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Olena Barabash

## ECOLOGICAL HAZARD ASSESSMENT OF THE ATMOSPHERIC AIR AT THE URBAN ECOSYSTEM BY THE STATE OF THE DEPOSIT ENVIRONMENT

National Transport University, 1, M. Omelianovycha-Pavlenka str., Kyiv, 01010, Ukraine

E-mail: el\_barabash@ukr.net

### Abstract

Industrial activity and emissions of road transport is one of the major sources of pollution in urban ecosystems and poses a significant threat to the health of urban populations due to dust emissions into the atmosphere. The high cumulative capacity of toxic metals, in particular the plumbum, leads to its entry into the atmospheric air, soil and groundwater, and ultimately to accumulation in the tissues and organs of plant organisms. There is a correlation between the content of toxic metals in the atmospheric air and their fallout within the sanitary protection zone of industrial and motor transport enterprises and distribution throughout the urban ecosystem. Snow cover stores pollution, thus, it is often used to assess the state of the air. The layer-by-layer sampling of the snow cover allows determining the pollution dynamics and the influence of the production capacities of enterprises on the state of the urban ecosystem. The bioassay methods using plant organisms as test objects is based on their sensitivity to exogenous chemical effects and is reflected in the response of plants to pollutants. Determination of physico-chemical parameters of the snow cover and calculation of phytotoxic effect based on the phytotesting methods allows to detect not only the presence of toxic metals in the snow cover, but also to obtain reliable information about their distribution in the atmospheric air of cities. According to the researches results, the indexes for the lengths of *Lepidium sativum* shoots were obtained. The test object was germinated in a snow cover sampled at a distance of 5 to 50 m near the WOG filling station enterprise. The data obtained were compared with the values of the shoots length of test objects germinated in snow samples from the territory of the park area. It was established that the level of atmospheric air pollution with toxic metals is the highest at a distance of 50 m from WOG filling station. The physico-chemical parameters of the snow cover and the phytotoxic effect indicate a high probability of toxic metals entry into the atmospheric air beyond the limits of the sanitary protection zone of WOG filling station and into the residential areas.

**Keywords:** phytoindication; test object; snow cover; phytotoxic effect; garden cress (*Lepidium sativum*); urban ecosystem

### 1. Introduction

According to the results of geochemical and hygienic studies, many scientists note the dependence between the content of toxic metals in the atmospheric air and their atmospheric fallout in the territory of cities, which is fixed in the form of anomalies in the snow cover as a natural environment [1]. During the formation and fall of snow due to processes of dry and wet washing, the concentration of pollutants in it is usually 2-3 times higher than in atmospheric air, since the snow cover deposits pollution, allowing to assess the conditions of the atmospheric air [2]. Layered sampling from the snow cover provides prospects for obtaining data on the dynamics of atmospheric air pollution in the cities during the winter, and sampling over the entire area of snow cover provides the opportunity to obtain pollution data from the formation of a stable snow cover until the time of sampling. The content of toxic substances in the snow

cover is determined by relatively simple methods with a high degree of reliability, especially since there is a limited number of stationary posts in the conditions of large cities with complex industrial-residential housing, which does not allow to obtain reliable information on the spatial distribution of polluting substances across the polluted areas [1]. The use of bio-indicative monitoring methods, in particular phytotesting using garden cress (*Lepidium sativum*) as a sensitive test object will allow to carry out cheap and easy environment quality control for the presence of toxic substances in the snow cover continuously and without prior identification of specific substances or physical effects [3].

### 2. Analysis of research and publications

From the geological standpoint, snow was first studied by P.N. Chyrvinskyi, who considered snow as an integral part of the system: the atmosphere - the

soil - the aquifer [4]. Issues of pollution monitoring in snow cover are revealed in scientific works of V.N. Vasylenko, I.M. Nazarov [5]; V.M. Artemov, etc. [6]. According to E.I. Yehorova [7], the cumulative effect for a variety of influences can be estimated only by biotesting methods. I.N. Tarasenko considers biotesting in his work [8] as an introduction to a more detailed and comprehensive analysis for the chemical composition of atmospheric air, soil or water. Control and evaluation of phytotoxic potential of the biospheric components are covered in many scientific works of domestic and foreign authors [9 - 14].

