ELSEVIER

Journal of Hazardous Materials A76 (2000) 59–70

Journal of Hazardous Materials

www.elsevier.nl/locate/jhazmat

Case study

# Hazardous materials in the environment of Dnepropetrovsk Region (Ukraine)

Natalia P. Gritsan *, Andrey P. Babiy

*Institute of Nature Management Problems and Ecology of National Academy of Sciences of Ukraine, 6, Moskovskaya Street, Dnepropetrovsk 49000, Ukraine*

Received 11 January 2000; accepted 10 March 2000

**Abstract**

The investigations were aimed at assessment of environmental pollution in one of the most industrialized regions of Ukraine — Dnepropetrovsk Region. The following types of environmental contamination were considered in the study: emissions and concentrations of 16 air pollutants; content and distribution of 15 elements in soils and plants at the polluted and unpolluted territories. The investigations were conducted at 28 urban sites and 18 rural sites of the Region during 1991–1998 years. Level and character of air, soil and plants contamination were investigated. Statistical methods were used to describe quantitatively the relationships between contents of hazardous materials in the environment. It was found that concentrations of fluoride, iron, copper, zinc, and lead in the soil and contents of fluoride, iron, nickel, cadmium, and aluminum in plants were several times higher than normal. 

*Keywords:* Air, soil and plants pollution; Ukraine

## 1. Introduction

Human activities have changed the landscapes of Southeast Ukraine. Only 0.8% of Dnepropetrovsk Region area remain for more or less natural ecosystems. The scope of the impacts was so wide and different that the Region has been transformed into the unique polygon for environmental and ecological investigations of any kind.

Dnepropetrovsk Region holds a wealth of natural resources including mineral resources (two of the metal ore reserves are among the largest in the world: iron ore in

* Corresponding author. Tel.: +380-562-464316; fax: +380-562-464316.
*E-mail address:* dea@email.dp.ua (N.P. Gritsan).

0304-3894/00/$ - see front matter 
PII: S0304-3894(00)00210-7

Krivoy Rog and manganese ore in the vicinity of the city of Nikopol), black coal, water resources, fertile soils and favorable climatic conditions.

Natural resources formed the basis for leading industries of the economy at the national and regional level. Heavy industries were founded and emphasis was put on the mining, metallurgical and chemical industries, which are the most environmentally dangerous ones. These types of industries use enormous quantities of resources and energy and pollute the environment as a result of obsolete production technologies and lack of relevant waste treatment facilities.

A complicated environmental situation has been created in Dnepropetrovsk Region at present. Concentrations of hazardous materials in atmosphere, soils, vegetation and water are much higher than in unpolluted areas. The negative effects of the industries lead to changes in chemical composition of the biosphere. Thus, the investigations were conducted to assess the level and character of environmental pollution, to select priorities for mitigation of the environmental situation and to prevent negative impact in future. Concentrations of elements were determined in soils and plants to understand if there was any quantitative relationship between concentrations of these elements in the environment.

## 2. Materials and methods

Dnepropetrovsk Region (province) is situated in the southeastern part of Ukraine on both banks of the river Dnepr and occupies an area of 31923 km$^2$ (5.3% of total territory of Ukraine) (Fig. 1). The Region area is comparable with the territory of the Netherlands.

The conditions of soil formation in the Region are in accordance with geographical zonality. The main type of soil is black soil — chernozem. The fertility of chernozem is


Fig. 1. Geographical location of Dnepropetrovsk Region.

famous around the world, and because of that the great part of Dnepropetrovsk Region (about 80%) can be characterized as arable. Artificial and natural forests occupy only 3.5% of total regional territory. In such conditions, the dominant form of natural plant life is tree-like (about 60% of regional flora).

Populations of the Roman tree (*Robinia pseudoacacia* (L.) of age of 40–60 years growing on typical black soil were selected as a test-species. The Roman tree is widely spread all over the territory. It grows in rural, urban and industrial areas. It is a species of plants, which determines the structure of phytocenosis and consequently the terrestrial ecosystem on the whole.

The investigations were conducted at 28 urban sites and 18 rural sites of the Region during the years 1991 to 1998. The area used for control was situated 60 km away from the city of Dnepropetrovsk in the opposite direction relative to prevailing winds and was free of industrial emissions.

