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Full Length Research Paper

Early Diagnosis of Ecosystem Pollution and Its Prognosis

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The article considers the issue of developing a geo-ecological indicator to assess the status of the soil and infiltration waters that could be both representative for the ecosystem and give assessment of its pollution. As an index a change in contents of chemical substances in the biogeochemical analysis of the flow in the system atmospheric deposition, soil and infiltration waters. The risk index in the developed model of chemical element streams is based on indication of the dominating role of lysimetric filtrates for determining transit streams of pollutants in ecosystems and evaluating pollution levels of infiltration waters which inflow to ground and surface waters. Employing biogeochemical analyses of the fluxes in the system on the example of mountainous massif indicated that concentrations of Pb, Ni and Mn in the lysimetric filtrates significantly exceeded threshold values and values of their concentrations in precipitation. It is demonstrated that applied indicators reflect the total range of changes in the structure of biogeochemical cycles in the terrestrial ecosystem and provide opportunity to integrate information on the pollution. Proceeding from results of analyses it is possible to assess the risk of environmental pollution of ground waters and soil.

Keywords: soil pollution**,** heavy metals, lysimetric filtrate, balance model.

INTRODUCTION

The aim of this work is to demonstrate that bio-geochemical cycling covering the main components of an ecosystem and allowing to reveal changes of its state at an early stage of pollution can not only serve an indicator but also provide a quantitative estimate of pollution. An early revealing of disturbances is decisive for prevention of irreversible change of an ecosystem health. In connection with this the definition of indicator has great importance for solution of tasks of an ecosystem state assessment.

Determining an index that will be representative with respect to response of ecosystem on the whole is very important for solving tasks on ecosystem state assessment. In solving the task the biogeochemical cycling of chemical elements appears to be one of the most effective ways due to capacity of cycles to cover all main components of the ecosystem and to respond on integral natural and anthropogenic impact resulting from different factors superposition (Revazyan, 1998, 2003).

There are other approaches and methods used for the ecosystem state assessment. One of them is a bio-indication method. It has been recognized that serious difficulties in its application arise with respect to obtaining information on the status, since reaction of plants to impact of different pollutant's greatly varies due to genetic features of plant reaction to pollutant. Some species can react to one pollutant, others to two, they could even show

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tolerance. Proceeding from this we can state that bio-indication investigations contributing to solution of a number of specific tasks in this field do not allow to assess the ecosystem state since they are conducted on the level of different species, which is connected with surmounting of several methodological problems [(Feder 1978), Roberts (1972), Revazyan (2003)].

The need for detailed elaboration of geochemical aspects of ecosystem transformations induced us to create a system of geochemical cycling research designed to assess ecosystem states namely at local level. Only at such level it appears to be possible to examine in most details complex series of interrelated reactions between flows of metals from atmospheric precipitation, soil solution, vegetative cover intended to reveal the general development of the process often hidden under peculiarities of regional level. Analyses of chemical elements fluxes in an ecosystem as well as bio-geochemical balance computation make possible to determine quantitative changes in ecosystem states. A significant condition for studying this question is an adequate representation of time scale peculiar to the system. For dynamics of bio-geochemical cycles under investigation we analyze average values for annual cycles.

Mass balance calculations present technique used for investigation of peculiarities of chemical elements cycles in an ecosystem. For case study of a terrestrial ecosystem we calculate fluxes of the various chemical species into and out of the soil module. An index calculation is based on the entropy analysis method, which provides metrics for measuring distribution of substances in the process of transition through the system (Ulanowicz 2001). The combination of lysimetric studies with mass balance calculations provides ground for modeling with entropy analysis. We describe calculations for one element from seven species of heavy metals studied in the investigated system to present examples of the preliminary results.

One of the attempts for calculation of balance of heavy metals in the soil in response to atmospheric deposition is based on a model described by a system of ordinary differential equations. A simplified model for heavy metals mass transfer in the system is used for approximate estimate of the range for flux rates. The equation for calculation of the load on the soil is built on the assumption of some critical level of concentration in the soil and comparison of observed values with critical for later definition of its status.

MATERIAL AND METHODS

The investigations were conducted in one of the complicated in ecological aspect physical-geographical subregions in the Republic.

