Biologia et Biotechnologia

UDC 574

Paper

Biogeochemical Standards as a Measure of Critical Loads on Ecosystems

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Citation:
Bashkin V.N. Biogeochemical Standards as a Measure of Critical Loads on Ecosystems. *Biologia et Biotechnologia* 2025, 2, 4. https://doi.org/10.61847/pbcras.bbt.2025.2.4

Received: 22.01.2025
Accepted: 13.03.2025
Published: 30.03.2025

Abstract: The calculation of biogeochemical standards for parameterization of anthropogenic impact on various ecosystems has been carried out within the framework of the biotechnological trend being developed - biogeochemical engineering. For the purpose of quantitative assessment of these standards, the application of critical loads methodology is shown. Methods for calculating the values of critical loads are given, in particular, for acid-forming and eutrophying sulfur and nitrogen compounds emitted by various industries, including oil and gas. Examples of calculations of biogeochemical standards for the impact zones of gas trunk lines are given: from tundra and forest ecosystems of Yamal gas transportation routes to the Central Asia-Center gas trunk line projected for reconstruction. Environmental risk probabilities have also been assessed.

Keywords: biogeochemical standards, critical loads, acid deposition, eutrophication, ecosystems, gas pipelines, environmental risk

Introduction

Biogeochemical standards are the most important element of biogeochemical technologies within the development of a new scientific direction - engineering biogeochemistry. This direction is developing at the interface of fundamental and applied research based on the study of physicochemical mechanisms governing biogeochemical organization of the biosphere. Biogeochemical technologies, as nature-like technologies, are actively used in reclamation and remediation of disturbed and polluted lands, as well as in environmental risk assessment [1-3].

The biogeochemical concept of the biosphere as the habitat of biota and the cycle of elements under the action of living matter proposed by V.I. Vernadsky [4] was supplemented by V.A. Kovda's fundamental ideas on the role of soil as the most important component of the biogeochemical cycle of elements [5]. M.A. Glazovskaya developed ideas about the interaction between the biosphere and the technosphere. Thus, technogenic compounds entering the environment as a result of emissions into the atmosphere, discharges and effluents into natural waters, storage and disposal of solid wastes or other ways, as a rule, are not preserved in an unchanged form, but transformed to a greater or lesser extent, are "included" in the migration flows of substances already existing in nature [6,7].

The stability of ecosystems with respect to most pollutants is determined by the intensity of development in them of processes of neutralization, long-term immobilization and removal of anthropogenic substances of different orientation of action. These loads should fit within the natural fluctuations of various links of the biogeochemical cycle and biogeochemical stability of ecosystems (Fig. 1).

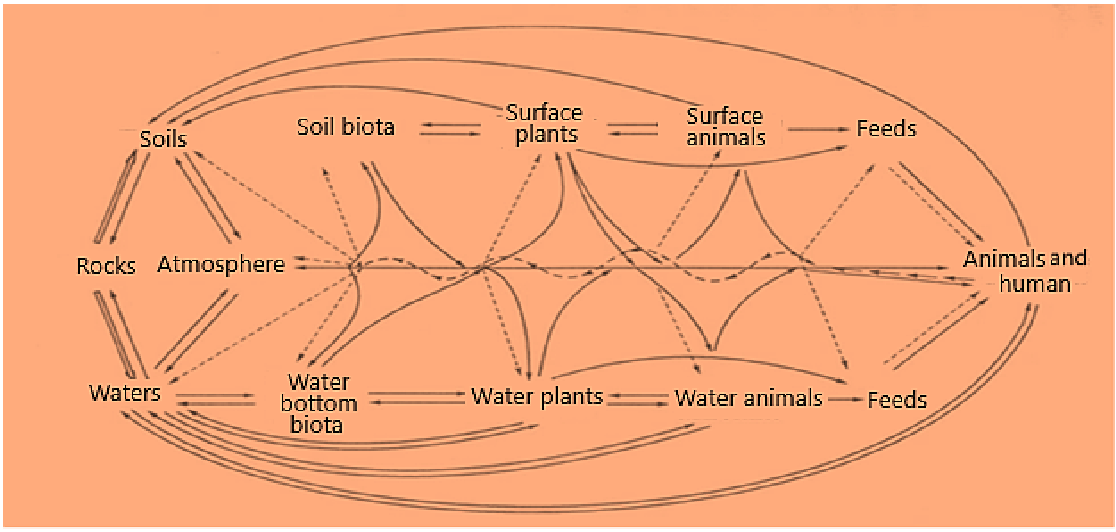

Figure 1. Conceptual diagram of the biogeochemical cycle

Consequently, it is necessary to develop methodological approaches for qualitative and quantitative assessment of the values of these permissible loads, considering them as biogeochemical standards of permissible impact of various pollutants on different ecosystems composing the environment.

This is taken into account within the framework of the critical load (CL) methodology [8,9]. Critical load is an acceptable level of pollutant input into an ecosystem that is not accompanied by disturbances in the biogeochemical structure of the ecosystem over a long-term period (50-100 years).

Assessment of CL values implies determination of the threshold of pollutants input into ecosystems, after exceeding which negative consequences for living organisms and the ecosystem as a whole are possible, while below this level no violations and adverse effects are observed. In contrast to the traditional for Russia and most other countries "environmental" indicators, which normalize the concentrations of pollutants in individual environments based on the values of maximum permissible loads (MPL), the value of CL is an ecosystem indicator and/or, accordingly, a biogeochemical standard. The main differences between these standards are summarized in Table 1.

Table 1. Difference in methodological approaches “embedded” in the concept of MPL and IP as a biogeochemical standard

Maximum permissible concentrations of pollutants	Critical load values
• Norms the content of pollutants in separate media (soil, vegetation, ground and surface waters) without taking into account chemical relations between ecosystem components and specificity of pollutant migration flows; • Developed mainly for assessing the quality of agricultural soils, water bodies for fishery use, drinking water, usually on the basis of laboratory tests; • As a rule, they do not take into account the specifics of functional use of territories; • They are anthropocentric - humans are considered as the main recipient of impacts; • Characterize the degree of anthropogenic changes in the chemical composition of the environment, without taking into account the intensity of previous, existing or permissible impacts; • Do not allow to establish quantitative dependencies between the impact and its consequences.	• Characterize the maximum input of pollutants into ecosystems, taking into account the potential for ecosystem resilience with respect to the effects of specific pollutants; • Take into account biogeochemical relationships between individual ecosystem components and existing natural variations in the parameters of individual environments; • Allow for assessing the permissible level of technogenic load taking into account the functional use of territories, including from the point of view of ensuring environmental safety of various recipients (humans, terrestrial or aquatic biota, soil fauna and microorganisms); • Provide an idea of the ratio of existing and permissible impact, allow for regulating the intensity of impacts and focus on the economic feasibility of reducing anthropogenic loads.

Estimates of CL values are oriented at establishing quantitative links between the impact of specific pollutants and environmental consequences resulting from these impacts, which is especially important from the point of view of ecological and economic justification of management decisions. Quantitative indicators characterizing the permissible level of anthropogenic impacts of certain pollutants on specific ecosystems can be established on the basis of experimental or monitoring studies. These are so-called empirical critical loads. However, when conducting regional studies for territories with high natural diversity, quantitative methods of estimation of CL values based on mathematical calculations with involvement of modern GIS-technologies are more demanded.

Therefore, the purpose of this article is to consider approaches to quantitative assessment of biogeochemical standards. At the same time, it shows the methods of their practical realization on the basis of using the concepts of critical loads as an indicator of ecologically acceptable levels of impact of atmospheric pollutants on natural ecosystems.

Critical loads as biogeochemical standards

For the purposes of analysis of environmental impact and justification of permissible parameters of atmospheric pollutants emission from various industrial facilities, including oil and gas enterprises, scientific and methodological approaches developed within the framework of internationally recognized methodology of critical loads are of the greatest practical interest. The basic provisions of the critical loads methodology have been used for scientific support of a number of international conventions on long-range transboundary air pollution in Europe, North America and Asia. The methodology is based on the notion of differentiated responses of different ecosystems to similar man-made impacts.

Quantitative methods of calculating CL values are based on the use of simple chemical mass-balance models of elements, which will be discussed in detail below. The assessment of critical loads may take into account one or another conservation priorities determined through the selection of recipients (preservation of specific natural objects) and establishment of appropriate biogeochemical standards. As already mentioned, exposure of recipients occurs as a result of their contact with polluted environments or involvement of pollutants in trophic chains. The level of exposure is determined by the concentration of pollutants in the boundary environments, and exceeding the threshold concentrations of pollutants in the environments established for different groups of recipients can lead to ecological disturbances. As threshold concentrations traditional for the Russian Federation MPC and APC values are used, or standards used abroad: no-effect concentrations (NOEC, NOEL), minimum effect concentrations (LC10, LC50 or EC10, EC50) and others. At the same time it is necessary to use biogeochemical standards (critical loads), the ecosystem validity of which has already been shown above (see Table 1).