Samples were analyzed for concentrations of 15 elements. Atomic absorption spectrophotometry was used for heavy metal determination in plants and soils [1]. Concentrations of potassium and sodium were determined by flame photometer [2]. For determination of soil fluorides, ion-selective electrode was used [3].

Statistical methods were applied to describe quantitatively the relationships between contents of hazardous materials in the environment.

Coefficient of concentration anomaly for certain element was elaborated by Gritsan et al. [4]:

$$C_{\mathrm{A}} = \frac{C_{\mathrm{found}}}{C_{\mathrm{normal}}}$$

where: $C_{\mathrm{A}}$ — coefficient of concentration anomaly; $C_{\mathrm{found}}$ — measured concentration; $C_{\mathrm{normal}}$ — background concentration.

## 3. Results and discussion

### *3.1. Hazardous substances in the atmosphere*

In the regional environmental pollution, industrial emissions play a crucial role.

Industries and transportation are the main contributors to atmospheric pollution in Dnepropetrovsk Region. As a result of industrial production processes, about 1 million tons of hazardous substances annually have been emitted into the atmosphere from about 25,000 industrial stationary sources. During recent years, there has been a trend towards decreasing emissions; but this was connected, mainly, with decreasing production.

The most polluting industries in Dnepropetrovsk Region are metallurgy and power industry. Now, there are 57 metallurgical companies in Dnepropetrovsk Region. A steel plant in Krivoy Rog is one of the largest in the world. The technologies used in most of the companies are outdated and energy inefficient, although there are modern sections found in individual plants. The metallurgical sector contributed of 64% of total regional emissions (about 530,000 tons per year) and was especially a source of the following substances: dust — about 90,000, $SO_2$ — about 50,000, CO — about 370,000, $NO_2$ — about 20,000, VOC — about 2000 tons per year.

There are 11 thermal power stations in Dnepropetrovsk Region, which caused high air pollution (total amount was about 250,000 tons per year, including dust — about 80,000, $SO_2$ — about 120,000, CO — about 15,000, $NO_2$ — about 50,000) as a result of obsolete equipment, treatment facilities and production technologies. The power stations use large quantities of black coal of very low quality as fuel, this gives more pollution than generating power with most other fuels.

The emissions from chemical companies (on average is about 2000 tons per year) are very different and particularly toxic for the environment.

Most of the emissions took place in the cities of Krivoy Rog (more than 10% of total emissions over Ukraine), Dnepropetrovsk and Dneprodzerzhinsk, where there is a high concentration of environmentally dangerous industries.

In Dnepropetrovsk Region, the main reasons, which determine the air quality, are volume and composition of industrial emissions. They play a crucial role in the atmospheric pollution. The quantity and quality of industrial emissions determined the spectra of pollutants in the cities of Dnepropetrovsk, Krivoy Rog and Dneprodzerzhinsk. In Table 1, the average daily concentrations of main pollutants in the atmosphere of these three large cities are shown. Oxides of sulfur, nitrogen and carbon, dust, phenols, ammonia, benzo(*a*)pyrene, formaldehyde and heavy metals are the most important pollutants in terms of their concentrations and toxicity. For comparison, the maximum permissible concentrations (according to Ukrainian law) are shown.

Table 1
Average daily concentrations of pollutants in the atmosphere of the cities on average for 1986–1998 ($mg/m^3$)

