticeable, about 10% of CLmaxS changed to negative values when increasing Bc:Al from 1 to 7, mainly occurring in the northern hemisphere (i.e. Sweden and Norway). Furthermore, we ran three SMB-Model simulations by setting the critical pH to 4.2, 5.0 and 6.2, respectively. In general, increasing the critical pH limit leads to a decrease in CLmaxS. Interestingly, an increase in pH to 5.0 and 6.2, respectively, led to drastic decrease in CLmaxS, even below zero. While 95% of total ecosystem area was protected by CLmaxS = 685 eq $ha^{-1}$ $yr^{-1}$ (10.96 kg $ha^{-1}$ $yr^{-1}$), CLmaxS protecting 95% of ecosystem area was about 70 eq $ha^{-1}$ $yr^{-1}$ (1.12 kg $ha^{-1}$ $yr^{-1}$) for pH = 5.0 and fell drastically below 0 when increasing pH to 6.2. We concluded therefore, that increasing pH, without respecting local site characteristics, does not result in any meaningful target. We summarised the results of the variations in pH in Figure 9

**Figure 8: Area-weighted 5th percentile CLmaxS maps. A: Bc:Al = 1, B: Bc:Al = 7, C: Bc:Al = 10, E: relative difference between Bc:Al = 7 and 10 [(A-B)/A]. The cumulative distribution functions of the different simulations (A, B, C) are shown in D.**




Source: own illustration, Environment Agency Austria

**Figure 9: Area-weighted 5th percentile CLmaxS maps. A: pH = 4.2, B: pH = 5.0, C: pH = 6.2, E: relative difference between pH = 4.2 and 6.2 [(A-C)/A]. The cumulative distribution functions of the different simulations are shown in D.**

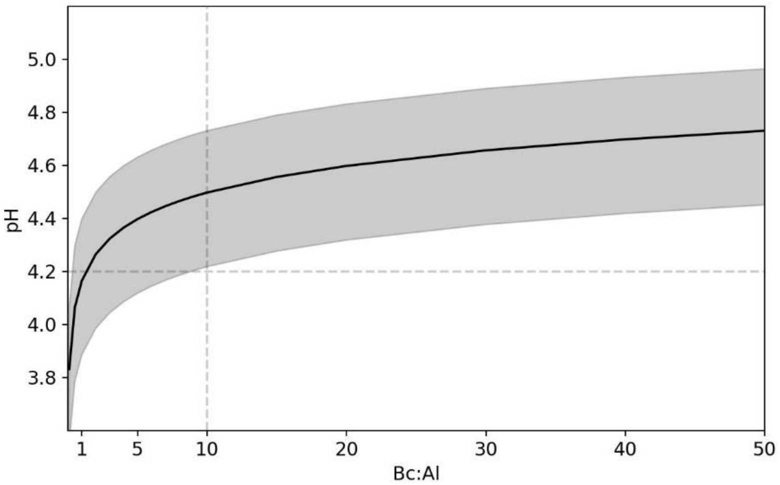



Source: own illustration, Environment Agency Austria

### 3.1.6 Interrelation of Bc:Al and pH

By definition, setting Bc:Al leads to the indirect setting of pH via the gibbsite equilibrium and vice versa. The same holds true for critical base saturation, which potentially can be back calculated from either Bc:Al or pH as described in Figure 2. Nonetheless, back calculating critical base saturation, requires a higher number of parameters for the Gapon model (see Equation 4), increasing the overall uncertainty, which is why it was omitted here. The relation between critical pH and Bc:Al, calculated based on all data points in the Background Database can be seen in Figure 10 and shows that 50% of the data points results in pH > 4.2 when Bc:Al = 10. Consequently, a decrease of Bc:Al leads to pH < 4.2 for a higher fraction of sites.

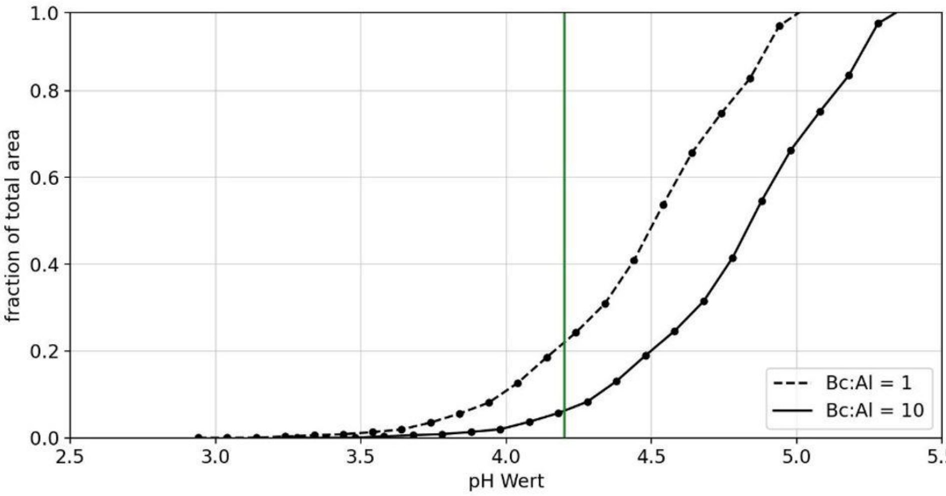
**Figure 10 SMB model defined interrelation between pH and Bc:Al for the Background Database sites. Interquartile range, representing 50% of data points is shown in grey.**




Source: own illustration, Environment Agency Austria

Furthermore, we considered the interrelation of Bc:Al and pH via the critical load Background Database taking into account the ecosystem area (Figure 11; exemplary for Bc:Al = 1 and Bc:Al = 10). As an example, when applying Bc:Al = 1, 21.5% of ecosystem area had a pH < 4.2; when setting Bc:Al = 10, only 6% of ecosystem area had a pH < 4.2.

**Figure 11 Cumulative distribution function of ecosystem area protected under various pH values for Bc:Al = 1 and Bc:Al = 10.**




Source: own illustration, Environment Agency Austria

## 3.2 Critical limits for nutrient nitrogen

Many temperate forests, shrublands, heathlands, and wetlands have, under natural conditions, been limited by N supply, i.e. plant production was hampered due to a deficit of N supply. The increase in N emissions, particularly after the Second World War and the subsequent decades of exceptional economic growth in Europe (Sutton et al. 2011), resulted in long-term accumulation of N in ecosystems overcoming natural N limitation and, with sustained N supply, even N saturation (Aber et al. 1998; Lovett and Goodale 2011). Consequences were manifold, ranging from biomass accumulation, tree growth reductions and mortality, nitrate losses to the groundwater, increased gaseous loss of $N_2O$, changes in the composition of plants, lichens, bryophytes and fungi species, and even species loss in some of the studied ecosystems (Bobbink et al. 2022). The decline in N deposition in Europe since the mid 1980s as a consequence of partly successful emission abatement measures rendered only limited ecosystem effects so far (Schmitz et al. 2019). Hence, a decline in N deposition during just some years cannot eliminate accumulated N due to elevated N deposition lasting decades. Negative effects of N deposition on ecosystems and biodiversity are expected to remain an issue in the next decades in Europe (EMEP 2017; Dirnböck et al. 2018).

The major N cycling processes in terrestrial ecosystems are bound to the soil (Butterbach-Bahl and Gundersen 2011). Critical load calculations take advantage of this fact by using soil N concentration or leaching rates respectively as a limit criteria, assuming that beyond a certain concentration level or leaching amount, an ecosystem is negatively affected by N deposition (CLRTAP 2017). Among the potential negative (harmful) effects, eutrophication, vegetation changes, nutrient imbalances in trees and plant sensitivity to frost and diseases are particularly addressed in the context of critical loads. According to the current Mapping Manual for the calculation of critical loads for nutrient nitrogen (CLRTAP 2017), N leaching ($N_{le}$) is set either directly or indirectly via its derivation from pre-defined soil N concentration levels and soil water drainage. For the sake of simplification, all $NH_4^+$ is assumed to be nitrified and dissolved organic N (DON) is not included in N leaching.

The latest assessment of the critical limit values for nitrogen was done between 2005 and 2007 by De Vries et al. (2007) including a series of expert workshops. Their results were taken up in the current version of the Mapping Manual (CLRTAP 2017) see Table 7. Regarding the derivation of critical soil N concentration limits for biological endpoints such as plants, the authors clearly stated that a direct link does not exist. However, with regard to vegetation changes, De Vries et al. (2007) have applied dynamic soil-plant models to calculate critical soil N availability for the Netherlands. While this new approach improved and specified the old values from Warfvinge et al. (1992) for their modelling domain (the Netherlands), they still point out that soil N concentration cannot directly be linked to plant response. Instead, soil N concentration is the result of complex soil and vegetation processes and differs from plant N availability, which is used in their modelling approaches (De Vries et al. 2007).

Moreover, De Vries et al. (2007) stated, that no process-based link exists for the relationship between soil solution N concentration and nutrient imbalances in trees. In critical load calculations focusing on nutrient imbalances, this difficulty is usually circumvented by using a "natural soil N concentration" of 0.2 mg N $l^{-1}$, a value stemming from unpolluted forest sites in Sweden (Rosén 1990), as the critical limit (Table 7). In contrast, the critical limit values for the impacts on fine roots, diseases, and frost effects are well documented (De Vries et al. 2007).

In summary we conclude that, while clear evidence is available regarding N deposition effects on ecosystems (Bobbink et al. 2022), the general validity of N leaching as a single indicator of ecosystem N saturation, as used in SMB modelling, is still under debate (Lovett and Goodale 2011).

**Table 7. Critical soil solution N concentrations according to the Mapping Manual (CLRTAP 2017) with details to the latest updates as suggested by De Vries et al. (2007).**

| Impact | [N]acc (mgN $l^{-1}$) | Source and comments |
|---|---|---|
| **Vegetation changes in forested ecosystems (data established in Sweden;):** | | Derived from Warfvinge et al. (1992); applicable in Nordic Countries and based on inverse SMB modelling (see De Vries et al. 2007) |
| Lichens to cranberry (lingonberries) | 0.2 - 0.4 | |
| Cranberry to blueberry | 0.4 - 0.6 | |
| Blueberry to grass | 1 - 2 | |
| Grass to herbs | 3 - 5 | |
| **Vegetation changes (data established in The Netherlands):** | | Alternative values from De Vries et al. (2007) used for application in the Netherlands |
| Ground vegetation in coniferous forest | 2.5 - 4 | |
| Ground vegetation in deciduous forest | 3.5 - 6.5 | |
| Grass lands | 3 | |
| Heath lands | 3 - 6 | |
| **Other impacts on forests:** | | |
| Nutrient imbalances | 0.2 - 0.4 | 0.2-0.4 mgN $l^{-1}$ is given for deciduous trees, 0.2 is given for conifers; no clear substantiation according to De Vries et al. 2007 |
| Elevated nitrogen leaching/N saturation | 1 | Based on a differentiation between undisturbed and |

| Impact | [N]acc (mgN $l^{-1}$) | Source and comments |
|---|---|---|
| | | "leaky" forest sites (Stoddard 1994), confirmed by De Vries et al. 2007 |
| Fine root biomass/root length | 1 - 3 | Derived from Matzner and Murach (1995); confirmed by De Vries et al. 2007 |
| Sensitivity to frost and fungal diseases | 3 - 5 | Well documented in the literature; confirmed by De Vries et al. 2007 |

Two sets of critical limit values are currently used in SMB modelling to define the acceptable N leaching ($N_{le(acc)}$), i.e., for the soil solution N concentration or for N leaching itself. Soil N concentration relates to N leaching through the percolation of precipitation water (i.e. precipitation surplus). It is common among several NFCs to use acceptable N leaching instead of thresholds of soil solution N concentration, particularly when high precipitation leads to unrealistically high $N_{le(acc)}$ and hence high soil base cation depletion (Figure 12). In case that no better regional assessments are available, the $N_{le(acc)}$ limit values shown in Table 8 are recommended in accordance with CLRTAP (2017). In addition, approaches such as elevation dependent $N_{le(acc)}$ values are used (Rihm and Achermann 2016).

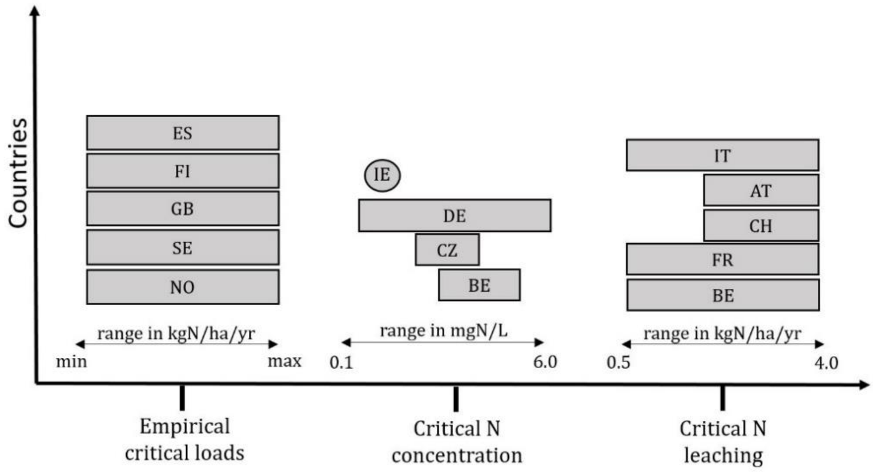
**Table 8. Critical N leaching values according to CLRTAP (2017).**

| Ecosystem type | Acceptable N leaching (kg N $ha^{-1}$ $yr^{-1}$) |
|---|---|
| Boreal and temperate heaths and bogs | 0 - 0.5 |
| Intensive coniferous plantations | 1 - 3 |
| Temperate deciduous forests | 2 - 4 |
| Temperate grasslands | 1 - 3 |
| Mediterranean forests | 1 - 2 |

### 3.2.1 National Focal Centre survey

Overall, we collected 14 NFC responses. Five out of 14 NFCs did not use the SMB-Model but did set critical loads directly via empirical critical loads. Four NFCs calculated critical loads based on critical soil N-concentration and five NFCs via directly using critical N-leaching values. All but Ireland implemented spatially varying, i.e. receptor-specific critical N-limits. Dynamic modelling was used by the Netherlands for the setting of critical limit values relating to critical N availability of plant species (Figure 12).

