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## ECOLOGICAL ASSESSMENT AND REGULATION OF SOIL POLLUTION

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# Assessment of Current Risks of Excessive Heavy Metal Accumulation in Soils Based on the Concept of Critical Loads: A Review

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**Abstract**—At the international level, the concept of critical loads developed under the Convention on Long-Range Transboundary Air Pollution directed by the United Nations Economic Commission for Europe is actively used to assess the risks of excessive inputs of pollutants into ecosystems. The review considers the main principles of the concept of critical loads and methods of its application for assessing the current risks of excessive accumulation of heavy metals (HMs) in soil as a component of terrestrial ecosystems from the standpoint of ecotoxicological effects (on plants, soil invertebrates, and microorganisms). Under this concept, the critical concentrations of Cd, Pb, Cu, and Zn for soils are for the first time estimated using the functions of critical concentrations taking into account the properties of soils (primarily, acidity and the contents of organic matter and clay). The main attention is paid to the rationale and development of the models for assessment of the critical concentrations and transfer functions connecting the concentrations of HM compounds in soils and soil solutions. The current environmental risks of excessive HM accumulation are assessed by comparing them with their critical concentrations. Current challenges and future prospects for analyzing the current environmental risks based on the concept of critical loads include the reduction in the uncertainty of estimates, combined effect of different metals in a multicomponent pollution, field validation of processes and modeling results, and the impacts of climate change and land use.

**Keywords:** environmental risks, critical concentration functions, bioavailability, ecotoxicity, biotic ligand models

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## INTRODUCTION

In the recent decades, ever increasing environmental pollution with heavy metals (HMs) caused by intensive industrialization, urbanization, and agricultural production has been accompanied by their accumulation in soil and toxic effect on plants, soil biota, and, eventually, humans [43, 50, 102]. Vast areas of soils affected by adverse anthropogenic impact in Europe [76, 101] and the world [43] demonstrate a global character of soil pollution. The environmental risk of soil pollution with HMs is especially high in the territories adjacent to large integrated industrial facilities [3, 6, 42, 60], megacities [26], and/or areas subject to long-term agricultural cultivation [52, 53], where the HM input from anthropogenic sources considerably exceeds the natural input.

Anthropogenic soil pollution belongs to the priority environmental challenges and their resolution requires basic knowledge and scientifically grounded methodological approaches. Soils play a special role in the interaction of biosphere and pollutants because the buffer properties of soils determine not only the

degree of changes in soils themselves caused by the anthropogenic impact, but also the amount of pollutants entering other components of ecosystems (living organisms, ground and surface waters, soil-forming rock, and, potentially, oceans) [50]. The accumulation of pollutants in soils is accompanied by a long-term negative impact on ecosystems. The problem is frequently aggravated by an unfavorable combination of natural and anthropogenic factors, leading to the level of pollutants exceeding the corresponding values toxic to biota. Thus, it is necessary to quantitatively analyze, estimate, and predict the limits of soil transformation and stability with regard to pollutants and the risks of their excessive accumulation in soils taking into account the integrated impacts of many factors in order to control the negative effects on ecosystems, to determine the priorities in remediation of polluted soils, and remediation efficiency.

The goal of the work was to analyze the capabilities, advantages, and limitations of the concept of critical loads in assessing the current risks of excessive HM accumulation in soils as components of terrestrial ecosystems at the present stage of development.

## THE CONCEPT OF CRITICAL LOADS

At the international level, the concept of critical loads developed under the Convention on Long-Range Transboundary Air Pollution (CLRTAP) directed by the United Nations Economic Commission for Europe is actively used to assess the risks of excessive inputs of pollutants into the ecosystems.

Critical load is the maximum input rate of pollutants (with precipitation, fertilizers, and other sources) below which long-term harmful effects on human health as well as the structure and function of ecosystem in the site of interest do not occur according to present knowledge [54]. The critical HM loads are calculated based on the balance of all significant input and output metal fluxes in a considered ecosystem in a future steady-state situation [27]. The potential risks or the exceedance of critical loads in different scenarios of pollutant emissions can be used for development of emission-abatement strategies that balance environmental risks and economic costs [54].

Initially, this concept was elaborated in the mid-1980s and has been widely used since that time for assessing the critical loads for acidifying pollutants (S and N), for comparing them with the current atmospheric load, and for devising the strategy to decrease the pollutant emissions to the atmosphere [27, 29, 70, 95]. The first approaches to assessment of the critical HM loads for terrestrial [31] and aquatic [32] ecosystems were proposed in the 1990s. The recent CLRTAP methodology manual was approved for the “priority metals”, namely, Cd, Pb, and Hg [27, 38, 104]. The focus on these metals is associated with the fact that they were included into the CLRTAP Protocol on Heavy Metals (1998), ratified by 29 countries, which entered into force at the end of 2003. The protocol pays attention not only to ecotoxicological risks for terrestrial ecosystems, where the atmospheric deposition of metals is the only external source, but also to toxicological risks for humans, agrosystems included. As for the agrosystems, the load there comprises the application of fertilizers, manure (sometimes, wastewater sludge), and atmospheric deposition. Currently, the list of metals and metalloids is extended to Cd, Pb, Cu, Ni, Zn, Cr, Hg, As, and Se [62, 82]. The Coordination Centre for Effects (CCE; [https://www.umweltbundesamt.de/en/Coordination\\_Centre\\_for\\_Effects](https://www.umweltbundesamt.de/en/Coordination_Centre_for_Effects)) and the International Cooperative Programme on Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends (ICP M&M; <https://unece.org/modelling-and-mapping>) are responsible for elaboration and agreement of the computation techniques and construction of the unified database and maps of critical loads and their exceedance.