| Pollutant | Maximum permissible concentration | Dnepropetrovsk | Krivoy Rog | Dneprodzerzhinsk |
|---|---|---|---|---|
| Dust | 0.1500 | 0.2000 | 0.4000 | 0.2000 |
| Sulfur dioxide | 0.0500 | 0.0100 | 0.1000 | 0.0100 |
| Carbon monoxide | 3.0000 | 2.1000 | 3.0000 | 1.8000 |
| Nitrogen dioxide | 0.0400 | 0.0020 | 0.0050 | 0.0020 |
| Nitrous oxide | 0.0600 | 0.0010 | 0.0010 | 0.0008 |
| Ammonia | 0.0400 | 0.1000 | 0.1000 | 0.1500 |
| Phenols | 0.0030 | 0.0040 | 0.0050 | 0.0060 |
| Formaldehyde | 0.0030 | 0.0040 | 0.0060 | 0.0040 |
| Benzo(*a*)pyrene, $\mu g$ per 100 $m^3$ | 0.1000 | 0.5000 | 0.5000 | 0.5000 |
| Chromium | 0.0015 | 0.0200 | 0.0700 | 0.1100 |
| Copper | 0.0020 | 0.1100 | 0.0700 | 2.8000 |
| Lead | 0.0003 | 0.0600 | 0.0200 | 0.0600 |
| Manganese | 0.0100 | 0.2300 | 0.0200 | 0.1700 |
| Zinc | 0.0500 | 0.3000 | 0.0800 | 0.3200 |
| Nickel | 0.0010 | 0.0300 | 0.0200 | 0.3400 |
| Cadmium | 0.0030 | 0.0100 | 0.0200 | 0.0300 |

Industrial activities and transportation have resulted in concentrations of the various greenhouse gases and acidifying components in the atmosphere far in excess of their natural values and in most cases greater than the legal maximum.

### 3.2. Hazardous substances in the soils

The soil is a very complex material that interacts with other elements of the biosphere. Under current conditions, the soil undergoes growing effects of human activities.

Table 2 includes information about background concentrations of elements and their contents in soil (typical chernozem) and plant (*R. pseudoacacia* (L.) of control area. Average concentrations of 15 elements in the soils of ecosystems formed on the basis of Roman tree populations are shown in Table 3.

One of the most important properties of black soil is high content of humus (up to 5.3%). From one hand, humus is the first factor of soil fertility, but from the other hand, it can accumulate different hazardous substances (heavy metals, pesticides, phenols, etc.).

In the cation exchange, capacity of chernozem calcium takes a significant place. Concentrations of Ca in the soils of studied areas were on average 40% higher than normal (background) level. Especially high content of Ca was determined in the soils of the cities of Krivoy Rog and Dnepropetrovsk. But Ca concentrations in the soils of different territories varied considerably.

Magnesium content in the black soil is about 15–20% from the cation sum. Mg content in the soils of studied sites was, mainly, about background level except the city of Krivoy Rog, and coefficients of variations were rather low.

Table 2
Background concentrations of elements and their content in plants (*R. pseudoacacia* (L.)) and soils (typical chernozem) of control area (mg/kg dry mass)

| Element | Background | | Control area | |
|---|---|---|---|---|
| | Plant leaves | Soil | Plant leaves | Soil |
| Mg | 4000 | 4000 | 3600 | 3600 |
| Cr | 10 | 30 | 10 | 34 |
| Mn | 100 | 600 | 10 | 500 |
| Fe | 500 | 22,000 | 900 | 16,170 |
| Co | 6 | 9 | 6 | 10 |
| Ni | 4 | 10 | 9 | 13 |
| Cu | 10 | 20 | 9 | 13 |
| Zn | 20 | 30 | 16 | 41 |
| Cd | 1 | 1 | 1 | 1 |
| Pb | 10 | 10 | 10 | 10 |
| Al | 300 | 30,000 | 500 | 30,000 |
| Ca | 20,000 | 20,000 | 21,000 | 10,000 |
| K | 10,000 | 20,000 | 11,400 | 8600 |
| Na | 500 | 2000 | 1300 | 2800 |
| F | 10 | 200 | 20 | 336 |

Table 3
Content of contaminants in soils of Dnepropetrovsk Region (mg/kg dry mass)