At present, the most widely used in calculations of CL are effect-oriented models, which are based (1) on the idea of relative biogeochemical equilibrium existing between different components of ecosystems under stable external conditions, as well as (2) on consideration of specific environmental consequences - effects of technogenic impacts. This allows us to calculate the permissible level of pollutant intake corresponding to the critical concentration of pollutants in one of the considered environments, and to fulfill the condition of preserving the quality of those environments, which are defined as ecologically priority for the given conditions. Norming of technogenic loads on the basis of such models is carried out for environmental situations when the level of pollution of individual components of ecosystems is below the established critical standards, and, from the economic point of view, more intensive use of territories is justified, which, however, should not lead to pollution of environmental components above the established standards and destruction of biogeochemical organization of ecosystems [10]. For conditions when the existing level of environmental pollution is higher than the established normative indicators, dynamic models are used to assess the permissible intensity of impact in the further use of these territories and (or) to determine the parameters of the necessary reduction of anthropogenic loads.

Currently, there are methods for calculating CL values as biogeochemical standards for the following pollutants:

- Sulfur and nitrogen oxides (SO_x, NO_x) in relation to the effects of ecosystem acidification ($CL(S)_{max}$);
- Nitrogen compounds (NH_4, NO_x) in relation to the effects of ecosystem eutrophication ($CL(N)_{min}$, $CL(N)_{nut}$, $CL(N)_{max}$);
- Heavy metals (Pb, Cd, Hg) in relation to the effects of toxicity for biota and humans (CL(Pb), CL(Cd), CL(Hg)).

This article will consider methods for calculating CN values to assess acidifying and eutrophying effects.

Methods for calculating the values of atmospheric pollutants for terrestrial ecosystems

Calculations of CL values include parameterization of the main migration fluxes of elements specific for different bioclimatic and landscape conditions. Simple biogeochemical models, which include two types of equations, are most often used to quantify IP values:

- Equilibrium equations of simple mass balance of elements and/or their compounds in the soil (the soil layer under consideration);
- Equations describing the intensity of the main biogeochemical flows of elements in ecosystems, taking into account the features of their formation.

A number of assumptions are made in these models, namely:

- The depth of the soil layer under consideration is conventionally equal to the depth of the root zone, which allows the nutrient cycle to be neglected;
- Evapotranspiration occurs on the surface of the soil profile;
- Infiltration of precipitation moisture is constant throughout the soil profile and occurs only vertically;
- Physicochemical constants are assumed to be homogeneous throughout the soil profile;
- Internal fluxes of elements (nitrogen fixation, etc.) are independent of soil chemical conditions (such as pH).

Internal ecosystem interactions and such processes as intraspecific competition or the presence of pests, the removal of elements from the soil with the growth of the part of terrestrial biomass that returns to the surface annually with the plant litter, and others are also not taken into account.

Since these models describe conditions of a relatively equilibrium biogeochemical state, they require the use of long-term averages of incoming fluxes as input information. Seasonal, inter-annual and other short-term dynamic changes of indicators are usually not taken into account in these models.

Methodology for calculating the CL values of acid-forming compounds

The purpose of calculating the CL values of acid-forming compounds (or CL acidity) is to quantify the potential of ecosystems to neutralize the acid component of atmospheric deposition, which depends on the balance of chemically active protons and cations in natural systems.

It is known that the main agent of acidity of atmospheric precipitation is sulfur oxides, with the excessive emission of which in the 60-80s of the twentieth century was associated with the magnitude of the problem of acid rain in Central and Northern Europe. Therefore, within the framework of studies under the UN Convention on Long-Range Transboundary Air Pollution, it was decided to use the term "critical load of maximum sulfur" i.e. $CL(S)_{max}$ to assess the permissible parameters of acid-forming compounds entering ecosystems. It is believed that this value corresponds to a safe level of sulfur oxide deposition in the absence of other acid-forming compounds in atmospheric deposition.

In case of presence of other acid-forming compounds, primarily nitrogen oxides, correction (reduction) of permissible sulfur intakes is necessary (Fig. 2). In recent years, after a noticeable reduction in SO_x emissions in Europe, in many industrial regions, including the Russian Federation, nitrogen oxides began to play a significant role in the formation of acid precipitation, reduction of atmospheric emissions of which is a more difficult practical task.

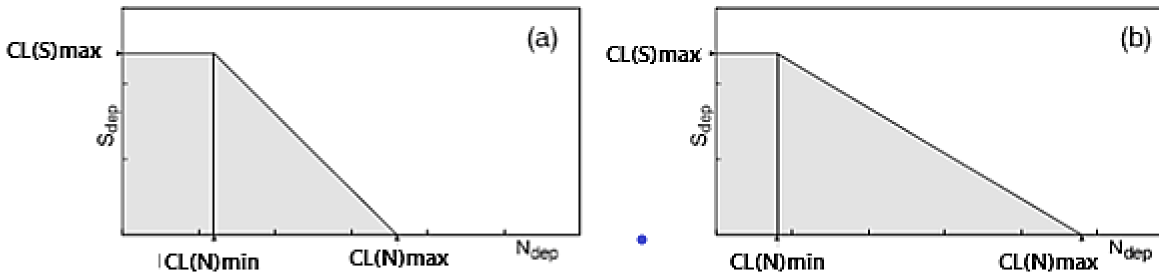

Figure 2. Schemes for correction of CL of maximum sulfur and acidifying nitrogen, determined by the calculated values of $CL(S)_{max}$, $CL(N)_{min}$ and $CL(N)_{max}$:

a - at constant denitrification value (function slope angle is 45°);

b - at denitrification parameters depending on nitrogen input with atmospheric deposition (more gentle slope of the function determined by the denitrification value, f_{de}).

The gray zone corresponds to "pairs" of deposition levels of S (S_{dep}) and N (N_{dep}), providing conditions under which soil acidity will not be below the permissible critical pH values.

The basic algorithm for calculating acidity CL values is based on the use of the law of equivalents according to Equation 1:

$$\mathbf{CL\ (S)_{max} = BC_{dep} + BC_{w} - Cl_{dep} - Bc_{upt} - ANC_{le(crit)}} \quad (1)$$

where, BC_{dep} - input of Ca, Mg, K, Na cations into the ecosystem with atmospheric deposition; BC_w -subsurface weathering of Ca, Mg, K, Na cations; Cl_{dep} – input of Cl anions with atmospheric precipitation; Bc_{upt} - removal of Ca, Mg, K cations from soils by vegetation due to root nutrition; $ANC_{le(crit)}$ – critical leaching of alkalinity. The units of measurement for the values of all parameters of this equation are gram equivalent per hectare per year (g-eq/ha per year).

Atmospheric inputs of cations and chlorine are usually estimated based on monitoring data of their deposition controlled in the Roskomgidromet system, or are estimated based on mathematical modeling of pollutant dispersion processes from natural and anthropogenic sources.

Another parameter of Equation 1 - intensity of soil mineral weathering (BC_w) depends on mineralogical and granulometric composition of soils and temperature conditions. There are several models to estimate the intensity of this parameter, e.g. using Equation 2:

$$\mathbf{BC_{w\_100} = BC_w(T^0) * 2{,}6^{(A/T0 - A/T)}} \tag{2}$$

where, $BC_w(T^0)$ – the intensity of in-soil weathering of Ca, Mg, K, Na for soils of different granulometric composition, corresponding to the average annual temperature 8°C. Values of T^0 and T, are respectively, the air temperature at 8°C and the average annual temperature for the study area, expressed in Kelvin degrees. The value of A is 3600. The values of $BC_w(T^0)$ for soils of different granulometric composition are presented in Table 2.

Table 2. Standard values of $BC_w(T^0)$ for soils of different granulometric composition; the values correspond to standard temperature conditions of 8 °C and a soil layer of 0-100 cm [11].

Granulometric composition	Value of $BC_w(T^0)$, g-eq/ha yr.
1. Sandy soils	750
2. Sandy loam and sandy light loamy soils	1250
3. Light and medium loamy soils	1750
4. Medium loamy soils	2250
5. Heavy loamy and clayey soils	2750

Another variant of calculations is based on the use of soil texture data, information about which can be obtained from soil map data at different scales, for example, from global [12,13], regional [14] to local [15]. In this case, the weathering parameters are estimated according to Equation 3.

The values of the weathering intensity of the main cations (**BC_w_100**) obtained according to equation 2 for the temperature conditions of the study regions correspond to a meter-thick soil layer and should be recalculated depending on the thickness of the considered layer in accordance with the specificity of soil of particular study regions. For bog soils and forest soils with developed peat horizon, the cations input due to weathering is assumed to be 0.

Another variant of calculations is based on the use of soil texture data, information about which can be obtained from soil map data at different scales, for example, from global [12,13], regional [14] to local [15]. In this case, the weathering parameters are estimated according to Equation 3:

$$BC_w = z \cdot 500 \cdot (WRc - 0.5) \cdot \exp\left(\frac{A}{281} - \frac{A}{273 + T}\right), \tag{3}$$

where, $BC_w(T^0)$ – intensity of subsurface weathering of Ca, Mg, K, Na for soils of different textures, corresponding to the average annual temperature of 8 °C, z is the depth of the soil layer. ***WRc*** is the value corresponding to the class of soil texture (Tables 3, 4); the properties of parent rocks for different types of soil can be obtained from the legend of the FAO map (Table 3). The other values are shown above.