**Figure 12 Methods applied in countries (in two-letter ISO codes) to calculate critical loads for N eutrophication. The bars represent the range used for receptor specific approaches. Circles indicate that a constant critical limit value was used. The ranges of empirical critical loads differ among countries and ecosystems. Note that Belgium appears two times since we got answers from Belgium Wallonia and Flanders, further the Netherlands do not appear in the figure since the apply dynamic modelling.**




Source: own illustration, Environment Agency Austria

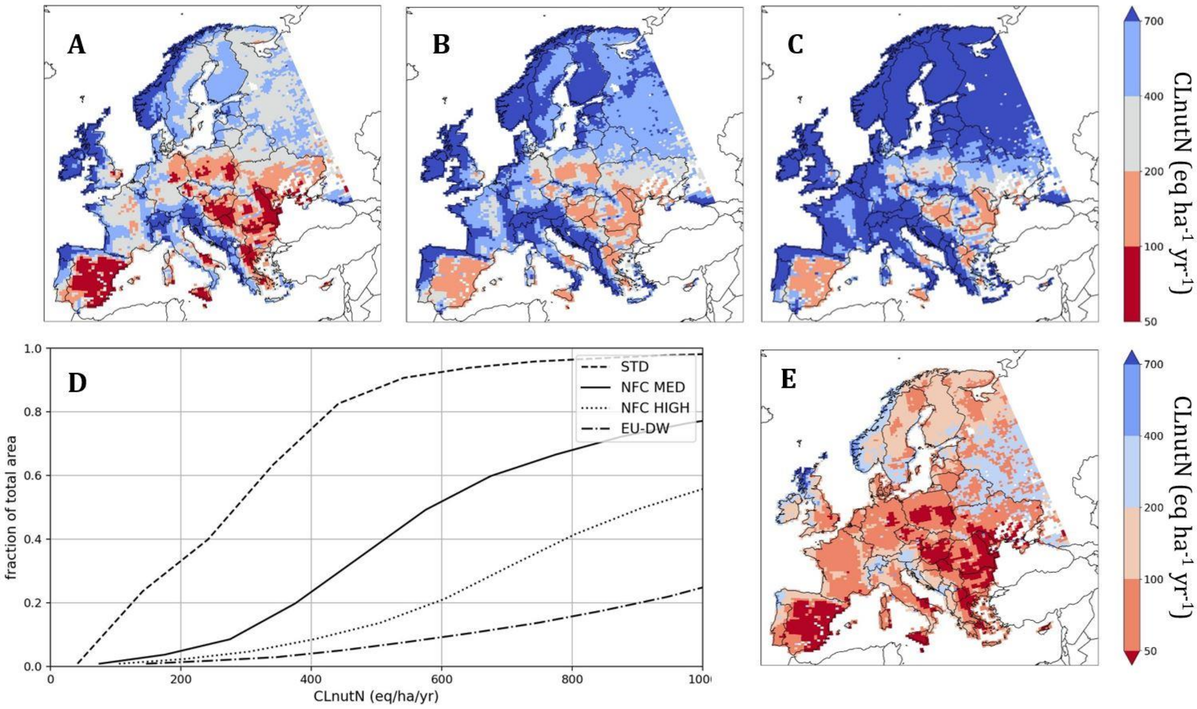
Critical N-concentration applied by the NFCs stayed within the ranges proposed in the Mapping Manual. Ireland used a value of 0.2 mg $l^{-1}$ for managed forests to avoid nutrient imbalances. The Czech Republic used 1 mg N $l^{-1}$ for coniferous and 2 mg N $l^{-1}$ for broadleaf forest and other ecosystems to avoid vegetation change. Belgium (Wallonia) used 2.5, 3.5 and 3 mg N $l^{-1}$ for coniferous-, deciduous- and mixed forests, respectively. Germany used critical N-concentrations ranging between 0.1 and 6 mg N $l^{-1}$ (being derived via the BERN-Database) based on community specific soil C:N ratios to prevent vegetation change.

Italy, France and Belgium (Flanders) used habitat specific critical N-leaching ranging from 0.5 to 4 kg $ha^{-1}$ $yr^{-1}$ referring to the Mapping Manual chapter 5, page 23 (CLRTAP 2017). Furthermore, Austria and Switzerland applied an altitude dependent N-leaching approach (CCE Status Report of 2007) in order to better account for areas with high precipitation. Hence, critical N-leaching ranges from 4 kg $ha^{-1}$ $yr^{-1}$ at 500 m.a.s.l to 2 kg $ha^{-1}$ $yr^{-1}$ at 2000 m.a.s.l with linear interpolation in between (see Switzerland's contribution to the CCE Status Report 2007).

### 3.2.2 Assessing changes in critical soil N concentration

Increasing critical limits of eutrophication (i.e. soil N-concentration or N-leaching) results in increasing critical loads. We conducted four simulations: a standard approach (STD APR) with soil N concentrations ranging from 0.2 – 0.3 mg N $l^{-1}$, a medium (NFC MED) and a high (NFC HIGH) scenario in accordance with the results obtained from the NFC survey, and a scenario, where the soil N concentration is set to the recommended EC Drinking Water Directive target value (EU-DW) see Table 1. In the medium model run (NFC MED) we increased the critical N-concentration by 5-10 times ranging from 1 – 2 mgN $l^{-1}$. In the high model run (NFC HIGH) we increased the critical N-concentration by 10-15 times ranging from 2.5 – 3.5 mgN $l^{-1}$ in comparison to the standard approach. Within these ranges, distinct critical N concentrations were applied to the four receptor types (non-forest, deciduous-forest, coniferous-forest, and mixed-forest). In EU-DW, soil N-concentration was set to 5.6 mg N $l^{-1}$ irrespective of the receptor. Consequently, the STD APR had the lowest critical loads with median (i.e. protecting 50% of total ecosystem area) of CLnutN = 290 eq $ha^{-1}$ $yr^{-1}$ (4.06 kg $ha^{-1}$ $yr^{-1}$). For NFC MED the median CLnutN = 585 eq $ha^{-1}$ $yr^{-1}$ (8.19 kg $ha^{-1}$ $yr^{-1}$) increased by a factor of 2, and for NFC HIGH by about a factor of 3 (CLnutN = 915 eq $ha^{-1}$ $yr^{-1}$ = 12.81 kg $ha^{-1}$ $yr^{-1}$) when compared to the STD APR. Comparing the EU-DW scenario with the STD APR resulted in a 5 times higher median CLnutN = 1470 eq $ha^{-1}$ $yr^{-1}$ (20.58 kg $ha^{-1}$ $yr^{-1}$).

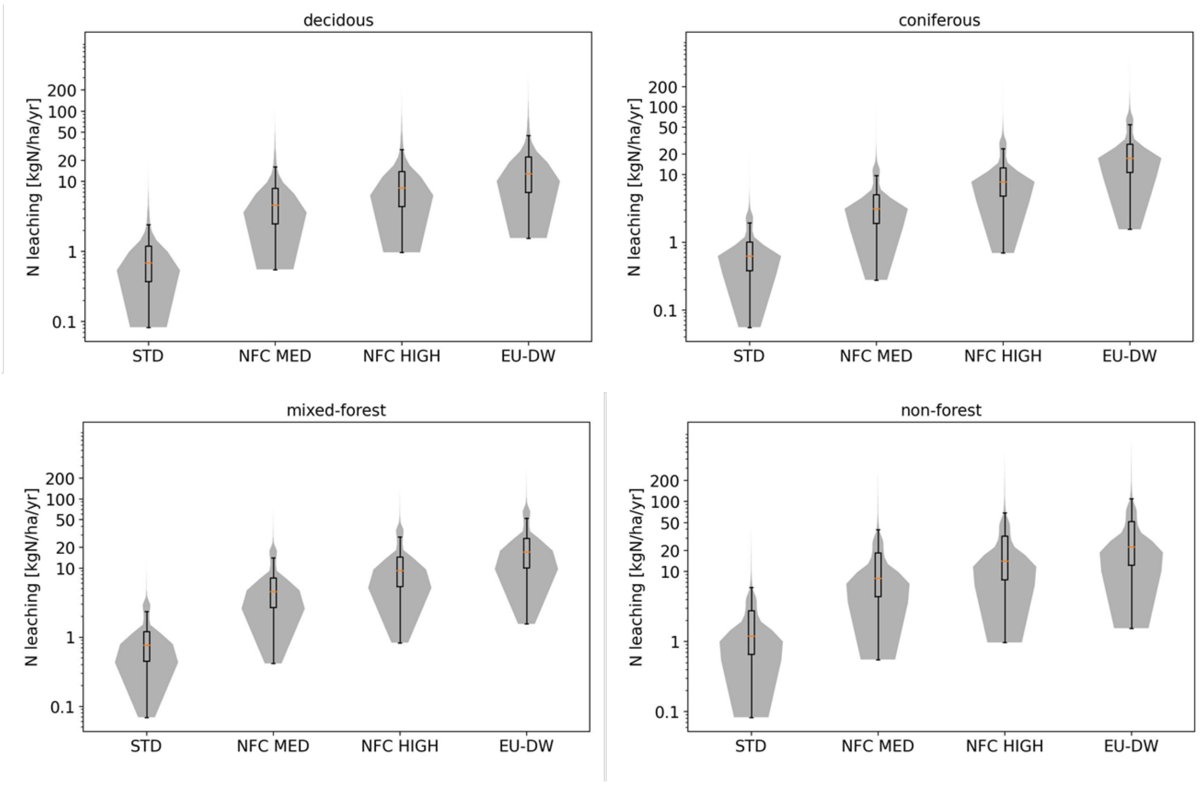
**Figure 13. Area weighted 5th percentiles CLnutN maps. A: NFC MED, B: NFC HIGH, C: EU-DW, E: STD APR. The cumulative distribution functions of the different simulations are shown in D.**




Source: own illustration, Environment Agency Austria

Our assessment was done across the entire geographical domain of the critical load Background Database. We compared the four critical soil N concentration scenarios regarding their implications for N leaching (Figure 14) in ecosystem types and further compared the resulting CLnutN values with CLempN of the same ecosystem types (Figure 15). Among the different critical values for soil N concentration, only the lowest scenario resulted in median annual N leaching of < 1 kg N $ha^{-1}$ $yr^{-1}$ in the different forest types (median: 0.62 – 0.76 kg N $ha^{-1}$ $yr^{-1}$) and slightly above in non-forest ecosystems (median: 1.21 kg N $ha^{-1}$ $yr^{-1}$) (Figure 14). All other scenarios showed significantly higher values in all ecosystem type. Only the forest ecosystems in the NFC MED scenario resulted in median N leaching values ranging from 3.1 – 4.6 kg N $ha^{-1}$ $yr^{-1}$ for deciduous, coniferous and mixed forest, being close to the upper value given in the Mapping Manual (Table 8). For the non-forest ecosystem, the median N-leaching of NFC MED (8.0 kg N $ha^{-1}$ $yr^{-1}$), is twice as high compared to the forest ecosystems.

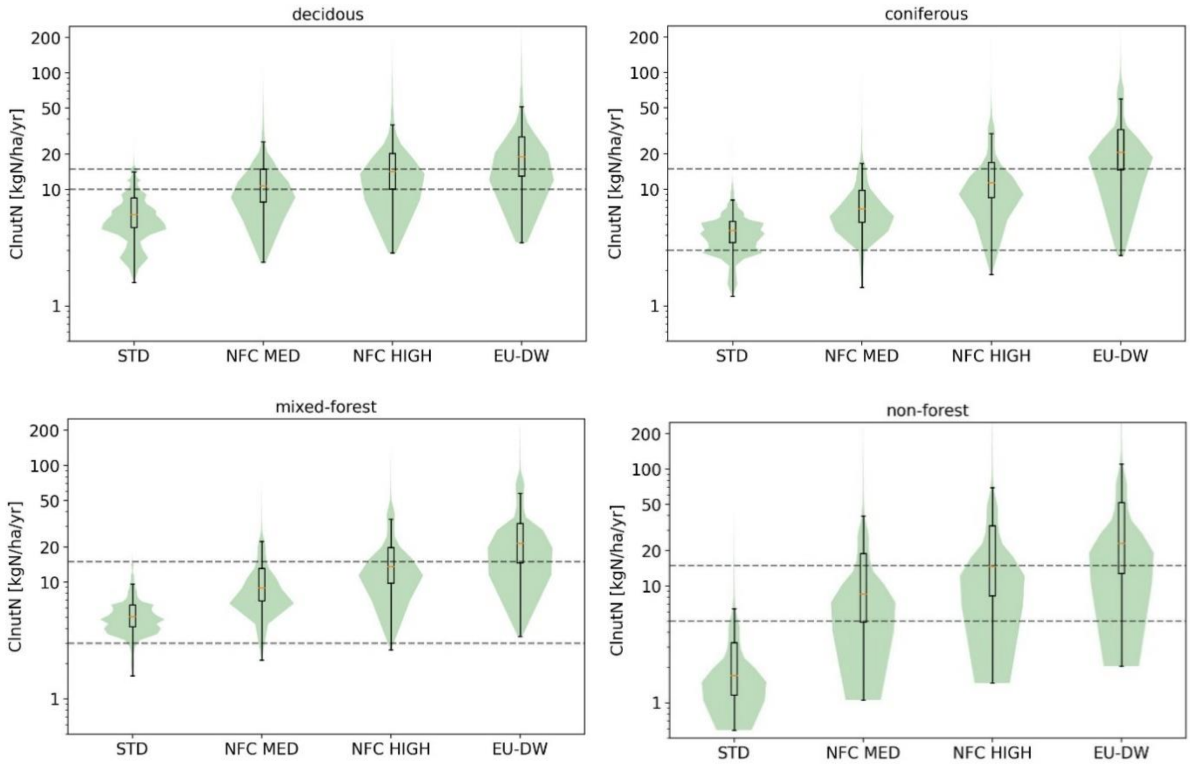
**Figure 14. Variability in N leaching per ecosystem receptor across the entire Background Database domain resulting from the four scenarios of critical soil solution N given in Table 1 (Note: the y-scale is logarithmic).**




Source: own illustration, Environment Agency Austria

Only when using the lowest and the median setting of the critical soil N concentrations (the approach [STD APP and NFC MED] in Table 1), the CLnutN values remained within the range of the minimum and maximum CLempN of the respective ecosystem types (Figure 15). For coniferous forests CLempN values were not strongly exceeded in the NFC HIGH scenario.