### 3. Materials and methods

Snow cover samples were obtained taking into account the boundaries of the gas station's sanitary protection zone [15]. The sampling density was 1-5 samples per km<sup>2</sup> due to the possibility for detecting the contamination epicenter. Samples were taken at the full capacity of the snow sampler, and the area of the exploratory well and snow day were recorded. The length and width of the hole were measured to calculate the area on which the fallout from the atmosphere is projected. The samples weight reached 6 kg, which allowed to obtain a mass of fallout sufficient for analysis. The sampling date was clearly recorded to determine the time of accumulation in the snow cover. The samples were melted and centrifuged to remove the solid precipitation fraction. The organoleptic index (odor) of snow samples was evaluated using a 5-point scale. Chemical methods were used for determining the pH index (pH) [15].

Phyto-testing of the snow cover using the test object was carried out for 10 days. A batch of garden cress taken for experiments was tested for germination. 90-95% of seedlings sprouted from the sown seeds were taken as the norm [3].

After measuring for each of the investigated variants, the mean length of the aboveground and root parts  $\bar{x} \pm m$  was calculated, where  $m$  is the arithmetic mean error, which was determined using the formula:

$$m = \sqrt{\frac{\sigma^2}{N}}, \quad (1)$$

where  $N$  – the number of results;  $\sigma^2$  – the variance defined using the expression:

$$\sigma^2 = \frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N}. \quad (2)$$

The significance  $t$  of the difference for the arithmetic mean was calculated by the Student-Fisher test:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{m_1^2 + m_2^2}}, \quad (3)$$

where  $x_1$  – the arithmetic mean of the indicator in the control experiment;  $x_2$  – the arithmetic mean of the indicator in the studied variant;  $m_1$  – arithmetic error in the control experiment;  $m_2$  – the same in the variant studied variant.

The phytotoxic effect was determined as a percentage by one bioparameter - shoot length, and was calculated using the formula:

$$PhE = \frac{M_0 - M_x}{M_0} * 100\%, \quad (4)$$

where  $M_0$  – the value of bioparameter (plant mass, height of shoots, root length, etc.) in the vessel with the control substrate;  $M_x$  – the value of a similar bioparameter in the vessel with the test substrate.

### 4. Results and discussion

Shevchenkivskyi district is one of the central districts of Kyiv and covers an area of 2,7 thousand hectares, with a population of 233,500 people. Shevchenkivskyi district combines high-productivity industry (Table 1) and construction, printing production and branched trade, health care and consumer services, a wide network of educational and cultural institutions.

Thus, the industry of the district includes various enterprises in Kyiv, in particular, State-owned enterprise Artem, PJSC KZBN "Rosynka", and JSC "NVK Kyiv Automation Plant named after H.I. Petrovsky", OJSC CEZ "Transsygnal", SE "Research Plant of Welding Materials named after Ye.O. Paton", SE Polygraph Enterprise "Ukraine", SE Press Publishing House, SE OJSC Kyivkhib Bakery and Confectionery Complex, SE OJSC Kyivkhib Experimental Bakery, JSC Kyivmedpreparat [16].

Table 1

## Enterprises of Shevchenkivskyi district of Kyiv

Number of enterprises, which reported using the Form 1P in 2018 - 59 companies	
Sectoral structure of industry by types of economic activity	Share, %
Industry	100.0
<i>Processing industry:</i>	15.8
food industry and processing of agricultural products	15.8
<i>Consumer goods industry:</i>	0.7
textile and sewing	0.7
leather and leather footwear manufacturing	
Manufacture of wood and wood products	0.3
Pulp and paper, printing industry and publishing	24.7
<i>Chemical and petrochemical industry:</i>	22.5
chemical production	22.3
rubber and plastic products production	0.2
Manufacture of other non-metallic mineral products (building materials and glassware)	
Metallurgy and metalworking	2.7
<i>Mechanical engineering, repair and installation of machines and equipment</i>	33.3
manufacture of machinery and equipment	2.5
manufacture of electrical and electronic equipment	5.8
manufacture of transport equipment	25.0

The threatening situation in the area is formed due to the rapid increase in traffic flows. Residents living in the immediate vicinity to the road interchange and intersection with insufficient vehicle capability are most affected. According to the results of observations performed by the Central Geophysical Observatory in Shevchenkivskyi district, the Permohy avenue, Permohy Square and Bessarabska Square are characterized by significant environmental danger. Bessarabska Square is the most polluted place in Kyiv, where the integral indicator of atmospheric pollution is constantly characterized as high. The levels of suspended solids, phenol, nitrogen dioxide and formaldehyde exceed for at least double the maximum permissible concentrations.