A conjugated selection and treatment of soil, plant, atmospheric precipitation samples, lysimetric filtrates were conducted on the monitoring station(at height 2100 m over the sea level). The top-soil is composed from mountainous-meadow and steppe soils. The latter is characterized with high humus concentration(8-10%), washing out water regime, high aggregation, weak-acid or neutral reaction. Vegetation of meadow-steppe zone, specified with high diversity and motley of species composition, was selected as material for biogeochemical investigation. The most spread of meadow-steppe vegetation types are grains, polygrass, grass-grain and leguminous, including Festuca versikolor Tausch, F. Ovina L., F. Pratensis, Huds., Stipa pulchezzima C. Koch, S. Tirsa Stev, etc.

Studying of vertical infiltration runoff was implemented with lysimetric method. A flatfit lysimeter was established under a layer of soil with depth 50 cm, without violating natural vegetation cover and underlay, while deformation of soil structure and constitution was the least [(Revazyan (2003), Roberts, (1972)]. The selection of lysimetric probes and atmospheric precipitation was performed seasonally. The conjugated selection of soil and plant samples, lyzimetric filtrates were taken on the monitoring station (altitude above sea level 2100 meters).

The contents of heavy metals in investigated objects (soil, plant, water) were defined with atomic -absorption method on Analyst 800 (Perkin Elmer).

The structure of bio-geochemical cycle includes: the flow of heavy metal (HM) input to an ecosystem with atmospheric precipitation, metals inflowing to the system with infiltration waters (lysimetric filtrate), the capacity of metal flux in phytocenoses of meadow-steppe zone. Besides the capacity of HM content in meadow-steppe zone was calculated by means of definition of plant productivity and metal concentration in plants. The productivity of the phytocenosis was determined with generally used weighing method, i.e. 25 meter patches were taken from 1 hectare over the vegetation period. The capacity of metal flow in the phytocenosis was calculated by multiplication of the plant productivity by concentration of metals in it. Capacity in this context is measured with flux which is defined as usual concentration multiplied by time.

Analyzing geochemical rankings it is not difficult to note that elements change places with respect to their types of contents: Mn and Ti, Pb and B, as well as Cu and Ni. Most strongly contents of elements in lysimetric filtrates and their gross contents in soils differ. Thus, Mn moved to the second place in the rank of elements in filtrates, while in soil and lithosphere it is on the third place. Boron moved from the last place to the middle one.

Interpretation of data, derived exclusively from contents of HM in soil solutions without data on concentrations and intensity of HM absorption, as well as removal of HM by plants does not convey the full picture of biogeochemical cycling.

Table 1. Geochemical series of element contents in infiltration waters, soils and lithosphere clarks on mountainous meadows.

Soil	Forms of content	Geochemical ranks of elements
Meadow-steppe	In lysimeter filtrates	Fe>Mn>Ti>Pb>B»Cu>Ni
	Gross contents	Fe>Ti>Mn»Ni>Pb»Cu>B
According clarks in lithosphere.		Fe>Ti>Mn>Ni>B»Cu> Pb

Model of the system formulation.

Soil presents the environmental compartment which serves as interface between atmospheric deposition, such as rains and fluxes to ground water. We describe it with a simple process consisting from one input and two output fluxes. A flux definition is adopted as the rate of transfer of material or energy and is defined by mass per unit area per time. In case study fluxes are computed g per (ha-year). Data for the region under investigation is given in table 2 for four successive years.

We consider the terrestrial part of the ecosystem as partially independent and elucidate the aspects of element transfer in the system presented in the form of a process in one compartment-soil, with one input that is external source from atmospheric deposition and two output flows that reflect loss from the soil compartment. In fact there are other factors having impact on the transition processes, such as fertilizers that could be an additional source for input, back processes reflecting precipitation. Simple calculations of balance *w* between intake and removal with the soil runoff and alienated biomass for each of elements in the series Fe, Mn, Ti, Pb, Cu, Ni indicates that in some cases, more exactly for Mn and Pb, the value of balance is negative. In these cases secondary sources of input exist that have not been taken in consideration, revealed to be significant.

For a steady state analysis we apply a network environ analysis to quantify the through flow analysis and environ through flow analysis as indicators, then we can decompose the system in terms of input-output. Thus the block soil in the system "atmospheric deposition, soil and infiltration waters" has links both with atmospheric deposition and infiltration waters. Let f_i be the i-th flow and F represent the sum of all the flows ($F = \sum_i f_i$), then $p_i = f_i / F$ becomes the fraction that the i-th flow comprises of the total system activity. To estimate the degree of uncertainty in the flows we will use an index proposed by MacArthur, for detailed description we refer to (Ulanowicz, 2001). It is defined by formula:

$S = -\sum_i p_i \log p_i$, where logarithms could be on base 2. Since this is a process based approach we need to define events "a quantum of material enters the node" and "a quantum of material leaves the node", then it will be possible to calculate the nodal contribution to the change of state [(Tolner and Kazanci, 2007)]. But we will calculate only the entropy of input and output for each of compartments we defined in our network, thus taking into account only direct relations in the system.. Denote $x_{i,k}^{input}$ the input flows to the compartment i for one of elements k with indices ranging from 1 to 4 (atmosphere- soil-lysimetric filtrates-ground waters) and 1 to 6 correspondingly. The single contaminant transfer coefficient defined for each compartment i as $\omega_{i,k} = x_{i,k}^{input} - x_{i,k}^{output}$ becomes most important. Though experimental data is not available for rates of all reciprocal flows, we consider soil solute as the most informative, since it is provides pathways for contaminant migration to trophic chains and the flow to ground waters. The value for the part retained in the lysimetric filtrates for Cu thus becomes:

$$\lambda_{lys,cu} = \frac{x_{lys,cu}}{x_{atm,cu}}$$

From data in table 2 for example, it can be defined that $\lambda_{lys,cu}$ was 0.134 in 2008. In the intra-annual perspective then we can estimate the level of pollution using the retention coefficients as single element indicators. To quantify pollution however, for pragmatic reasons, we calculated the geoaccumulation index.

The index of geo accumulation was calculated by the following formula:

$I_{geo} = \log_2[C_i / (1.5C_{ri})]$,

where C_i is the measured concentration in the soil solute and C_{ri} is the reference value of the metal i ., factor 1.5 in original formula was used for possible variations in background concentrations or very small antropogenic influences (Qingjie et al, 2008). We used threshold values as referenced one, limiting threshold values are brought in (Sakhaev et al,1986).

Table2. The mass balance of heavy metals in the ecosystem of meadow-steppe zone

Years	Name of the component	Heavy metal species					
		Fe	Ti	Mn	Ni	Cu	Pb
2008	Atmospheric precipitation flux given in g/(ha-yr)	9620	2040	1370	321	687	229
	Flux in intra-soil runoff (lysimetric filtrate). g/(ha-yr)	2700	1240	3110	92	92	229
	Removal of chemical species in alienated phytomass(hay), g/(ha-yr).	920	180	950	38	62	12
2009	Atmospheric precipitation flux given in g/(ha-yr)	6230	2420	2080	415	761	242
	Flux in intra-soil runoff (lysimetric filtrate) g/(ha-yr)	2530	1180	1560	104	138	311
	Removal of chemical species in alienated phytomass(hay), g/(ha-yr).	680	385	1100	51	85	18
2010	Concentration in the atmospheric precipitation flux given in g/(ha-yr)	16480	3300	1650	412	733	247
	Concentration of chemical species in intra-soil runoff (lysimetric filtrate) g/(ha-yr)	3630	1900	2640	412	412	659
	Concentration of chemical species in alienated phytomass (hay). g/(ha-yr)	1400	290	600	61	105	14
2011	Concentration in the atmospheric precipitation flux given in g/(ha-yr)	15030	2460	1082	120	601	120
	Concentration of chemical species in intra-soil runoff (lysimetric filtrate)in g/(ha-yr)	4030	902	3130	301	180	361
	Removal of chemical species in alienated phytomass(hay), g/(ha-yr).	1700	220	750	21	93	20

A Simple Dynamic Model for the Balance Evaluation

The main mechanisms of exchange between soil and ground waters are sorption and desorption. As it mentioned in [Venetsianov, (2009)], the rate of absorption and movement into deeper layers of soil depends on specific features of the local soil, but in this model they are not taken in the account. Let $m_{1,i}$ be the content of some component i , then i takes values from 1 to 6 in the case study, in the module "atmospheric precipitation", $m_{2,i}$ и $m_{3,i}$ be the contents of the same component in the soil and removal with the dead biomass. The rates of the flows change are supposed to be linear. The model is defined with the following system of differential equations:

$$\frac{dm_{1,i}}{dt} = -\alpha_1 m_{1,i} + \beta_1 m_{2,i}$$

$$\frac{dm_{2,i}}{dt} = m_{2,i}(k_1 m_{1,i} - \alpha_2 m_{3,i}) \quad (2)$$

$$\frac{dm_{3,i}}{dt} = \alpha_3 m_{2,i}$$

The main difficulty of analytical investigation and numerical solution consists in definition of parameters,