**Figure 15. Comparison of CLnutN and CLempN per ecosystem type resulting from the four scenarios of critical soil solution N (Table 1) across the entire geographical domain of the Background Database. Minimum and maximum CLempN according to Bobbink et al. (2022) are presented as horizontal lines (Note: the y-scale is logarithmic).**




Source: own illustration, Environment Agency Austria

### 3.2.3 Inorganic soil N concentration literature studies

New studies linking soil N concentration and impacts remain rare. The largest data set on soil solution chemistry of forests in Europe originates from ICP Forests. In their latest assessment, long-term median $NO_3^-$ soil solution concentration was 0.23 and 0.10 mg N $l^{-1}$ at 10–20 and 40–80 cm, respectively (Johnson et al. 2016). At 10–20 cm, 46 plots (44%) had median concentrations greater than 1 mg N $l^{-1}$ (the threshold where an ecosystem is assumed to be leaky, Table 7). At 40–80 cm, the number of plots with median soil N concentrations > 1 mg N $l^{-1}$ was 51 (31%). Note, that $NO_3^-$ soil solution concentration remained unchanged at 10–20 cm but showed a relative decrease of 30% at 40–80 cm, which the authors interpreted as a first sign of a recovery from N saturation. A regional difference was not detected. However, in a previous ICP Forests study, Waldner et al. (2015) found that the soil inorganic N solution concentration relate to whether a site's SMB derived critical load was exceeded or not.

Non-forest ecosystems are rarely modelled in SMB applications. However, as an example, Helliwell et al. 2010 provide a good overview for alpine heathland habitats. They found mean inorganic N concentrations of 0.11 mg N $l^{-1}$ in the control plots of an N addition experiment with ambient N deposition of 9 kg N $ha^{-1}$. N concentrations, N leaching and base cation loss increased immediately after N addition.

### 3.2.4 N leaching literature studies

The classical relationship between N deposition and N leaching (Gundersen et al. 1998; Dise and Wright 1995) defines N deposition > 10 kg N $ha^{-1}$ $yr^{-1}$, and a forest floor C:N ratio of <25 a risk of enhanced N leaching. The importance of the soil C:N ratio stems from the significance of a large and stable organic matter pool for long-term storage of deposited N (Curtis et al. 2011). Nonetheless, these thresholds have some variety. Dise et al. (2009), by using a global dataset, identified a forest floor C:N threshold of 23. In addition, they stated that: 1) N deposition below 8 kg N $ha^{-1}$ $yr^{-1}$ does not result in N leaching or the fluxes are very low (mostly <1 kg N $ha^{-1}$ $yr^{-1}$) and no relationship between C:N and N leaching occurs; 2) sites with N deposition > 8 kg N $ha^{-1}$ $yr^{-1}$ and mean annual temperature <7.5 °C leach 2-5 more inorganic N than warmer sites. Hence, regarding critical N leaching rates, 1 kg N $ha^{-1}$ $yr^{-1}$ is a reasonable lower bound threshold for forests, because this is the onset of N leaching as affected by N deposition (Table 8).

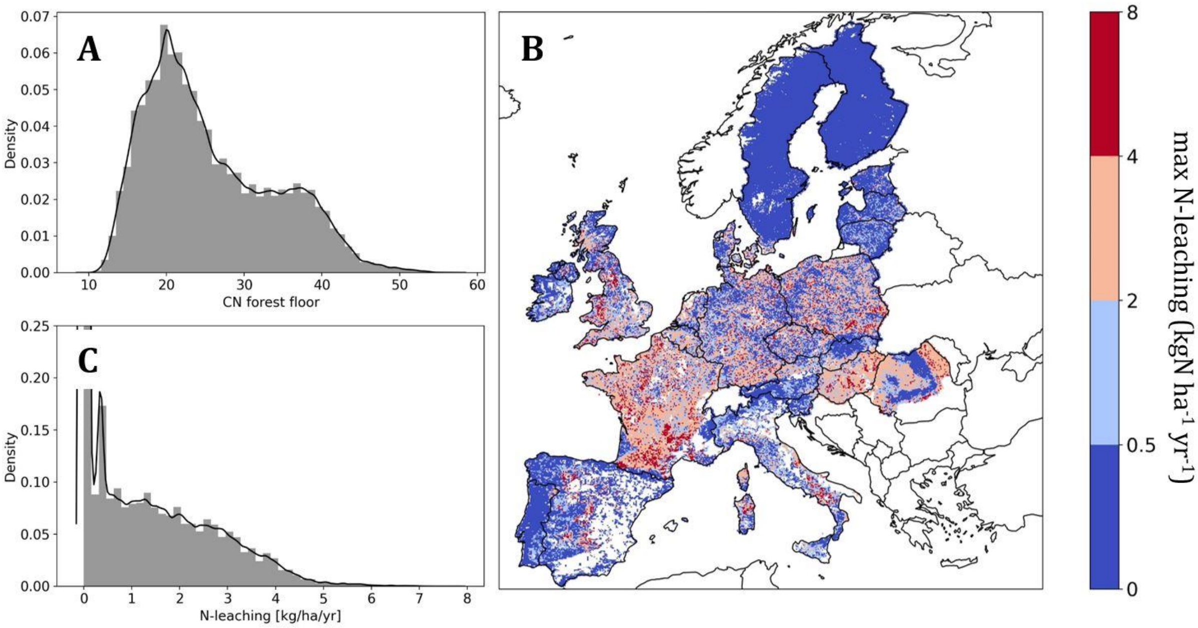
An upper bound value for critical N leaching, as given in Table 8 is not as easily found. From the studies cited in the Mapping Manual (Hornung et al. 1990; Dise and Wright 1995) we could not comprehend the given differentiation in $N_{le(acc)}$. Empirical critical loads tell us, that for European temperate deciduous and coniferous forests deposition of up to 10-15 N $ha^{-1}$ $yr^{-1}$ does not lead to detrimental effects in soils and trees, but causing leaching (Bobbink et al. 2022) eventually. In the six ICP Forests (Level II) sites in Italy, N leaching remained <1 kg N $ha^{-1}$ $yr^{-1}$ when N deposition was <17 kg N $ha^{-1}$ $yr^{-1}$. Please note, that the authors state an underestimation of N leaching at two of the high-deposition sites. ICP Integrated Monitoring sites across Europe showed long-term mean annual N leaching below or only slightly above 1 kg N $ha^{-1}$ when exposed to <10 kg N $ha^{-1}$ , while sites above this deposition, showed clearly elevated values (Vuorenmaa et al. 2018). The large majority of the Swiss monitoring sites experienced substantial N deposition during the last decades and are therefore not well suited to set critical N leaching levels. Braun et al. (2020) showed that even substantially high deposition resulted in low leaching - the sites with leaching of <1 kg N $ha^{-1}$ $yr^{-1}$ experienced a mean annual deposition of 27 N kg $ha^{-1}$. Taking these results together, it is not possible to adapt the existing critical N leaching values of the Mapping Manual.

### 3.2.5 Constraining critical N-leaching via soil C:N and empirical critical loads

Deriving critical loads for eutrophication via the forest floor C:N and mean empirical critical loads approach (CN EMP APR), as described in detail in section 2.5.2, led to an increase of critical loads when compared to the standard approach (STD APR) using N-concentration as described in section 2.5.1.

The mean critical N-leaching of all ecosystems within the respective grid cells (Figure 16) was 0.49 kg N $ha^{-1}$ $yr^{-1}$. The maximum critical N-leaching was 7.8 kg N $ha^{-1}$ $yr^{-1}$. In total 71 % of all N-leaching values were negative and were therefore set to zero. The forest floor C:N ratios ranged from 12 – 57. We visualized the distribution of forest floor C:N and critical N-leaching in Figure 16 A and B.

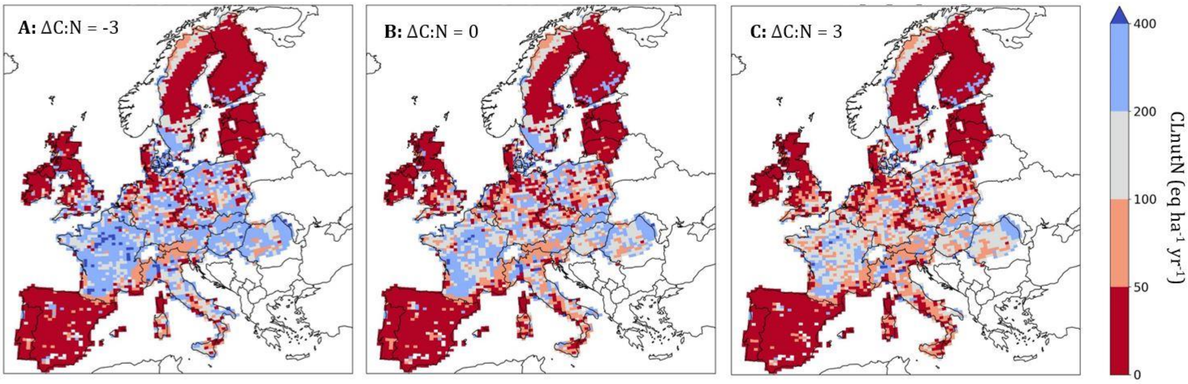
**Figure 16: Critical N-leaching (kg N ha-1 yr-1) based on the CN EMP APR. A: distribution of forest floor C:N ratios; B: map of the maximum critical N leaching in respective grid cells; C: distribution of critical N-leaching values. Since the underlying calculations are based on the European LUCAS database, the results are only available for EU countries.**




Source: own illustration, Environment Agency Austria

Furthermore, we investigated how changes in forest floor C:N, which may have happened due to N deposition over the last decades, affect overall CLnutN when using CN EMP APR. For this, we increased and decreased the C:N ratios by up to 3 units, which is the assumed N deposition impact in forest soil (see chapter 3.2.5). As defined in Equation 2, a decrease in C:N results in an increase in N-leaching. When C:N rations were changed by -3, 0 and 3 units, the average CLnutN of CN EMP APR was 341 eq $ha^{-1}$ $yr^{-1}$ (4.7 kg $ha^{-1}$ $yr^{-1}$), 587 eq $ha^{-1}$ $yr^{-1}$ (8.2 kg $ha^{-1}$ $yr^{-1}$), and 259 eq $ha^{-1}$ $yr^{-1}$ (3.6 kg $ha^{-1}$ $yr^{-1}$) respectively. We also visualized the area weighted 5$^{th}$ percentiles maps for the different changes in soil C:N (Figure 17).

**Figure 17: CLnutN area weighted 5th percentile maps when changing soil C:N by different units. A: ΔCN = -3, B: ΔCN = 0, C: ΔCN = 3.**

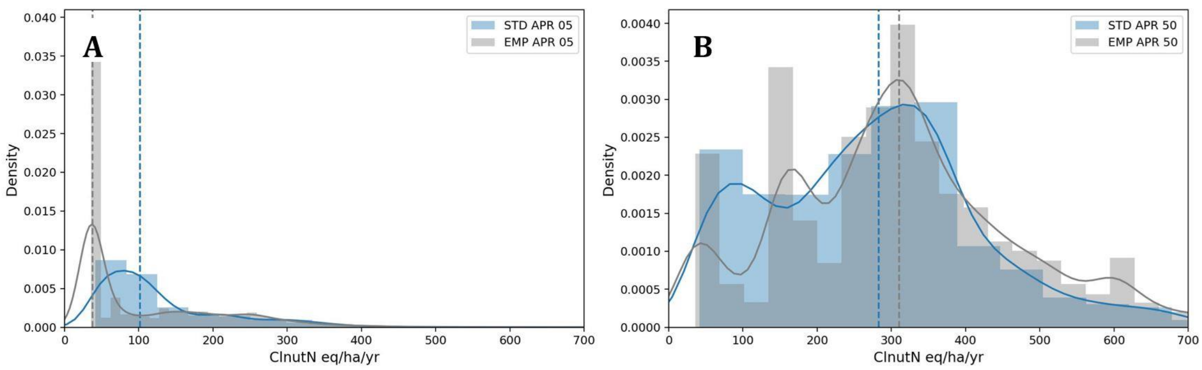



Source: own illustration, Environment Agency Austria

When comparing the STD APR with the CN EMP APR via the area 5th percentile maps, we see that median CLnutN of all grid cells is 54 eq $ha^{-1}$ $yr^{-1}$ higher in STD APR (median CLnutN = 101 eq $ha^{-1}$ $yr^{-1}$ = 1.4 kg $ha^{-1}$ $yr^{-1}$) compared to the CN EMP APR (median CLnutN = 46 eq $ha^{-1}$ $yr^{-1}$ = 0.64 kg $ha^{-1}$ $yr^{-1}$) as shown in Figure 20.

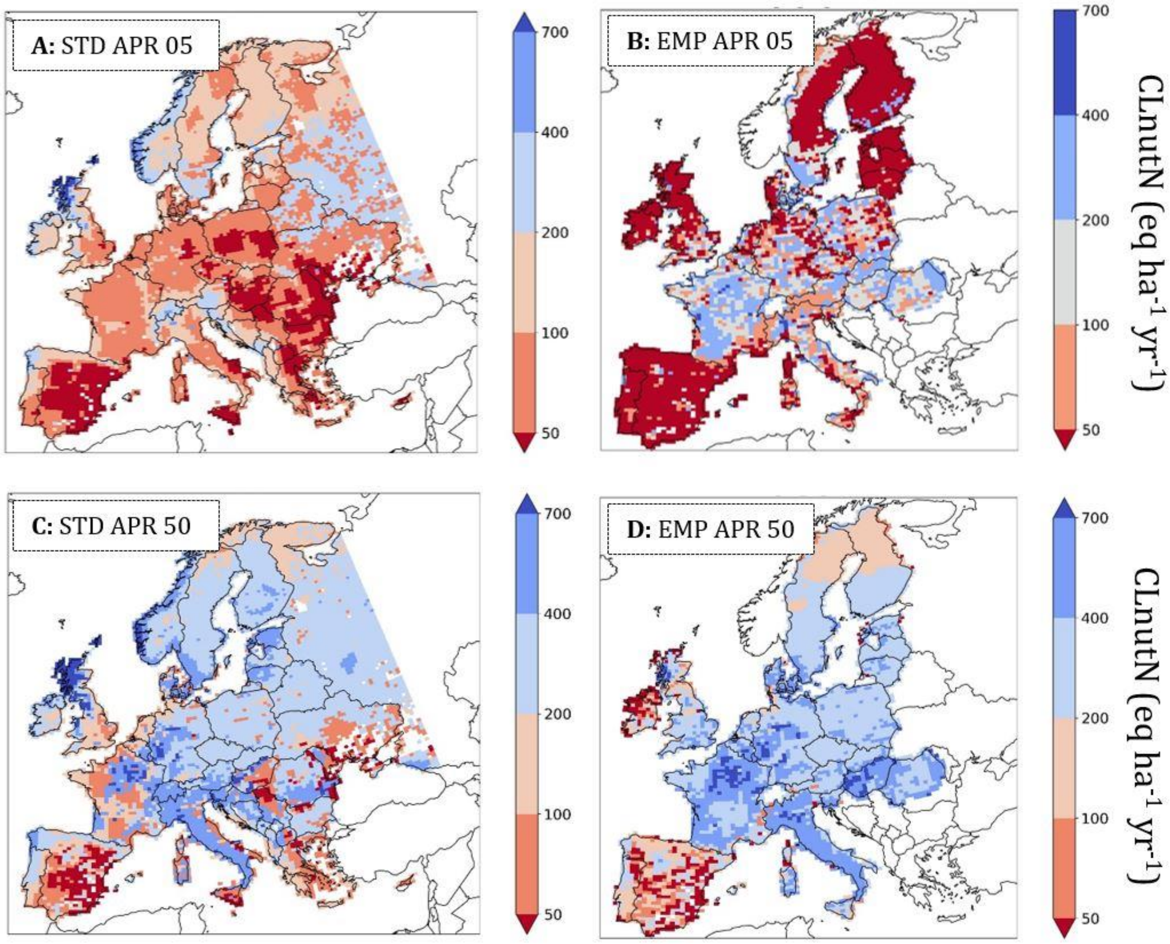
When comparing the STD APR with the CN EMP APR via the area 50th percentile maps, we note that median CLnutN of all grid cells is 28 eq $ha^{-1}$ $yr^{-1}$, lower than in the STD APR (median CLnutN of 283 eq $ha^{-1}$ $yr^{-1}$ = 3.96 kg $ha^{-1}$ $yr^{-1}$) compared to CN EMP APR (median CLnutN of 311 eq $ha^{-1}$ $yr^{-1}$ = 4.35 kg $ha^{-1}$ $yr^{-1}$). The respective distributions of both CLnutN 5th and 50th percentile maps, comparing STD APR and CN EMP APR can be found in Figure 18 together with and the respective CLnutN (for the 5th percentile) maps in Figure 19.