Table 3. Data for determining soil texture classes depending on the properties of parent rocks: average values for East-European soils [10]

Parent material	Texture class values (WRc)				
Acid class	1	2	3	4	5
Middle class	1	3	3	6	6
Basic class	2	4	4	6	6
Organic	2	5	5	6	6
	Class 6 for peat bog soils and class 1 for other organic soils				

Table 4. Classes of parent material for the main soil types presented in the FAO classification [13,14]

Parent material	Soil types presented in the FAO classification
Acid class	Ah, Ao, Ap, B, Ba, Be, Bf, Bh, Bm, Bx, D, Dd, Dg, Gx, I, Id, Ie, Jd, P, Pf, Pg, Q, Qa, Qc, Qh, Ql, Rd, Rx, U, Ud, Wd
Middle class	A, Af, Ag, Bv, C, Cg, Ch, Cl, G, Gd, Ge, Gf, Gh, Gi, Gl, Gm, Gs, Gt, H, Hg, Hh, Hl, J, Je, Jm, Jt, L, La, Ld, Lh, Lo, Lp, Mo, R, Re, V, Vg, Vp, W,We
Basic class	F,T, Th, Tm, to, Tv
Organic	O, Od, Oe, Ox

The intensity of consumption of Ca, Mg and K cations by terrestrial vegetation (***Bc_{upt}***) depends on the species characteristics of edifiers. In calculations of CL values, only physiologically active cations are estimated for biomass removal by root nutrition, excluding sodium. As noted above, the mass balance equation includes only the pool of cations that can be removed from ecosystems or relatively long-term deposited in some part of plant biomass. In ecosystems dominated by woody vegetation, the relatively long-term deposition of these elements as part of stem wood growth can be taken into account. Calculation of cation removal with biomass growth is carried out according to Equation 4:

$$Bc_{upt} = Y * ([Ca] + [Mg] + [K]) \quad (4)$$

where, ***Y*** – annual production of that part of biomass that can be removed outside ecosystems, (kg/ha per year); ***[Ca], [Mg], [K]*** – concentration of corresponding cations in the considered part of biomass, (g-eq./kg).

The parameter of Equation 1, *critical alkalinity leaching* (***$ANC_{le(crit}$***) sets a criterion that takes into account the effects of acidic influences on sensitive recipients, which in terrestrial ecosystems are usually edificatory plant species. Since the sensitivity of different species to the same environmental factors is significantly differentiated, the different values of the criteria used determine the difference in the values of the CL of acidity. At the same time, if for one and the same ecosystem the CL is calculated using different criteria, the final value will be the smallest of the calculated ones. The decision to establish one or another criterion for the effects (consequences) of acid impacts depends on what the selected recipient is more sensitive to. It can be excessive soil acidity associated with low pH, or toxic effects determined by increased concentrations of aluminum in the soil solution, or imbalance between physiologically active cations and aluminum, etc.

For soils with a relatively high content of poorly mineralized organic matter in the upper part of the profile, the proton criterion is recommended, *i.e.* the estimation of the ANC le(crit) parameter based on the use of values of permissible concentrations of hydrogen ions expressed through pHcrit or [H]crit. This critical level corresponds to the pH value below which negative effects are possible for different groups of plant species. For forest soils of the boreal zone, taking into account the predominant coniferous species in them, the recommended value of pHcrit = 4.0, which corresponds to [H]crit = 0.1 g-eq/m^3. For herbaceous ecosystems, the pHcrit value may be higher. For example, the standard of soil quality in terms of acidity for urban park soils in Moscow is 5.5.

Taking into account the proton criterion, the value of ***$ANC_{le(crit)}$*** can be calculated according to the Equation 5:

$$ANC_{le(crit)} = -10^4 * Q * ([H]_{(crit)} + K_{gibb} * [H]^3_{(crit)}) \quad (5)$$

where, ***Q*** – average annual volume of moisture percolating through the topsoil, (m/year); ***$[H]_{(crit)}$*** – critical concentration of hydrogen ions, (g-eq./m^3); ***K_{gibb}*** – constant, (m^6/g-eq.^{2}).

The volume of moisture (***Q***), which determines the intensity of removal (leaching) of elements from soils with radial in-soil moisture flow, can be estimated on the basis of the water balance equation characterizing the ratio between precipitation, evaporation and transpiration values. Average parameters of hydrological runoff or results of model calculations can also be used. The values of K_{gibb} constant for different soil variants are given in the Table 5.

Table 5. Values of the K_{gibb} constant for soils with different organic matter contents ($pK_{gibb}=-\log_{10}(K_{gibb})$)

Soil type (horizon)	Organic matter content, (%)	K_{gibb}, ($m^6/g\text{-eq.}^2$)	$-pK_{gibb}$
▪ Mineral soils (horizon C)	< 5	950-9500	8.5-9.5
▪ Soils with low organic matter content (horizons B/C)	5-15	300-3000	8-9
▪ Soils with high organic matter content (horizons A/E)	15-30	100	7.6
▪ Peat and sod soils (organogenic horizons)	> 70	9.5	6.5

For peat and peat-bog soils that do not contain aluminum hydroxides, it is proposed to use the critical molar ratio of basic cations to protons $(Bc/H)_{crit}$ as a criterion for assessing permissible acidity. Then critical leaching $ANC_{le(crit)}$ can be calculated according to Equation 6:

$$ANC_{le,crit} = 0.5 \cdot \frac{Bc_{dep} - Bc_u}{(Bc/H)_{crit}}, \quad (6)$$

where, Bc_{dep} and Bc_{up} account for the atmospheric supply and uptake of Ca, Mg and K by vegetation. A factor of 0.5 is used to convert moles to equivalents. The $(Bc/H)_{crit}$ value is derived from the critical ratio $(Bc/Al)_{crit}$ and the relationship between H and Al described by Equation 7:

$$[Al] = K_{gibb} \cdot [H]^3, \quad (7)$$

The following ratios $(Bc/Al)_{crit}$ have been established: for coniferous species – 1, for deciduous species and ground vegetation cover – 0.3 [4].

Methodology for calculating the CL values of eutrophic nitrogen compounds

For nitrogen compounds, several variants of critical loads are calculated, which is necessary to quantify the relationship between the permissible levels of nitrogen and sulphur oxides inputs when they are present together in atmospheric deposition.

- The minimum nitrogen load characterizes the lowest level of nitrogen input that ensures the preservation of productivity of the ecosystems under consideration.
- The "nutrient" nitrogen load makes it possible, on the contrary, to quantify the nitrogen input that does not cause its excess in ecosystems (eutrophication), which may be the cause of change in species diversity of biocenoses.
- Maximum nitrogen load determines the permissible parameters of nitrogen oxide input into ecosystems, at which the acidity level (pH values) does not fall below the critical level and, at the same time, the nutrient regime of soils favorable for biota is preserved.

The critical load of minimum nitrogen $(CL(N)_{min})$ is calculated according to Equation 8:

$$CL(N)_{min} = N_{im} + N_{upt}, \quad (8)$$

where, N_{im} – the amount of nitrogen annually fixed (immobilized) in the soil due to the processes of soil organic matter creation (g-eq./ha per year); N_{upt} – nitrogen accumulated in the growth of vegetation biomass, (g-eq./ha per year).

Long-term N immobilization (N_{im}) is determined by its accumulation as part of a stable pool of soil organic matter. This N immobilization should not lead to a change in the C/N ratio compared to similar background soils. For boreal forests, the multiyear dynamics of soil N deposition is reported to be 0.2-0.5 kg N/ha per year. Nitrogen removal with biomass growth (Equation 9) is calculated similarly to estimates of cation uptake by vegetation:

$$N_{upt} = Y * [N] \text{ ,} \tag{9}$$

where, Y is the annual production of that part of biomass that can be removed from ecosystems, [kg/ha/year]; [N] is the N concentration in the part of biomass under consideration, [g-eq/kg].

As with estimates of cation fixation in phytomass, productivity and N concentrations in the removed or long-term deposited portion of the biomass of plant communities are used to calculate this parameter.

Critical load of nutrient nitrogen ($CL\ (N)_{nutr}$) is calculated according to Equation 10:

$$CL\ (N)_{nutr} = CL\ (N)_{min} + N_{le(acc)} / (1 - f_{de}) \text{ ,} \tag{10}$$

where, $CL(N)_{min}$ is the critical load value of minimum nitrogen; $N_{le(acc)}$ is the permissible leaching of nitrogen from soils into groundwater; f_{de} – is the denitrification coefficient.

The f_{de} coefficient depends on the intensity of denitrification processes in soils. For soils characterized by good drainage conditions, it is suggested to use the value f_{de} =0.1, for soils of heavy granulometric composition with difficult drainage conditions – f_{de} =0.4-0.8 (Table 6).

Table 6. Recommended values of the denitrification coefficient depending on soil drainage conditions

Denitrification coefficient	Soil drainage conditions					
	Excessive	Good	Moderate	Imperfect	Poor	Very poor
f_{de}	0	0.1	0.2	0.4-0.5	0.7	0.8

Direct estimates of denitrification values based on the amount of nitrous oxide (N_2O) emissions can also be used, as well as indirect estimates when conducting experiments with ^{15}N [16].

