Studia Universitatis "Vasile Goldiş", Seria Ştiinţele Vieţii
Vol. 25 issue 2, 2015, pp. 125-130

ENVIRONMENTAL ASSESSMENT OF ATMOSPHERIC POLLUTION IN DNIPROPETROVSK PROVINCE (UKRAINE)

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ABSTRACT: Atmospheric pollution in Ukrainian industrial cities poses a serious environmental threat. Intensive mining and industrial activities, power and heating plants, construction enterprises, have contributed to increase in the number of atmospheric pollution sources .The purpose of our study is to estimate pollution with NO_2 and SO_2 in Dnipropetrovsk region. Assessment of air pollution with NO_2 and SO_2 is carried out using the new GIS system and weather data from stationary networks of Dnipropetrovsk Hydrometeorological Regional Center. Elevated concentrations of nitrogen dioxide (excess of Maximum Permissible Concentration in 1.25-2.25 times) is observed during last 5 years in the atmosphere of this region. Atmospheric pollution estimated above average according to accepted gradation of air pollution index. Three years of data interpolation from monitoring stations in the above two industrial cities has allowed to build maps to assess the risk level of atmosphere contamination with nitrogen and sulfur dioxides (individually and collectively). In terms of total soil pollution with heavy metals near the metallurgical plant are rated as "moderately threatening". Bioassay of technogenic soils pollution revealed weight decrease of 4-days radish sprouts from 15 to 45%.

Key words: air, soil, pollution, industry, emissions, networks, monitoring.

INTRODUCTION:

Air quality has increasingly become a great concern to the public, researchers, and policy-makers, as extensive research has demonstrated that air pollutants affect the health of humans and animals, damage vegetation and materials, reduce visibility and solar radiation, and affect weather and climate (Arya, 1998). Air pollution in urban areas of the Ukraine, as well as in the other countries of the region, has reached levels which cause negative impact on people's health. Some pollutants exceed the maximum permissible concentrations (MPC) according to the Ukrainian legislation (Timshenko, 2003).

Dnipropetrovsk region is a major industrial center in the south-east of Ukraine. The main sources of technogenic air pollution in large industrial cities are metallurgical, chemical plants, enterprises of construction materials, thermal power plants and heating plants. Nitrogen dioxide, sulfur dioxide, carbon monoxide, phenol and other substances that can react chemically with each other to form highly toxic compounds. These substances are corresponding for the formation of photochemical smog during summer months in the atmosphere of large industrial agglomerations (Kharytonov *et al.,* 2008, Loghin, 2010). To a certain extent the concentration of NO_x affects the budget of tropospheric ozone formation. It is known that tropospheric ozone is a gas with a powerful "greenhouse effect", identically to the negative processes of growth in air temperature due to increased amounts of CO_2 and CH_4 (Kharytonov *et al*., 2013). Connected to acid rain form aerosols of HNO_3 and H_2SO_4 lead to a decrease in soil pH, ground, and groundwater leaching of heavy metals (Duccer *et al.*, 1970). Consequently, studies are a rather actual emission of oxides of nitrogen and sulfur and assessment of possible risk of acid rain around industrial agglomerations. Together with fog and some other natural phenomena in areas of high Concentrations of Chemical Substances arises in photochemical smog. Nitrogen oxides and sulfur dioxide combines with water to form nitric and sulfuric acids that fall with rain forming acid rain. Damage that acid rain cause to forestry, horticulture is associated with the extinction of plantings, decrease in growth of wood pulp, as well as increased susceptibility of trees to disease and pest damage (Yatsyshyn *et al.,* 2009).

The purpose of this article was to analyze risks of air born environmental pollution due to acid rain formation in the atmosphere of industrial cities of Dnipropetrovsk region.

MATERIAL AND METHODS:

Current information using the network of stationary posts in three the industrial cities in Pridneprovsk region conducted by regional network of the Hydrometeorology laboratory for air pollution evaluation .This network has been established in several cities of Dnipropetrovsk region. In order to assess air pollution using laboratory, express and automatic control methods. The information-analytical system combines the results of aerotehnogenic pollution modeling and averaging data from the air quality monitoring networks (Yatsyshyn *et al.*,2009).