The development and use of these scientifically grounded approaches have made it possible to assess the long-term permissible HM input into the terrestrial ecosystems of Europe [34–37, 51, 81, 90, 92] and

Canada [40, 67]. As for Russia, the Meteorological Synthesizing Centre—East (MSC-E; <http://www.msceast.org>) is involved in the assessment of the HM transboundary transfer and deposition on a regular basis. However, the critical loads for terrestrial ecosystems have been estimated only in few cases for acid deposition [1, 4, 7, 12, 19, 58] and even more rare cases for HMs [5, 51], which, unfortunately, has had no effect on the actual regulation practices.

## ASSESSMENT OF CURRENT RISKS OF EXCESSIVE HEAVY METAL ACCUMULATION IN SOIL

The above-considered approach to the analysis of risks relying on the comparison to critical loads, which reflect the acceptable rates of pollutant input to terrestrial ecosystem, is intended for a preventive estimation of the risk associated with future input of pollutants. However, this does not allow the current risks of excessive HM content in soils resulting from the accumulated pollution to be assessed [62]. This problem is solved by comparing to the threshold values (critical concentrations or environmental quality standards). The HM concentrations in soils and/or soil solutions that have no significant adverse effect on plants and soil biota are regarded as critical concentrations [35, 37]. The critical (threshold) impact corresponds to a conventional probability to observe negative biological effects or, in other words, conventionally acceptable risk.

The key stages in the assessment of current risks for excessive HM accumulation comprise (1) selection of recipients; (2) determination of the critical HM concentrations for plants, microorganisms, and invertebrates in soil; and (3) finding of the transfer functions describing the links between different compounds of HMs in soil solid and liquid phases depending on their properties [35, 37].

**Selection of recipients.** The concern over the input of metals to terrestrial ecosystems is associated with (1) ecotoxicological effect on soil organisms, plants, and aquatic organisms because of the runoff to surface waters and (2) the uptake by animals via the food chain, which may have adverse consequences for the health of animals and humans [35, 37]. The impact on soil organisms, including microorganisms and invertebrates, such as nematodes and earthworms, leads to a decrease in species diversity, abundance, and biomass [20]. The effect on vascular plants manifests itself in toxic (slowdown of root and shoot growth and development), physiological (an increase in starch and total sugar concentrations and a decrease in nutrient content in leaf tissues), and biochemical (a decrease in enzyme activities) [17, 18, 23, 80] symptoms. The influence on hydrobionts, including algae, crustaceans, and fish affects the respiratory function, nervous system, as well as the growth and reproduction rates. The environmental quality standards or the critical limits for metals in soil and surface water based

**Table 1.** Critical concentrations of heavy metals determined in early ecotoxicological studies, mg/kg

Indicator (medium)	Cd	Cu	Ni	Pb	Zn	Reference
Mean content in soil	0.35	30	50	19	70	[49]
Critical/ecotoxicological concentrations						
Plants (soil)	3–5	60–125	100	50–400	70–400	[55]
Plants (solution*)	0.01–0.11	0.02–0.1	–	0.1–0.21	0.1–1.0	[103]
Decomposition and accumulation of plant residues**	1.1–885	41.4–1400	640–1300	255.6–8500	282–25750	[17]
Carbon mineralization**	1.1–600	25–1400	6.6–1200	78–11872	71–2000	[17]
Nitrogen transformation**	2–200	15–1445	2–50	200–8000	30–26000	[17]
Enzyme activity**	1.56	25–1900	1200	78–1700	71–1900	[17]
Enzyme activity	3–>100	–	–	700–>1000	300–>10000	[8]
Microbial biomass**	4.7–1120	15–61139	6.6–1900	22–21320	139–75826	[17]
Microbial biomass (forest litter/humus)	19–1120	71–2600	1900	260–7562	300–41 100	[103]
Soil invertebrates in forest litter	–	657–2509	–	132–230	1165–3585	[103]
Soil invertebrates mineral layer (0–2 cm)	26–885	78–2500	–	34–4800	171–25750	
Soil invertebrates	10–50	<100	–	100–200	<500	[20]
Soil organisms (litter)	1.7	–	–	320	110	[107]
Threshold limit values						
Total content in soil	3–3.5	50–100	30–50	50–100	150–300	[55]
	$0.4 + 0.007 \times (L + 3H)^{***}$	$15 + 0.6 \times (L + H)^{***}$	–	$50 + L + H^{***}$	$50 + 1.5 \times (2L + H)^{***}$	[32]
Concentration in soil solution*	0.02	0.02	–	0.1	0.2	[32]
Mobile metals in soil		3.0	4.0		23.0	[11]

\* mg/L; \*\* field experiments with forest litter, soil mineral layer, and peat; and \*\*\* L, clay and H, organic matter, %.

on these impacts are used in the assessment of environmental risks [35].