The general level of air pollution according to the atmospheric pollution index (API) in the Shevchenkivskyi district of Kyiv is estimated as high [17]. In general, the content of nitrogen dioxide, formaldehyde, nitrogen oxide and phenol exceed the average daily maximum permissible concentrations (ADMPC) in the district. These are substances of 2 and 3 classes of danger, which are the most polluting in the studied area throughout the year. Nitrogen dioxide content at average and maximum concentrations exceeds the corresponding MPC level in all posts of Shevchenkivskyi district. The content of heavy metals was below the admissible levels in 2018, and the average annual concentrations of cadmium, iron, manganese, cuprum, nickel, plumbum, chromium and zinc at all posts were at the

level of 0.0 - 0.1 ADMPC [17].

Exceedance in MPC for nitrogen dioxide, carbon monoxide, formaldehyde dust is established for all highways in the district. The largest exceedances were found on the Sichovykh Striltsiv Str., O. Teliyh Str., Permohy ave., B. Khmelnytsky Str., T. Shevchenko Blvd. In the area of the industrial enterprises influence within the Shevchenkivskyi district, the content of nitrogen dioxide exceeds the MPC for the following objects: PJSC "Kyivoblenergo" 1, Stetsenko Str.; State-owned enterprise Artem, 2/10, Melnykov Str.; PE Company "KIMS" 18-24, Dmytrivska Str.; WOG gas station 11-B Permohy ave.; AMIS gas station 53, Dehtyariivska Str.; AMIS gas station 46/48, Tabirna Str.; Plastmash PJSC; MAUP boiler house.

Considering that the snow cover composition varies depending on its distance from the source of pollution, snow samples were taken at sites of at least 1 m<sup>2</sup> at a distance of 5, 10, 20 and 50 m from the WOG gas station in order to obtain reliable data on the air pollution level. The control sample was a sample taken in the A.V. Fomin Botanical Garden. The contact time for the snow cover with the environment from the time of snowfall to sampling was 10 days in late January and 14 days in mid-February. The study found that the highest content of soluble impurities was observed in the sample taken at a distance of 5 m from the gas station in January, whereas in February, the highest content of dissolved impurities was observed for the samples taken at a

distance of 50 m from the gas station. The lowest soluble impurity content was detected in the control sample. Such indicators are related not only to the activity of the gas station, but also with the presence of intensive road traffic at the Peremohy Avenue.

Analyzing the pH in snow cover, it was noted that it can be caused by the presence of not only by solids, but also by gaseous pollutants in the atmosphere: SO<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, NO, NO<sub>2</sub>, which will be transferred into the soil environment after snowmelt. Pure snow, like pure rain water, has a pH = 5.6, due to the presence of CO<sub>2</sub> in the air, which acidifies precipitation [15]. If the concentration of nitrogen oxides, sulfur dioxide and other acidic substances in the air is high, the snow will have a pH value of <5.6. In cases, when a pH of snow is above 5.6 there is a probability of its contamination with metal oxides. The average pH in the tested snow samples ranged from 5.25 (5-10 m from the gas station) to 5.75 (20 m from the gas station), proving the heterogeneity of the pollutants distribution and the extreme impact of road transport emissions. Thus, most of the snow samples taken at a distance of 5 and 10 m from the gas station in January and estimated by their pH index contain nitrogen oxides and sulfur dioxide. Alkaline environment and metal oxide contamination were detected in samples taken at a distance of 20 m from the gas station in January and February.