Nitrogen leaching ($N_{le(acc)}$) as a result of infiltration of atmospheric precipitation through the soil layer is calculated using Equation 11:

$$N_{le(acc)} = 10^4 * Q * [N]_{acc} \text{ ,} \tag{11}$$

where, Q is the average annual volume of moisture percolating through the upper soil layer (see above), [m/year]; $[N]_{acc}$ is the allowable concentration of nitrogen in the soil solution, characterizing the conditions of nitrogen nutrition in different types of ecosystems, [g-eq./m^3]. The values of this parameter in relation to different effects of disturbances in terrestrial ecosystems are presented in Tables 7 and 8.

Table 7. Critical levels of nitrogen in soil solution in relation to the effects of disturbance on species diversity for different types of terrestrial ecosystems

Change of types - edificators	**Critical nitrogen content in soil solution**	
	mg N/m^3	**g-eq./ m^3**
Lichens and oligotrophic shrubs	0.2-0.4	0.0143-0.0276
Oligotrophic shrubs and mesotrophic shrubs	0.4-0.6	0.0276-0.0428
Mesotrophic shrubs and cereal species	1-2	0.0714-0.143
Cereal species and broad-grass species	3-5	0.2143-0.3571

Table 8. Critical levels of nitrogen in soil solution in relation to nutrient imbalance effects for different types of terrestrial ecosystems

Ecosystem types	**Critical nitrogen content in soil solution**	
	mg N/m^3	**g-eq./ m^3**
Coniferous forests	0.2	0.0143

Deciduous forests	0.4	0.0276
Herbaceous biocenoses with a predominance of oligotrophs	1-3	0.0714-0.2143
Herbaceous biocenoses with a predominance of mesotrophs and eutrophs	3-5	0.2143-0.3571

Maximum critical load of nitrogen ($CL(N)_{max}$) is calculated according to Equation 12:

$$CL\ (N)_{max} = CL\ (N)_{min} + CL\ (S)_{max}\ /\ (1 - f_{de}), \quad (12)$$

The parameters included in Equation 12 and their calculation methods are discussed above.

Deterministic and probabilistic methods of calculating CLs. Describing the conditions of the equilibrium biogeochemical state, the model for calculating CL is static. As an input, it usually uses deterministic indicators (constants and averaged values of various parameters). Seasonal, inter-annual and other short-term dynamic changes are not taken into account. In Europe, where in most countries there is a rather detailed network of in-situ monitoring observations, measured averages characterizing areas of territories with a high degree of detail are used to calculate the CL values.

However, when estimating CL for large regions with poorly studied or complex natural structure, there are problems associated with high spatial variability of natural indicators and increased uncertainty of available data. In addition, deterministic calculations do not take into account the natural interannual dynamics of bioclimatic conditions characteristic of all natural-territorial complexes, which from the point of view of long-term assessments also increases the uncertainty of the obtained results (conclusions), reducing their significance for the analysis of environmental risks. A possible solution to this problem is the use of probabilistic methods of calculating CL. In this case, for the input parameters of mass-balance equations and migration flows, ranges or a set of possible (probable) values are determined from literature and cartographic data, which are included in model calculations "randomly", using, for example, the Monte Carlo method. Thus, for each ecosystem (spatial section) a multiple number of "runs" of the model (e.g., 10,000) is performed, which allows for obtaining a range of probable values of CL corresponding to the combination of natural conditions of a particular territory. Analysis of the distribution of the obtained probable values of CL makes it possible to justify the intensity of anthropogenic loads depending on environmental priorities and/or economic feasibility of using territories and their natural resources (Fig. 3).

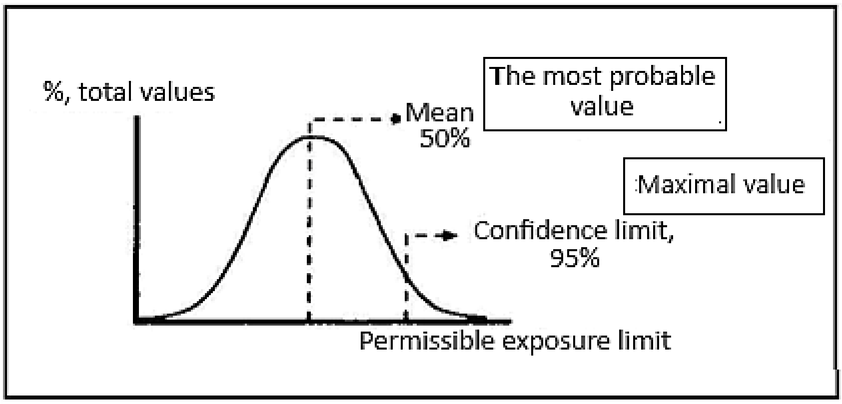

Figure 3. Distribution curve of probable values of CL (permissible loads) of pollutants for a conditional ecosystem.

Below is an example of assessment of permissible levels of impact of acidifying and eutrophying compounds on natural ecosystems, which illustrates the range of possible applications of the CL methodology for the analysis of environmental risks within the framework of environmental protection activities of economic entities and scientific support of the management decision-making process.

Biogeochemical standards for assessing anthropogenic critical loads in impact zones of main gas pipelines

Critical loads of acidifying and eutrophying compounds for ecosystems of the impact zone of the Central Asia-Center main gas pipeline

Estimates of acceptable parameters of anthropogenic nitrogen compounds for arid ecosystems in the zone of the Central Asia-Center main gas pipeline (CAC MGP), during its planned reconstruction, were made on a landscape basis using a probabilistic approach due to the limited nature of the required input information. The available soil, climate and phytogeochemical data were incorporated in the GIS project consisting of several layers of thematic cartographic information (soils, parent rocks, type of land use, precipitation, temperature, cation and anion fallout) and an attribute table of parameters required for calculating the CL values. The spatial distribution of the obtained values of CL of acid-forming compounds (CL (S)max), CL of eutrophying compounds (CL (N)nut) and CL of maximum nitrogen (CL (N)max) within the territory under consideration is shown in Figures 4 - 6.

In accordance with biogeochemical approaches of the CL methodology, the potential of the considered ecosystems resistance to the impact of eutrophying compounds, expressed through the CL $(N)_{nut}$ value, varies in a wide range of values – from 125 to 1400 g-eq./ha per year, which corresponds to the permissible input from 1.5-2 to 18-20 kg N/ha per year. Maximum values of CL $(N)_{nut}$ were calculated for highly productive phytocenoses on meadow-brown semi-desert soils used for pastures; minimum values were for highly sparse communities of solonetz complexes. However, taking into account the potential for additional nitrogen accumulation in the vegetation of the *Chenopodiaceae* family prevailing on solonetz complexes, the values of the permissible nitrogen input for these types of ecosystems, apparently, may be higher – about 5 kg N/ha per year. Ecosystems with the level of CL $(N)_{nut}$ values corresponding to the permissible input of eutrophying compounds of 300-450 g-eq./ha or 4.5-7 kg N/ha per year prevail in most of the territory (Fig. 4).

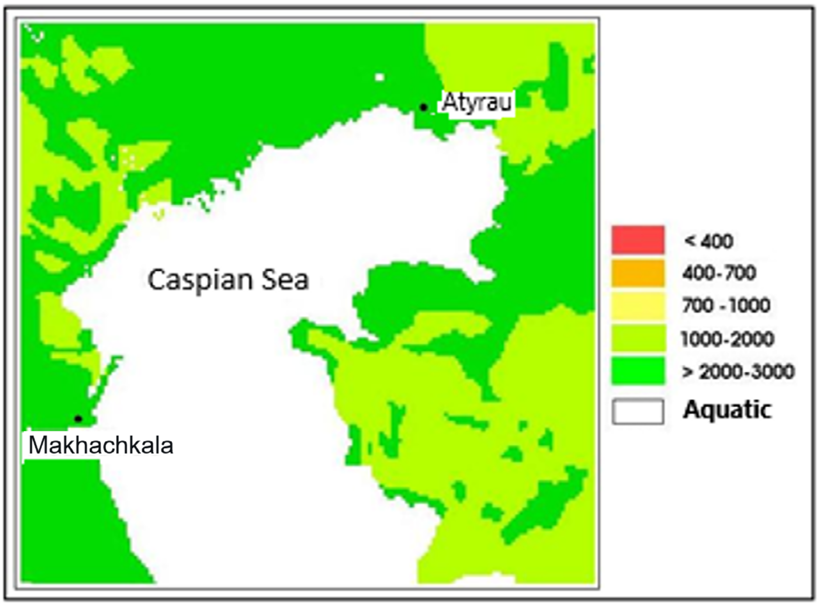

Figure 4. Spatial distribution of CL $(N)_{nut}$ values, g-eq./ha per year

The increased potential of arid zone ecosystems with respect to the acid component of atmospheric deposition determined a high level of calculated values of CL $(S)_{max}$, which in most of the territory are estimated at more than 1000 g-eq./ha per year, which corresponds to the permissible total intake of acidifying compounds equal to 12-15 kg (S+N)/ha per year and higher (Fig. 5).