In addition to a direct impact on soil organisms, metals can be transferred via the food chain, causing an adverse effect on animals and humans (secondary intoxication). The accumulation of HMs in food chain is especially relevant for Cd and Hg and, to a lesser degree, for Pb, the biological functions of which in terrestrial organisms are vague [35]. The concern over an excessive input of Cd, Cu, and Zn into crops is also observed in several countries [52, 53]. The excessive amounts of these metals can decrease the crop yields and food quality [35].

In general, a wide range of selected recipients is determined by the tasks of environmental protection and, correspondingly, has a certain political aspect. It is possible to select a priori the most important recipients and to determine the major exposure pathways based on the factors, such as land use or social and political considerations [62]. This review concerns exclusively soils as components of terrestrial ecosystems and the critical HM concentrations are justified depending on the ratio of direct and indirect impacts

on the recipients, such as plants, soil microorganisms, and invertebrates.

**Selection of threshold or critical concentrations,** which guarantee protection of the most sensitive components of ecosystems, is an exclusively important and difficult problem. The critical concentrations for plants and soil microorganisms determined under laboratory conditions vary in a wide range depending of the recipient organisms and the type of biogeochemical processes (Table 1).

Ecotoxicologists utilize the concentrations that have no observed effect (No Observed Effect Concentrations, NOECs), causing a minimum observed effect (Lowest Observed Effect Concentrations, LOECs), or maximum acceptable toxicant concentrations (MATCs; the geometric means of NOEC and LOEC) as the ideal threshold values for the impact of pollutants. Experimentally measured toxicological characteristics  $EC_5$  and  $EC_{10}$  (or calculated from the most reliably measurable  $EC_{50}$  when the exposure-response model is known) are quantitatively close to these ideal criteria; here  $EC_x$  is the concentration of

pollutant at which its effect is observed in  $x\%$  cases as compared with the control group of measurements. As typically being more reliably determinable (less variable comparing with NOEC, LOEC and MATC), the conventional characteristics  $EC_5$  and  $EC_{10}$  are ever more frequently used as the threshold concentrations of the pollutant impact causing the minimum share of negative effect [109]; they are figuratively referred to as surrogate NOECs.

Note that the majority of limit values accepted in the regulation are mainly associated with the total metal contents in organic or mineral soil layers [8, 17, 103]. In addition, these limits are still frequently expressed as unified values for soil or calculated as a weighted mean for soil components omitting the ecotoxicological estimates [35].

The use of unified total content of metals in soils does not comply with the requirements of correct indication of potential negative impacts and receives fair criticism [2, 10, 15, 35, 37, 93]. Indeed, the use of the content of metals as a critical limit for ecotoxicological effect on soil organisms does not take into account the observed specific features in the toxicity of metals in the soils differing in their chemical properties [94]. Currently, most scientists believe that the differences in toxicity for many organisms are determined by the uptake of metals from soil solution [83]. It is only the soluble and mobile fraction that can be leached or taken up by plants and further enter the food chain [84]. Solubility, mobility, and bioavailability of metals depend on diverse soil, microbial, and plant factors as well as on the properties of metals themselves. The soil properties, such as pH, cation exchange capacity, and the content of organic matter and clay particles considerably influence the bioavailability and toxicity of metals to biota [13, 37, 48, 94, 108].

**Rationale and development of the models for assessing critical concentrations.** The assessment of the risk of HM pollution of terrestrial ecosystems is based on the concept of the hazard of HM accumulation in living organisms, their direct input to soil biota and uptake by vegetation by roots, and their further impact on animals via the food chain. Among these processes, those at the boundary between the living organism and water are decisive [9, 71], while the conceptual frameworks of the chemical toxicity model coincide for the aquatic and terrestrial (soil) ecosystems. Initially, it was believed that among the mobile HM compounds, the concentration of HM free ions or their chemical activity in soil solution correlates best with their uptake by vegetation and function of microorganisms [25, 79] and, as a consequence, determines the toxic general impact on ecosystems.

The activity of HMs may not be the optimal chemical characteristic of their toxic effects; in particular, the biological response of hydrobionts better correlates with the HM accumulation in individual organs as compared with the concentration of free HM ions

in water [25]. As has become clear, it is necessary to take into account the chemical interaction of HMs directly with biomolecules of organism's target organs considered as an ensemble of individual positions where metals can be bound [56, 77]. The chemical model describing the binding of HM ions to biomolecules [39, 91, 96] is among the most advanced tools for analyzing the HM toxicity. This model permits one to simultaneously consider the competitive formation of HM complexes with abiotic ligands (dissolved organic matter, carbonates, chlorides, sulfides, etc.) and the competition between the free cations of toxic HMs and natural cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $H^+$ ,  $K^+$ ,  $Na^+$ , etc.) in surface and ground waters for binding to biotic ligands. At first, the free HM ions interact with physiologically active zones of biomembranes (for example, ion channels and translocases) and then usually (but not necessarily) enter the living organism. The direct binding of toxic HMs and competitive inhibition of the uptake of cations necessary to the organism are the main factors that determine the toxic effect of HMs [72, 91].

