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Approaches for establishing threshold concentrations of priority pollutants in urban ecosystem components

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Quality management of urban ecosystem components should be based on adequate determination of threshold values for concentrations of priority pollutants, otherwise it is difficult to assess the severity of negative consequences of anthropogenic activities. Currently, there is no officially approved or generally accepted method for setting concentration thresholds for urban ecosystem components at the regional level in Russia. Setting such thresholds requires the use of effective indicators that can reflect man-made multi-component and multi-factor effects. Quantitative characteristics of accumulating and dynamic biosubstrates of sensitive representatives of the population can act as an informative marker of the response of biological components of the urban ecosystem to anthropogenic impact. Territorial correspondence of sampling points of components of the urban ecosystem and biosubstrates of the body will allow to establish relationships between their contents. The priority of the study of metals among the entire variety of pollutants subject to control is their stability in the components of the urban ecosystem, their high ability to biogenic migration, and the danger of accumulation with the manifestation of toxic effects, due to a long period of excretion from the human body. The use of modern neural network technologies and chemical analysis of metals has allowed to define threshold concentrations of metals in depositing components of the urban ecosystem at the upper limits of acceptable concentrations of their content in biological substrates of children and adolescents which do not lead to an increase of regional reference values in blood and hair.

Keywords: metals, biosubstrates, depositing media, threshold concentrations, neural network modeling.

УДК 504.064

Подходы для установления пороговых концентраций приоритетных загрязняющих веществ в компонентах урбоэкосистемы

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Управление качеством компонентов урбоэкосистемы должно основываться на адекватном определении пороговых значений концентраций приоритетных загрязняющих веществ, в противном случае сложно оценить выраженность негативных последствий антропогенной деятельности. В настоящее время в России не существует официально утверждённой или общепринятой методики установления пороговых значений концентраций для компонентов урбоэкосистем на региональном уровне. Установление таких порогов требует использования эффективных индикаторов, способных отразить техногенное поликомпонентное многофакторное воздействие. Количественные характеристики аккумулирующих и динамичных биосубстратов чувствительных представителей населения могут выступать информативным маркером отклика биологических компонентов урбоэкосистемы на антропогенное воздействие. Территориальное соответствие точек пробоотбора компонентов урбоэкосистемы и биосубстратов организма позволит установить взаимосвязи между их содержаниями. Приоритетность исследования металлов среди всего многообразия подлежащих контролю загрязняющих веществ, обусловлена их устойчивостью в компонентах урбоэкосистемы, высокой способностью к биогенной миграции, опасностью накопления с проявлением токсического действия, вследствие длительного периода выведения из организма человека. Использование современных нейросетевых технологий, химико-аналитических исследований содержания металлов позволило определить пороговые концентрации металлов в депонирующих компонентах урбоэкосистемы по верхней границе приемлемых концентраций их содержания в биосубстратах детей-подростков, не приводящих к превышению их региональных референсных значений в крови и волосах.

Ключевые слова: металлы, биосубстраты, депонирующие среды, пороговые концентрации, нейросетевое моделирование.

In the process of the formation of a large urban agglomeration, the degradation of the natural ecosystem and the formation of a new anthropogenic ecosystem – the urban ecosystem – are gradually taking place. Anthropogenic flows of matter formed during the functioning of urban ecosystems are extremely diverse and contain high concentrations of a wide range of chemical elements, including toxic ones. Being included in natural migration cycles, anthropogenic flows lead to the rapid spread of pollutants in the components of the urban ecosystem, where their interaction with humans is inevitable. A special role in this context is played by the migration flows of metals, which are not only the most important pollutants, but also substances that form their own biogeochemical cycles in urban ecosystems [1, 2]. The dominant pathway for the supply of metals to the territory of the urban ecosystem is the aerogenic pathway. Aerogenic influx of metals with emissions from stationary and mobile sources of pollution is the main input part of their balance [2, 5, 8].

The influx of metals into the territory of the urban ecosystem usually occurs over a long period with low intensity, exerting a chronic polymetallic load on organisms, especially sensitive groups of the population [1–2].

It is known that metals with carcinogenic potential have a negative effect on various organs and systems of the human body. A high level of input of Cr and Pb is often found in the territory of urban ecosystems of industrialized countries, and chronic exposure to these metals is still a serious problem [3–4].

Estimates show that the integral rather than isolated intake of metals into the body most often occurs in the territory of urban ecosystems, although the latter has been the subject of the largest number of studies. Essays on assessing the impact of the polyelement spectrum of metals present in the components of urban ecosystems at a level below hygienic standards are practically absent today [4–7]. The main role of the transport of metals in the body belongs to the blood due to binding metals by blood proteins. The availability and simplicity of sample preparation determined the choice of blood serum as one of the objects for investigation of the metal content [6–11]. Various tissues, nails, hair, the stratum corneum of the skin can be used as indicators of chronic polymetallic exposure. Hair is a particularly representative and easily obtained object of research [3, 12].