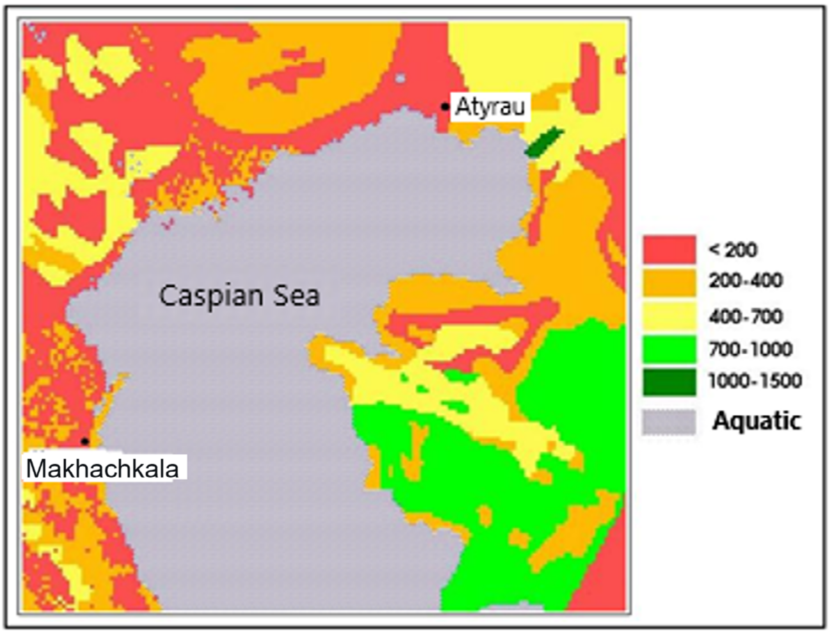

Figure 5. Spatial distribution of CL $(S)_{max}$ values, g-eq./ha per year

The calculated values of critical loads of maximum nitrogen, reflecting the total potential of ecosystem stability in relation to acid and eutrophying components of atmospheric deposition, vary for the territory under consideration from 2450 to 3500 g-eq./ha per year (Fig. 6). For the most part of the territory under consideration, the permissible level of total nitrogen load, according to the results of the performed assessments, is 2600-3100 g-eq./ha or 35-40 kg N/ha per year (in the absence of other acid depositions).

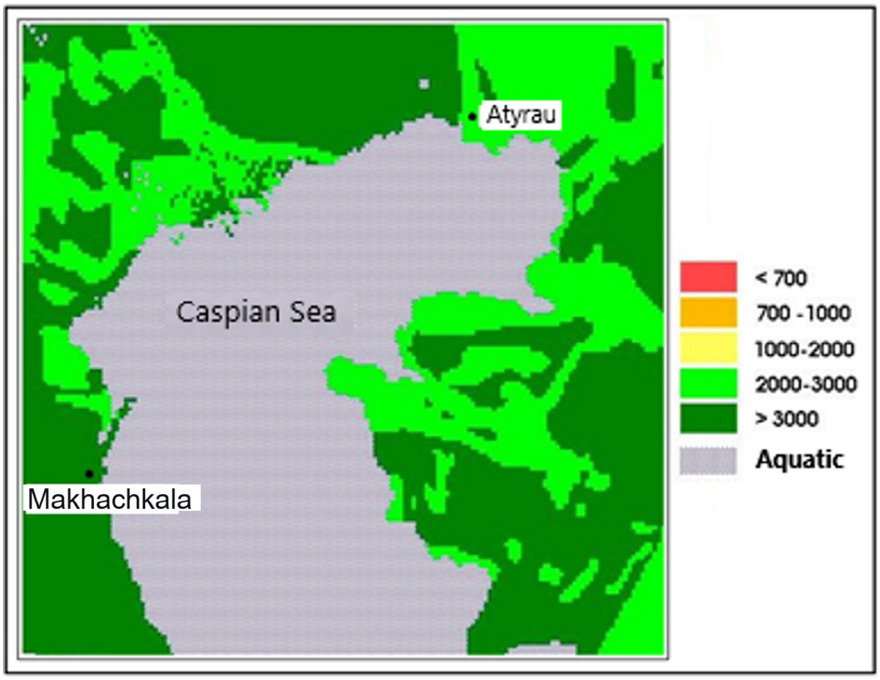

Figure 6. Spatial distribution of CL $(N)_{max}$ values, g-eq./ha per year

The current level of nitrogen oxide deposition within the considered territory of the northern eastern regions of the Caspian region is about 3 kg N/ha per year, which is lower than the calculated CL values.

The spatial distribution of atmospheric NO_x delivery tends to decrease from west to east, being evidence of transboundary transport of nitrogen oxides. As a result of the projected increase in gas transportation volumes via the CAC GMP, the level of nitrogen load is estimated to increase by 4 kg N/ha per year. Comparative analysis of the data shows that at the same time it is possible to slightly exceed the calculated values of nutrient nitrogen load for some ecosystems of solonetz complexes, which are characterized by low parameters of nitrogen removal with vegetation biomass and nitrogen accumulation in soil organic matter. However, despite the results of calculations, the risk of eutrophication of these ecosystems is minimal. No exceedances of critical loads of maximum nitrogen under the considered scenario of the main gas pipeline Central Asia - Center development were revealed.

Anthropogenic critical loads on tundra and forest ecosystems in the impact zone of the head section of the Yamal-West gas trunkline.

Most natural indicators are characterized by natural variability of possible values within certain intervals of values, which is associated with spatial heterogeneity of natural-territorial complexes at the micro- and mesolevel, species and physiological characteristics of living organisms, as well as with daily, seasonal and interannual dynamics of functioning of the biosphere components. The parameters of biogeochemical balance of elements in ecosystems also depend on a large number of biotic and abiotic factors. Taking into account the general concepts of geochemical ecology and environmental epidemiology, disturbances in the structure and/or functions of biological objects under external impacts manifest themselves after exceeding a certain threshold or critical level of recipient exposure (Fig. 7). Naturally, in complex biological systems (including ecosystems) characterized by a variety of components of the biogeochemical cycle and the already mentioned variability of indicators in time and space, it is very difficult to determine the value of the critical level of impact as a reliable point value, especially when it comes to assessments in a relatively long-term perspective (25-50 years). More correct parameters of permissible impacts - critical loads as biogeochemical standards can be obtained using probabilistic calculation methods that make it possible to determine the most reliable interval of possible CL values.

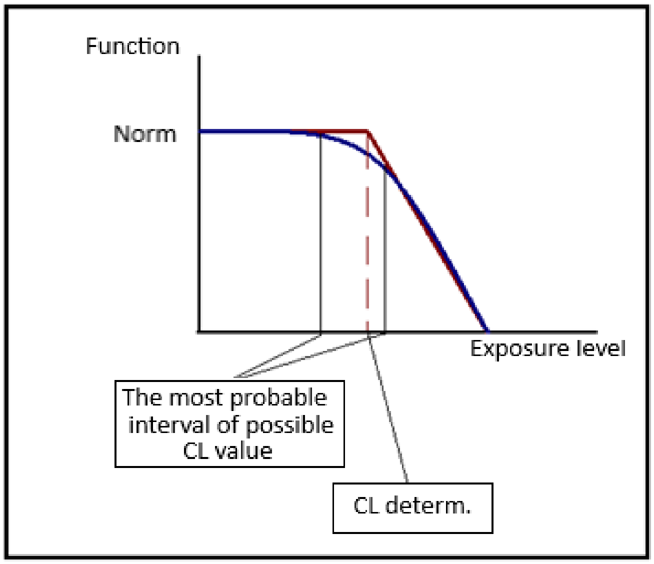

Figure 7. Correlation of the CL indicators calculated using deterministic and probabilistic methods

Using the example of terrestrial ecosystems in the impact zone of the Yamal-West gas pipeline head section, the above traditional algorithm for calculating nitrogen CL values with respect to eutrophying and acidifying effects (Table 9) was used for probabilistic IP assessments. For the input parameters of mass-balance equations and the equations characterizing the intensity of migration fluxes of elements in ecosystems, the ranges of possible values were determined from literature and cartographic data and included in the calculations using the Monte Carlo method. The total number of model “runs” for each ecosystem was 10,000, which made it possible to obtain a probabilistic distribution of possible CL values at different ratios of factors determining the resulting value. Subsequent verification showed that such a number of “runs”, despite the randomness of the samples obtained, ensure high repeatability of the results.

