Formation of the xenobiotic profile in anthropogenic systems

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Abstract. The article deals with the issue of formation of the xenobiotic profile of a biogeocenosis as a combination of foreign substances in the environment in a form that allows them to enter into chemical and physicochemical interactions with biological objects of the ecosystem. At the initial stage, patterns of distribution of xenobiotics in various natural environments (water, soil, air, and living organisms) and their subsequent effects on the biogeocenosis were determined.

1. Introduction
At the beginning of the twentieth century, a new sphere of the Earth's shell began to form. It is a technosphere which is part of industrial and non-productive human activities with its own laws of material and energy flows. Being part of the biosphere, humans interact with it developing within the limits of physical, chemical, biological and other states of the biosphere. Natural processes are increasingly intertwined with man-made ones, increasing the exchange of matter, energy and information.

At the initial stage, transformation of the natural system takes into account possible transformations of its biosphere framework (biological, biocenotic, ecological, etc.). In the future, changes take place under the influence of both anthropogenic activities and dynamic processes characteristic of open self-organizing natural systems.

Patterns of the processes of entry, distribution, transformation and metabolism of pollutants are complex and rely on environmental information whose core is a live matter in all forms of its manifestation and a human as a socio-biological species. All other variables must be considered in relation to the overall biological nucleus.

2. Methods and materials
Currently, there are no methods describing patterns of xenobiotic behavior in the environment. The available research materials are devoted to environmental problems and methods of analytical chemistry of persistent organic pollutants, including monitoring which generally does not identify patterns of their migration and transformation in various natural objects. This article is a phenomenological description of formation of a xenobiotic profile as one of the most important environmental factors.

3. The xenobiotic profile and man-made migration paths
The xenobiotic profile should be considered as one of the most important environmental factors (along with temperature, light, humidity, trophic conditions, etc.) which can be described by qualitative and quantitative characteristics.
Xenobiotic profiles of the environment developing forming during evolutionary processes belong to natural xenobiotic profiles (XBP). They are different in different regions. The biocenoses in these regions are more or less adapted to the corresponding natural XBP.

The evolution of natural XBE is determined by biogeochemical laws and controlled by the geochemical balance in the processes of biogeochemical cycles of biogenic components of the natural environment.

Determination of the balance of nutrient components of the oceans and land, identification of geochemical processes caused by implementation of large land-reclamation projects, prediction of the impact of production and economic activities on the environment are some problems of migration flows, geochemical balances of territories with different spatial dimensions.

Geochemical development and the balance of the substance of territories are determined by a surface and underground runoff, a biogenic and technogenic migration, a movement of air and water masses of seas and oceans.

At the present stage, migration of the substance with a surface runoff is well studied. For individual river basins, indicators of ionic and solid runoff were determined. For the most studied basins of the underground runoff, it is possible to determine the specific distribution of salt removal or supply over the entire area of the basin; for less studied ones, it is possible to determine the overall balance of solutes.

The atmospheric transfer occurs as a result of general circulation of the atmosphere and local movements of air masses. The main elements of the atmospheric transfer of salts from the ocean are chlorine and sodium, and a number of trace elements (iodine, boron, bromine, lithium). Estimates of the atmospheric transfer of substances differ by tens and hundreds of times due imperfect methods [1, 2].

Technogenic migration is characterized by a direct movement of substances as a result of economic activities. It is understudied, although it is of paramount importance.

The chemical products entering the environment are distributed and transformed in the atmosphere, soil and water bodies; they enter food chains and are accumulated by living organisms. Many ecotoxicants extend over long distances and retain dangerous properties for a long time. The ability of ecotoxicants to spread over long distances depends on their physical, chemical, physicochemical properties (evaporation, volatility, solubility, soil absorbability, resistance to decomposition).

The study of anthropogenic migration is of great importance.

In the geochemical aspect, the anthropogenic impact involves transition of a substance from man-made migration flows into the natural ones. Since products of anthropogenic production that migrate with the anthropogenic flow have different resistance, they are transformed into natural migration flows with different intensity.

To characterize the technogenic geochemical impact, in addition to elements involved in the technogenesis, a number of indicators are used.

One of these indicators is technophilicity of chemical elements (N) [3] which characterizes the degree of utilization of the chemical elements of the lithosphere.

\[
N = \frac{Q}{Q_c}
\]  

where \(Q\) – annual element mining (t), \(Q_c\) – clarke.

To assess a possible impact of technogenesis on living organisms, an indicator of destructive activity of elements (A\(^t\)) has been introduced. It is the ratio of the weight of an element in the annual production plus its release into the environment from the burning of combustible minerals to the weight of this element in the annual biological production of terrestrial vegetation [4].

The geochemical analysis of toxicity of chemical elements and compounds ensures purity of the atmosphere of urban agglomerations, preserves the natural composition of soils and natural waters. Currently, around 500 thousand compounds are used; 40 thousand compounds are harmful, and 112 thousand are extremely toxic. Technogenic pollution affects ecological systems and is determined by the ability of chemical elements to be included in natural migration cycles.