The obtained daily, monthly and annual averages data of background monitoring of tested substances in atmospheric air compared to the maximum permissible concentration (MPC) (Tarasova *et al*., 2006). The simultaneous presence of different air pollutants in some cases leads to the effect of increasing actions, firstly, with the similarity actions of some toxic substances, and secondly, by increasing mutual action

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Article published: May 2015

(synergistic effect) of various substances. In case of presence of several substances in atmospheric air which have the ability to use the cumulative effect of two indicators: summation coefficient and air pollution index API_n (*Tarasova et al.,* 2006).To calculate effect of summation the following formula is used:

$$ES = \sum_{i=}^{n} \frac{C_i}{MPC_i} \leq 1 \quad (1)$$

where C_i - concentration of harmful substances; *ES* - effect of summation;
MPC_i - corresponding to the maximum permissible concentration.

The sum of their concentration should not exceed the unity. For determining the state of air pollution by several substances acting at the same time, is used air pollution index, which indicates how many times the total level of air pollution by several substances exceeds the MPC of sulfur dioxide. For each settlement is determined a specific priorities list of contaminants for which the air pollution index is calculated on formula:

$$API_n = \sum_{i=1}^{n} \frac{C_i}{K_i} \quad (2)$$

where K_i; coefficient of maximum permissible concentration of *i* - substance relative to the MPC of sulfur dioxide.

$$K_s = \frac{MPC^{subsance}}{MPC^{SO_2}} \quad (3)$$

If API ≤5 - the level of air pollution is considered to be below average,
5 < API ≤8 - equal to the average;
if 8 < API ≤15 - above average, API> 15 - significantly above average.

Information-analytical system (IAS) was used to construct aerotehnogenic maps of atmospheric pollution in two industrial centers Dnipropetrovsk and Dniprodzerzhynsk.

For determining the impact of aerotehnogenic pollution on soil in Dnipropetrovsk ,soil samples were collected nearby the stationary monitoring networks (SMN), stations №10, 20, 13, 25. For details of determining the impact of main environmental pollutant in Dniprodzerzynsk city, soil samples were collected in four stations.

The level of soil contamination with heavy metals is characterized by concentration coefficient of chemical element anomalies (Pinygin ,2001):

$$Z_c = \sum_{i=1}^{n} \left(K_{c_i} - (n-1)\right), \quad (4)$$

$$K_c = \frac{c_i}{c_b}, \quad (5)$$

where c_i – actual pollutant concentration of pollutant in soil, mg/kg; c_b – background pollutant, mg/kg.
Where n: number of elements. If concentration factor $K_c \geq 1$ then $Z_c \geq 1$, which means that the threat to technogeneous exists from pollutants the degree of which is graded as follows: Z_c <16: degree of threat of the territory pollution estimated as permissible one; 16< Z_c <32: moderately threating; 32< Z_c<128: threating; $Z_c \geq 128$: extremely threating.

Soil sampling was carried out by the envelope methode.Soil was selected at a depth of 10 cm, 800-900 g of each sample. In each section were selected two samples from different areas of stationary monitoring networks. Thereafter soil samples were dried at room temperature and crushed; then have been removed impurities and particles using a sieve with holes of different diameters from 5 to 1 mm. To reduce weight of sample we used the quartering method: particulate material is thoroughly mixed and sprinkled evenly thin layer in the form of a square, divided into four sectors. The contents of the two opposite sectors were discarded, and the remaining two were mixed again. After many repetitions of trial has remained, dried to obtain ammoniac-acetat buffer (AAB) pH 4.8 extracts from the soil. The ratio of AAB: soil - 1: 5. Acid-soluble form of heavy metals was obtained after processing soil samples with 1NHCl. Determination of heavy metals was carried out on the atomic absorption spectrophotometer (S-115). 4-days seedlings of radish (Raphanus sativus L.) grown on soil water extracts of technogenic zones of the city. The content of soluble protein in coleoptiles 4-days seedlings of radish variety "French Breakfast" was determined by the Bradford method (Bradford ,1976).