The key papers [39, 78, 88] have formed the conceptual and technical background for the process-oriented modeling of biotic ligands and demonstrated the usefulness of this model in prediction of the acute HM toxicity to hydrobionts. Although these papers are based on the assumption of a short-term HM load on a biotic ligand as the key factor inducing a long-term toxicity, they demonstrate that it is easier to assess the HM load when constructing the model by solving the inverse problem utilizing the experimental data on toxicity rather than to measure this load. As compared with the number of models of this kind developed later, the studies that determine the physiological mechanisms of actual HM accumulation in biotic ligands are rather few. Actually, the transition to this kind of modeling of the correlation between the load on a biotic ligand and environmental toxicity supports only the conceptual mechanistic framework that the theoretical critical load of HMs on the ligand causes the critical toxicity level. In part, this approach has emerged out of practicability associated with human efforts, technical complexity, and high cost of experimental measurements of HM loads and, in part, is determined by the fact that such measurements in many cases are simply unfeasible. Even when measuring the HM concentration in a tissue or an organ, this concentration at the site of HM toxic impact is most likely not the only measured load. Instead, it is usually assumed that the measured concentration in a tissue or in an organ is proportional to the concentration at the site of the impact, which cannot be currently measured. For most HMs, the mechanisms of chronic toxicity and, correspondingly, biotic ligand targets are still poorly studied [68].

It is the adequacy of the made simplifications of both chemical and, especially, biological submodels (consideration of extremely complex living systems—individual organisms and communities—as a “mathe-

mathematical construct" described by the same relationships as a usual molecular ligand) that has led to rather good approximation of the observed links and, eventually, recognition of the biotic ligand models. Certainly, this approach considers a biotic ligand as an effective parameter/operator of the model and chemical load, as effective variable, i.e., they are not real directly measurable values but rather the values to be assessed basing on the observed effects. As for the response of biological system (toxic effect) to the external chemical load, it remains the only directly measured variable.

In the initial formulation of the model (Fig. 1), the biotic ligand carrying a negative charge was regarded as a set of monodentate positions for binding cations, mainly, to simplify the consideration and because of insufficient experimental data restricting the use of more complex interactions in the model. It is assumed that the formation of complexes has an electrostatic nature since the chemical bond is formed owing to attraction of oppositely charged ions. The laws of chemical masses, connecting the equilibrium activities of the initial substances and reaction products in chemical thermodynamics, can be put down in the case of binding different cations to certain positions of a biotic ligand as

$$[M_i BL] = K_{M_i BL} (M_i^{z+}) [BL], \quad (1)$$

where  $K_{M_i BL}$  are the stability constants for the cation–biotic ligand complexes;  $[M_i BL]$  and  $[BL]$  are the concentrations of the  $M_i$  cations bound to biotic ligand and the total number of positions available for binding, respectively; and  $(M_i^{z+})$  is the activity of free ion in water ( $z$ , charge of the ion). The values of activities are usually replaced with the corresponding concentrations for the reactions in solutions in the cases of a considerable contribution of uncertainties associated with our limited knowledge as well as in the computations that do not require any special accuracy. Along with Eq. (1), the general system of equations comprises the analogous equations for binding cations to other inorganic and organic ligands of ground waters and the balance equations integrating all reactions. Note that Eq. (1) contains in equal terms both the cations of the nutrients vitally important to plants and the HM cations adversely affecting them: both kinds of cations merely compete for the same binding positions.

The binding of cations to other organic ligands or to the soluble organic matter of initially biological origin transformed in soil, quantitatively represents a considerable part of the total formation of complexes and the complexity of this module is comparable to that of the model itself (this module forms a separate block in Fig. 1). The biotic ligand models for hydrobiota as a mechanistic module of chemical equilibria used the WHAM models of different generations [99], NICA–Donnan model [58], and Stockholm

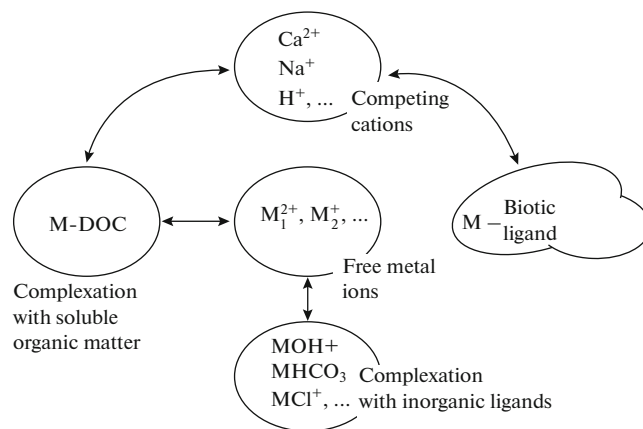


Fig. 1. Scheme of biotic ligand model (modified from [39]).

humus model [47]. Since the concentrations of dissolved organic matter in groundwaters frequently exceed the corresponding concentrations in surface waters, a happy choice of the module for chemical equilibria tuned for modeling groundwaters appears no less important than in the case of modeling aquatic media.