Table 9. Algorithm for calculating CL values of cidifying and eutrophying nitrogen compounds and sources of the data used

Conventional designations	Parameter name	Units	Formula for calculation/data source
$*CL(S)_{max}$	Critical load of maximum sulfur	g-eq./ha/year	$= BC_{dep} - Cl_{dep} + BC_{w} - Bc_{upt} - ANC_{le(crit)}$
$*BC_{dep}$	Input of main cations (Ca, Mg, K, Na) from the atmosphere	g-eq./ha/year	Modeling data of atmospheric deposition of major cations from MSC-East (www.msc-east.org)
$*Cl_{dep}$	Chlorine ions entering from the atmosphere	g-eq./ha/year	Modeling data of atmospheric deposition of major cations from MSC-East (www.msc-east.org)
$*BC_{w}$	Intrasoil weathering of cations (Ca, Mg, K, Na)	g-eq./ha/year	$= BC_w(T^0) * 2{,}6^{(A/T0 - A/T)}$
$BC_w(T^0)$	Total weathering of cations for a 1m soil layer at a temperature T^0=281 ^{O}K	g-eq./ha/year	It was assessed depending on the class of soil texture in accordance with: [11]
*T	Average annual temperature for the study area	^{O}K	Spatially distributed data (www.cru.uea.ac.uk)
A	Coefficient	-	= 3600
$*Bc_{upt}$	Immobilization of cations (Ca, Mg, K) in wood biomass removed by logging or grazing	g-eq./ha/year	$= Y_{wood} * ([Ca] + [Mg] + [K])$
$*Y_{wood}$	Mass of wood removed by logging per year (or biomass removed by grazing)	kg/ha/year	$= Z * f_{wood}$
*Z	Timber reserves	kg/ha	[10]
$*f_{wood}$	Proportion of timber removed by felling	%	[10]
* [Ca]+[Mg] +[K]	Concentration of cations in wood (or pasture biomass)	g-eq./kg	[10]
$*ANC_{le(crit)}$	Critical alkalinity leaching	g-eq./ha/year	$= - Q_{le} * ([H]_{(crit)} + K_{gibb} * [H]^3_{(crit)})$
$*Q_{le}$	Precipitation infiltration layer	m	Spatially distributed data calculated based on: www.cru.uea.ac.uk
$[H]_{(crit)}$	Critical concentration of hydrogen ions in soil solution	г-экв./м^3	According [8] = 0.1 for coniferous species; = 0.01 for deciduous species
K_{gibb}	Gibbsite coefficient	m^6/g-eq.^{2}	= 300
$*CL(N)_{nut}$	Critical load of nutrient nitrogen	g-eq./ha/year	$= N_{im} + N_{upt} + N_{le(acc)} / (1 - f_{de})$
$*N_{im}$	Long-term immobilization of nitrogen in the soil	g-eq./ha/year	[10]

$*N_{upt}$	Nitrogen fixation in wood biomass	g-eq./ha/year	$= Y_{wood} * [N]$
* [N]	Nitrogen concentration in wood	g-eq./kg	[10]
$*N_{le(acc)}$	Permissible N leaching	g-eq./ha/year	$= Q_{le} * [N]_{acc}$
$*[N]_{acc}$	Critical N concentration in soil solution	g-eq./m^3	[8]
f_{de}	Coefficient of N denitrification in soil	-	= 0.1 (soils with good drainage conditions); = 0.4 (soils with variable moisture); = 0.5 (soils with constant moisture)
$*CL\ (N)_{max}$	Critical load of maximum nitrogen	g-eq./ha/year	$= N_{im} + N_{upt} + KH\ (S)_{max} /(1 - f_{de})$

* - probable values

The database for probabilistic calculations of CL values was formed as a GIS project in the ArcView software environment, which allowed for current analysis and visualization of the obtained data. The spatial resolution (detail) of the input data and the obtained CL values correspond to the spatial allocation of 1x1 km^2. When analyzing the obtained results of probabilistic estimates of individual mass-balance parameters and CL values, 25%, 50%, 75% and 95% levels of values corresponding to each "ecosystem" were considered (Fig. 8).

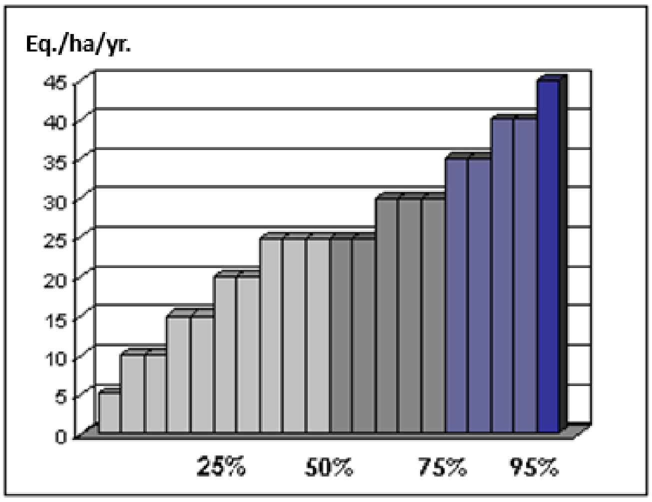

Figure 8. Example of a cumulative distribution of possible CL values for a conditional ecosystem

As a result of these studies, an extensive array of spatially distributed information characterizing the specifics of biogeochemical cycling of nitrogen and associated macroelements in different zonal and intrazonal types of impact tundra and taiga ecosystems was obtained. The most typical harvesting scenarios (selective, gradual, sanitary) were considered for forest ecosystems. For grass and shrub-grass ecosystems of the forest zone and forest tundra, the considered management scenario included the "use" of territories as pastures, including in the northern areas for reindeer herding.

The analysis of the obtained results indicates a high differentiation of the ecosystems of the considered zone with respect to most parameters of the mass balance of nitrogen and associated macroelements. For example, according to the obtained estimates (Fig. 9), the removal of nitrogen from forest ecosystems of the taiga zone with wood growth under different logging options varies from 0.5-1.5 kg N/ha per year (or 35-100 g-eq/ha) in tundra mixed forests to 6-10 kg N/ha per year (or 400-700 g-eq/ha) in mid-taiga spruce forests.

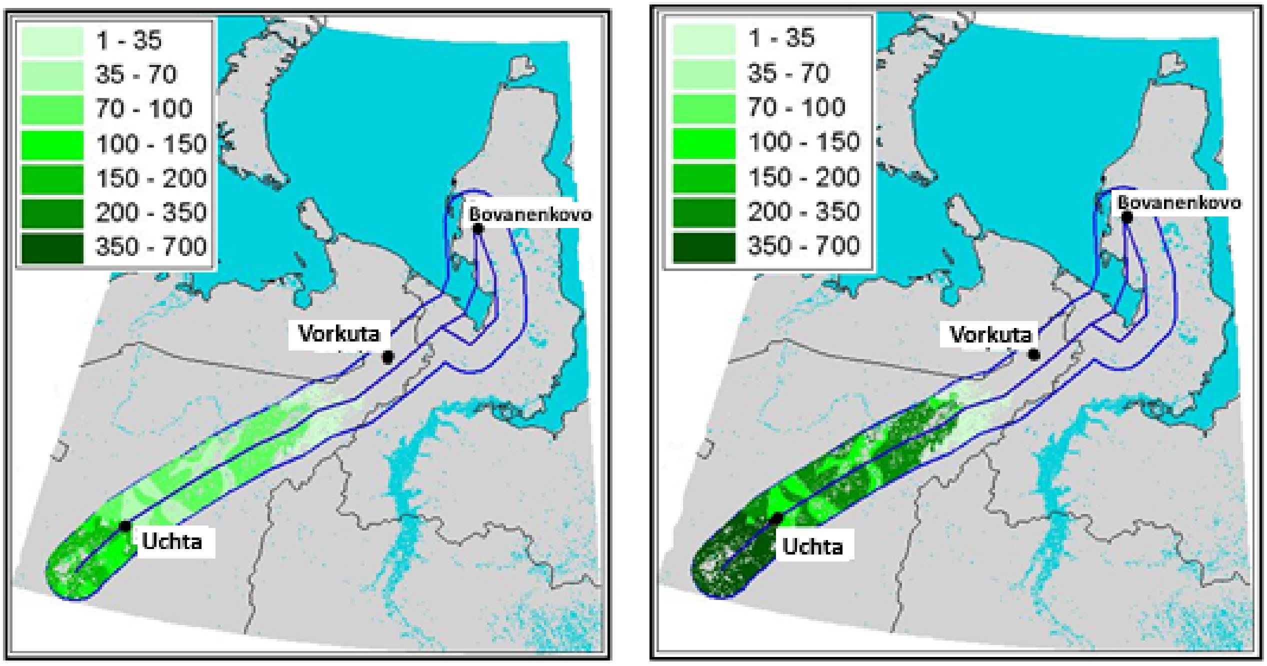

Figure 9. Distribution of nitrogen fixation values (g-eq/ha per year) in wood products at 25% (left scheme) and 95% (right scheme) levels of values

Two scenarios were considered when assessing the allowable levels of N removal with soil-soil water, corresponding to the prevention of the effects of N nutrition imbalance for edifiers (woody species in forests and terrestrial species in herbaceous biocenoses) and the effects of reduced biodiversity of ground cover (Fig. 10). In the first case, these values can be 70-160 g-eq/ha per year (or 1-2.5 kg N/ha), while the level of nitrogen concentrations in the soil solution corresponds to 0.2-0.4 mg N/l depending on the edifier species. The effects of biodiversity disturbance, manifested in the change of species due to the increase in the share of nitrophilous vegetation and the disappearance of oligotrophic vegetation, are manifested in conditions when nitrogen concentrations in the soil solution exceed 0.2-0.4 mg N/l for lichens and mosses, 1 mg N/l for dwarf shrub species, and 1-3 mg N/l for sedges and grasses. Taking into account the high level of precipitation and climate humidity typical for the study area, the calculated parameters of the permissible leaching of nitrogen with soil and groundwater runoff ranged from 100 to 700 g-eq/ha per year (or from 1.5 to 10 kg N/ha) for subarctic and typical tundra, and from 500 to 1000-1200 g- eq/ha per year (or from 10 to 15-18 kg N/ha) for forest areas.