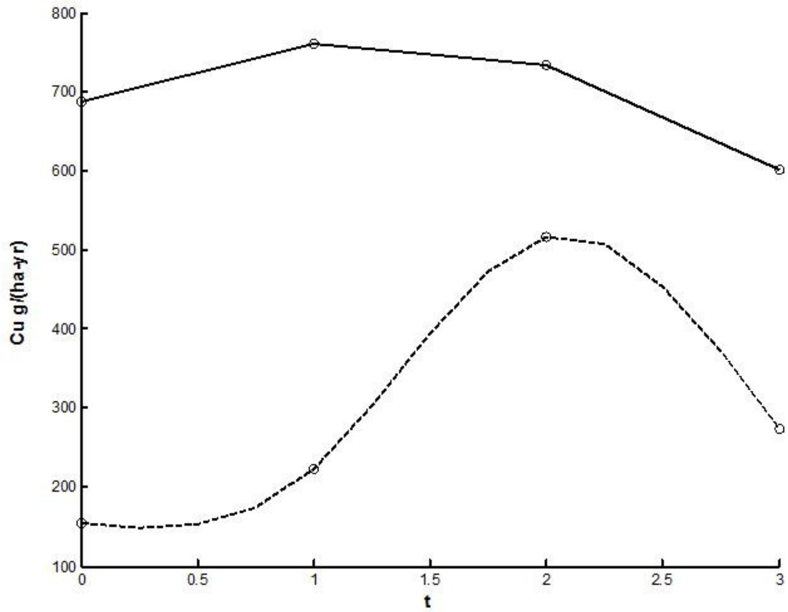

Figure 1. Rates of input and output fluxes for Cu, i.e. the flow coming from precipitation plus recycled biomass and mass removed with lysimetric filtrates plus hay. Time is given in years. Curves are obtained with interpolation.

which could be non-linear, but we assume investigation near the steady state of the system. Main sources of uncertainty include the stochastic nature of input flux change, the need to include anthropogenic load (fertilizers for example). Obviously some range of the variable change should be accepted. Provided parameters are fixed the system numerical solutions can be easily derived.

Denote N the concentration of one of the elements Fe, Mn, Ti, Pb, B, Cu, Ni in the soil, we omit the index for simplicity of the expression, N(t) is assumed to be a continuously differentiable function. We adapt the equation for the logistic growth for determining the rate of change in the soil. The input flux of some element is assumed constant, B=n= const. We denote D(N) losses from soil, then the local growth is determined through the following expression:

$D(N) = m + \mu N$,

where μ is the growth parameter, m -some initial rate of decrease of the element concentration in the soil, considered as content in the filtrate. We come to the following equation for N(t)

$$\frac{dN}{dt} = ((n-m) - \mu N)N \qquad (4)$$

After making notations $n - m = r$, $n - m / \mu = K$ the equation can be brought to the following:

$$\frac{dN}{dt} = rN(1 - \frac{N}{K}) \qquad (5).$$

Such equation was applied for description of dynamics of an isolated population, called population with logistic growth(Svirezhev, (1987)). Obviously the population has two steady states, the unstable one, $N_1^*=0$, and stable $N_2^* = K$.

The greatest simplification in the model (5) is the assumption that the parameter r is constant, the other difficulty is selection of the value for K. The curves on figure 2 are obtained with $K = 900$ and initial annual values 668, 944, 1212, 1408 that correspond the monitoring data for Cuprum over four successive years.

The picture shows that changing of the model variable is rather slow. The main difficulty with prediction of events related to the input fluxes and loss is the stochastic nature of processes. It is possible to imitate with scenarios of the ecosystem state changes to determine appropriate values for model parameters. Having estimated the parameter values the model allows predicting an approximate range of the change in the following year, provided the assumptions are valid.