As is mentioned above, the conceptual chemical measure of the biological response of all living organisms to the chemical effect of toxic HMs is their binding to the most critical organs of living organisms or the corresponding  $[M_i BL]$  values for HMs. Assuming a weak dependence of the total number of  $[BL]$  positions available for binding on  $(M_i^{z+})$ , it is natural to expect a linear dependence between the concentrations of the cations bound to biotic ligand and free cations. However, this inference is not evident because of a complex and, strictly speaking, nonlinear character of the model. Soon after Di Toro et al. [39], it was demonstrated [30] that this model gave a good linear approximation of the dependences between chemical activities of competing cations and the activity of free HM ions, corresponding to the  $EC_x$  effect observed with a probability  $x$  (%), in a wide range of the observed activities. Thus, it has been shown that the stability constants of the competing cations may be assessed using simple linear regression. The introduction of ecotoxicological characteristics and the HM stability constants calculated basing on these characteristics explicitly reflect the biological component of biotic ligand model.

The paper by De Schamphelaere and Janssen [30] triggered an avalanche growth in the interest to the model and relatively simple one-factor experimental determinations of effective stability constants for many HMs, different living species, and chemical compositions of the studied waters. This direction of research as well as filling of the model with the relevant values (constants) has gradually transformed the

model from a purely theoretical construct into a working tool for analysis of waters and prediction of environmental situation. Further, the model concurrently developed in two opposite directions. On the one hand, it was somewhat complicated by including the previously ignored phenomena. On the other hand, an opposite process of fundamental model simplification on the basis of the achieved new level of knowledge commenced with the gradual accumulation of the operational databases linking the initial measured concentrations and ecotoxicological characteristics with the calculated activities.

Currently, the biotic ligand models include both the classical variants, predicting acute toxicity from the measured loads [28, 39], and the variants adapted to the data on acute and chronic toxicities [73, 89] as well as the models predicting toxicity by using humic acid or other surfaces as the substitutes for biotic ligands [100]. Although it has been clear from the very emergence of the model by Di Toro et al. [39] that the biotic ligand models are principally applicable to toxicity assessment of HM mixtures, the applied research in this direction is hindered because of a combinatorially large number of the necessary variants of experiment. However, the recent progress in this area is evidently observed [44, 45, 69, 74].

Strict requirements of the biotic ligand models to the detailed knowledge about the input chemical environmental parameters, on the one hand, limits a wide application of the models in assessing the quality of environment and, on the other hand, prevents a direct use of the accumulated geochemical knowledge because of the absence of a number of parameters necessary for modeling. However, gradual accumulation of the experience in using mechanistic biotic ligand models and accumulation of the simulation results automatically led to the search for empirical relationships between the predicted variable and the arrays of modeled activities of different compounds rather than all available data, including concentrations. Correspondingly, the generalized models have been constructed that can be as simple as the linear regression with a single variable, for example, the toxicity of free HM ions versus pH [68, 106]. A significant advantage of this approach consists in that only the variables included into the mechanistic models are studied, i.e., the variables that cannot be connected in a “cause–effect” manner with the predicted variable (for sure, within rather general conceptual limitations of the mechanistic model) are discarded.

A wide recognition of the HM bioavailability models in the scientific community does not always correlate with their use by the regulatory authorities [68]. The biotic ligand model was included into the regulatory guidelines for copper in the water bodies by the United States Environmental Protection Agency [41]. The environment quality standards in the European Union Water Framework Directive are based on the

use of several similar models developed for protection of algae/plants, vertebrates, and fish ([73] for Ni, [105] for Cu and Zn, and [106] for Pb; [68]). In Russia and several other countries, the categorical norms for threshold limit pollution are legislatively approved for both the aquatic objects and soils. Although it is generally accepted that the variation of soil properties directly influences the HM bioavailability and toxicity in soil, the unified threshold limit value for the overall territory or a limited set of the approximate limit values each of them characterizing a wide class of soils are specified for each regulated potentially hazardous metal [11]. The use of this simplified approach is after all associated with our limited knowledge about the effects of pollutants on living organisms. Thus, comparatively simple regression models based on bioavailability models are preferable for ecological regulation. With accumulation of the relevant knowledge, it is possible to take into account the variation of environment during the regulation in more detail (and even continuously for the best studied properties). Development of the continuous approach aims at a gradual transition to the regulation on a whole ecosystem scale.

Find below the description of empirical models for the partitioning of metals between soil and soil solution, which link the metal concentrations in solution to their concentrations in the solid phase and to soil properties (the so-called transfer functions) as well as the approach to the use of these models for determining the critical limits associated with the ecotoxicological impact for Cd, Pb, Cu, and Zn in soils and soil solutions.