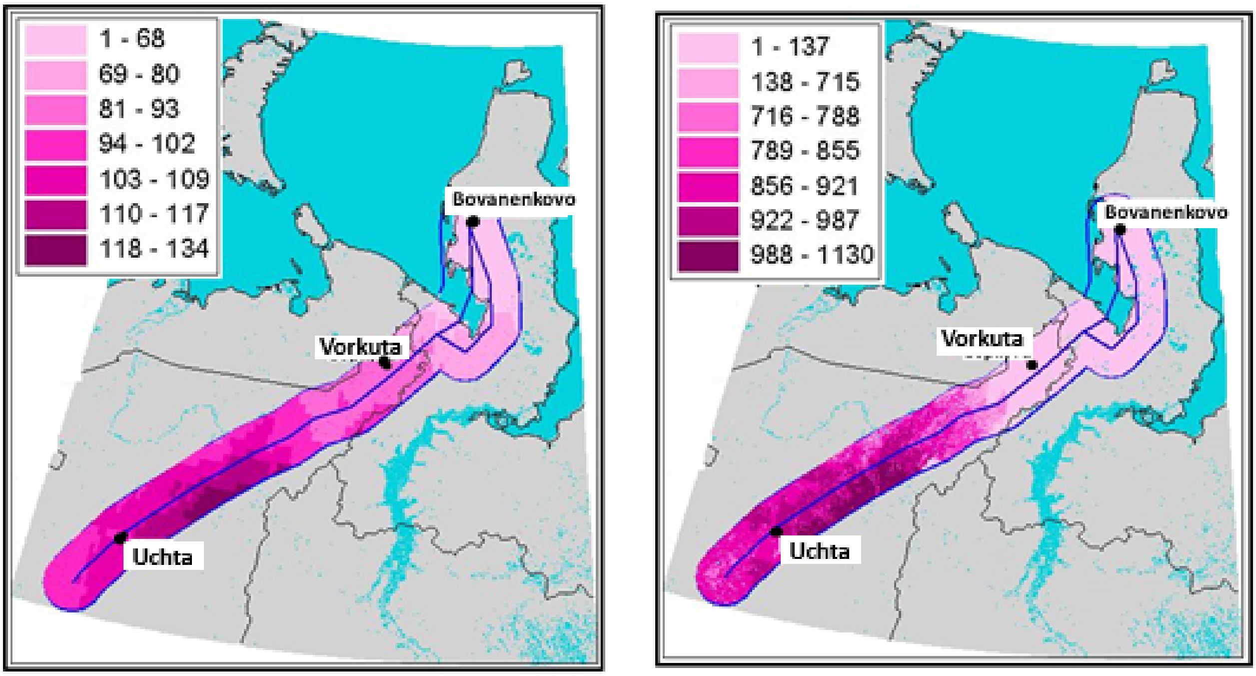

Figure 10. Distribution of allowable nitrogen leaching rates (g.-eq/ha/year) at 75% level of values for nitrogen nutrition imbalance effects (left scheme) and biodiversity disturbance effects (right scheme)

The distribution of acidity CL corresponding to 25%, 50%, 75% and 95% levels of values is shown in Figure 11. As can be seen from the above schemes, the entire study area can be conditionally divided into 2 parts according to the neutralization potential of the acid component of atmospheric precipitation: northern (tundra) and southern (forest). Within the forest zone, the minimum CL acidity values are characteristic of wetland ecosystems. This differentiation is caused by a whole complex of factors related to temperature conditions, moisture regime of territories, soil texture and vegetation types. According to the calculated values, the permissible level of acid deposition for tundra and waterlogged grass ecosystems averages 100-200 g-eq/ha per year, while in forest ecosystems the range of values obtained varies from 300 to 700 g-eq/ha per year. It was revealed that middle taiga forests have a reduced potential for neutralizing acid deposition compared to northern taiga phytocenoses, which can be explained by more active deposition of soil cations in the biomass of more productive forest stands of the middle taiga subzone

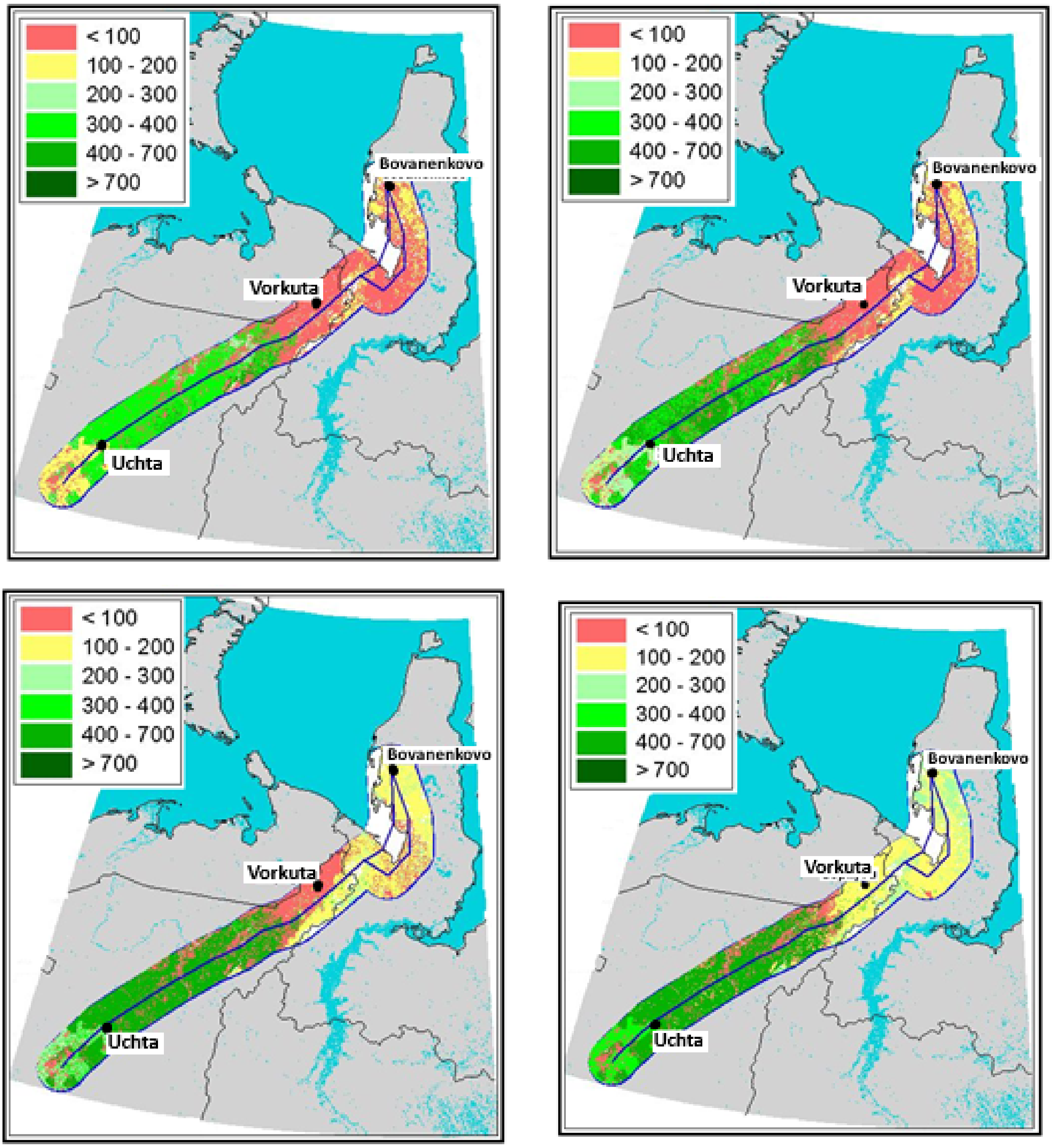

Figure 11. Distribution of CL values of acidifying compounds (g-eq/ha per year) at 25%, 50%, 75% and 95th levels of probable values

The calculated CL values with respect to the effects of nutrient imbalance for ecosystems in the forest-tundra zone are 150-350 g-eq/ha per year (or 2-5 kg N/ha). For forest ecosystems, the level of allowable nitrogen input with atmospheric deposition is estimated at 350-700 g-eq/ha per year (or 5-10 kg N/ha), Fig. 12. With respect to the effects associated with the risk of disturbance of species diversity, close CL values were obtained for tundra ecosystems, since similar critical nitrogen concentrations in the soil solution were used in the calculations. For forest ecosystems, the CL values are higher and amount to 700-1000 g-eq/ha per year and higher, which corresponds to an input of 10-15 kg N/ha per year or more (Fig. 13).

The obtained results of estimation of CL values make it possible to rank ecosystems in the impact zone according to the degree of their resistance to atmospheric nitrogen deposition, which can be used in environmental risk management during gas transportation from the Far North fields to various consumers.