The sensitivity of adolescent children to the chronic intake of metals from their environment differs significantly from that of young children and adults for various reasons associated with the physiological characteristics of metabolism [1, 4].

Abroad, approaches based on the creation of models and the development of scenarios for the development of urban ecosystems are actively practiced. Ecological and geochemical studies based on the chemical analysis of samples of various natural environments are traditional in our country [8–10]. The combination of these approaches seems to us promising for determining the threshold values of metal concentrations in the components of urban ecosystems.

In the case of deficiency of systematic observations of the content of metals in the surface layer of the atmosphere, it is informative to determine them in the snow cover and soils as the depositing components of the urban ecosystem. The advantages of studying the depositing components of the urban ecosystem are the relative cheapness, the characterization of the accumulation of polluting components over a long period, the ability to cover large areas by sampling, and the accuracy of the results in terms of sensitivity and reproducibility.

Snow has a high sorption capacity for metals sedimented from the atmosphere in dissolved and suspended forms. The composition of the snow allows us to obtain information on the spatial distribution of metals and the intensity of the impact of emission sources for a certain period – during one snowfall or for the entire period of snow. Observations of the composition of snow in the same territory allow us to identify a general trend in the change in the levels of polymetallic load, to find new foci of pollution that are not detected by less dynamically reacting objects such as soils, and to quantitatively calculate the influx of metals during a period with a stable snow cover [2, 9].

The soil cover, being at the intersection of all migration paths of metals, fixes the total effect of long-term accumulation of atmospheric impurities, and is one of the most informative blocks in the study of the urban ecosystem condition. At the same time, the soil is a source of dust containing a certain pool of metals and forms secondary air pollution in residential areas [2, 8].

Thus, the aim of the study was to determine the threshold concentrations of metals in the depositing media of the urboecosystem – soil and snow cover, at which the content of the same metals does not exceed regional reference values in biosubstrates of adolescent children (blood as dynamic medium and hair as accumulating one).

Materials and research methods

To study the content of metals in the soil and snow cover (essential Zn, Cu and toxic Pb, Cr), 170 points of depositing media were selected throughout the territory of Kazan city, which are under the influence of stationary and mobile sources of metal input. Metals of the studied series are present in emissions of 154 out of 291 enterprises in the consolidated database, and the location of the sampling points was determined after analyzing the structure of emissions and calculating the fields of metal concentrations with the determination of pollution epicenters using the licensed software "Ecolog-Gorod" 4.5 with an additional module for calculating averaged concentrations developed by Firma Integral Ltd, which is described in detail in [10]. Sampling of snow cover was carried out according to the recommendations [13] and was carried out by the through-breakdown method. As a result of the study the concentrations of metals (μg/L) were obtained in soluble (water phase) and suspended (solid phase) forms. At the same time, the content of metals in the solid residue (mg/kg dust) was calculated.

Under aerogenic pollution, the maximum concentrations of metals are usually recorded in the uppermost soil horizon. Down the profile, their content usually decreases and reaches the background level [2, 8].

At each point, one mixed sample was taken from the surface horizon by the envelope method from a depth of 0–20 cm.

Determination of the content of metals in the obtained aqueous extracts was carried out by atomic absorption spectrometry on the Perkin Elmer AAnalyst 400 device. Statistical processing of the obtained results of the study was carried out using the "STATISTICA v.6.0" package. The significance of the differences in the means was determined by the standard Student's t-test with Keuls' correction for small samples, and using the Mann-Whitney U-test for samples with pronounced asymmetry. The frequency characteristics of the variational series were evaluated, with an assessment of the normality of the distribution of samples, their 95% confidence intervals, medians and means with standard deviations.

Results and discussion

As a result of evaluating the data series of variations, a significant variability in the content of metals in the solid and liquid phases of snow was established (coefficient of variation 47.4–123.5%). The distribution of gross and mobile forms of metals in urban soils is also subject to very large variability. The maximum values are reached by the coefficients of variation of mobile forms of zinc (216%), and, especially, copper (732%). The high variability of the values, as well as the pronounced asymmetry of the samples, indicate the presence of dynamic factors that determine this variability. It should also be noted that there are direct correlations between the content of lead in hair and in the solid phase of snow (r = 0.28, p = 0.036); zinc in the blood and in the water (r = 0.44; p = 0.005) and solid (r = 0.45; p = 0.004) phases of snow; chromium in blood and its gross forms in soil (r = 0.33, p = 0.011). This circumstance allows us to make an assumption about the presence of objective prerequisites for the variability of the concentrations of these metals in the body, depending on the air route of intake, including dust.