**Critical limits of metal concentrations in soil associated with ecotoxicological impact.** In principle, *the critical concentrations of free metal ions in soil solution* are assessable from the critical concentrations of reactive metals with the help of transfer functions [35]. Formally, these are merely simple empirical solutions of Eq. (2) type (see below) but they approximate the solutions of the above-described chemical models for experimental data of different authors and different waters concurrently taking into account the ecotoxicological constraints; thus, correspondingly, they reflect the “cause–effect” (rather than only correlation), geochemical, and ecological characters of the predicted relationships. The critical concentrations of free metal ions ( $[M_{free; crit}]$ , mol/L) were obtained as a function of the pH of soil solution according to

$$\log [M_{free; crit}] = \alpha_{crit} pH + \gamma_{crit} \quad (2)$$

Lofts et al. [63, 64] devised the algorithm for determining the parameters of transfer function (2), which connects the calculated (based on the available data on the critical HM concentrations for soil organisms and plants, namely, NOEC, LOEC, and their “surrogates”) critical activities of free metal ions and the main cation activities in soil solution affecting the HM availability. The parameters of this equation calculated

for Cd and Pb according to the described logic are listed in Table 2. Note that the  $[M_{free,crit}]$  values thus determined by no means reflect the calculated contribution of hydrogen ions. In fact, Eq. (2) describes the integrated result of the effect of all cations,  $H^+$  included; however, the  $H^+$  contribution gives only a certain correction to the total effect. The easily measurable variable  $pH$  is merely a convenient measure that aggregates the effect of all cations in the solution. According to the sign of coefficient  $\alpha_{crit}$ , the total result can be also regarded as a protective effect determined by the major cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ , and  $Na^+$ ) along with  $H^+$ .

These critically important functions of free metal ions in solution are based on (a) the sets of data on toxicity, NOEC or  $EC_{10}$ , for the main organisms in soils, including the information on soil properties that influence bioavailability; (b) the transfer functions, describing the links between free metal ion concentrations in solution and the content of reactive metal in soil solid phase (as is assumed, it amounts to the content of added metal in toxicological experiments); and (c) statistical approaches to finding the limit functions and 95% protection level [35]. The set of data extracted from the risk assessment reports on TMs in the European Union comprised (a) decomposers (microorganisms or the associated soil processes, for example, enzyme activity); (b) consumers, such as invertebrates (earthworms and arthropods); and (c) primary producers, in particular, plants (see [35, 37, 64] for details).

Based on the critical concentrations of free metal ions, the critical total concentrations of metals in soil solution must be the sum of concentrations of (a) free metal ions,  $[M_{free}]$ ; (b) dissolved inorganic complexes,  $[M_{DIC}]$ , such as  $MOH^+$ ,  $MHCO_3^+$ , and  $MCl^+$ ; and (c) the metals,  $[M_{DOM}]$ , bound to dissolved organic matter,  $[DOM]$ , namely,

$$[M]_{tot} = [M]_{free} + [M]_{DIC} + [M]_{DOM} \times [DOM], \quad (3)$$

where  $[M]_{tot}$  is the total concentration of metals ( $mol/m^3$ );  $[M]_{DOM}$  is the concentration of metals bound to dissolved organic matter ( $mol/kg$  DOM); and  $[DOM]$ , the concentration of dissolved organic matter ( $kg/m^3$ ). Once the chemical equilibrium is established, it is possible to calculate the partitioning of metals among fractions. Taking into account the activity of free metal ions, the concentrations of other metal compounds are assessable with the help of the equilibrium geochemical model. The WHAM models are frequently used for this purpose [97, 99]. The calculations take into account the dependence of metal binding to DOM on pH and the competitive effects determined by the Mg, Al, Ca, and Fe cations [98].

The critical concentrations of reactive (potentially available) metals in soil associated with the ecotoxicological impact on soil organisms and plants were determined in laboratory experiments based on the

**Table 2.** Values of  $\alpha_{crit}$  and  $\gamma_{crit}$  coefficients in Eq. (2) for calculation of critical concentrations of free metal ions in soil solutions (according to [35])

Metal	$\alpha_{crit}$	$\gamma_{crit}$
Cd	0.32	6.34
Pb	1.23	2.05

**Table 3.** Values of  $b_0$ – $b_2$  coefficients in Eq. (4) for calculation of critical concentrations for the reactive (potentially available) Cd and Pb as a function of soil properties (according to [35, 37])

Metal	$b_0$	$b_1$	$b_2$
Cd	2.27	0.33	1.00
Pb	0.58	0.11	0.11

NOECs of the used metals [64]. It is assumed that these concentrations are equal to the concentrations of reactive metals in soil potentially available to the exchange with soil solution (Fig. 2). The metals incorporated into the crystalline lattices of minerals and directly inaccessible to dissolution are not included into this fraction. The reactive fraction in soil is frequently determined using the extraction with 0.43 M  $HNO_3$  solution [46]. The effect of soil properties that determine the bioavailability and toxicity of metals was taken into account by comparing the critical values with the pH of soil solutions and the content of organic matter in soil [37, 64]:

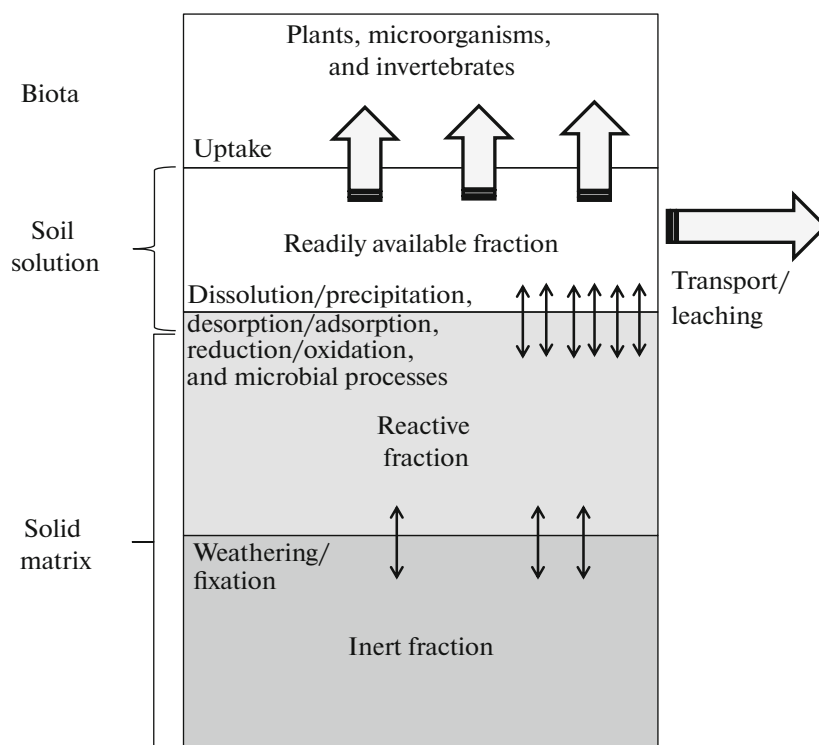
$$\log M_{re,crit} = b_0 + b_1 pH + b_2 \log SOM, \quad (4)$$

where  $M_{re,crit}$  is the critical concentration of reactive metal in soil ( $mg/kg$ );  $pH$ , the pH of soil solution; and  $SOM$ , the content of soil organic matter (%). The values of  $b_0$ ,  $b_1$ , and  $b_2$  are listed in Table 3. The results are based on the same sets of that were used for the critical concentrations of free metal ions.

Critical total concentrations of metals, which are important for regulatory bodies, are obtainable using the transfer functions based on the concentrations of reactive metals [35, 86]:

$$\log M_{tot,crit} = c_0 + c_1 \log M_{re,crit} + c_2 \log SOM + c_3 \log clay, \quad (5)$$

where  $M_{tot,crit}$  is the critical pseudo-total (added) concentration of metal in soil ( $mg/kg$ ) and  $clay$ , the content of clay (%); the  $c_0$ – $c_3$  values are listed in Table 4. The regression equations are based on the Netherlands dataset, comprising 630 samples covering a wide range of soil types differing in their properties, including the contents of organic matter and clay as well as background and polluted soils. All samples were analyzed for the metals extracted by both 0.43 M  $HNO_3$  and aqua regia [35, 86]. Indeed, a high diversity of soils depending on different geochemical and biocli-



**Fig. 2.** Distribution of the total pool of heavy metals in soil: readily available fraction (free metal ions and complexes with dissolved organic matter); reactive fraction (sediments, metals sorbed by clay and organic matter, amorphous metal oxides, carbonates, and metal–organic complexes); and inert fraction (incorporated into crystalline lattices, sulfide minerals, and crystalline oxides of metals). The fractions vary in size and the most important soil processes vary in their intensity depending on particular metal and environmental conditions (modified from [85]).

matic conditions requires preliminary testing the transfer functions to take into account the specific regional features, when necessary.

### PROBLEMS AND PROSPECTS

*The processes of mobilization and binding*, for which the potential quantitative estimates considerably vary, are the key factors in the control of HM behavior, including their effect on the recipients. The main processes of HM binding in soil are complexation, sorption, ion exchange, and precipitation; these processes are sufficiently well studied under laboratory conditions. However, the difficulties in studying the HM partitioning between the soil solid phase and solution remain for the real soil-to-solution ratios under field

conditions. In particular, the latter include the addition of soluble HM salts in laboratory adsorption and ecotoxicological experiments that ignore the long-term processes of metal binding and a decrease in their bioavailability, characteristic of the field conditions [61, 65, 75, 87, 93]. The efforts to model the ageing process depending on soil properties and duration of interaction are necessary [110]. In particular, field research into the partition of metals between soil and soil solution are of evident priority [62].

*Spatial scale and resolution.* Being the functions of soil properties, the critical concentrations considerably vary in space. In the assessment of critical concentrations and their exceedance, the spatial resolution depends on the resolution of the input data, namely, the spatial availability of soil properties taking

**Table 4.** Values of  $c_0$ – $c_3$  coefficients in Eq. (5), linking the pseudo-total and reactive (potentially available) concentrations of Cd and Pb depending on soil properties; determination coefficient ( $R_{adj}^2$ ), and mean square root error  $se(Y)$  (according to [35, 86])

Metal	$c_0$	$c_1$	$c_2$	$c_3$	$R_{adj}^2$	$se(Y)$
Cd	0.028	0.877	0.009	0.081	0.96	0.10
Pb	0.323	0.810	0.035	0.136	0.92	0.13



into account their natural variation and the uncertainty caused by the absence of data. The resolution of data on HMs varies from the local to regional and even continental levels [62].