**Figure 18: Density distribution plots comparing the STD APR (in blue) with the CN EMP APR in black of the area weighted 5th percentile maps in A and of the 50th area weighted percentile maps in B. Dashed, vertical lines indicate median values of the respective distributions.**




Source: own illustration, Environment Agency Austria

**Figure 19 Comparison of area weighted 5th percentile (upper row, A and B) and 50th percentile (lower row, C and D) maps calculated via the standard approach (STD APR) in part A and C and via the CN EMP APR in B and D.**




Source: own illustration, Environment Agency Austria

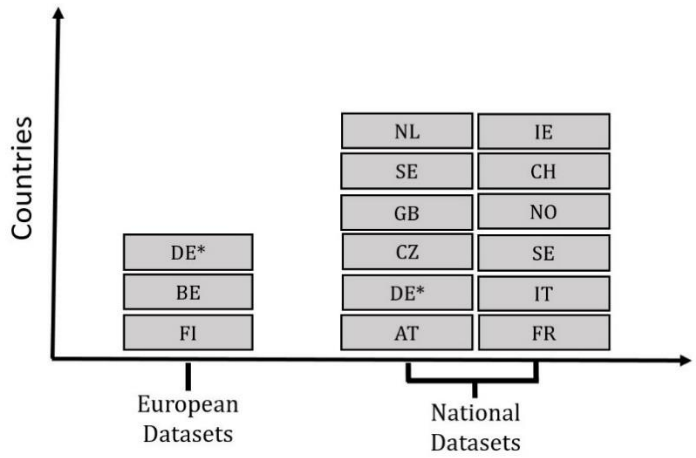
## 3.3 Spatial datasets of critical limits

Information on receptor specific critical limits is scarce. While the information on critical limits of nutrient nitrogen (N-leaching or critical N-concentration) is only available at a coarse ecosystem level, for the aluminum criteria, Bc:Al ratios are available at the species level. The introduced inverse approach (CN EMP APR) relating empirical critical loads to critical N-leaching (chapter 2.5.2) is an exception and is available for forest ecosystem only. In chapters 3.3.1 - 3.3.3 we list a potential collection of land cover and soil datasets, available for critical load calculations for acidification and nutrient nitrogen.

### 3.3.1 Land cover datasets

Land cover maps can be used to directly link critical limits for critical load calculation for nutrient nitrogen and acidification. Currently, twelve out of fourteen NFCs have implemented national land cover datasets to compute critical loads for either acidification or nutrient nitrogen as shown in Figure 20 (information taken from CCE status reports of the years 2015 – 2017).

**Figure 20 National versus European land cover maps used by the NFCs to compute critical loads for acidification or nutrient nitrogen. *Note that in Germany the CORINE Land Cover dataset is used as a basis being extended via national soil and climate datasets, were the final receptors are then derived via the BERN model.**




Source: own illustration, Environment Agency Austria

We list five relevant land cover datasets in descending thematic resolution (Table 9). The Receptor Map represents an update of the harmonized European Land Cover Map and covers the entire region of the Geneva Air Pollution Convention and comes with a high thematic resolution of EUNIS level 3 classes (219 classes). CORINE Land Cover maps represent a dataset for the entire EU region and a high thematic resolution (44 land cover classes). The Copernicus Land Cover gridded maps (for 22 land cover classes) are available at the global scale and since 1992 at the annual base. Similarly, the Copernicus Land Cover is available at the global scale and provides a resolution of 21 land cover classes. The World Cover is available for 11 classes for the year 2020/21.

The so-called Receptor Map is a recently created product provided by the CCE. It represents a version, updated in many aspects, of a land use map formerly used by the CCE and other bodies of the CLRTAP. It was created with the assistance of the external company Earth Observation Solutions and Services (EOSS) GmbH and was developed with a particular focus on the requirements of critical load modelling. Using this product, it is possible to distinguish between land uses that are relevant to CL modelling and those that are not. The receptors are mostly identified up to EUNIS level 3 and the areal coverage includes all of Europe and the countries of the EECCA region. The results have already been presented at various meetings within the WGE and the data can be obtained from the CCE. The final report on the project is expected to be published by the end of 2023 and can be accessed through the CCE website.

**Table 9 selected land cover maps with their temporal, thematic and spatial resolution.**

| Dataset | Year | Thematic resolution | Spatial resolution | Web-Link |
|---|---|---|---|---|
| Receptor Map | 2023 | 219 classes | EU+ and EECCA/100 m | https://www.umweltbundesamt.de |

| Dataset | Year | Thematic resolution | Spatial resolution | Web-Link |
|---|---|---|---|---|
| CORINE Land Cover | 2018 (latest) | 44 classes | EU+/100 m | https://land.copernicus.eu |
| Copernicus Land Cover gridded maps | 1992 – 2023 | 22 classes | global/300 m | https://doi.org/10.24381/cds.006f2c9a |
| Copernicus Land Cover | 2015 - 2019 | 21 classes | global/100 m | https://doi.org/10.5281/zenodo.3939050 |
| World Cover | 2020/21 | 11 classes | global/10 m | https://doi.org/10.5281/zenodo.7254221 |

### 3.3.2 Soil datasets

Soil data is indispensable for the calculation of the critical loads via the SMB-Model (e.g., weathering rates or allocation of $K_{gibb}$ etc.). We used LUCAS soil maps to derive forest floor soil C:N ratios, and to estimate N-leaching via CLempN. Apart from the LUCAS database, the European soil database version 2 (ESDB 2004) is currently used in the SMB model run by CCE. (Table 10) On a global scale, the harmonized world soil database is available for selected soil parameters. For critical limits of acidification the German NFC uses national soil maps and reference soil profiles to map the critical pH via the pH soil buffer system available for the soil reference profiles (Schlutow et al. 2017). Reference soil profiles to derive critical pH values on a Pan-European scale are not available. The mentioned soil datasets are listed in Table 10.

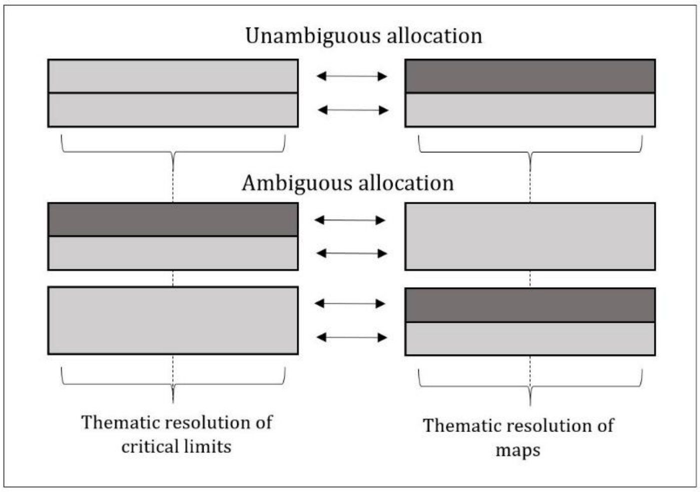
**Table 10: Selected soil datasets with their thematic and spatial resolution as well as reference.**

| Dataset | Thematic resolution | Spatial resolution | Reference/Link |
|---|---|---|---|
| LUCAS Database | various - depending und parameter | EU - Various | https://esdac.jrc.ec.europa.eu |
| European soil database version 2 | 73 attributes | Pan-European- 1km | Panagos et al. (2022) |
| Harmonized World Soil Database | Selected soil parameters | Global - 30 arc seconds by 30 arc seconds | Nachtergaele et al. (2023) |

### 3.3.3 Linking critical limits to spatial datasets

Linking critical limits with available map resources is not straightforward since the thematic resolutions of critical limits and map resources differ, often resulting in an ambiguous allocation. In contrast, an unambiguous allocation means that a direct link between critical limits and map resources without further aggregation or disaggregation is feasible. Both ambiguous and unambiguous allocation of critical limits and map resources are visualized in Figure 21 below.

**Figure 21 Unambiguous and ambiguous allocation of critical limits to map entities.**




Source: own illustration, Environment Agency Austria

#### 3.3.3.1 Ambiguous allocation of Bc:Al

Sverdrup and Warfvinge (1993) published species-specific Bc:Al ratios for different levels of growth reduction ranging from 5 - 20% for a vast number of species. As the resolution of critical limits exceeds the resolution of land-cover classes, in most cases we deal with an ambiguous allocation of Bc:Al ratios with land cover classes. In addition, Bc:Al ratios are not available for all species occurring in, for example, EUNIS Level 3 classes, used in the Receptor Map. This could potentially be resolved by selecting the highest available Bc:Al ratio within a respective land cover/vegetation classes, ensuring the highest level of protection for all species within a respective class, as conducted by Schlutow et al. (2017). We tested this approach for the CORINE land cover classes, as well as for a selection of EUNIS Level 3 classes occurring in the Receptor Map by selecting the highest Bc:Al ratio of species occurring in respective land cover classes. The results for CORINE land cover classes and for EUNIS Level 3 classes can be seen in Table 11 and Table 12, respectively. The underlying approach is schematically presented in Figure 22 . The Bc:Al ratios listed in the tables represent the 20% reduction limit for tree growth. This selection is neither complete nor representative and may vary within the different land cover class itself. Accordingly, the limitations of this approach come down to the species specific Bc:Al ratios being available and the remaining species for which this information is missing. It remains uncertain if the highest Bc:Al ratio of available species protects all species within a land cover class.

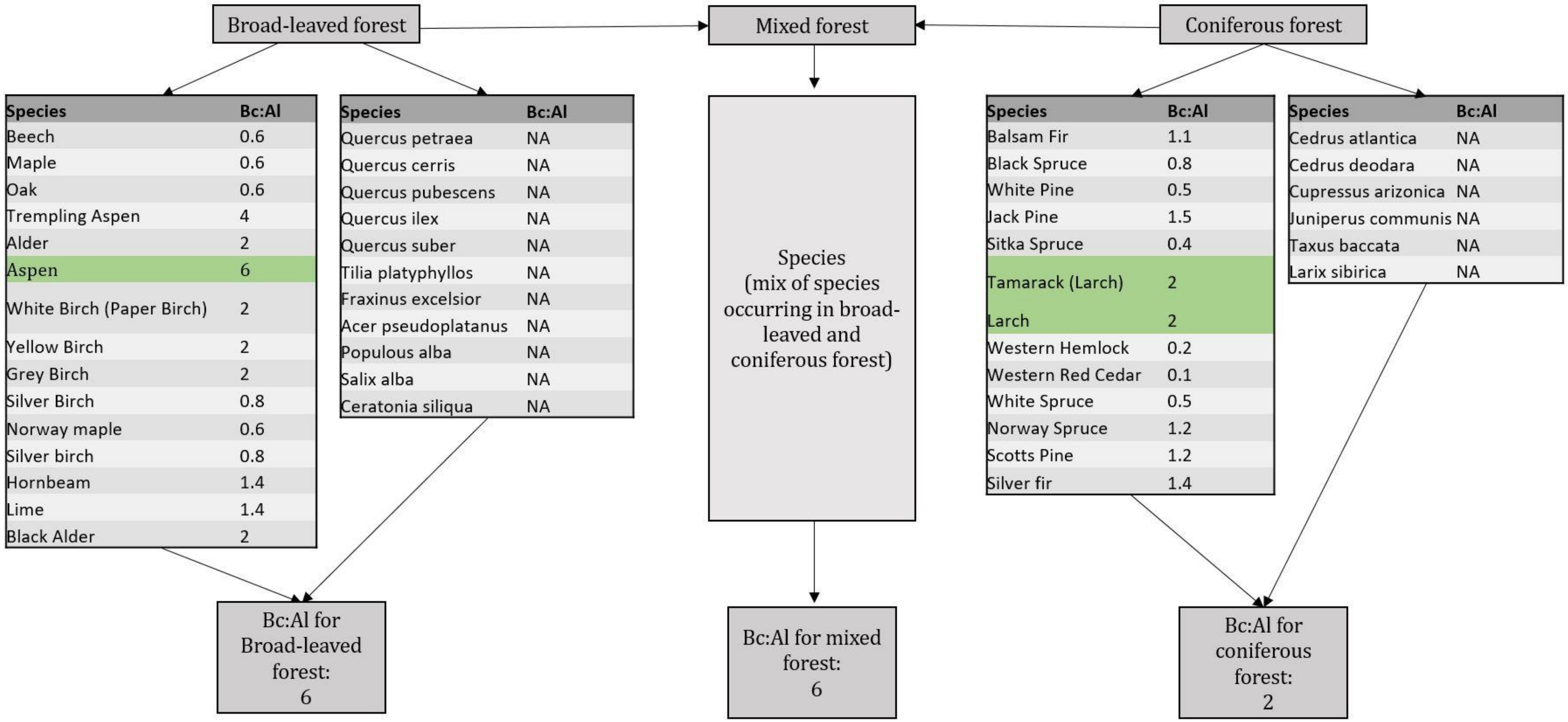
**Table 11 CORINE land cover classes and highest selected Bc:Al ratio based on Sverdrup and Warfvinge (1993).**

| CORINE land cover class | CORINE land cover code | Bc:Al |
|---|---|---|
| Broad-leaved forest | 311 | 6 |
| Coniferous forest | 312 | 2 |
| Mixed forest | 313 | 6 |
| Natural grassland | 321 | 10 |
| Moors and heathland | 322 | 5 |
| Sclerophyllous vegetation | 323 | 0.7 |
| Transitional woodland/shrub | 324 | 6 |