Technogenic migration occurs in gaseous, liquid and solid forms. Caused by intense human activities, it accelerates the movement of various substances so that the cycles of substances become
incomplete. The products of material production involved in the living cycle partially accumulate in the biosphere creating obstacles to natural processes.

The mechanism of specific toxicity is understudied. For ecotoxicology, toxicity of the substance that enters the environment and products of its transformation is important. When contaminated with industrial waste, fuel combustion products, garbage, a mixture of products of complex composition is formed. The total toxic effect of the mixture may differ from the total toxicity of its individual components.

Of particular interest are molecules with bioavailability, i.e. molecules able to interact non-mechanically with living organisms. As a rule, these are compounds that are in a gaseous or liquid state, aqueous solutions; finely dispersed dust (the particle size less than 50 microns); substances entering the body with food.

Some bioavailable compounds are utilized by organisms participating in the processes of their plastic and energy exchange with the environment, i.e. act as habitat resources. Other ones are not used as sources of energy or plastic materials; they modify normal physiological processes. These are xenobiotics.

An important element of the xenobiotic profile is a foreign substance in the organs and tissues of living beings; all of them are consumed by other organisms (they have bioavailability). In contrast, chemicals that are fixed in solid, non-dispersible objects (rocks, solid industrial products, glass, plastic, etc.) do not have bioavailability. They can be considered as potential sources of XBP formation.

Economic activities change the natural XBP of many regions (especially urbanized ones). Chemical substances that are not typical of the environment accumulate in the medium in sufficient quantities to initiate the toxic process in the biocenosis, change the natural XBP and transform into an eco-toxicant (xenobiotic).

Determination of quantitative parameters at which an eco-politanant is transformed into an eco-toxicant is a difficult task. When solving it, it is necessary to take into account that in real conditions, the whole xenobiotic profile of the environment acts on the biocenosis modifying the biological activity of a particular pollutant. Therefore, in different regions, different xenobiotic profiles, different biocenoses, quantitative parameters of transformation of the pollutant into ecotoxicants are different.

Assessment of technogenic pollution is used to identify the amount of an element or substances entering the human body according to the scheme: natural objects (soil, water, air) - organisms (plants, animals) - food products (vegetable, animal) - food - human.

Even if according to hygienic standards, environmental pollution is not dangerous, it is advisable to assess the MPC of pollutants and their effects to determine the maximum allowable load taking into account all the pathways of harmful substances.

Environmental studies analyze a) the relationship between accumulation of harmful substances and severity of toxic effects; b) the statistically significant dependence (positive or negative) between the content of xenobiotics in various natural environments and diagnostic substrates; c) the comparison of identified patterns in the distribution of xenobiotics in various natural environments with data on the health status of the population obtained on the basis of medical statistics.

Implementation of this approach is important with respect to priority organic pollutants: pesticides (aldrin, chlordane, DDT, mirex, etc.), industrial substances (PCB, hexabromobiphenyl, chlorine paraffins, etc.), by-products (PCDD, PCDF, PAH), organic metal compounds. Their danger is due to their ability to cumulate; various diseases can develop after exposure to these substances.

Persistent organic pollutants that are part of priority pollutants do not fall into any of the five hazard classes, since most of them have a powerful toxic effect and can have mutagenic, teratogenic and carcinogenic effects on humans and animals [5].

Pollution with persistent organic pollutants (POPs) is caused by their migration between natural environments; all elements of the biosphere are subject to the anthropogenic pressure regardless of its sources [6].

4. Theoretical substantiation of xenobiotic migration in natural environments
Atmospheric air is a nonstationary, inhomogeneous, multiphase, multicomponent system associated with the problems of transboundary transportation of POPs. Entering from various sources, POPs are carried by air currents and spread throughout the globe. Based on the data on POP sources, the model of horizontal transportation and turbulent diffusion of substances in the atmosphere [7] complemented by models of the POP exchange with soil and water surfaces was built. “Dry” deposition of POPs (D) is calculated as a stream on the underlying surface for a certain period of time using the deposition rate Wg:

\[ D = (C(x,y,0)) W_g dt \] (2)

To calculate the amount of POPs that fall out with precipitation (F), the following formula is used:

\[ F = C(x,y,0) h \gamma dt \] (3)

The total amount of pollutants. Pollutants entering with atmospheric transfers (Q) are

\[ Q = C(x,y,0) (W_g + h \gamma) dt \] (4)

Calculations show that atmospheric transportation of POPs is one of the main sources of environmental pollutants.

Natural water is an open-type multiphase heterogeneous system exchanging substances and energy with other media and a biological component. Accumulating POPs, bottom sediments contribute to their removal from water; on the other hand, they are a constant source of water pollution. Hundreds of thousands of tons of POPs are deposited in the bottom sediments of large river deltas, including OCPs, PCBs, PCDDs, PCDFs.