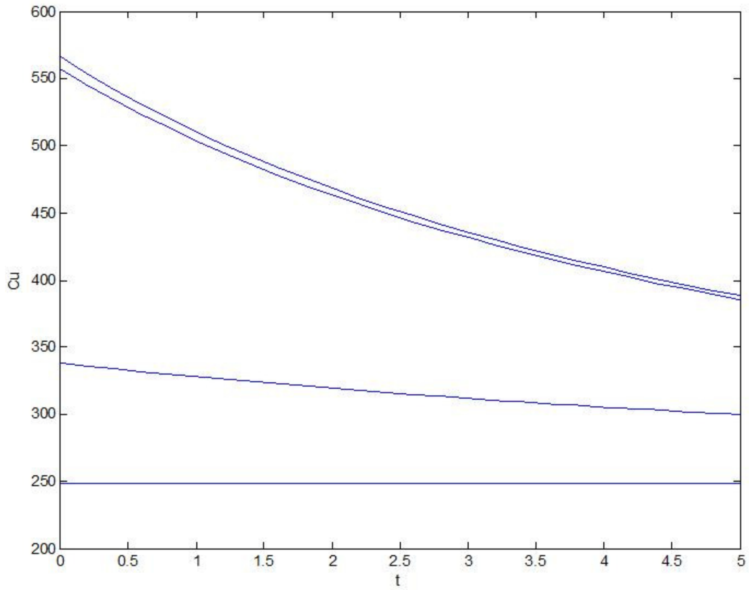

Figure 2. Solutions of the model for contents of Cu in the soil

Thus playing different potential scenarios of the state change allows defining functions for parameters of the model. Having prescribed values to parameters the model could give assessment of conditions, particularly time intervals for potential change of the load and significant change of element contents in the soil.

RESULTS

Our investigations were held on an example of mountainous-meadow ecosystems, where the ecological tension achieved high limits. The need of simultaneous study of all the components, from atmospheric precipitation to lysimetric filtrates, occurred. The lysimetric filtrate is affected with all the spectrum of polluting substances entering the soil, that is integration of all active pollutants takes place. The statement was confirmed with ranking of elements composed on the base of calculation of some biochemical parameters.(table 1).

Analyses of HM flow in phytocenoses of mountainous meadows revealed disequilibrium between fluxes alienated out of the ecosystem boundary and repeatedly coming in it. Thus, the volume of metal flow removed with grass organic mass beyond the ecosystem exceeded significantly the store of elements in organic mass flow remained in limits of the ecosystem.

Since pollution of the environment presents a migration flow of substances in biosphere having its regularities connected with migration and accumulation processes necessity of quantitative definition of migration arises. The process is based on construction of balance of chemical elements [Revazyan (1998), Saghatelyan, (2004)].

It is demonstrated that statistical entropy analysis can be used to assess the level of pollution. We used a rather simple dynamic model which nevertheless allows to catch the qualitative features of the process. In fact it is a food chain model, that it is indicated in [Svirezhev, (1987)] are proper models for biogeochemical cycles. We made simplification by assuming linear dependence between flux rates, but is sufficient approximation in vicinity of the existing state. The model is based on assumption of migrating element balance, but the long term predictability is not possible. The model allows easy approximation of solution. The system does not provide long term predictability, since the estimate of an external resource, i.e. flux with the atmospheric precipitation, is not possible and seems rather random. But the investigation makes basis for developing scenarios proceeding from quantifying the level of rate in precipitation and predict the evolution depending on observed data.

As data showed total input of HM with atmospheric precipitation is, in general, substantially lower than the module of removal, except for Ni and Co. Thus, misbalance of metals arising in the system in the process of its functioning is the result of transformation of migrating flow of elements, starting from input with atmospheric precipitation up to output in infiltration waters and alienation with removed phytomass.

DISCUSSION

Lysimetric solutions occupy a special place in the list of components since they accumulate pollutants from the atmosphere and soil and their composition has reflection of main regularities peculiar to an ecosystem internal processes dynamics [Shilova,(1972) Revazyan (1998)]. The obtained data presents evidence on dominating informative role of lysimetric filtrate capable to provide encoding of element mobility in top-soil and estimates of pollution of infiltration waters inflowing to ground and surface waters.

CONCLUSION

The results of research showed that on the base of the early diagnosis of the ecosystem state with application of lysimetric method and balance estimation it is possible to detect disturbances in contents of heavy metals in biogeochemical series and assess the level of pollution of the infiltration waters which inflow to ground waters through transition flows.

The model imitating dynamics of the mentioned indicators under different assumptions on element flows coming from precipitation was built on the description of links between model parameters.

The balance approach to identifying of the ecosystem state allows estimating quantitatively the processes of heavy metals input, leaching and removal in the ecosystem. The landscape geochemical study with lysimetric method makes ground for the biogeochemical assessment of the element balance.

The results of investigations showed that it is possible to assess quantitatively the processes of input, taking out, alkalinity of heavy metals in the ecosystem on the base of bio-geochemical approach to ecosystem's state diagnostics and landscape-geochemical study with using lysimetric method and bio-geochemical balance of elements.

In further work we will describe the results of application of entropy analysis to all elements. What should be done includes analysis of the dynamical model, including parameter determination and comparing predictions of model with the observed values.

The conducted research does not naturally broach all spectrum of questions related to the processes of elements migration. However the results prove that the investigations can be effective in solution of questions regarding assessment of ecosystem states, arranging monitoring of level of their pollution, as well as for prognostic estimates.

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