| Element | Dnepropetrovsk | | Krivoy Rog | | Dneprodzerzhinsk | | Rural areas | |
|---|---|---|---|---|---|---|---|---|
| | Content | Coefficient of variation | Content | Coefficient of variation | Content | Coefficient of variation | Content | Coefficient of variation |
| Mg | 3589 | 37.7 | 8150 | 44.0 | 4600 | 37.6 | 4884 | 42.6 |
| Cr | 42 | 29.6 | 48 | 13.9 | 48 | 25.9 | 41 | 18.0 |
| Mn | 791 | 83.2 | 733 | 34.8 | 1563 | 47.7 | 662 | 26.3 |
| Fe | 27,913 | 107.5 | 62,675 | 84.8 | 55,033 | 97.3 | 20,643 | 25.2 |
| Co | 11 | 20.4 | 14 | 25.2 | 13 | 34.5 | 12 | 12.2 |
| Ni | 16 | 27.7 | 48 | 47.4 | 22 | 46.3 | 19 | 26.8 |
| Cu | 29 | 61.8 | 17 | 20.7 | 44 | 67.3 | 18 | 24.4 |
| Zn | 126 | 45.8 | 85 | 68.2 | 177 | 75.6 | 70 | 41.9 |
| Cd | 1 | 22.1 | 6 | 142.7 | 2 | 93.2 | 1 | 14.4 |
| Pb | 27 | 57.7 | 21 | 25.0 | 45 | 89.5 | 16 | 35.3 |
| Al | 27,372 | 29.6 | 31,200 | 52.9 | 25,300 | 43.7 | 33,613 | 34.2 |
| Ca | 23,644 | 58.8 | 95,250 | 150.7 | 128,800 | 87.9 | 15,421 | 37.5 |
| K | 10,412 | 26.8 | 9875 | 40.0 | 6470 | 58.4 | 13,189 | 18.4 |
| Na | 4100 | 41.7 | 2950 | 64.0 | 4240 | 33.3 | 4242 | 23.8 |
| F | 387 | 31.5 | 554 | 58.6 | 715 | 43.9 | 320 | 32.5 |

Oxides and hydroxides of Fe and Mn are ordinary components of chernozem soil. But in terms of other element behavior, they are very important. These compounds have ability to absorb other elements due to their form of membrane in soil [5]. High content of Fe and Mn oxides and hydroxides in soil may lead to significant changes in territorial geochemical balance. Maximal concentration of Fe (on average 10 times higher than normal) were observed in the soils of the city of Krivoy Rog because of high natural background level of Fe in this area (natural reserve of iron ore).

Manganese is not considered as a contaminant.

Copper is a low movable soil element. But a tendency towards increasing the amount of Cu in the atmosphere, soils and plants have appeared during recent years. Cu is one of the most polluting components in Dnepropetrovsk Region because, from one hand, the ratio of its measured concentration to the background one was 1.5–3.0, and, from another hand, Cu is one of the most toxic elements for biota even in lower concentrations [5,6].

Content of zinc in the soils of the cities of Dnepropetrovsk and Krivoy Rog is on average three times higher than its background level. It seems to be another environmental problem.

Concentrations of chromium are four times higher on average in the soils of large cities than normal content. More attention should be paid to this element.

Rural areas and big industrial centers of Dnepropetrovsk Region had excess of nickel — 3–5 and 5–7 times higher than background level, respectively.

Lead is an element of the first class of danger (according to Ukrainian classification). Among heavy metals, Pb is less movable element [5]. It was determined that concentrations of Pb in the soils were higher than normal and were higher in the cities than in the rural areas.

The soils of studied territories were also contaminated by fluorides.

The spectra of soil contamination are shown in Fig. 2.

Thus, the highest level of soil contamination took place in the cities of Krivoy Rog, Dnepropetrovsk and Dneprodzerzhinsk because of the high concentration of environmentally dangerous industries and their location in the cities. The level and character of soil pollution depended, mainly, on quantity and quality of industrial emissions and type (or mixture) of industries. It was found that among the contaminants iron, copper, zinc, lead and fluoride were most important in terms of soil contamination.

### 3.3. Hazardous substances in the plants

Nature protects the soil by covering it with vegetation. Plants are able to absorb from the environment almost all elements of periodic system. However, for normal plant development, only certain groups of elements (macro- and micro-elements) are needed. Concentrations of elements in plants may vary widely and depend upon the different environmental factors. Some elements (for example, heavy metals and fluorides) may accumulate in plants in extremely high concentrations, which are not normal for plants. Mineral elements accumulate, mainly, in plant leaves, the ash of which may reach up to 15% [5,6].

Average concentrations of 15 elements in Roman tree (*R. pseudoacacia* (L.) of studied areas are shown in Table 4. The spectra of plant contamination are shown in Fig. 3.