**Table 12 EUNIS land cover classes and highest selected Bc:Al ratio based on Sverdrup and Warfvinge (1993)**

| EUNIS CODE | EUNIS LABEL | Bc:Al |
|---|---|---|
| N1D | Atlantic and Baltic broad-leaved coastal dune forest | 2.0 |
| R1B | Continental dry grassland (true steppe) | 10 |
| T1F | Ravine forest | 2.0 |
| T3F | Dark taiga | 6.0 |
| T1B | Acidophilous Quercus forest | 0.6 |
| T16 | Broadleaved mire forest on acid peat | 2.0 |
| T31 | Temperate mountain Picea forest | 1.2 |
| T5 | Mixed deciduous and coniferous woodland | 6.0 |
| S41 | Wet heath | 6.0 |
| T21 | Mediterranean evergreen Quercus forest | 6.0 |
| T33 | Mediterranean mountain Abies forest | 1.4 |
| T13 | Temperate hardwood riparian forest | 6.0 |

**Figure 22 Selection procedure of Bc:Al exemplary for forest CORINE land cover classes (i.e. broad leaved forest, mixed forest and coniferous forest), based on tree species and associated Bc:Al ratios (protection level = 20%) based on Sverdrup and Warfvinge (1993).**




Source: own illustration, Environment Agency Austria

#### 3.3.3.2 Hydrogen ion criteria

Species-specific pH values, applicable on a Pan-European scale are not available. To our knowledge, only the German NFC applied spatially explicit critical pH values. As outlined by Schlutow et al. (2017) critical pH values are set based on the different soil buffer systems, which are available in Germany for so-called reference soil profiles. Subsequently, specific soil types have a specific reference buffer system and pH ranges which can then be linked with soil type maps. The respective soil buffer systems are listed in Table 6. Nonetheless, applying such approach on a Pan-European scale is not easily done since soil classification systems differ and soil reference profiles are not openly available. In the case that critical pH values are being implemented at the Pan-European scale, the feasibility of the cited soils maps for the derivation of soil buffer systems could be studied in more detail.

#### 3.3.3.3 Spatial allocation of N-leaching and soil N concentration

In accordance with the Mapping Manual critical N-leaching and critical N concentrations are available mainly at a coarse ecosystem level (i.e. coniferous forest, deciduous forest, grasslands and heathlands). Newer literature does not allow for a finer scale definition either. In the CN EMP APR we further distinguished critical N-leaching for forest ecosystems based on empirical critical loads via the developed framework. When linking critical N-leaching/N-concentration to the CORINE land cover an unambiguous allocation is feasible. The thematic resolution of the Receptor Map (with 218 EUNIS level classes) exceeds the resolution of N-leaching und N-concentration, making it tricky to take advantage of the high resolution of the Receptor Map.

## 3.4 Reflection on the expert workshop

### 3.4.1 Critical limits for acidification

The workshop participants did not question our conclusions from the literature review, not recommending an update of critical limit values or methods regarding the three geochemical criteria (aluminium, hydrogen and base saturation). Further, we suggested Bc:Al > 1 (e.g., 7 or 10 as already applied by Switzerland and Canada), in particular when Bc:Al is applied as a constant. The rationale behind an increase of Bc:Al originates from considering Bc:Al not as a stand-alone criterion but in relation to base saturation and critical pH and generally higher levels of tree growth protection. Additionally, the German NFC presented their national approach, where soil reference profiles and allocated pH buffer ranges are the basis to define critical pH values. While this approach might be worth considering, it is however, highly dependent on national data availability (i.e. chemical soil profile information). The base saturation criterion was not discussed in depth, apart from mentioning that the Gapon coefficient is also dependent on the pH-range. The beforehand presented criteria interrelations were brought up during the workshop and stimulated our assessment of indirect violation of critical limits using the critical load Background Database (see chapter 3.1.6).

### 3.4.2 Critical limits for nutrient nitrogen

There has been a discussion among the participants over the question whether the currently recommended critical limit values of soil solution N concentrations in the Mapping Manual are too high. The long-term data from Switzerland shows that at N deposition of 15 kg N $ha^{-1}$ $yr^{-1}$ the

N concentration was approximately 0.2 mg $l^{-1}$. Hence, a soil N concentration of 3 mg $l^{-1}$ (as it is included in the Mapping Manual) would result in a very high critical load (N deposition of approximately 50 kg N $ha^{-1}$ $yr^{-1}$). In accordance, choosing a critical N concentration of >0.4 mg $l^{-1}$ would allow a high eutrophication in forest ecosystems. In contrast, the lower critical limits for soil N concentrations seem to be in line with CLempN (e.g., N deposition of 15 kg N $ha^{-1}$ $yr^{-1}$ resulted in 0.1-0.4 mg N $l^{-1}$ in Switzerland).

The currently recommended critical limit values for critical/acceptable critical N leaching should be equal the leaching under pristine conditions while the high range should be equal to EU Drinking Water Directive thresholds (e.g., 11 mg N $l^{-1}$, or advised value, which is half of that). Note that the high values derived from the EU Drinking Water Directive would lead to significant ecosystem damage; hence, their application can be questioned in the context of critical loads. All related critical limit values were assessed in chapter 3.2.2 and elaborated with further data from literature in chapter 3.2.3 and 3.2.4.

Critical limits used to derive critical loads for nutrient nitrogen are rarely related to plant response. For example, acceptable N concentrations in soil solution given in the Mapping Manual for vegetation changes in Northern Europe are based on critical load values derived by visual inspection and SMB model application. The acceptable N concentrations in soil solution in Western Europe are based on Ellenberg indicators for N and are linked to N availability. Derivation of critical limits for the impacts on plant species composition follows a dose-response relationship, where given N and S depositions exert an influence on diverse soil parameters (pH, Bsat, Bc/Al, C:N, N availability), which in turn might generate an impact on the plant species composition. The impacts on soil parameters and plant species composition are in general modeled. Optionally, critical limits for N and acidity indicators related to plant response can be derived using databases with measured soil and vegetation parameters (e.g., PROPS, BERN, etc.). Regarding plant response, an additional issue is that the SMB approach defines N leaching below the rooting zone of plants. We discuss these conceptual issues in chapter 4.2.2.

#### 3.4.2.1 Usefulness of the soil C:N ratio to derive critical N leaching

Using the empirical relationship between forest floor C:N ratios and N leaching as a tool to detail critical N leaching has been discussed. The main concerns were that N deposition influences soil C:N ratios (see chapter 3.2.5) and that the empirical relationship has a wide error range. Following recommendations of Dise et al. (2009) (see chapter 3.2.5), i.e. using the lower confidence bound of the empirical functions, we updated the calculation. Also, the soil C:N:P stoichiometry for N leaching might have a significantly better empirical fit (Oulehle et al. 2021) - and could therefore be taken into the consideration. The limitations of our approach are addressed (chapter 4.2.4) and the NFCs are encouraged to use their national data sources to improve its accuracy.

#### 3.4.2.2 Potential use of $NH_4^+$, DON and $N_2O$ in the SMB context

During the expert workshop we discussed newer findings in soil N cycling, namely the role of $NH_4^+$ and dissolved organic nitrogen (DON) in determining plant available N, as well as $N_2O$ gaseous emission rates and their significance for SMB modelling.

There has been an agreement that a better representation of $NH_4^+$ and DON in the SMB model might be worthwhile but with a risk of increasing complexity without major changes to the results. Similarly, the relationship between N leaching and $N_2O$ losses are highly variable due the importance of soil type and climate (chapter 4.2.3.).

# 4 Discussion

## 4.1 Critical limits for acidification

### 4.1.1 State of knowledge of critical limits for acidification

Elevated levels of inorganic Al concentration in soil solution, as a consequence of acid rain during the 1980's, have been related to inhibited root growth or disrupted nutrient uptake (e.g., Marschner 1991), and consequently to forest dieback (Ulrich et al. 1980). Thereupon, the scientific community established critical limits for acidification based on three geochemical criteria (aluminium criteria, hydrogen criteria and critical base saturation) to prevent adverse effects and implemented them in the SMB model (CLRTAP 2017). Critical limits based on the aluminium criteria are either defined to prevent tree growth reduction (Sverdrup and Warfvinge 1993; Cronan and Grigal 1995; Cronan et al. 1989) or to comply with EU drinking water regulation (EC 2020; CLRTAP 2017). Following the Mapping Manual, a critical Al concentration of 0.2 eq $m^{-3}$ (about 0.2 mg $l^{-1}$) is based on Cronan et al. (1989) and aims to prevent tree growth inhibition. Similarly, species specific Bc:Al ratios provided by Sverdrup and Warfvinge (1993) aim to prevent tree growth reduction as well. Setting a critical Al concentration of 0.02 eq $m^{-3}$ aims to comply with the Al concentration of 200μg $l^{-1}$ referring to the drinking water guideline (EC 2020). For the hydrogen criteria, even though not explicitly stated in the Mapping Manual, a critical pH limit of 4.2 aims to prevent inorganic Al species from reaching unfavourable concentration in soil solution (Ulrich 1987). Selecting a critical pH from pH range 4.0 – 4.5, as presented in section 3.1.2.2, refers to the increasing solubility of aluminium, i.e. $Al^{3+}$ species becoming the dominating cation in soil solution (Ulrich 1987). Similar to the hydrogen criteria, a decreasing critical base saturation is foremost linked to an increasing concentration of Al in soil solution (Reuss and Johnson 1985). In accordance with Posch et al. (2015), base saturation is an indicator of the soil acidity state.

All three geochemical criteria for acidification are applied in national critical load calculations. The aluminium criteria were by far the most widely applied, aiming to avoid biological effects (i.e. elevated levels of Al in relation to tree growth) or to avoid exceedances of recommended Al concentration in drinking water. The Bc:Al ratio was mainly applied as a constant (Bc:Al = 1; Figure 4). The scientific basis of critical limits of the different geochemical criteria as currently used is described in the second chapter of the book "Critical Loads and Dynamic Risk Assessments" (De Vries et al. 2015). Overall, they indicated that the results were somehow ambiguous, especially when speaking of direct effects of elevated aluminium concentration in relation to inhibited tree growth. As summarised by De Vries et al. (2015), many studies provided evidence that Al as a stand-alone indicator fails to pinpoint inhibited tree growth, root damage or adverse crown condition (Nygaard and Wit 2004; Eldhuset et al. 2006; Šrámek et al. 2014; Binkley and Högberg 2016). As mentioned by De Vries et al. (2015), contrasting the findings by Huber et al. (2004) with the results from Alewell et al. (2000), healthy trees can be found among sites with elevated Al concentrations and also with low Al concentrations. Some additional studies showed that under field conditions, elevated Al concentrations are not necessarily implying adverse effects such as constrained root and tree growth (Van Schöll et al. 2004; Ross et al. 2008; Richter et al. 2007; Nygaard and Wit 2004; Meesenburg et al. 2016), indicating that Al being one among many factors such as N deposition, phosphorus availability, water availability, and climate change etc., possibly constraining tree growth (De Vries et al. 2015; Sverdrup et al. 2007; Hedwall et al. 2017). De Vries et al. (2015) summarized that according to the present literature, a clear link between elevated Al concentrations in soil solution and reduced plant vitality (e.g., root growth, tree growth, crown condition) could not be identified. Our recent literature review does not reveal new evidence relevant for an improved differentiation or updates of the current values for critical limits.

Although, an update of critical limits was not feasible, a discussion on increasing of Bc:Al >1 has taken place. The current version of the ICP Modelling and Mapping manual states that Bc:Al = 1 might not sufficiently protect ecosystems from harmful effects. Nonetheless, a Bc:Al = 1 is most widely applied by the NFCs. To our knowledge, only Switzerland and Canada have implemented Bc:Al > 1, i.e. 7 and 10, respectively. Increasing Bc:Al makes sense due to a number of reasons. Firstly, different species-specific ratios are available for different levels of protection (i.e. 20%, 10%, 5% and 2% growth reduction), with higher levels of protection being achieved by setting higher Bc:Al ratios (Sverdrup and Warfvinge 1993). Secondly, increasing Bc:Al >1 is required in order to sustain a critical base saturations > 20%, which are of importance for increasing rooting depth and decreasing uprooting (Braun 2013; Watmough and Dillon 2003; Ouimet et al. 2006; Braun et al. 2020). Thirdly, an increase of Bc:Al would make sense taking the multi constrains of tree growth into account. For example, Göransson and Eldhuset (2001) mentioned the importance of essential nutrients such as Ca, Mg and K as well as N for plant vitality. Although they argued that tree growth can be limited even at Bc:Al > 1 due to scarcity of only one essential nutrient, higher Bc:Al ratios increase the likelihood of sufficient base cation supply. Finally, increasing Bc:Al makes sense in order to avoid indirect violation of other critical limits (see chapter 3.1.6).

### 4.1.2 Interrelation between Bc:Al and pH

All three geochemical criteria are interrelated through the gibbsite equilibrium (see Figure 2), which is incorporated in the SMB-model structure. This means, no matter which geochemical criteria is used, to calculate critical ANC leaching and thus critical loads for acidity; an indirect definition of critical limits is given via the gibbsite equilibrium (see chapter 3.1.6). Therefore, indirect critical limit violation may occur when setting only one of the criteria too low. We suggest that critical limits should be chosen by keeping the criteria gibbsite interrelation in mind, so that indirect critical limits comply with pre-defined values. Independently of the criteria interrelation, all three criteria encompass different levels of uncertainty based on the way they are calculated. One way to taking this uncertainty into account is to calculate the critical load based on a multi-criteria approach. The German NFC conducts such a multi-criteria approach, i.e. calculates critical loads based on all criteria and then selects the smallest respective critical load for acidity. However, the required input data to calculate critical limits based on all criteria is not readily available on a Pan-European scale.

## 4.2 Critical limits for nutrient nitrogen

### 4.2.1 Acceptable inorganic N leaching

NFCs apply the entire range of $N_{le(acc)}$ as given in the Mapping Manual and use both soil N concentrations and N leaching flux thresholds. We assessed the critical load Background Database standard approach - using lowest soil N concentrations - with two NFC approaches using medium and high soil N concentrations. Only the standard approach and the medium NFC approach for forests resulted in N leaching rates lower than those recommended in the mapping manual. When comparing the SMB derived CLnutN values with empirical critical load values, only the standard approach and the NFCs medium setting of the critical soil N concentrations compared with the CLempN values. An exception were coniferous forests, for which the high NFC approach did not strongly exceed CLempN values.