RESULTS AND DISCUSSION:

The permanent excess of one MPC by the average concentrations of nitrogen dioxide in the atmosphere of industrial cities, the maximum excess of MPC content of NO_2 in the atmosphere of the cities has reached twice. Over the last 5 years in the atmosphere of industrial cities in the region there was an increased level of nitrogen dioxide (excess of MPC in 1.25-2.25 times). It was established that in the first place on air pollution with nitrogen dioxide is Dnipropetrovsk. Interpolation of three-year data from monitoring stations in the above two industrial cities has allowed to build maps of atmospheric pollution of nitrogen and sulfur dioxide (Fig. 1-4).

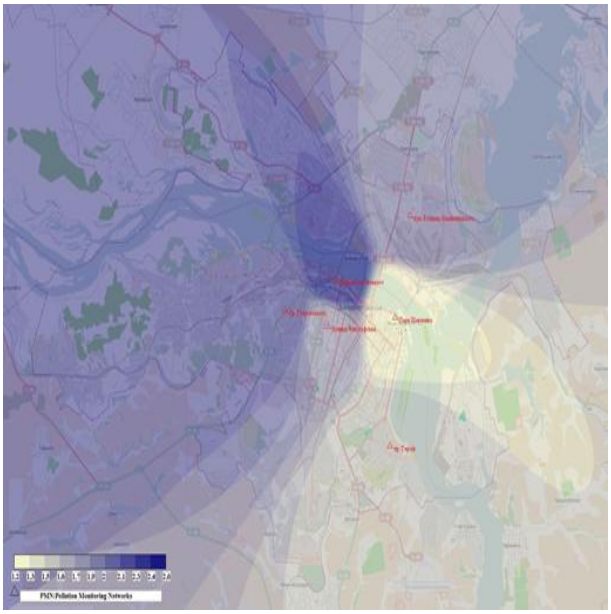

Fig 1. NO_2 in atmosphere of Dnipropetrovsk

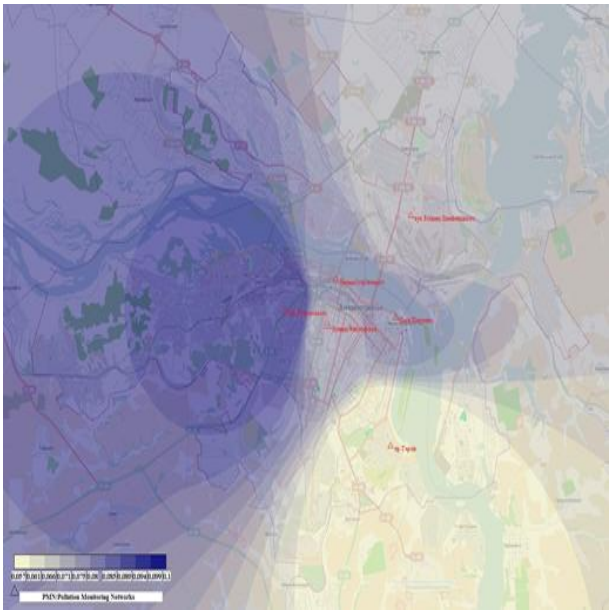

Fig 2. SO_2 in atmosphere of Dnipropetrovsk

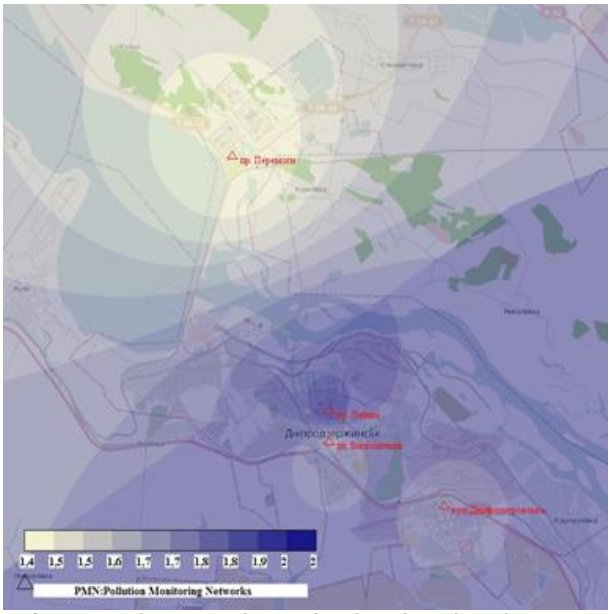

Fig 3. NO_2 in atmosphere of Dniprodzerzhynsk

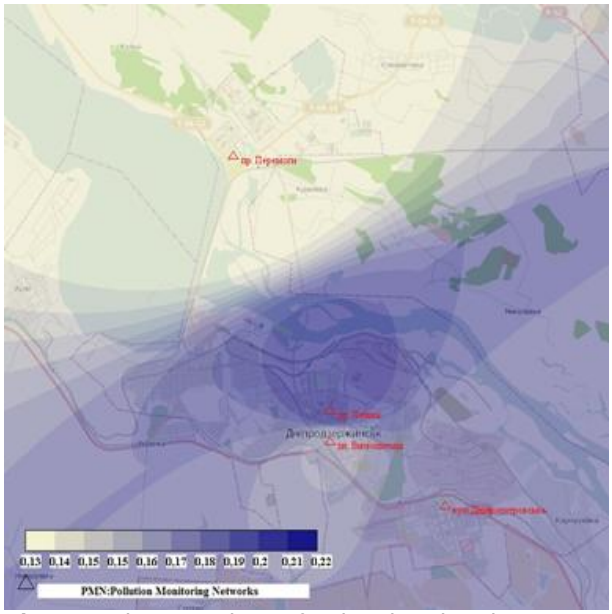

Fig 4. SO_2 in atmosphere of Dniprodzerzhynsk

The analysis contour of the spread aerosol streams of nitrogen dioxide in the center of Dnipropetrovsk indicates the formation of expressed torch in the north - west direction in excess of 2.5 times MPC. In addition, the stream diverges into two sides in the south - west and north - easterly direction and passes through areas which are under the constant influence of a number of industrial enterprises (including metallurgical and coke plants). The aureole formation of aerosol spread of sulfur dioxide is shown in the right-bank part of the city and is connected with the activity of the metallurgical plant. In the city of Dniprodzerzhynsk greatest concentration of nitrogen dioxide recorded in neighboring with metallurgical plant area (in excess of MPC achieves 1.8).

As a result, the right-bank part of the city is constantly covered with plume in excess of MPC in 1.5-1.6 times. Some areas of Dniprodzerzhynsk, which are under the constant impact of the coke industrial enterprises and under prevailing southerly winds, are the most contaminated with sulfur dioxide. It is necessary to take into account that a number of aerosols nitrogen dioxide, sulfur dioxide and other have an effect of summation. The current values of the maximum of single concentrations of Dnipropetrovsk and Dniprodzerzhynsk are shown in Table 1.