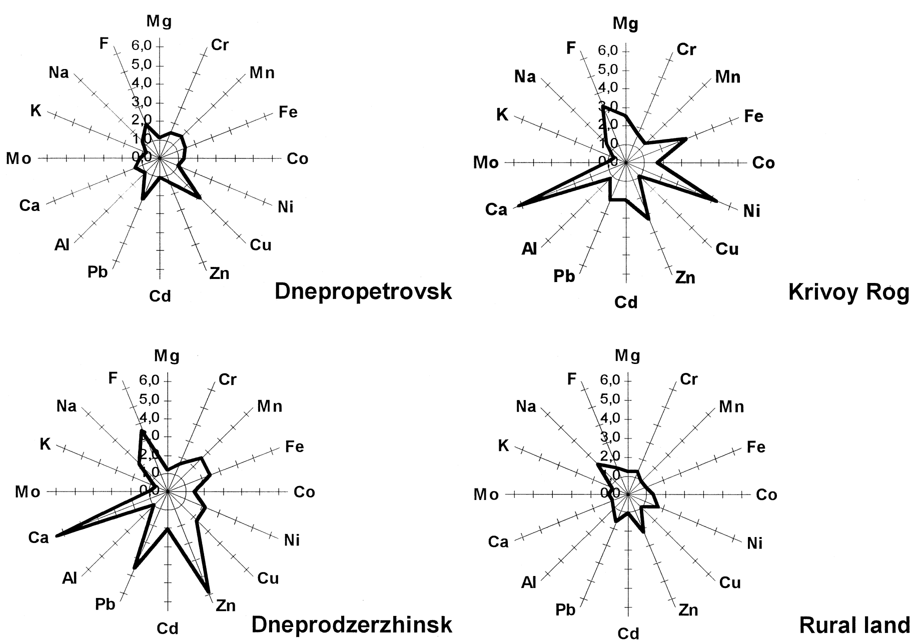


Fig. 2. Spectra of soil contamination. Number on the radius is ratio of measured concentration to background concentration of element (coefficient of concentration anomaly).

Table 4
Content of contaminants in plants of Dnepropetrovsk Region (mg/kg dry mass)

| Element | Dnepropetrovsk | | Krivoy Rog | | Dneprodzerzhinsk | | Rural areas | |
|---|---|---|---|---|---|---|---|---|
| | Content | Coefficient of variation | Content | Coefficient of variation | Content | Coefficient of variation | Content | Coefficient of variation |
| Mg | 4464 | 29.2 | 4500 | 17.3 | 3666 | 23.1 | 4101 | 19.5 |
| Cr | 15 | 29.9 | 16 | 31.7 | 17 | 35.5 | 12 | 22.2 |
| Mn | 88 | 69.3 | 100 | 16.3 | 92 | 57.2 | 100 | 42.0 |
| Fe | 1821 | 78.1 | 4000 | 59.2 | 1020 | 63.2 | 813 | 29.7 |
| Co | 8 | 15.9 | 9 | 20.4 | 8 | 19.2 | 8 | 9.3 |
| Ni | 8 | 35.8 | 34 | 73.6 | 20 | 60.1 | 14 | 79.6 |
| Cu | 13 | 26.4 | 11 | 27.8 | 14 | 25.3 | 10 | 21.2 |
| Zn | 35 | 56.2 | 18 | 38.6 | 23 | 41.8 | 19 | 37.5 |
| Cd | 1 | 19.1 | 5 | 147.0 | 3 | 120.0 | 1 | 11.2 |
| Pb | 13 | 37.8 | 14 | 19.6 | 13 | 57.4 | 11 | 10.9 |
| Al | 986 | 101.1 | 543 | 46.1 | 1037 | 122.2 | 691 | 63.1 |
| Ca | 33,999 | 31.6 | 45,750 | 15.0 | 42,667 | 78.5 | 25,632 | 14.5 |
| K | 10,222 | 41.3 | 7075 | 74.5 | 6470 | 101.7 | 11,126 | 19.9 |
| Na | 589 | 33.7 | 700 | 26.1 | 600 | 38.7 | 625 | 34.1 |
| F | 38 | 35.7 | 32 | 78.0 | 58 | 44.9 | 19 | 96.4 |

It was found that the spectra of plants contamination were different from the soils ones. The plants from rural areas were very polluted by iron (on average 1.7 times