New studies linking soil N concentration and impacts remain rare, so that a definition of new suitable critical values remains unfeasible. The review of the ICP Forests soil solution data revealed significant insights on the impact of N deposition on soil solutes but no further information on the relationship between soil N concentration and ecosystem impacts (Johnson et al. 2018). Nonetheless, their published median soil N concentration value (0.10 mg N $l^{-1}$ at 40–80 cm soil depth) and elevated N deposition in Europe over some decades does not indicate that a significantly higher critical values could be recommended.

Our findings show that only the lower end of critical soil N concentration values, as used in SMB modelling and defined in the Mapping Manual, seem to result in reasonable CLnutN values. Consequently, some NFCs apply too high critical limit values.

### 4.2.2 The N saturation concept and SMB

Mass balance critical loads rely on the concept of ecosystem saturation (Aber et al. 1989). Since this concept has been challenged in its original form by Lovett and Goodale (2011), we first discuss whether or not it is still useful in this context. According to the original model of nitrogen saturation an ecosystem undergoes sequential change (stages 1 to 3) through which enhanced N deposition renders N to N-limited plants, which enriches plant tissues and litter, the litter N is transferred to soil organic matter, stimulating N mineralization and nitrification, and eventually resulting in elevated nitrate leaching from the ecosystem (stage 3). These changes are thought to be accompanied first by an increase in net primary productivity (stage 1 and 2) and a decrease thereafter, when other nutrients than N become limited as indicated by decreasing foliage Ca:Al or Mg:N ratios. These sequential effects have been updated with new findings by Emmett (2007) but the framework in principle remained the same. The assumption in critical load mass balance calculations regarding the critical (acceptable) N leaching is that (i) a certain amount of N deposition pushes an ecosystem towards one of the three aforementioned stages, and (ii) that the nitrogen saturation is indicated by enhanced dissolved inorganic nitrogen (DIN) leaching. However, empirical evidence of the last two to three decades does not support that these temporal changes, which are assumed to be triggered by an increase of N in litter, can be generalized. Rather, deposited N can simultaneously move to plants, soil, and to leaching water. Lovett and Goodale (2011) point out that "This makes it very difficult to predict temporal patterns of response of various parts of the system […], because the patterns depend on the relative strength of the sinks, rather than the timing of transfer between one sink to the other. Hence, uptake kinetics (sink strengths) become the dominant mechanism rather than N storage capacities as was stated in Aber's model (Niu et al. 2016). In addition, the widespread decline in N leaching and availability, is explained by sink strength (Mason et al. 2022). They summarized that 1) elevated $CO_2$ increased foliar C:N and lowered foliar N concentrations through increased assimilation of C by plants; 2) plants may invest more in acquiring N from soil but may not be able to obtain sufficient N to meet increased N demand; 3) higher C:N in litter may reduce net mineralization of N, lowering soil N supply and plant N uptake and further reducing foliar N concentrations. These processes reduce the amount of inorganic N, which can be mobilized during hydrological events and finally lost to the groundwater.

Another saturation model, the "multiple substrate - multiple consumer reaction network" has been proposed by Tang and Riley (2013). It is conceptually similar to the kinetic framework of Lovett and Goodale (2011) but describes better the patterns found in observation and experimental data. It also calls into question the current approach in critical load calculations, using N leaching as the single indicator of N saturation. However, there are pros and cons of simple (the original SMB model) and more complex (e.g., Tang and Riley 2013) representations of N saturation in critical load calculations (Binkley and Högberg 2016).

From the aforementioned studies, we conclude that even though empirical data (used to define $N_{le(acc)}$) indicates thresholds of N deposition for N loss through leaching (Dise et al. 2009; Gundersen et al. 2006), and that this relationship is substantiated by experiments (Schmitz et al. 2019), N leaching per se is not indicative for setting critical loads for nutrient N (e.g., nutrient imbalances, vegetation changes). In general, we can say, that the use of $N_{le(acc)}$ in the SMB model, for the derivation of CLnutN is a strongly simplified approach and should therefore be supported by additional data such as empirical critical loads. Moreover, models are continuously in development and improvements should be incorporated in order to keep pace with the latest scientific knowledge.

### 4.2.3 Nitrogen cycling in soils

Here we summarize newer findings in N cycling in soils, which are relevant for SMB modelling. First, in the context of critical load research, it has already been criticized that soil N concentration and N leaching respectively are not indicative of specific ecosystem effects such as vegetation changes and tree nutrient imbalances (see chapter 4.2.2). Second, apart from soil N concentrations, several other (better) indicators of plant available N have been described by De Vries et al. (2007) but all of them are prone to some kind of issue when used in dynamic soil-plant models. Third, novel insights during the last two decades have reshaped our knowledge about the N cycle in ecosystems (Schimel and Bennett 2004; Rennenberg et al. 2009; Van Groenigen et al. 2015). For instance, the focus on net N mineralization being merely the remaining N, which is exceeding the microbial demand and, thus, is available for plant uptake, was dropped and gross mineralization rates came into the center. In addition, the significance of bioavailable DON for plant nutrition was introduced as the rate-limiting step in N mineralization.

The current knowledge on soil N cycling can in short be summarized in the following way. Total dissolved N in soils occurs as dissolved inorganic N (DIN; i.e. $NO_3^-$ and $NH_4^+$), and dissolved organic N (DON). The main driver of the production of DIN and DON is plant litter (above- and belowground). Bacteria and fungi depolymerize organic macromolecules to DON, which is further processed to $NH_4^+$ (= N mineralization or N ammonification). Subsequently, specific microorganisms oxidize $NH_4^+$ to $NO_3^-$ (= nitrification). Plants compete against microbes for both DIN and DON. Part of the DIN and DON leaches to the groundwater, DIN is additionally prone to gaseous N production and is hence partly lost to the atmosphere. The proportion of dissolved inorganic soil N (1-10 kg N $ha^{-1}$) is tiny compared to the large pools of N in soil organic matter of natural ecosystems (1350–9000 kg N $ha^{-1}$ in mineral soil; Butterbach-Bahl and Gundersen 2011). In addition, turnover rates through microbial processes in the soil are much higher than any losses of N to the environment. Hence, even small changes in process rates can therefore drastically change the concentrations of inorganic N in soil solutes. Plants are effective competitors for N. Stable isotope measurements with $N^{15}$ showed that plants take up N at remarkably low, even negative net N mineralization rates, and effective N accumulation under N limiting conditions haven been reported (Rennenberg et al. 2009; Schimel and Bennett 2004). As a result, plants together with microbes control effectively N concentrations in the soil.

For SMB modelling, two aspects are important: 1) Despite the linkage between soil N solute and plants, it is difficult to determine any thresholds targeted at plant impacts (nutrient imbalances, growth) because of the significant importance of gross rather than net transformation rates for plant N availability. The expert's opinion at the workshop reflected also this dilemma. 2) Plants, particularly in nutrient-poor ecosystems, are strong competitors for DON. Depolymerization of organic macromolecules rather than N mineralization is the rate-limiting factor of plant N availability (Rennenberg et al. 2009; Schimel and Bennett 2004). Since plants competitive strength for DON has been related to mycorrhiza fungi it is noteworthy that mycorrhiza composition proved particularly sensitive to N deposition (Suz et al. 2021). Usually, DON is not included when calculating the $N_{le}$ term in SMB modelling. We discussed this issue with the experts at the workshop (chapter 3.4.2). They concluded that including DON in SMB is not useful because it adds a lot of complexity without additional information.

### 4.2.4 Constraining critical N leaching based on soil C:N ratios

Many studies have shown a rather tight relationship between the forest floor or soil C:N ratio, N deposition, and N leaching (Gundersen et al. 2006; Dise et al. 2009; Dise et al. 1998; Dise and Gundersen 2005). Findings from isotope studies confirm the important role of C for the retention of N deposition (Curtis et al. 2011). Furthermore, limitation in available P co-determines N leaching rates, so that high leaching rates occur where forest floor C:N ratios are low and N:P ratios are high (Oulehle et al. 2021). P limitation occurs naturally due to sorption but also because of N deposition (Braun et al. 2020), and climate warming increasing plant uptake and leaching losses (Tian et al. 2023). The Mapping Manual does not propose the C:N ratio as a criterion. Nevertheless, using the empirical relationships between N deposition, forest floor C:N ratios and N leaching as developed by Dise et al. (2009) for European forests together with empirical critical loads (Bobbink et al. 2022) as the N deposition term, technically critical N leaching can be calculated. But note that the variation of the relation between N leaching and forest floor C:N ratios is relatively high.

A couple of limitations exist regarding the use of soil C:N ratio as a criterion for N leaching. First, although the forest floor C:N ratio indicates how leaky a site is, the N leaching is determined by the rate of N deposition. Hence, the N deposition is used for an indirect estimation of critical N leaching and subsequently for calculation of CLnutN in an SMB approach. Second, soil C:N ratios are affected by cumulative N deposition. N can accumulate in the soil with a constant C:N ratio through C accumulation and through a change in the C:N ratio. In the case of a C:N decrease in the soil organic or mineral layer, a stoichiometric N sink occurs (Lovett and Goodale 2011). As an example, soils accumulate considerable amounts of N after stand replacing disturbances (1.5-2.5 kg N $ha^{-1}$ $y^{-1}$, Berg and Dise 2004). However, the N that deposited since the onset of high emissions in the mid-19$^{th}$ century in Europe rendered much lower N accumulation in soils as indicted by spatial differences in C:N ratios and correlations of N deposition with C:N ratios. Mineral soil (9-30 cm) C:N ratios of the semi-natural ecosystems differ significantly between high and low N deposition areas in Europe using modelled deposition and the LUCAS soil data (Ballabio et al. 2019). In that study, C:N differences amount to 2.35 and were restricted to semi-natural ecosystems. Cools et al. (2014), using ICP Forest data, showed that N deposition were of only minor importance for forest floor and mineral soil C:N ratios, being mostly determined by tree species, followed by the biogeographic zone. Since the range of the spatial variability (2.5 and 97.5 percentile) of the C:N ratio was 16 – 44 and 17 – 32 in the forest floor and mineral soil respectively (Cools et al. 2014), and was driven by less than 10% (< 5% relative importance in the forest floor) by N deposition, the related C:N impact remains < 3 units. Offsetting current soil C:N ratios using this value could give a rough estimate of reference C:N ratios and the respective critical N leaching (Figure 17).

In order to further reduce uncertainty of the aforementioned empirical relationship, P limitation could be included in order to account for its significant role (Oulehle et al. 2021). However, no spatial data exists to our knowledge suitable for such an approach yet.

# 5 Conclusions

Here we summarize our main findings, which, together with the newly updated empirical critical loads for nitrogen and the new receptor map, could be used as a basis for an review of the Mapping Manual.

## 5.1 Acidification

- Empirical studies towards the impact of acidification on ecosystem receptors (e.g., tree growth, root damage) stagnated since the mid-nineties in Europe so that no significant improvement of the scientific knowledge, as already presented in the ICP Modelling and Mapping Manual, can be achieved.
- Among the three available limit criteria we suggest Bc:Al as a criterion for its direct effect on tree growth. Most NFCs already comply with this suggestion.
- As Bc:Al = 1 is probably not sufficient to ensure high enough levels of base saturation, a Bc:Al > 1 is suggested for consideration.
- Using Bc:Al > 1 is moreover reducing indirect hydrogen criteria violation (e.g., with a Bc:Al = 10 pH > 4.2 is mostly guaranteed).
- In case a receptor specific approach for Bc:Al is feasible, selecting the highest Bc:Al critical limit for all respective species within the mapping unit is recommended.

## 5.2 Eutrophication

- Causation from either soil N concentration or N leaching towards other biotic ecosystem effects such as vegetation changes or nutrient imbalances in trees lacks empirical foundation or are based on a small number of studies only (root impacts, susceptibility to droughts and insects). Newer literature, allowing for an improvement in the derivation of critical $N_{le(acc)}$ values, is also not available.
- Improvements of insights in soil N cycling and N saturation processes are summarized in the report and should be closely followed in order to continuously keep pace with the advance in scientific knowledge.
- The limit criteria related to nitrate concentrations in seepage water and runoff (e.g., drinking water regulations) are, from a mechanistic point of view, the most evidence-based approach. However, such an approach does not directly relate to ecosystem effects and can therefore only be seen as an upper bound criterion.
- We recommend using only the lower end of the values of soil N concentration (<0.4 mg $l^{-1}$) for ecosystem protection. This approach guarantees the consistency with the ranges of empirical critical loads and simultaneously does not exceed the onset of N leaching when an ecosystem becomes leaky (1 kg N $ha^{-1}$ $yr^{-1}$).
- We explored a new method that uses soil C:N ratios, a known explanatory factor contributing to the amount of N leaching, for the regionalisation of critical N leaching values. This method has its limitations and is therefore not seen as a stand-alone approach but rather as an additional information, supporting the results derived from traditional critical limit values as given in the Mapping Manual.

# 6 References

Aber, J.; McDowell, W.; Nadelhoffer, K.; Magill, A.; Berntson, G.; Kamakea, M. et al. (1998): Nitrogen saturation in temperate forest ecosystems: Hypotheses revisited. In *BioScience* 48 (11), pp. 921–934.

Aber, J. D.; Nadelhoffer, K. J.; Steudler, P.; Melillo, J. M. (1989): Nitrogen Saturation in Northern Forest Ecosystems. In *BioScience* (39 (6)), 378-286.

Alewell, C.; Manderscheid, B.; Gerstberger, P.; Matzner, E. (2000): Effects of reduced atmospheric deposition on soil solution chemistry and elemental contents of spruce needles in NE-Bavaria, Germany. In *Journal of Plant Nutrition and Soil Science* Vol. 163, No. 5, pp. 509–516. Available online at https://edoc.unibas.ch/13020/.

Alexeyev, V. A.; Markov, M. V.; Birdsey RA (2004): Statistical data on forest fund of Russia and changing of forest productivity in the second half of the XX-th century.

Arp, P. A.; Oja, T.; Marsh, M. (1996): Calculating critical S and N loads and current exceedances for upland forests in southern Ontario, Canada. In *Can. J. For. Res.* 26 (4), pp. 696–709. DOI: 10.1139/x26-080.

Augustin, S.; Bolte, A.; Holzhausen, M.; Wolff, B. (2005): Exceedance of critical loads of nitrogen and sulphur and its relation to forest conditions. In *Eur J Forest Res* 124 (4), pp. 289–300. DOI: 10.1007/s10342-005-0095-1.

Balla, S.; Uhl; Kiebel, K.; Mueller-Pfannenstiel, A.; Luettmann, J.; Lorentz, H. et al. (2013): Untersuchung und Bewertung von straßenverkehrsbedingten Nährstoffeinträgen in empfindliche Biotope. In : Forschung Straßenbau und Straßenverkehrstechnik. 0344-0788. Available online at https://trid.trb.org/view/1327910.