Table 1.
Maximum single concentration, mg / m^3

Substance	The maximum single concentration, mg / m^3				
	Dniprodzerzhynsk		Dnipropetrovsk		MPC
	2012	2013	2012	2013	
Ammonia	0.20	0.15	0.18	0.15	0.2
Nitrogen dioxide	0.20	0.17	0.48	0.44	0.085
Carbon monoxide	5	6	9	8	5
Hydrogen sulfide	0.025	0.016	0.030	0.052	0.008
Sulphur dioxide	0.020	0.028	0.044	0.091	0.5
Phenol	0.034	0.017	0.049	0.024	0.003

Since the effect of summation (ES) of the above substances possess the only nitrogen dioxide, carbon monoxide, sulfur dioxide and phenol, the calculation will be carried out in accordance with formula (1) only for these four substances without taking into account the emissions of ammonia and hydrogen sulfide. The results of calculations of ES and API for atmosphere of the two industrial cities are shown in Table 2.

Table 2 .
ES and API in the atmosphere of two industrial cities

Index	Dniprodzerzhynsk		Dnipropetrovsk	
	2012	2013	2012	2013
ES	14.6	8.8	23.7	14.8
API	9.5	5.8	14.2	11.0

It was found a significant effect of summation in both cases, due to the excess of the limit values for all maximum single concentrations of these substances. However, the downward trend level of air pollution is fixed in both cities for the two indicators by 1.3-1.6 times. In presence of diffuse sources are super imposed individual emissions and formed the total torch actually located over the whole of the industrial agglomeration. Spatial structure of such torch is very complicated, instant concentration of impurities at various points in the city are substantially different from each other. However, the average levels of air pollution resulting from the interaction of many factors differ insignificantly. To assess the risk of total exposure to nitrogen dioxide and sulfur in the two industrial cities were built maps (Figure 5 and 6).