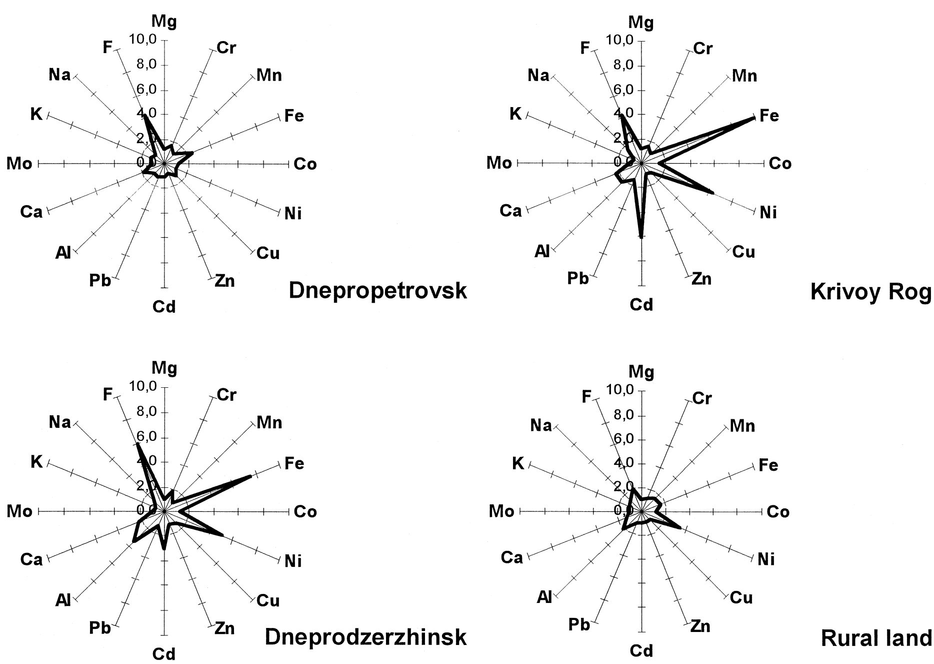


Fig. 3. Spectra of plant contamination. Number on the radius is ratio of measured concentration to background concentration of element (coefficient of concentration anomaly).

Table 5
Correlation between elements in soils of the city of Dnepropetrovsk

| | Mg | Cr | Mn | Fe | Co | Ni | Cu | Zn | Cd | Pb | Al | Ca | K | Na | F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mg | | 0.49 | 0.24 | 0.08 | 0.60 | 0.75 | 0.46 | 0.15 | 0.07 | 0.26 | 0.81 | 0.45 | 0.67 | 0.66 | 0.40 |
| Cr | | | 0.70 | 0.71 | 0.74 | 0.50 | 0.65 | 0.72 | 0.67 | 0.64 | 0.43 | 0.34 | 0.09 | 0.27 | 0.61 |
| Mn | | | | 0.84 | 0.75 | 0.40 | 0.51 | 0.68 | 0.75 | 0.53 | 0.14 | 0.45 | −0.15 | 0.08 | 0.47 |
| Fe | | | | | 0.62 | 0.21 | 0.27 | 0.61 | 0.85 | 0.35 | 0.02 | 0.16 | −0.16 | −0.16 | 0.46 |
| Co | | | | | | 0.58 | 0.49 | 0.48 | 0.59 | 0.58 | 0.46 | 0.46 | 0.17 | 0.34 | 0.61 |
| Ni | | | | | | | 0.37 | 0.21 | 0.32 | 0.18 | 0.55 | 0.38 | 0.53 | 0.50 | 0.35 |
| Cu | | | | | | | | 0.73 | 0.29 | 0.79 | 0.53 | 0.62 | 0.08 | 0.56 | 0.67 |
| Zn | | | | | | | | | 0.65 | 0.69 | 0.12 | 0.54 | −0.25 | 0.18 | 0.58 |
| Cd | | | | | | | | | | 0.34 | 0.09 | 0.14 | −0.14 | 0.01 | 0.57 |
| Pb | | | | | | | | | | | 0.21 | 0.40 | −0.23 | 0.46 | 0.56 |
| Al | | | | | | | | | | | | 0.22 | 0.60 | 0.69 | 0.48 |
| Ca | | | | | | | | | | | | | 0.01 | 0.34 | 0.43 |
| K | | | | | | | | | | | | | | 0.49 | 0.15 |
| Na | | | | | | | | | | | | | | | 0.44 |
| F | | | | | | | | | | | | | | | |

higher than background level), nickel (3–5 times higher), aluminum (2 times higher), fluorine (1.5 times higher). The spectrum of contamination of plants growing in urban territories of the large industrial cities was wider and included the following elements: F, Fe, Ni, Cd, Al, Co, Cu, Pb, and Cr.