Ballabio, C.; Lugato, E.; Fernández-Ugalde, O.; Orgiazzi, A.; Jones, A.; Borrelli, P. et al. (2019): Mapping LUCAS topsoil chemical properties at European scale using Gaussian process regression. In *Geoderma* 355, p. 113912. DOI: 10.1016/j.geoderma.2019.113912.

Berg, B.; Dise, N. (2004): Calculating the long-term stable nitrogen sink in northern European forests. In *Acta Oecologica* 26 (1), pp. 15–21. DOI: 10.1016/j.actao.2004.03.003.

Binkley, D.; Högberg, P. (2016): Tamm Review: Revisiting the influence of nitrogen deposition on Swedish forests. In *Forest Ecology and Management* 368, pp. 222–239. DOI: 10.1016/j.foreco.2016.02.035.

Bobbink, R.; Loran, C.; Tomassen, H. (2022): Review and revision of empirical critical loads of nitrogen for Europe. Dessau-Roßlau (Texte, 02/2022). Available online at https://www.umweltbundesamt.de/publikationen.

Bonten, L. T. C.; Reinds, G.J.; Groenenberg, J.E.; De Vries, W.; Posch, M.; Evans, C. D. et al. (2015): Dynamic Geochemical Models to Assess Deposition Impacts and Target Loads of Acidity for Soils and Surface Waters. In Wim De Vries, Jean-Paul Hettelingh, Maximilian Posch (Eds.): Critical Loads and Dynamic Risk Assessments: Nitrogen, Acidity and Metals in Terrestrial and Aquatic Ecosystems. Dordrecht: Springer Netherlands, pp. 225–251.

Braun, S. (2013): Untersuchungen über die Zusammensetzung der Bodenlösung Bericht 2012. INSTITUT FÜR ANGEWANDTE PFLANZENBIOLOGIE, Schönenbuch (CH).

Braun, S.; Tresch, S.; Augustin, S. (2020): Soil solution in Swiss forest stands: A 20 year's time series. In *PLOS ONE* 15 (7), e0227530. DOI: 10.1371/journal.pone.0227530.

Butterbach-Bahl, K.; Gundersen, P. (2011): Nitrogen processes in terrestrial ecosystems. In M. A. Sutton, C. M. Howard, J. W. Erisman, Gilles Billen, A. Bleeker, P. Grennfelt et al. (Eds.): The European Nitrogen Assessment: Cambridge University Press, pp. 99–124.

Cinderby, S.; Emberson, L.; Owen, A.; Ashmore, M. (2007): LRTAP land cover map of Europe. In: Slootweg J, Posch M, Hettelingh J-P (eds) Critical loads of nitrogen and dynamic modelling, CCE Progress Report 2007.

CLRTAP (2017): Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends. Chapter V Mapping Critical Loads for ecosystems. In *UNECE Convention on Long-range Transboundary Air Pollution*. Available online at https://www.umweltbundesamt.de/en/cce-manual.

Cools, N.; Vesterdal, L.; Vos, B. de; Vanguelova, E.; Hansen, K. (2014): Tree species is the major factor explaining C:N ratios in European forest soils. In *Forest Ecology and Management* 311, pp. 3–16. DOI: 10.1016/j.foreco.2013.06.047.

Cronan, C.S.; Grigal, D. F. (1995): Use of Calcium/Aluminum Ratios as Indicators of Stress in Forest Ecosystems. In *Journal of Environmental Quality* 24 (2), pp. 209–226.

Cronan, C.S.; April, R.; Bartlett, R.J.; Bloom, P.R.; Driscoll, C.T.; Gherini, S.A. et al. (1989): Aluminum toxicity in forests exposed to acidic deposition: The ALBIOS results. In *Water, Air, & Soil Pollution* 48 (1-2), pp. 181–192. DOI: 10.1007/BF00282377.

Curtis, C.; Evans, C.; Goodale, C.; Heaton, T. (2011): What Have Stable Isotope Studies Revealed About the Nature and Mechanisms of N Saturation and Nitrate Leaching from Semi-Natural Catchments? In *Ecosystems*, pp. 1–17. DOI: 10.1007/s10021-011-9461-7.

Davies, C.E; Moss, D.; Hill, M. O. (2004): EUNIS habitat classification revised 2004: European Topic Centre on Nature Protection and Biodiversity.

De Vries, W.; Kros, H.; Reinds, G. J.; Wamelink, W.; Mol, J.; van Dobben, H. et al. (2007): Development in deriving critical limits and modeling critical loads of nitrogen for terrestrial ecosystems in Europe. In *Wageningen, Alterra, 206pp* ((Alterra-rapport 1382)).

De Vries, W.; Posch, M.; Sverdrup, H.U.; Larssen, T.; De Wit, H.A.; Hettelingh, J.P.; Bobbink, R. (2015): Geochemical Indicators for Use in the Computation of Critical Loads and Dynamic Risk Assessments. In De Vries, W.; Hettelingh J.P.; Posch, M. (Eds.): Critical Loads and Dynamic Risk Assessments: Nitrogen, Acidity and Metals in Terrestrial and Aquatic Ecosystems. Dordrecht: Springer Netherlands, pp. 15–58.

Dirnböck, T.; Pröll, G.; Austnes, K.; Beloica, J.; Beudert, B.; Canullo, R. et al. (2018): Currently legislated decreases in nitrogen deposition will yield only limited plant species recovery in European forests. In *Environmental Research Letters* 13 (12), p. 125010. DOI: 10.1088/1748-9326/aaf26b.

Dise, N.; Gundersen, P. (2005): Leaching of nitrogen deposition into the ground water. in The condition of forests in Europe: executive report. Federal Research Centre for Forestry and Forest Products (BFH), pp. 23–24.

Dise, N. B.; Matzner, E.; P, Gundersen (1998): Synthesis of nitrogen pools and fluxes from European forest ecosystems. In *Water Air and Soil Pollution* (105), pp. 143–154.

Dise, N. B.; Rothwell, J. J.; Gauci, V.; van der Salm, C.; Vries, W. de (2009): Predicting dissolved inorganic nitrogen leaching in European forests using two independent databases. In *The Science of the Total Environment* 407 (5), pp. 1798–1808. DOI: 10.1016/j.scitotenv.2008.11.003.

Dise, N. B.; Wright, R.F. (1995): Nitrogen leaching from European forests in relation to nitrogen deposition. In *Forest Ecology and Management* 71, pp. 153–161.

Duarte, N.; Pardo, L.H.; Robin-Abbott, M. J. (2013): Susceptibility of Forests in the Northeastern USA to Nitrogen and Sulfur Deposition: Critical Load Exceedance and Forest Health. In *Water, Air, & Soil Pollution* 224 (2), pp. 1–21. DOI: 10.1007/s11270-012-1355-6.

EC (2020): Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption. Source: Brussel: European Commision.

EEA (2004): Ecoregions for Rivers and Lakes. Available online at http://www.eea.europe.eu/data-andmaps/data/ecoregions-for-rivers-and-lakes.

Eldhuset, T. D.; Lange, H.; Wit, H. A. de (2006): Fine root biomass, necromass and chemistry during seven years of elevated aluminium concentrations in the soil solution of a middle-aged Picea abies stand. In *Science of The Total Environment* 369 (1-3), pp. 344–356. DOI: 10.1016/j.scitotenv.2006.05.011.

EMEP (2017): Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components. Edited by Norwegian Meteorological Institute. Oslo, Norway (Status Report).

Emmett, B. A. (2007): Nitrogen Saturation of Terrestrial Ecosystems: Some Recent Findings and Their Implications for Our Conceptual Framework. In *Water Air Soil Pollut: Focus* 7 (1), pp. 99–109. DOI: 10.1007/s11267-006-9103-9.

ESDB (2004): The European Soil Database distribution version 2.0.

Göransson, A.; Eldhuset, T. D. (2001): Is The Ca + K + Mg/Al Ratio in the Soil Solution a Predictive Tool for Estimating Forest Damage? In *Water, Air and Soil Pollution: Focus* 1 (1/2), pp. 57–74. DOI: 10.1023/A:1011507216827.

Graf Pannatier, Elisabeth; Walthert, Lorenz; Blaser, Peter (2004): Solution chemistry in acid forest soils: Are the BC : Al ratios as critical as expected in Switzerland? In *Journal of Plant Nutrition and Soil Science* 167 (2), pp. 160–168. DOI: 10.1002/jpln.200321281.

Gundersen, P.; Callesen, I.;De Vries, W. (1998): Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. In : Nitrogen, the Confer-N-s: Elsevier, pp. 403–407.

Gundersen, P.; Schmidt, I. K.; Raulund-Rasmussen, K. (2006): Leaching of nitrate from temperate forests - effects of air pollution and forest management. In *Environmental Review* 14, pp. 1–57.

Hall, J.; Reynolds, Brian; A., Julian; Hornung, M. (2001): The Importance of Selecting Appropriate Criteria for Calculating Acidity Critical Loads for Terrestrial Ecosystems Using the Simple Mass Balance Equation. In *Water Air Soil Pollut: Focus* 1 (1/2), pp. 29–41. DOI: 10.1023/A:1011519619553.

Hastings, D. A.; Dunbar, P. K. (1998): Development & assessment of the Global Land One-km Base Elevation digital elevation model (GLOBE).

Hedwall, P.O.; Bergh, J.; Brunet, J. (2017): Phosphorus and nitrogen co-limitation of forest ground vegetation under elevated anthropogenic nitrogen deposition. In *Oecologia* 185 (2), pp. 317–326. DOI: 10.1007/s00442-017-3945-x.

Helliwell, R. C.; Britton, A. J.; Gibbs, S.; FISHER, J. M.; Potts, J. M. (2010): Interactive Effects of N Deposition, Land Management and Weather Patterns on Soil Solution Chemistry in a Scottish Alpine Heath. In *Ecosystems* 13 (5), pp. 696–711.

Hettelingh, J. P.; Downing RJ; De Smet, P.; De Vries W.; Schopp W.; Chadwick M.J. et al. (1991): Mapping Critical Loads for Europe. CCE Technical Report no. 1. Rijksinstituut voor Volksgezondheid en Milieu RIVM (ISBN 90-6960-011-0). Available online at https://rivm.openrepository.com/handle/10029/260554.

Hettelingh, J. P.; Posch, M.; Slootweg, J. (2017): European critical loads: database, biodiversity and ecosystems at risk. In *CCE Status Report*. DOI: 10.21945/RIVM-2017-0155.

Holmberg, M.; Mulder, J.; Posch, M.; Starr, M.; Forsius, M.; Johansson, M. et al. (2001): Critical Loads of Acidity for Forest Soils: Tentative Modifications. In *Water Air Soil Pollut: Focus* 1 (1/2), pp. 91–101. DOI: 10.1023/A:1011575704531.

Hornung; R.; Langan (1990): A review of small catchment studies in western Europe producing hydrochemical budgets. Air Pollution Research Report 28.

Huber, C.; Kreutzer, K.; Röhle, H.; Rothe, A. (2004): Response of artificial acid irrigation, liming, and N-fertilisation on elemental concentrations in needles, litter fluxes, volume increment, and crown transparency of a N saturated Norway spruce stand. In *Forest Ecology and Management* 200 (1-3), pp. 3–21. DOI: 10.1016/j.foreco.2004.05.058.

Iost, S.; Rautio, P.; Lindroos, A-J. (2012): Spatio-temporal Trends in Soil Solution Bc/Al and N in Relation to Critical Limits in European Forest Soils. In *Water Air Soil Pollut* 223 (4), pp. 1467–1479. DOI: 10.1007/s11270-011-0958-7.

Johnson, J.; Cummins, T.; Aherne, J. (2016): Critical loads and nitrogen availability under deposition and harvest scenarios for conifer forests in Ireland. In *Science of The Total Environment* (541), pp. 319–328.

Johnson, J.; Graf Pannatier, E.; Carnicelli, S.; Cecchini, G.; Clarke, N.; Cools, N. et al. (2018): The response of soil solution chemistry in European forests to decreasing acid deposition. In *Glob Chang Biol* 24 (8), pp. 3603–3619. DOI: 10.1111/gcb.14156.

Langan, S. J.; Hall, J.; Reynolds, B.; Broadmeadow, M.; Hornung, M.; Cresser, M. S. (2004): The development of an approach to assess critical loads of acidity for woodland habitats in Great Britain. In *Hydrol. Earth Syst. Sci.* 8 (3), pp. 355–365. DOI: 10.5194/hess-8-355-2004.

Lorenz, M.; Nagel, H-D.; Granke, O.; Kraft, P. (2008): Critical loads and their exceedances at intensive forest monitoring sites in Europe. In *Environmental pollution (Barking, Essex : 1987)* 155 (3), pp. 426–435. DOI: 10.1016/j.envpol.2008.02.002.

Lovett, G-M.; Goodale, C-L. (2011): A new conceptual model of nitrogen saturation based on experimental Nitrogen addition to an oak forest. In *Ecosystems* 14 (4), pp. 615–631. DOI: 10.1007/s10021-011-9432-z.

Maas, R.; Grennfelt, P. (2016): Towards Cleaner Air. Scientific Assessment Report 2016. EMEP Steering Body and Working Group on Effects of the Convention on Long-Range Transboundary Air Pollution. Oslo, Norway. Available online at www.unece.org/environmental-policy/conventions/envlrtapwelcome/publications.html.

Marschner, H. (1991): Mechanisms of adaptation of plants to acid soils. In *Plant Soil* 134 (1), pp. 1–20. DOI: 10.1007/BF00010712.

Mason, R. E.; Craine, Joseph M.; Lany, N. K.; Jonard, M.; Ollinger, S. V.; Groffman, P. M. et al. (2022): Evidence, causes, and consequences of declining nitrogen availability in terrestrial ecosystems. In *Science (New York, N.Y.)* 376 (6590), eabh3767. DOI: 10.1126/science.abh3767.

Matzner, E.; Murach, D. (1995): Soil changes induced by air pollutant deposition and their implication for forests in central Europe. In *Water Air Soil Pollut* 85 (1), pp. 63–76. DOI: 10.1007/BF00483689.

McDonnell, T. C.; Cosby, B. J.; Sullivan, T. J.; McNulty, S. G.; Cohen, E. C. (2010): Comparison among model estimates of critical loads of acidic deposition using different sources and scales of input data. In *Environmental pollution (Barking, Essex : 1987)* 158 (9), pp. 2934–2939. DOI: 10.1016/j.envpol.2010.06.007.

