Application of index of general toxic effects of biologically available polycyclic aromatic hydrocarbons as leading indicator in assessing the quality of industrial-urbanized territories

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Abstract. The authors consider the important issue relating to the assessment towards the territory exposed to some toxic effects of man-made polycyclic aromatic hydrocarbons (PAHs). As the main criterion applied in referring a territory to a particular level, it is proposed to use indices of the total toxic effects of bioavailable PAHs. Depending on the values of these indicators, we point out seven levels and propose for each one some evidence-based recommendations on the most rational use of industrialized urban territories.

1. Introduction
The level of technogenic pressure on all components of the environment is growing rapidly, which is the inevitable consequence of the technical development of society. The global scale of environmental challenges and their consequences began to be realized relatively recently, about 60-70 years ago, and in some countries even later. Owing to a gradual understanding of the seriousness of environmental issues, over the past few decades, there have been identified some technogenic factors that have the most critical impact on certain components of the environment. Including identified groups of pollutants, the content of which must be controlled in the soil, water, atmosphere and in objects of wild nature. The list of such compounds includes polycyclic aromatic hydrocarbons, related to persistent organic pollutants and having a carcinogenic and mutagenic toxic effect [1].

Today, new methods of recultivating land contaminated by various ecotoxicants, including PAHs, continue to be actively introduced in the world [2]. However, the limited land area suitable for living and conducting human activities, with an increasing population in the world and its needs, necessitate development of a scientific approach to management applied towards polluted territories, not only in terms of improving their quality. In our view, it is required also the substantiated distribution of the land resources between the tenant farmers, based on urgent data of geo-ecological monitoring.

2. Methods and materials
Recommendations towards the lands use exposed to man-made and technogenic impacts were given on the basis of the levels of toxic effects of bioavailable PAHs in the designated territory.
The indices of the total toxic effects of bioavailable PAHs, proposed by the authors, were used as an indicator determining these levels: $I_{2,3}$ (for light polyaromatic hydrocarbons, containing less than 4 aromatic rings in the structure) and $I_{4,6}$ (for heavy ones, containing 4-6 aromatic rings), each ring was calculated using the formula (1).

$$ I = \sum_{i=1}^{n} c_i \cdot f_i \cdot \frac{1}{\lg K_{oc}} $$

(1)

where $c_i$ is the concentration of $i$ PAH in the soil sample; $f_i$ - a toxic equivalence factor of that PAH [3]; $K_{oc}$ is the binding constant of $i$ PAH of this soil [4].

A feature of these indices is that, unlike most of these indicators, they take into account not only the total concentration of polyaromatic compounds in the soil, but also the biological effects of each of them.

The division of the index into two indicators $I_{2,3}$ and $I_{4,6}$ is due to the fact that the pressure of saturated vapors significantly decreases when a fourth aromatic ring appears in the PAH structure. This is the reason why heavy polyaromatic hydrocarbons are more characteristic of being in the form of solid particles adsorbed by soil than of light PAHs, which are largely present in the atmosphere as vapors [1].

The territories allocation within the level classification was conducted in line with the scale, based on not mathematical laws but on qualitative changes which were observed in the environment when transferring from one level to another. The assignment of a territory to one or another level was made by comparing the current values $I_{2,3}$ and $I_{4,6}$ for this territory with their maximum possible values and between each other.

3. Results and Discussion

Proposals for the most rational use of lands (in the authors' opinion) exposed to man-made impact, depending on the level of some toxic effects of bioavailable polyaromatic hydrocarbons are presented in Table 1. The indicator $I_{2,3}$ allows to indirectly judge about the state of atmospheric air in a certain territory, and the indicator $I_{4,6}$ - mainly about the quality of the soil, for the reasons mentioned above. Thus, the recommendations are given on the basis of the synergy of these two indicators.

The advanced analytical equipment, used to measure the concentration of poly-aromatic hydrocarbons in the soil, possesses the completely low limit of the detection [5]. Thus, in the case of complete absence of analytical signals corresponding to compounds of the PAH class, it is possible to speak of the most favorable ecological condition of the territory (level 1), which is best suited to accommodate recreational zones, children's and medical institutions, as well as agricultural lands, on which food products are produced (especially those which are not subjected to further heat treatment).

If heavy PAHs begin to be detected in the soil, while volatile substances (level 2) are also completely absent, then there is a low-hazardous toxic effect of polyaromatic hydrocarbons. Most likely, light PAHs are predominantly present in the atmosphere, but they are not highly toxic. Thus, the territory is suitable for housing residential areas.