The calculation of the threshold concentrations of metals was carried out in such a way that their content in the components of the external environment in the study area did not lead to increasing regional reference values in the blood and hair of adolescent children. The reference values were determined statistically (as the median of a ranked series of experimental measurements) based on retrospective population studies of the metal content in biosubstrates of adolescent children (9–16 years old) in the cities of the Republic of Tatarstan. The total sample size was 342 people.

To calculate the threshold concentrations of metals, it was necessary to construct a model capable of reflecting the relationship between their content in human biosubstrates and depositing media. Input parameters of the model: metal content in hair (x_1) and in blood serum (x_2); output parameters: metal content in snow cover (y_1) and mobile forms in soils (y_2).

It should be noted that the form of the regression dependence is not obvious and is clearly non-linear. At the same time, it is likely that the content of one or another metal in the blood and in human hair is interrelated. However, this relationship has a significant time lag, determined by the coefficients of biological accumulation of certain metals and the rate of hair growth, which makes it possible to identify it only with constantly acting (chronic) factors of influence. Under such conditions, artificial neural networks, which are universal approximators capable of reflecting an arbitrary implicit dependence of any complexity with a given accuracy, are best suited to the modeling task.

For regression tasks, the most suitable paradigms of neural networks are multilayer perceptrons (MLP networks) with linear (linear MLP networks) and nonlinear neurons (neuron activation functions). Thus, at the preliminary stage of modeling, a team of neural network experts is built. Under the conditions of the permanent influence of the factor that determines the influx of metals into the environment, the main calculation models should be built taking into account the mutual influence of the inputs during the formation of the output, that is, the models should contain the values of the metal content in both biosubstrates simultaneously.

To model the relationship between the content of metals in the snow and soil cover and the content of metals in the hair and blood of adolescent children in a given territory, MLP type neural networks with two inputs and one output were built. The internal structure of the computational MLP model for each metal was selected individually in the course of experiments from the condition of minimizing the root mean square error on the training set.

The simulation results are presented in the Table. In this case, the learning error characterizes the accuracy of the model on the training data and is used to assess the adequacy of the proposed neural network topology. The other two parameters (the standard deviation and the relative error) characterize the accuracy of the model's operation on data that is not involved in direct training. The most informative is the second of these parameters, since it gives an idea of the deviations of the model data from the real ones on a scale of measured values.

Thus, the models shown in the Table have a sufficient degree of accuracy and, according to the results of the analysis, are recognized as adequate. Consequently, they can be used to determine the threshold concentrations of metals in soils and snow cover based on the condition that the regional reference concentrations in the hair and blood of adolescents are not exceeded.

For further calculations, pairs of input values were compiled, processed by sequentially developed models 1–8 shown in the table. As a

Table

Indicators of relative errors and training errors of neural network models for different depositing media

No. of model	Metal, depositing media		Training error	Standard deviation	Relative error, %
1	Zn	snow	0.21	26.37	7.82
2		soil	0.19	15.87	37.65
3	Cu	snow	0.13	10.51	5.98
4		soil	0.28	1.68	34.76
5	Pb	snow	0.26	5.61	8.95
6		soil	0.08	1.48	6.18
7	Cr	snow	0.06	1.06	2.30
8		soil	0.12	0.16	3.98

Regional reference concentration in biosubstrates	Model	Threshold concentrations in depositing media
Zn, hair – 135.0 mg/kg Zn, blood – 0.91 µg/mL	1	Zn, snow – 21.16 µg/L
	2	Zn, soil – 2.40 mg/kg
Cu, hair – 11.3 mg/kg Cu, blood – 0.96 µg/mL	3	Cu, snow – 13.59 µg/L
	4	Cu, soil – 2.56 mg/kg
Pb, hair – 2.99 mg/kg Pb, blood – 0.03 µg/mL	5	Pb, snow – 4.99 µg/L
	6	Pb, soil – 6.92 mg/kg
Cr, hair – 0.51 mg/kg Cr, blood – 0.03 µg/mL	7	Cr, snow – 5.10 µg/L
	8	Cr, soil – 0.32 mg/kg

Fig. Threshold metal concentrations in depositing media

result, the threshold concentrations of metals in the depositing media were obtained, which are shown in the diagram (Fig.).

Conclusion

In conditions of constant supply of metals into the environment, the main calculation models should be built taking into account the values of the metal content in dynamic (blood) and accumulating (hair) biosubstrates simultaneously. To determine the threshold concentrations of metals, artificial neural networks, which are universal approximators, have shown a good ability to reflect an arbitrary implicit dependence of high complexity. A small relative error, taking into account the complexity of modeling (2–38%), allows the developed models to be used to determine the threshold concentrations of metals in the soil and snow covers, based on the condition that their regional reference concentrations in the hair and blood of the child population do not exceed. Determination of threshold concentrations in the depositing components of the urban ecosystem (soil and snow cover) is intended for the development of an emission control system, ecological substantiation of schemes for the development and placement of production facilities, master plans of cities, etc.

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