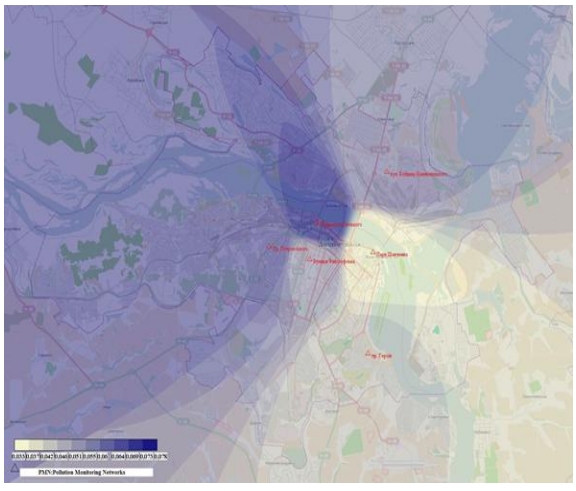

Fig 5. Risk of total air pollution with NO_2 and SO_2 in Dnipropetrovsk

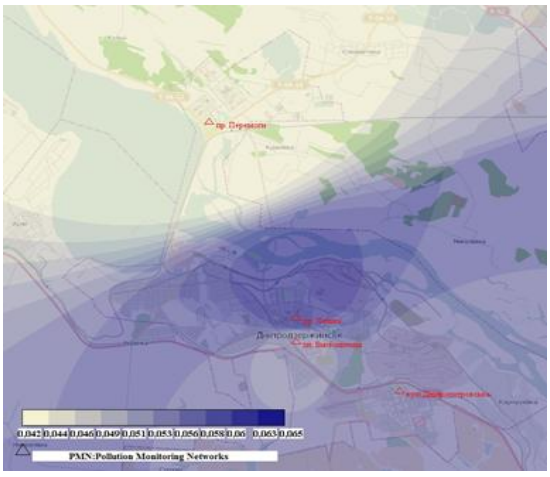

Fig 6. Risk of total air pollution with NO_2 and SO_2 in Dniprodzerzhynsk

Summary torch formed over each city from the merger of numerous enterprises emissions. Results of chemical analysis of heavy metals in the buffer-soluble and acid-soluble form of extracts (BSF and ASF) from the soil, which were selected on certain testing sites of two industrial cities are shown in Table. 3.

Table 3.
The content of heavy metals in soils of urban territories Dnipropetrovsk and Dniprodzerzhynsk mg / kg

Dnipropetrovsk								
Metal	**Plot 1**		**Plot 2**		**Plot 3**		**Plot 4**	
	BSF	**ASF**	**BSF**	**ASF**	**BSF**	**ASF**	**BSF**	**ASF**
Lead	9.42	42.72	11.70	60.75	7.06	22.41	7.70	24.04
Cadmium	0.28	1.40	0.37	0.78	0.30	0.45	0.32	0.55
Nickel	1.40	9.62	1.51	11.03	1.77	10.99	1.62	9.63
Zinc	52.87	254.60	65.77	393.75	41.16	232.06	48.24	267.39
Copper	1.02	25.57	1.24	29.89	1.06	26.32	1.14	38.29
Iron	2.00	1563.64	2.24	1670.82	2.69	1508.29	2.50	1308.34
Manganese	11.81	681.91	10.08	591.29	7.48	519.61	6.91	449.63
Dniprodzerzhynsk								
Lead	6.31	36.09	8.00	36.48	6.33	42.90	3.23	4.61
Cadmium	0.26	0.39	0.60	1.15	0.44	0.71	1.64	2.70
Nickel	1.25	7.96	1.30	6.85	0.89	6.72	0.57	6.89
Zink	15.29	59.90	43.48	258.54	45.59	230.92	15.66	120.24
Copper	0.56	7.43	1.14	27.69	0.63	14.36	0.61	21.92
Iron	1.93	1177.77	9.66	4553.38	2.13	2145.87	2.60	1392.95
Manganese	13.24	494.56	23.13	1598.55	22.10	1338.53	13.02	706.64

Polyelement level of soil contamination were calculated to summarize the results obtained. Determination of Zc was conducted with regard to the content of heavy metals in the form of acid-soluble extract from soil (Table 4).