Meesenburg, H.; Ahrends, B.; Fleck, S.; Wagner, M.; Fortmann, H.; Scheler, B. et al. (2016): Long-term changes of ecosystem services at Solling, Germany: Recovery from acidification, but increasing nitrogen saturation? In *Ecological Indicators* 65, pp. 103–112. DOI: 10.1016/j.ecolind.2015.12.013.

Nachtergaele, F.; van Velthuizen, H.; Verelst, L.; Wiberg, D. Henry, M.; Chiozza, Frederica et al. (Eds.) (2023): Harmonized World Soil Database. Version 2.0. Rome: Food and Agriculture Organization of the United Nations.

NEG/ECP Forest Mapping Group (2001): Forest Mapping Group Protocol for assessment and mapping of forest sensitivity to atmospheric S and N deposition. The Conference of the New England Governors and Eastern Canadian Premiers, Article 76 Summer St. Boston, MA 02110 79 p. Available online at http://www.ecosystems-research.com/fmi/Protocol.pdf.

Nilsson, J.; Grennfelt, P. (1988): Critical Loads for Sulphur and Nitrogen. Report from a workshop held in Skokloster, Sweden, 19–24 March, 1988: Nordic Council of Ministers.

Niu, Shuli; Classen, A. T.; Dukes, J. S.; Kardol, P.; Liu, L.; Luo, Y. et al. (2016): Global patterns and substrate-based mechanisms of the terrestrial nitrogen cycle. In *Ecol Lett* 19 (6), pp. 697–709. DOI: 10.1111/ele.12591.

Nygaard, P. H.; Wit, H. A. de (2004): Effects of elevated soil solution Al concentrations on fine roots in a middle-aged Norway spruce (Picea abies (L.) Karst.) stand. In *Plant Soil* 265 (1-2), pp. 131–140. DOI: 10.1007/s11104-005-0333-9.

Ouimet, R.; Arp, P. A.; Watmough, S. A.; Aherne, J.; DeMerchant, I. (2006): Determination and Mapping Critical Loads of Acidity and Exceedances for Upland Forest Soils in Eastern Canada. In *Water, Air, & Soil Pollution* 172 (1-4), pp. 57–66. DOI: 10.1007/s11270-005-9050-5.

Oulehle, F.; Goodale, C. L.; Evans, C. D.; Chuman, T.; Hruška, J.; Krám, P. et al. (2021): Dissolved and gaseous nitrogen losses in forests controlled by soil nutrient stoichiometry. In *Environ. Res. Lett.* 16 (6), p. 64025. DOI: 10.1088/1748-9326/ac007b.

Panagos, P.; van Liedekerke, M.; Borrelli, P.; Köninger, J.; Ballabio, C.; Orgiazzi, A. et al. (2022): European Soil Data Centre 2.0: Soil data and knowledge in support of the EU policies. In *European J Soil Science* 73 (6), Article e13315. DOI: 10.1111/ejss.13315.

Pardo, L. H.; Duarte, N.; van Miegroet, H.; Fisher, L. S.; Robin-Abbott, M. J. (2018): Critical loads of sulfur and nitrogen and modeled effects of deposition reduction for forested ecosystems of Great Smoky Mountains National Park. In *Gen. Tech. Rep. NRS-180. Newtown Square, PA: U.S. Department of Agriculture, Forest Service, Northern Research Station. 26 p.* 180, pp. 1–26. DOI: 10.2737/NRS-GTR-180.

Posch, M.; Reinds, G. J. (2017): The European background database of N and S critical loads. Hettelingh J-P, Posch M, Slootweg J (eds), European critical loads: database, biodiversity and ecosystems at risk: CCE Final Report 2017. RIVM Report 2017-0155, Coordination Centre for Effects, Bilthoven, Netherlands, pp 49-63; ISBN 978-90-6960-288-2. DOI: 10.21945/RIVM-2017-0155.

Posch, M.; Duan, L.; Reinds, G. J.; Zhao, Y. (2015a): Critical loads of nitrogen and sulphur to avert acidification and eutrophication in Europe and China. In *Landscape Ecol* 30 (3), pp. 487–499. DOI: 10.1007/s10980-014-0123-y.

Posch, M.; De Vries, W.; Sverdrup, H. U. (2015b): Mass Balance Models to Derive Critical Loads of Nitrogen and Acidity for Terrestrial and Aquatic Ecosystems. In Wim De Vries, Jean-Paul Hettelingh, Maximilian Posch (Eds.): Critical Loads and Dynamic Risk Assessments: Nitrogen, Acidity and Metals in Terrestrial and Aquatic Ecosystems. Dordrecht: Springer Netherlands, pp. 171–205.

Reinds, G. J.; Posch, M.; Vries, W. de; Slootweg, J.; Hettelingh, J.-P. (2008): Critical Loads of Sulphur and Nitrogen for Terrestrial Ecosystems in Europe and Northern Asia Using Different Soil Chemical Criteria. In *Water Air Soil Pollut* 193 (1-4), pp. 269–287. DOI: 10.1007/s11270-008-9688-x.

Reinds, G. J.; Thomas, D.; Posch, M.; Slootweg, J. (2021): Critical loads for eutrophication and acidification for European terrestrial ecosystems: German Environment Agency. Available online at https://www.umweltbundesamt.de/sites/default/files/medien/5750/publikationen/2021-07-12_doku_03-2021-critical_load.pdf.

Rennenberg, H.; Dannenmann, M.; Gessler, A.; Kreuzwieser, J.; Simon, J.; Papen, H. (2009): Nitrogen balance in forest soils. nutritional limitation of plants under climate change stresses. In *Plant Biology* 11, pp. 4–23. DOI: 10.1111/j.1438-8677.2009.00241.x.

Reuss, J. O.; Johnson, D. W. (1985): Effect of Soil Processes on the Acidification of Water by Acid Deposition. In *J. Environ. Qual.* 14 (1), pp. 26–31. DOI: 10.2134/jeq1985.00472425001400010005x.

Richter, A. K.; Walthert, L.; Frossard, E.; Brunner, I. (2007): Does low soil base saturation affect fine root properties of European beech (Fagus sylvatica L.)? In *Plant Soil* 298 (1-2), pp. 69–79. DOI: 10.1007/s11104-007-9338-x.

Rihm, B.; Achermann, B. (2016): Critical Loads of Nitrogen and their Exceedances. Swiss contribution to the effects-oriented work under the Convention on Long-range Transboundary Air Pollution (UNECE). (Environmental studies no. 1642: 78 p). Available online at https://www.bafu.admin.ch/bafu/en/home/topics/air/publications-studies/publications/Critical-Loads-of-Nitrogen-and-their-Exceedances.html.

Rosén, K. (1990): The critical load of nitrogen to Swedish forest ecosystems (Internal Report).

Ross, D. S.; Matschonat, G.; Skyllberg, U. (2008): Cation exchange in forest soils: the need for a new perspective. In *European Journal of Soil Science* 59 (6), pp. 1141–1159. DOI: 10.1111/j.1365-2389.2008.01069.x.

Schelhaas, M. J.; Varis, S.; Schuck, A.; Nabuurs G.J. (2006): EFISCEN Inventory Database.

Schimel, J.P; Bennett, J. (2004): Nitrogen mineralization. Challenges of a changing paradigm. In *Ecology* 85 (3), pp. 591–602.

Schlutow, A.; Kraft, P.; Scheuschner, T.; Schröder, W. (in prep): Bioindication for Ecosystem Regeneration towards Natural conditions – the BERN data base and BERN model. DOI: 10.21203/rs.3.rs-3249069/v1.

Schlutow, A.; Bouwer, Y.; Scheuschner, T.; Nagel, H.-D. (2017): Ermittlung und Bewertung der Einträge von versauernden und eutrophierenden Luftschadstoffe in terrestrische Ökosysteme (PINETI2) - Teilbericht II. Critical Load, Exceedance und Belastungsbewertung.

Schmitz, A.; Sanders, T.; Bolte, A.; Bussotti, F.; Dirnböck, T.; Johnson, J. et al. (2019): Responses of forest ecosystems in Europe to decreasing nitrogen deposition. In *Environmental Pollution* 244, pp. 980–994. DOI: 10.1016/j.envpol.2018.09.101.

Skeffington, R. A. (2006): Quantifying Uncertainty in Critical Loads: (A) Literature Review. In *Water Air Soil Pollut* 169 (1-4), pp. 3–24. DOI: 10.1007/s11270-006-0382-6.

Slootweg, J.; Posch, M.; Warrink, A. (2009): Status of the harmonised European land cover map.

Šrámek, V.; Fadrhonsová, V.; Jurkovská, L. (2014): Ca/Al ratio in Norway spruce fine roots on monitoring plots in the Czech Republic. In *J. For. Sci.* 60 (No. 3), pp. 121–131. DOI: 10.17221/85/2013-JFS.

Stoddard, J. L. (1994): Long-term changes in watershed retention of nitrogen. Its causes and aquatic consequences. In : Environmental Chemistry of Lakes and Reservoirs, vol. 237, pp. 223–284. Available online at https://www.researchgate.net/publication/257972244_Long-term_changes_in_watershed_retention_of_nitrogen_Its_causes_and_aquatic_consequences.

Sutton, M. A.; Howard, C. M.; Erisman, J. W.; Billen, Gilles; Bleeker, A.; Grennfelt, P. et al. (Eds.) (2011): The European Nitrogen Assessment: Cambridge University Press.

Suz, L. M.; Bidartondo, M. I.; van der Linde, S.; Kuyper, T. W. (2021): Ectomycorrhizas and tipping points in forest ecosystems. In *New Phytologist* 231 (5), pp. 1700–1707. DOI: 10.1111/nph.17547.

Sverdrup, H.; Warfvinge, P. (1993): The effect of soil acidification on the growth of trees, grass and herbs as expressed by the (Ca+Mg+K)/Al ratio. Department of Chemical Engineering II, Lund University. In *Reports in ecology and environmental engineering*.

Sverdrup, H.; Belyazid, S.; Nihlgård, B.; Ericson, L. (2007): Modelling Change in Ground Vegetation Response to Acid and Nitrogen Pollution, Climate Change and Forest Management at in Sweden 1500–2100 a.d. In *Water Air Soil Pollut: Focus* 7 (1-3), pp. 163–179. DOI: 10.1007/s11267-006-9067-9.

Sverdrup, H.; De Vries, W.; Henriksen, A. (1990): Mapping critical loads. A guidance to the criteria, calculations, data collection and mapping of critical loads ; prepared for the Workshop and Task Force on Mapping Critical Loads and Levels (Bad Harzburg, 6.-9.11.1989, and 22.-23.5.1990). Copenhagen: NMR (NORD, 1990,98).

Tamis, W.L.M.; Bakker, N.V.J de; van 't Zelfde, M. (2008): Integrating Natura2000 into critical load calculations for nitrogen.

Tang, J. Y.; Riley, W. J. (2013): A total quasi-steady-state formulation of substrate uptake kinetics in complex networks and an example application to microbial litter decomposition. In *Biogeosciences* 10 (12), pp. 8329–8351. DOI: 10.5194/bg-10-8329-2013.

Tian, Ye; Shi, Chupei; Malo, Carolina Urbina; Kwatcho Kengdo, Steve; Heinzle, J.; Inselsbacher, Erich et al. (2023): Long-term soil warming decreases microbial phosphorus utilization by increasing abiotic phosphorus sorption and phosphorus losses. In *Nature Communications* 14 (1), p. 864. DOI: 10.1038/s41467-023-36527-8.

Ulrich, B. (1981): Theoretische Betrachtung des Ionenkreislaufs in Waldökosystemen. In *Z. Pflanzenernaehr. Bodenk.* 144 (6), pp. 647–659. DOI: 10.1002/jpln.19811440613.

Ulrich, B. (1987): Stability, Elasticity, and Resilience of Terrestrial Ecosystems with Respect to Matter Balance. In Ernst-Detlef Schulze, Helmut Zwölfer (Eds.): Potentials and Limitations of Ecosystem Analysis. Berlin, Heidelberg: Springer Berlin Heidelberg, pp. 11–49.

Ulrich, B.; Mayer, R.; Khanna, P. K. (1980): Chemical changes due to acid precipitation in a loss-drived soil in central Europe. In *Soil Science* 130 (4), p. 193.

UNECE (2001): Workshop on Chemical Criteria and Critical Limits. Geneva, Switzerland: United Nations Economic Commission for Europe.: UN. Available online at https://digitallibrary.un.org/record/444836.

Van Groenigen, J. W.; Huygens, D.; Boeckx, P.; Kuyper, Th W.; Lubbers, I. M.; Rütting, T.; Groffman, P. M. (2015): The soil N cycle. new insights and key challenges. In *SOIL* 1 (1), pp. 235–256. DOI: 10.5194/soil-1-235-2015.

Van Schöll, L.; Keltjens, W. G.; Hoffland, E.; van Breemen, N. (2004): Aluminium concentration versus the base cation to aliminium ratio as predictors for aluminium toxicity in Pinus sylvestris and Picean abies seedlings. In *Forest Ecology and Management* (195), pp. 301–309.

Veerhoff, M.; Roscher, S.; Brümmer, G. W. (1996): Ausmaß und ökologische Gefahren der Versauerung von Böden unter Wald: Forschungsbericht 107 02 004/14. Berlin: Erich Schmidt Verlag.

Vuorenmaa, J.; Augustaitis, A.; Beudert, B.; Bochenek, W.; Clarke, N.; De Wit, H. A. et al. (2018): Long-term changes (1990–2015) in the atmospheric deposition and runoff water chemistry of sulphate, inorganic nitrogen and acidity for forested catchments in Europe in relation to changes in emissions and hydrometeorological conditions. In *Science of The Total Environment* 625, pp. 1129–1145. DOI: 10.1016/j.scitotenv.2017.12.245.

Waldner, P.; Thimonier, A.; Graf Pannatier, E.; Etzold, S.; Schmitt, M.; Marchetto, A. et al. (2015): Exceedance of critical loads and of critical limits impacts tree nutrition across Europe. In *Annals of Forest Science* 72 (7), pp. 929–939. DOI: 10.1007/s13595-015-0489-2.

Warfvinge, P.; Sverdrup, H.; Rosén, K. (1992): Calculating Critical Loads for N to forest soils. In Peringe Grennfelt, E. Thörnelöf (Eds.): Critical Loads for Nitrogen. NORD, vol. 41. Copenhagen (NORD, 41), pp. 403–418.

Watmough, S. A.; Dillon, P. J. (2003): Do critical load models adequately protect forests? A case study in south-central Ontario. In *Canadian Journal of Forest Research* 33 (8), pp. 1544–1556. DOI: 10.1139/x03-075.

Wellbrock, N.; Bolte, A. (Eds.) (2019): Status and Dynamics of Forests in Germany : Results of the National Forest Monitoring. Cham: Springer International Publishing.