The evaluation of organoleptic parameters for snowfall samples according to DSTU ISO 7027: 2003 "Water quality. The definition of turbidity" revealed that the high level of transparency comparing to other samples differs for snow water of the control sample [18]. High turbidity is observed in samples taken near the gas station at a distance of 5 m and 10 m, which may be explained by the presence of inorganic and organic fine suspensions, sand, clay, inorganic compounds (aluminum hydroxide, carbonates of various metals), as well as organic impurities, oxidation of iron and manganese compounds with oxygen in the air. The most intense earthy odor was recorded in samples taken in January in the area closest to the gas station (5 and 10 m). In the rest of

the samples, the smell of snowmelt water also had a natural origin, which is associated with the activity of living and dead organisms, the presence of plant residues, specific substances released by certain microorganisms.

Plants as primary links of trophic chains play a major role in the absorption of various substances and are the most convenient environmental pollution indicators. Therefore, using the plants permits to perform the accurate assessment of the environmental situation in the study area. The purpose of the growth test is to track the changes in the germination indices of the indicator plant grown on the samples of soil, water, water extracts of soil, etc. This method allows to evaluate both the inhibitory and the stimulating effect of various pollutants on plants.

The level of contamination in the snow cover at the WOG gas station was determined by the method of T.Ya. Ashihmina using garden cress seeds. The experiment was carried out for 10 days, after melting snow and reaching room temperature of snowmelt water. 50 seeds of garden cress were placed in Petri dishes on filter paper moistened in the test samples of snowmelt water. The length of the shoots was measured after 24 hours, and then every day throughout the allotted time for the experiment. The length of the shoots was measured using a caliper to the nearest 0.1 cm.

Analyzing the reaction of the test object to the toxic metals content in the snow cover sampled at different distances from the gas station, it was established that the degree of growth inhibition of the plant organisms is about 53% in January and more than 60% in February compared to the control. It should be noted that the highest percentage of inhibition was observed for plants sprouted in samples taken at 10 and 50 m distance from the source of contamination in January and February.

Based on the obtained data, the phytotoxic effect of the gas station emissions on the garden cress as a sensitive indicator for the toxicity of toxic metals in the environment was calculated (Table 2).

Table 2

#### Phytotoxic effect

Parameter	WOG gas station (Shevchenkivskyi district of Kyiv)							
	Garden cress (%) (January)				Garden cress (%) (February)			
	5 m	10 m	20 m	50 m	5 m	10 m	20 m	50 m
PhE	46.48	56.34	36.62	49.30	21.03	66.67	28.21	30.77

Thus, the growth inhibition in comparison with the control were the most significant in the samples taken at a distance of 10 and 50 m from the pollution source.

## 5. Conclusions

It was established that the level of pollution of the atmospheric air by toxic metals is relatively high both near and at a distance from the gas station located in the Shevchenkivskiy district of Kyiv. The obtained results for the lengths of shoots, physicochemical indicators of snow cover and phytotoxic effect of the activity of the "WOG" gas station on plant organisms in comparison with the control sample indicate a high likelihood of presence of toxic metals in the atmosphere both outside the sanitary zone and the within the residential area of the district.

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**О. В. Барабаш**

**Оцінка екологічної небезпеки атмосферного повітря урбоєкосистеми за станом депонуючого середовища**

Національний транспортний університет, вул. М. Омеляновича-Павленка, 1, Київ, Україна, 01010