Special attention has been paid to plant contamination by fluorides. Natural background concentrations of fluorides in plant leaves are low (20 mg/kg of dry mass maximum). Fluorides are widely spread in earth-crust (average content is 0.07%, like phosphorus and sulfur). But only a small part of soil fluorides is available for plants. It

Table 6
Correlation between elements in plants of the city of Dnepropetrovsk

| | Mg | Cr | Mn | Fe | Co | Ni | Cu | Zn | Cd | Pb | Al | Ca | K | Na | F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mg | | 0.04 | 0.02 | −0.24 | 0.46 | 0.05 | 0.02 | −0.19 | 0.40 | 0.35 | −0.30 | 0.52 | −0.41 | −0.15 | 0.05 |
| Cr | | | −0.11 | 0.16 | 0.22 | 0.31 | 0.43 | 0.76 | −0.19 | 0.07 | 0.32 | 0.17 | 0.12 | −0.40 | 0.42 |
| Mn | | | | −0.15 | 0.25 | 0.03 | −0.19 | −0.15 | 0.03 | 0.08 | 0.26 | 0.11 | 0.14 | −0.43 | −0.11 |
| Fe | | | | | 0.27 | 0.10 | 0.33 | 0.29 | 0.01 | 0.08 | 0.02 | 0.40 | −0.23 | −0.22 | 0.68 |
| Co | | | | | | 0.17 | 0.01 | 0 | 0.75 | 0.75 | 0.05 | 0.62 | −0.46 | −0.45 | 0.26 |
| Ni | | | | | | | 0.17 | 0.18 | 0.02 | 0.01 | 0.56 | 0.12 | 0.37 | −0.12 | 0.03 |
| Cu | | | | | | | | 0.53 | −0.19 | 0.03 | 0.42 | 0.20 | 0.02 | −0.23 | 0.76 |
| Zn | | | | | | | | | −0.20 | 0.13 | 0.27 | 0.13 | 0.36 | −0.33 | 0.62 |
| Cd | | | | | | | | | | 0.90 | −0.11 | 0.24 | −0.47 | −0.07 | −0.02 |
| Pb | | | | | | | | | | | 0.02 | 0.34 | −0.60 | −0.12 | 0.08 |
| Al | | | | | | | | | | | | −0.12 | 0.12 | −0.13 | 0.13 |
| Ca | | | | | | | | | | | | | −0.71 | −0.27 | 0.34 |
| K | | | | | | | | | | | | | | −0.02 | −0.12 |
| Na | | | | | | | | | | | | | | | −0.44 |
| F | | | | | | | | | | | | | | | |

Table 7
Correlation between elements in plants and in soils of the city of Dnepropetrovsk