Irrigation waters are a significant source of POPs. Calculation of the removal of chlorine-containing pesticides from agricultural land is a complex multi-dimensional task [8]. The determining factor is a dose of pesticides. The total amount of removal is proportional to the amount of precipitation and the area of agricultural lands.

For small and medium catchments, the average concentration of pesticides in the river in the closing section without taking into account the transformation in the riverbed is calculated by formula

\[ C_{op} = \frac{(M_1C_1F_1 + M_2C_2F_2 + \cdots + M_nC_nF_n)}{M_0F_0} \] (5)

where \( M_1 \cdots M_n \) – rainwater flow modules on selected agricultural fields; \( C_1 \cdots C_n \) – pesticide concentrations in the surface runoff; \( F_1 \cdots F_n \) – areas of individual agricultural land treated with pesticides; \( M_0 \) – rainwater flow module in the river station; \( F_0 \) – catchment area [6].

In the total balance of POPs in sludge, the share of metabolites becomes larger than the share of initial compounds.

In the category of global functions, the lithosphere with its surface layers determines a direction and diversity of the soil-forming process and depends on the thin layer of soil that covers. A weathering crust and a sedimentary layer experience effects of soil formation. Due to the fact that the soil does not have mobility characteristics of other natural environments, it is a place for the collection and storage of all types of xenobiotics, including POPs.

When xenobiotics enter the soil, they are subject to complex physico-chemical and biological transformations. Under the influence of some microorganisms, the POPs are oxidized to carbon dioxide and turn into less toxic metabolites. The rate of destruction depends on climatic conditions, the degree of pollution and conditions of reproduction of microorganisms. Unlike other natural objects (water, air) in which self-purification is quick, they are slow. Moreover, lead and mercury compounds accumulate in soils. Substances entering the soil migrate. It is obvious that modeling the space-time behavior of POPs taking into account their persistence, synergism and antagonism is a difficult task. Monitoring of the soils of industrial centers and adjacent territories indicates a certain regularity in the spatial distribution of xenobiotics according to the degree of contamination:

- risk zones - areas with a high level of soil pollution with POPs;
- potential risk areas - areas affected by POP sources;
- areas of POP unloading or degradation - areas around eliminated or modernized sources of POPs, reclaimed land;
- zones not subject to risks - background areas.
Xenobiotic pollution can be assessed only at the qualitative level. When creating a quantitative model of xenobiotic profile formation, it is necessary to take into account that XBP effects on the biocenosis manifest themselves as qualitative, step-wise changes in the state of the system or the mode of its development in response to monotonous and slow changes in parameters. These processes belong to non-linear dynamical systems.

The theory of "point" dynamic systems is based on differential equations

$$\frac{du_i}{dt} = \frac{1}{\tau_i} F_i(u_1, u_2, \ldots, u_n)$$  \hspace{1cm} (6)

where $u_i$ - concentration of reactants, $F_i(u_i)$ - nonlinear functions describing the interaction, $\tau_i$ - characteristic time of change of variables $u_i, i = 1, 2, \ldots, n$.

When specifying a type of function $F_i$, their solutions are determined by the initial conditions. However, surprises arise when decisions lose their stability with small deviations from the corresponding decision.

Equation (6) describes the development of processes in time rather than in space. However, in these processes, dynamic variables of concentration or a number of living organisms move in space due to diffusion or migration.

In the simplest case, changes in the flow of particles $\Delta u_i$ for $\Delta t$ due to space effects is proportional to the gradient of variables

$$\left(\frac{\Delta u_i}{\Delta t}\right)_{xy} = D \text{div} j = D \text{div} \left(\frac{\partial}{\partial x} u_i + \frac{\partial}{\partial y} u_i\right)$$  \hspace{1cm} (7)

Equation (6) takes into account spatial effects

$$\frac{\partial u_i}{\partial t} = \frac{1}{\tau_i} F_i(u_1, u_2, \ldots, u_n) + D \Delta u_i; i = 1, 2, \ldots, n$$  \hspace{1cm} (8)

where $D_i$ - diffusion coefficients.

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

Equation (8) describes important phenomena of self-organization of systems in which diffusion occurs. Functions $F_i(u_1, u_2, \ldots, u_n)$ describe chemical reactions at $x$, and variables $u_i, i$ - concentrations of substances involved in the reaction, values $\tau_i$ is a typical time of reactions.

The study of solutions of equation (8) will allow for the analysis of the phases of formation of xenobiotic profiles which may involve fronts, traveling pulses, spiral waves, dissipative structures and other processes in active media.

5. Conclusion

Anthropogenic human activities change the natural xenobiotic profile of territories, especially urbanized ones. Chemicals accumulating in the environment and causing changes in the natural xenobiotic profile act pollutants. A change in the xenobiotic profile may be a result of excessive accumulation of eco-pollutants.

Along with experimental studies of POPs in the atmosphere, water and bottom sediments, soils, plants, biological media and food products, we can trace patterns of migration, transformation and deposition of pollutants into eco-toxicants and assess their impact on the biosphere.

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