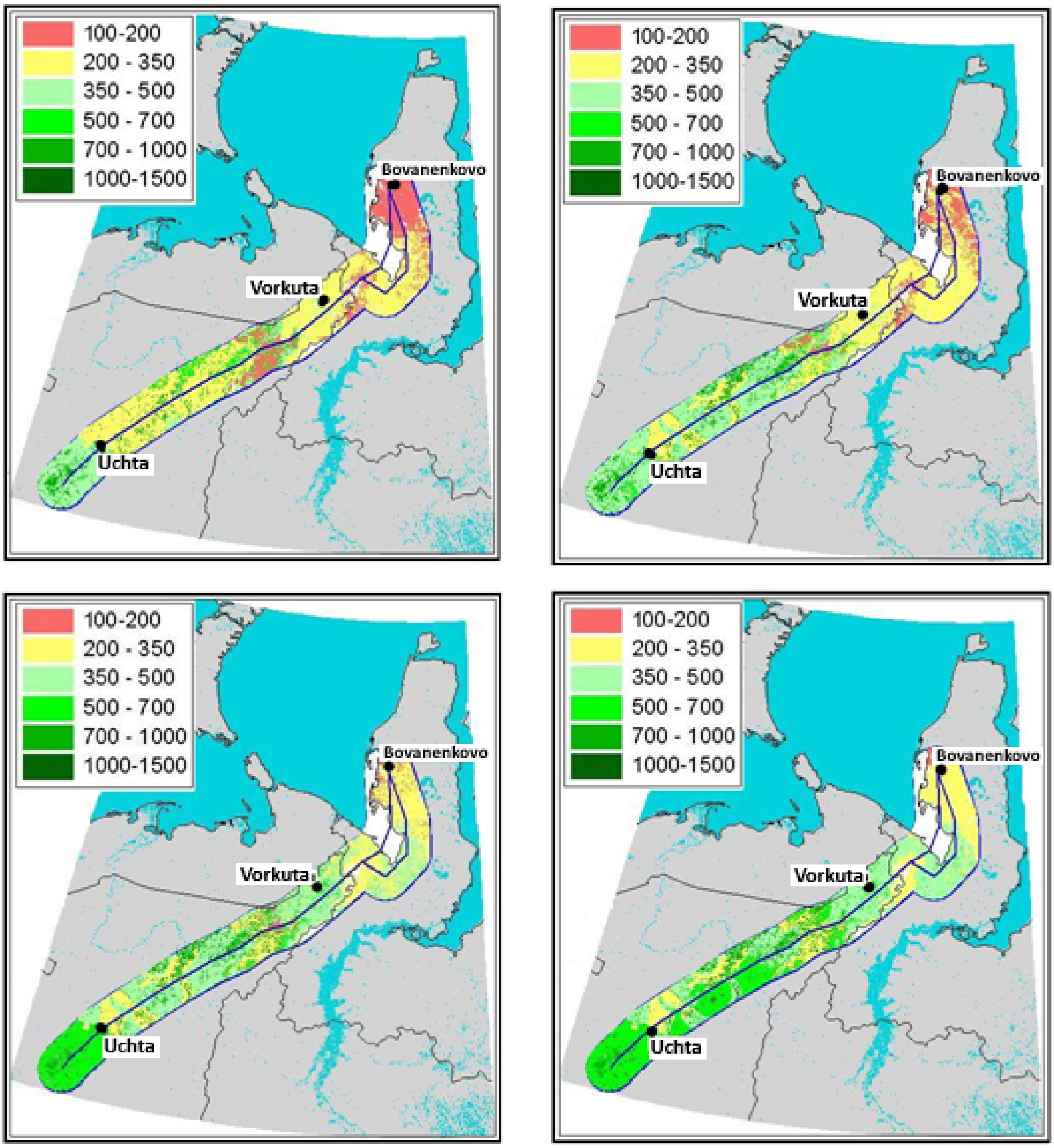

Figure 12. Distribution of CL values of the of eutrophying compounds in relation to nutrient element imbalance (g-eq/ha per year) at 25%, 50%, 75% and 95th levels of probable values

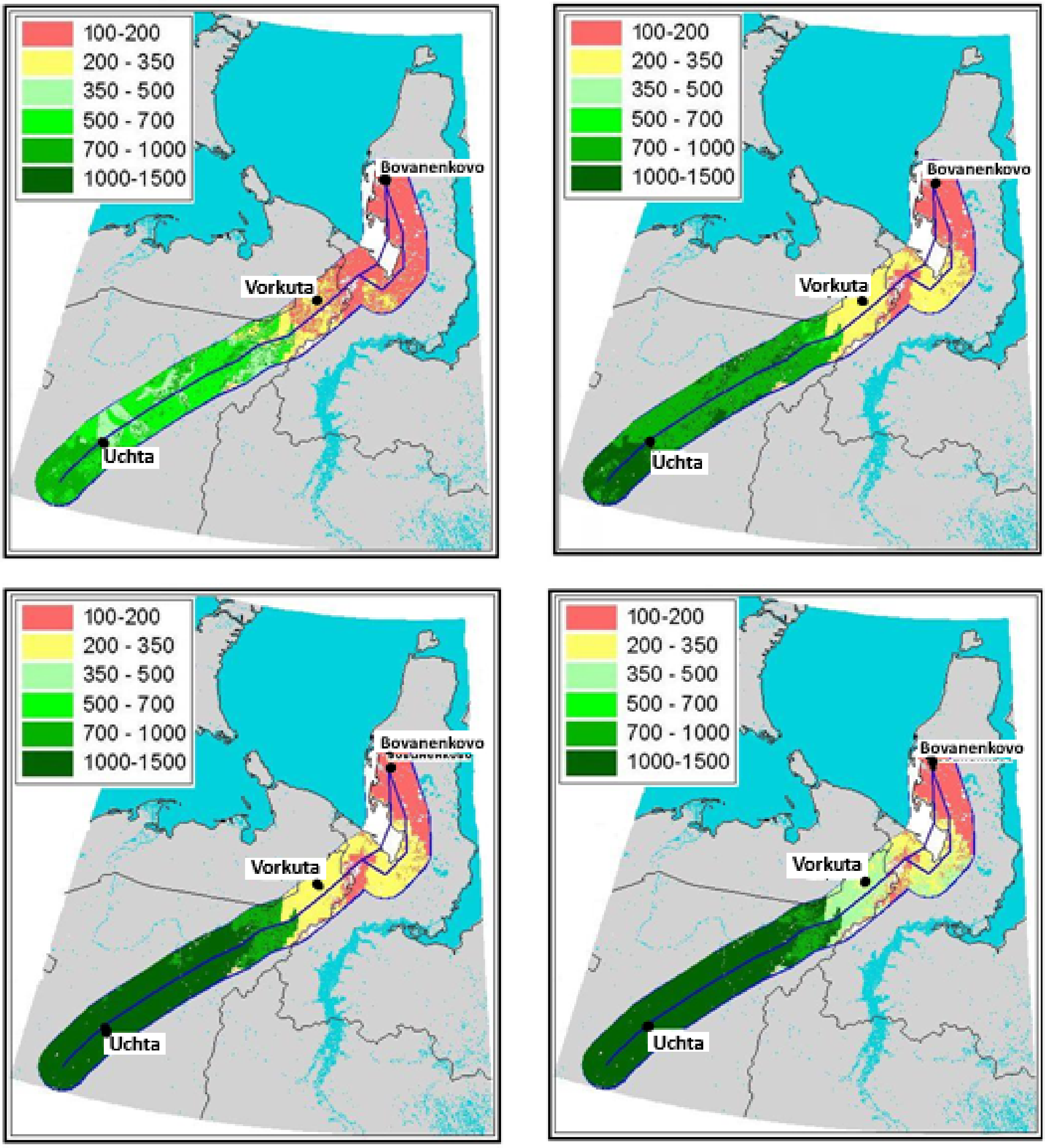

Figure 13. Distribution of CL values of eutrophying compounds in relation to disturbances of species diversity of phytocenoses (g-eq/ha per year) at 25%, 50%, 75% and 95th levels of probable values

Conclusion

Thus, quantitative methods for calculating critical loads as biogeochemical standards are based on the use of simple biogeochemical mass-balance models of elements. The assessment of critical loads can take into account certain conservation priorities determined through the selection of recipients (preservation of specific natural objects) and the establishment of appropriate biogeochemical indicators. Currently, biogeochemical standards are used in the development of biogeochemical technologies as technological parameters, which is relevant, in particular, in reclamation and remediation works, and risk probability assessment.

Financing

The work was carried out within the framework of the theme of the Ministry of Science of the Russian Federation ‘Biogeochemical processes of transformation of mineral and organic matter of soils at different stages of the evolution of the biosphere and technosphere (0191-2021-0004).

Acknowledgments

The author thanks I.V. Priputina (Ph.D), Institute of Physicochemical and Biological Problems of Soil Science, Russian Academy of Sciences; A.V. Tankanag (Ph.D), Institute of Cell Biophysics, Russian Academy of Sciences; and R.A. Galiulina, Institute of Fundamental Problems of Biology, Russian Academy of Sciences, for their assistance in collection, analysis and representation of materials.

Conflict of interests

The author declares that he has no conflict of interest.

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