E-mail: el\_barabash@ukr.net

Діяльність промислових підприємств та викиди автомобільного транспорту є основними джерелами забруднення урбоєкосистем і становлять суттєву загрозу здоров'ю населення міст в результаті емісії пилу в атмосферу. Висока кумулятивна здатність токсичних металів, зокрема плумбуму призводить до його надходження в атмосферне повітря, ґрунти та підземні води, а в кінцевому підсумку – до накопичення в тканинах та органах рослинних організмах. Існує залежність між вмістом токсичних металів в атмосферному повітрі і випадінням їх в межах санітарно-захисної зони промислових та автотранспортних підприємств й розповсюдженням по всій території урбоєкосистеми. Сніговий покрив депонує забруднення, тому досить часто використовується для проведення оцінки стану атмосферного повітря. Пошаровий відбір проб снігового покриву дозволяє встановити динаміку забруднення та вплив виробничих потужностей підприємств на стан урбоєкосистеми. Застосування методів біотестування за допомогою рослинних організмів, які використовуються в якості тест-об'єктів засноване на їх чутливості до екзогенного хімічного впливу і відображується в реакції-відповіді рослин на забруднюючі речовини. Визначення фізико-хімічних показників снігового покриву та розрахунок фітотоксичного ефекту на основі методів фітотестування дозволяє виявити не лише присутність у сніговому покриві токсичних металів, але й отримати достовірну інформацію про їх розподіл в атмосферному повітрі міст. За результатами проведених досліджень отримано показники довжини пагонів *Lepidium sativum*. Тест-об'єкт був пророщений у пробах снігового покриву відібраного на відстані 5-50 м поблизу підприємства АЗС «WOG». Отримані дані порівнювались із значеннями довжини пагонів тест-об'єктів пророщених у пробах снігу з території паркової зони. Встановлено, що рівень забруднення атмосферного повітря токсичними металами на відстані 50 м від АЗС «WOG» є найвищим. Фізико-хімічні показники снігового покриву та фітотоксичний ефект вказують на високу ймовірність потрапляння токсичних металів в атмосферне повітря за межі санітарно-захисної зони АЗС «WOG».

**Ключові слова:** фітоіндикація, тест-об'єкт, сніговий покрив, фітотоксичний ефект, крес-салат (*Lepidium sativum*), урбоєкосистема

**Е. В. Барабаш**

**Оценка экологической опасности атмосферного воздуха урбоэко системы по состоянию депонирующей среды**

Национальный транспортный университет, ул. Омеляновича-Павленка, 1, Киев, Украина, 01010

E-mail: el\_barabash@ukr.net

Деятельность промышленных предприятий и выбросы автомобильного транспорта являются основными источниками загрязнения урбоэко систем и составляют существенную угрозу здоровью населения городов в результате эмиссии пыли в атмосферу. Высокая кумулятивная способность токсичных металлов, в частности свинца приводит к его поступлению в атмосферный воздух, почвы и подземные воды, а в конечном итоге - к накоплению в тканях и органах растительных организмах. Существует зависимость между содержанием токсичных металлов в атмосферном воздухе и выпадением их в пределах санитарно-защитной зоны промышленных и автотранспортных предприятий, а так же их распространением по всей территории урбоэко системы. Снежный покров депонирует загрязнения, поэтому довольно часто используется для проведения оценки состояния атмосферного воздуха. Послойный отбор проб снежного покрова позволяет установить динамику загрязнения и влияние производственных мощностей предприятий на состояние урбоэко системы. Применение методов биотестирования с помощью растительных организмов, используемых в качестве тест-объектов основано на их чувствительности к экзогенному химическому воздействию и

отображается в виде реакций-ответов растений на загрязняющие вещества. Определение физико-химических показателей снежного покрова и расчет фитотоксического эффекта на основе методов фитотестирования позволяет выявить не только наличие в снежном покрове токсичных металлов, но и получить достоверную информацию об их распределении в атмосферном воздухе городов. По результатам проведенных исследований получены показатели длины побегов *Lepidium sativum*. Тест-объект был пророщен в снежном покрове отобранном на расстоянии от 5 до 50 м у предприятия АЗС «WOG». Полученные данные сравнивались со значениями длины побегов тест-объектов пророщенных в пробах снега с территории парковой зоны. Установлено, что уровень загрязнения атмосферного воздуха токсичными металлами на расстоянии 50 м от АЗС «WOG» является самым высоким. Физико-химические показатели снежного покрова и фитотоксический эффект указывают на высокую вероятность попадания токсичных металлов за пределы санитарно-защитной зоны АЗС «WOG».

**Ключевые слова:** фитоиндикация, тест-объект, снежный покров, фитотоксический эффект, кресс-салат (*Lepidium sativum*), урбоэкосистема

**Olena Barabash** (1975). Ph.D., Associate Professor.

Department of Ecology and Safety of Vital Functions, National Transport University, Kyiv.

Education: Ternopil State Pedagogical University, Ternopil, Ukraine, 1997.

Research area: Environmental Safety; Environmental management systems.

Publications: 82.

E-mail: el\_barabash@ukr.net.