Table 4.
Total index of soil pollution with heavy metals

Dnipropetrovsk			**Dniprodzerzhynsk**		
Plots	**Zc**	**Technogenic Pollution Degree**	**Plots**	**Zc**	**Technogenic Pollution Degree**
Plot.2	21	Moderately threating	**Plot.2**	14	Permissible
Plot.3	6	Permissible	**Plot.3**	8.5	Permissible
Plot.4	2	Permissible	**Plot.4**	9.3	Permissible

According to the above gradation of the environmental situation of soil pollution with heavy metals near the metallurgical plants in the two cities, it tends to be judged as "moderately hazardous". One of the fastest methods for biotesting environment is the cultivation of plant test objects in aqueous extracts of soil taken from different levels of man-made pollution zones. In this regard it was conducted bioassay of soil samples taken near the areas of metallurgical coke production in Dnipropetrovsk and Dniprodzerzhynsk. The evaluation results of morpho-physioloogical indexes changing in 4-days radish sprouts grown on water extracts of soil from Dnipropetrovsk city are given in Table 5.

Table 5.
Indicators of soil bioassay of Dnipropetrovsk City

Plant Organ	**Soil sampling plots**			
	Plot.1	**Plot.2**	**Plot.3**	**Plot.4**
Weight seedling in mg				
Seedling	105.3 ± 2.03	91.3 ± 5.04	87.3 ± 3.01	100.0 ± 7.01
Protein concentration in mg / ml				
Root	2.60 ± 0.03	1.41 ± 0.05	2.32 ± 0.07	2.54 ± 0.02
Leaves	1.65 ± 0.04	1.86 ± 0.11	1.42 ± 0.05	2.22 ± 0.08

Morpho-physioloogical indexes changing in 4-days radish sprouts grown on water extracts of soil from different sites of Dniprodzerzhynsk city are shown in Table 6.

Comparative analysis of data in Tables 5 and 6 allows to reveal a direct correlation between the degree of contamination and the mass escape. Reduced mass escape of soils in Dnipropetrovsk was 15-21% for Dniprodzerzhynsk was 25-45%. To a certain extent, changes in protein concentrations in the roots and leaves are in inverse proportion to the mass of escape..

Table 6 .
Indicators of soil bioassay of Dniprodzerzhynsk City

Plant organ	Soil sampling plots			
	Plot.1	Plot.2	Plot.3	Plot.4
Weight seedling in mg				
Seedling	81.2 ± 9.05	61.3 ± 4.11	65.6 ± 3.21	56.0 ± 2.03
Protein concentration in mg / ml				
Root	2.32 ± 0.06	2.41 ± 0.10	2.44 ± 0.04	2.44 ± 0.03
Leaves	1.20 ± 0.01	1.75 ± 0.05	2.58 ± 0.07	1.82 ± 0.13

CONCLUSION

1. Elevated concentrations of nitrogen dioxide (excess of MPC in 1.25-2.25 times) was observed during the last 5 years in the atmosphere of the sudied region. The risk of exceeding 1 MAC for SO_2 levels yet. Thus, due to the effect of summation, overall toxicity of newly formed photochemical smog can be significantly more.

2. Atmospheric pollution estimated above average according to accepted gradation of air pollution index (IPA).

3. Three years of data interpolation from monitoring stations in the above two industrial cities has allowed to build the map and level of risk of contamination of the atmosphere of nitrogen and sulfur dioxides (individually and collectively). Application of information-analitical system will ultimately make the definition of the distribution of concentrations of contamination in various scenarios.

4. In terms of Zc soil pollution with heavy metals near the metallurgical plant are rated as "moderately threatening."

5. Bioassay of soils technogenic pollution revealed weight decrease of 4-days radish sprouts from 15 to 45%.

ACKNOWLEDGMENTS:

The authors would like to thank the Dnipropetrovsk State Agrarian-Economic University, the Dnipropetrovsk Center of Hydrometeorology and Pukhov Institute for Modeling in Energy Engineering, National Academy of Sciences Kiev, Ukraine for their suport to cary out this work.

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