In the long run, the spatial scale of the estimates of critical concentrations and their exceedance must depend on the type of the pollution problem to be solved. A decrease in the atmospheric emissions by large industrial pollution sources brings about the need to deal with a direct input of pollutants with fertilizers, manure, and biosolids, as well as diffuse atmospheric sources, such as vehicle emissions [35, 62]. A more precise spatial resolution of critical concentrations may become important on a local scale, for example, zinc spreading because of tire wear within 10–100 m from highways may well require a large-scale mapping. However, the advantages of more precise resolution must be checked against the likely higher costs of the monitoring [62].

A large part of the *uncertainty* in the estimates of the current risks of excessive HM accumulation with regard to ecotoxicological impact stems from the uncertainty of the used critical concentrations; moreover, this uncertainty is influenced by the uncertainties of the critical limit functions [34, 82]. The critical concentrations of Cr, As, and Se rely on very few sources and, correspondingly, are rather uncertain as well. The more reliable estimates for the critical loads of these elements require a careful analysis of the available ecotoxicological data [82]. The uncertainty of critical concentrations to a considerable degree depends on the uncertainty of transfer functions that link the metals in the solid phase to the metals in soil solutions as well as on the soil properties influencing this link (in particular, pH and organic matter content) [34].

*Assessment of environmental risks for multicomponent pollution* is the challenge requiring special attention. The conditions of real multicomponent pollution require that different synergistic effects are taken into account, including a combined (simultaneous or sequential effects of several substances entering via the same route), composite (when one hazardous substance enters the organism via different routes and with different media, such as air, water, food, or through the skin), and a joint impact of the overall diversity of physical, chemical, and biological factors. In these cases, the measurement of toxic load is an intricate problem having no unambiguous solution [45, 48, 74]. Further studies are necessary to assess the response of ecosystem to the joint effect of stress factors in the situation of multicomponent pollution.

In terms of environment risk assessment, analysis of potential *effect of the climate change* on HM mobility, bioavailability, and toxicity is especially relevant. This effect is likely to manifest in the Arctic, currently exposed to the most rapid transformation. No less than one-third of the circumpolar Arctic area belongs to the Russian sector; the terrestrial area of the Arctic zone

accounts for 18% of the territory of this country [14]. Many aspects in the functions of natural ecosystems in the high latitudes are sensitive to climate changes. The main mechanisms underlying the effect of climate change on environmental risks are the likely alteration in ecotoxicological impact of pollutants and the transformation of their transfer pathways associated with the changed amount of precipitation, surface runoff, and evaporation [21, 57]. In addition, the climate change transforms soil conditions, including the temperature; moisture; pH; redox potential; contents of organic matter, nitrogen, phosphorus, and mineral fractions; and microbiological activity, eventually altering the processes of binding/release, oxidation/reduction, and composition of HM compounds in soil [21]. In particular, the current climate in Arctic determines a slow decomposition of organic matter, resulting in its accumulation together with the bound elements despite a low input. Climate warming with a rapid increase in temperature in high latitudes [16] can accelerate the cycles of carbon and other elements, especially in soil, which can be accompanied by initial HM release [24].

The climate change can influence the water regime and vegetation types and alter the land use. The change in the amount of fertilizers and biosolids applied to croplands, the rate and degree of industrialization and urbanization, and natural plant successions influence the HM behavior as well [62]. Traditionally, the effects of atmospheric pollution and climate have been considered separately. However, their integrated impact may considerably differ from the sum of the individual effects [22, 33].

## CONCLUSIONS

This review demonstrates that the critical concentrations of HMs in soils and soil solutions associated with ecotoxicological effects should be determined as the function of main properties of soils and soil solutions. HMs affect microorganisms, plants, and, to a considerable degree, invertebrates via the soil solution [83]. In terms of the free-ion activity model [25, 71] and biotic ligand model [39, 96], the uptake of HMs that cause a toxic effect can be considered as the interaction between free metal ions in soil solution and the organism. The extent of this interaction and, correspondingly, the degree of the toxic effect of a given concentration of free metal ions will also depend on the concentrations of other cations in this solution, which compete with the toxic metal for binding with an organism. Thus, the environmental risk assessment is based on the determination of critical limits for free metal ions [35]. In particular, the pH-dependent function of critical activities of free metal ions is an adequate tool for the description of impacts of Cd, Pb, Cu, and Zn [35, 37, 64]. The most important variables of the transfer functions for the calculation of HM critical values in soil are pH and the contents of organic matter and clay [35, 86]. These properties

considerably differ depending on the soil type; correspondingly, the range of critical concentrations of metals may be wide [37]. A decrease in the uncertainties for the functions of critical concentration of metals is the most important direction of the further studies. A high priority of the field validation of the obtained estimates is beyond question [62].

A new challenge is the joint effect of anthropogenic pollution and other environmental changes. The processes underlying the HM behavior in ecosystems are influenced by climate changes, which, in turn, affect the level of their integral impact. So far, this basic problem in soil science and ecology has not been studied in detail although the understanding of climate effects is most relevant with respect to science and practice to provide the soil security and sustainable environmental management [66]. Correspondingly, the research into soil tolerance of HMs, the risks of excessive HM accumulation in the terrestrial ecosystems, priorities for remediation of technogenic territories, and response to climate changes are of evident basic and applied importance.

#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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