The territory should be attributed to level 3, if low molecular weight and heavy PAHs are present in the soil, with the additional condition that the index $I_{2,3}$ attributed to the maximum value of this indicator exceeds the similar ratio for the index $I_{4,6}$. This indicates to the prevailing effect of light PAHs on the territory. It is quite acceptable to place agricultural lands on which technical and other crops are growing, largely being subject to further processing. Lipophilic compounds like polyaromatic hydrocarbons are likely to penetrate plant cells, mostly settling on the leaves from the atmosphere, rather than with nutrient juices from the soil (although, the question about what effects more PAHs sorbing by plants is still open - their content in the soil or in the atmosphere) [6, 7]. However, as mentioned above, volatile PAHs are low carcinogenic and the low value of the indicator $I_{4,6}$ for the soil indicates low concentrations of highly toxic polyaromatic hydrocarbons in the atmosphere. Thus, a territory with a relatively high level of PAH in the atmosphere, but low in the soil should have a weak effect on the quality of agricultural products under production.

The territories assigned to level 4 differ from the previous group because here the ratio of the index $I_{2,3}$ to its maximum value is less than the same ratio for the index $I_{4,6}$. This indicates that the soil...
contains mostly polyaromatic hydrocarbons with a high toxic equivalence factor close to 1. At the same time, the probability of a rather high content of light PAHs in the air (at the level of values close to the MPC value) is high. Conducting agricultural activities on these lands is inappropriate because of rather high concentrations of PAHs in the soil and in the atmosphere. The continuous presence of people in the territory is also undesirable, however, non-permanent exposure to low carcinogenic compounds in quantities below MPC is acceptable. Therefore, in the territories of level 4, it is advisable to place the working areas of enterprises (with a working day of not more than 8 hours) and transport roads.

Table 1. Recommendations for lands use to be subject to human impact

| Level of carcinogenic effects on territory | \( I_{2-3} \) | \( I_{4-6} \) | Objects whose accommodation or location is most rational in given territory |
|------------------------------------------|--------------|--------------|--------------------------------------------------------------------------------|
| (1) Below the detection limit Below the detection limit | \( I_{2-3} < I_{\text{max}} \) \( I_{4-6} < I_{\text{max}} \) | Recreations, children's and medical institutions, agricultural lands for food production Residential dwellings |
| (2) \( I_{2-3} < I_{\text{max}} \) \( I_{4-6} < I_{\text{max}} \) | Work areas of industrial enterprises with the possibility of permanent presence of employees in the territory without the use of personal protective equipment, transport and other communications. |
| (3) \( \frac{I_{2-3}}{I_{\text{max}}} > \frac{I_{4-6}}{I_{\text{max}}} \) | Agricultural lands for industrial and other crops undergoing to further processing/treatment |
| (4) \( \frac{I_{2-3}}{I_{\text{max}}} < \frac{I_{4-6}}{I_{\text{max}}} \) | |
| (5) \( I_{2-3} \geq I_{\text{max}} \) \( I_{4-6} < I_{\text{max}} \) | Technological buildings, a long stay in the territory of which requires the use of personal protective equipment (warehouses, remote controlled industrial installations, etc.) |
| (6) \( I_{2-3} < I_{\text{max}} \) \( I_{4-6} \geq I_{\text{max}} \) | Technological buildings of I and II class of danger, even a short stay in the territory of which requires the use of personal protective equipment |
| (7) \( I_{2-3} \geq I_{\text{max}} \) \( I_{4-6} \geq I_{\text{max}} \) | The territory is not suitable for living and carrying out any types of economic activity. Land reclamation is required. |

Exceeding the maximum index \( I_{2-3} \) with a relatively low value of the indicator \( I_{4-6} \) gives evidence to refer the territory to level 5, from which the term "pollution" can be used. In the air of these areas, obviously, an excess of the MPC of light PAHs should be observed, with a relatively low content of the most toxic high-molecular compounds. It is allowed to place household buildings (warehouses, industrial facilities that do not require the constant presence of personnel nearby, etc.). If necessary, a long stay in the area should be accompanied with the use of some personal protective equipment, primarily respirators.

In case of exceeding the maximum value \( I_{4-6} \), but with the value \( I_{2-3} \) below the maximum, the territory can be attributed to 6 level of toxic effects. Such a territory is contaminated with PAH with a high toxic equivalence factor. The probability of exceeding MPC of light polyaromatic hydrocarbons in the
atmosphere is high. These lands are suitable only for the placement of technological facilities, for which I and II class of danger is obviously established and even a short-term stay within their limits requires the use of some personal protective equipment.

Finally, exceeding the maximum values for both indicators shows the critical pollution of the territory with polyaromatic hydrocarbons. No economic activity here should be carried out, reclamation is required.

4. Conclusion

It is obvious that timely and well-planned measures for the rehabilitation and improvement of the quality of the territory should be aimed at reducing the toxic effect of bioavailable polyaromatic hydrocarbons. However, conducting these events are not always possible due to financial, technical or other reasons. In this case, the recommendations given in the article can be used as a basis in land management of unclaimed lands. Knowing the current level of toxic effects of PAHs on the territory, it is possible to limit the choice of infrastructure facilities located on it.

Also, with the help of the proposed recommendations, the inverse challenges can be solved, namely, the selection of the most optimal place for a new infrastructure object, from the point of ecology location, taking into account its future toxic effects on some neighbouring territories and the nature of their building.

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