| Soil | Plant | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mg | Cr | Mn | Fe | Co | Ni | Cu | Zn | Cd | Pb | Al | Ca | K | Na | F |
| Mg | 0.33 | 0.04 | −0.29 | 0.28 | 0.31 | 0.16 | 0.40 | 0.27 | 0.13 | 0.12 | −0.04 | 0.40 | −0.11 | 0.02 | 0.36 |
| Cr | −0.18 | 0.42 | −0.53 | 0.73 | 0.15 | 0.07 | 0.48 | 0.36 | −0.07 | 0.02 | 0 | 0.20 | −0.05 | −0.15 | 0.56 |
| Mn | −0.20 | 0.13 | −0.13 | 0.59 | 0.07 | −0.17 | 0.22 | 0.12 | −0.02 | −0.11 | −0.14 | 0.16 | 0.08 | −0.12 | 0.37 |
| Fe | −0.20 | 0.20 | −0.17 | 0.71 | 0.11 | −0.16 | 0.03 | 0.11 | −0.12 | −0.15 | −0.22 | 0.21 | 0 | −0.17 | 0.34 |
| Co | 0 | 0.03 | −0.26 | 0.68 | 0.20 | −0.07 | 0.27 | −0.08 | 0 | 0.03 | −0.14 | 0.49 | −0.24 | −0.03 | 0.33 |
| Ni | 0.30 | 0.39 | −0.25 | 0.25 | 0.24 | −0.01 | 0.37 | 0.20 | 0.05 | −0.03 | −0.14 | 0.44 | −0.23 | −0.21 | 0.48 |
| Cu | −0.22 | 0.37 | −0.29 | 0.57 | 0.04 | −0.11 | 0.79 | 0.56 | −0.07 | 0.08 | 0.24 | 0.20 | −0.03 | −0.10 | 0.71 |
| Zn | −0.24 | 0.40 | −0.14 | 0.66 | 0.28 | 0.08 | 0.57 | 0.47 | 0.02 | 0.12 | 0.10 | 0.18 | 0.13 | −0.39 | 0.68 |
| Cd | −0.04 | 0.16 | −0.31 | 0.55 | 0.14 | −0.13 | 0.15 | −0.04 | −0.08 | −0.08 | −0.31 | 0.30 | −0.11 | −0.01 | 0.35 |
| Pb | −0.41 | 0.22 | −0.15 | 0.57 | 0.19 | −0.16 | 0.42 | 0.21 | 0.07 | 0.22 | 0.19 | 0.24 | −0.17 | −0.11 | 0.35 |
| Al | 0.32 | 0.37 | −0.47 | 0.13 | −0.01 | 0.11 | 0.61 | 0.30 | −0.13 | 0.02 | 0.06 | 0.28 | −0.09 | 0.25 | 0.31 |
| Ca | 0.09 | −0.13 | 0.04 | 0.47 | 0.33 | −0.07 | 0.50 | 0.22 | 0.36 | 0.30 | −0.04 | 0.20 | −0.01 | −0.28 | 0.64 |
| K | 0.81 | 0.30 | −0.25 | −0.20 | 0.36 | 0.20 | 0.06 | 0.03 | 0.26 | 0.25 | −0.19 | 0.39 | −0.24 | −0.09 | −0.03 |
| Na | 0.39 | 0.28 | −0.11 | 0.04 | 0.33 | −0.02 | 0.58 | 0.07 | 0.21 | 0.32 | 0.19 | 0.55 | −0.38 | 0 | 0.28 |
| F | 0.14 | 0.14 | −0.57 | 0.59 | 0.20 | −0.34 | 0.43 | 0.17 | 0.11 | 0.29 | −0.32 | 0.54 | −0.44 | 0.05 | 0.51 |

explains the low concentrations of fluorides in vegetation. The main source of fluorides for plants is industrial emissions. Fluorine is not an element of biological importance for plant. Its role for plant development is not known. It does not take part in plant metabolism. An excess of fluorides content in plant is a diagnostic test for atmospheric pollution [4,5]. It was determined that concentrations of fluorides in plants growing near large or specific industrial companies were up to 15 times higher than normal.

### *3.4. Relationships between hazardous substances*

The relationships between concentrations of studied elements in plant leaves, soil and between plant and soil were investigated using statistical methods. Seventeen matrixes of pair correlation were calculated. Unfortunately, it was not possible to estimate the correlation between contents of heavy metals in the atmosphere and in plants or soils because of the lack of systematic data about concentrations of air pollutants.

Interaction of chemical elements is important for plant and soil development as a phenomenon of deficiency and toxicity. It can be antagonistic or synergetic. Antagonism may occur when the common effects of the component elements are less than the sum of the effects of the component elements taken separately, and synergism is vice versa.

Coefficients of pair correlation between elements in soil, in plants and relationships between concentrations of elements in soil and in plants in the city of Dnepropetrovsk are presented in Tables 5–7, respectively.

It was found that there was a strong positive correlation between Fe and Cu contents in the soil and their concentrations in plants and high correlation for Mg, Cr and Zn. It suggests that the plants absorb these elements from the soil.

Strong positive correlation between Cr and Mn contents in the soil and moderate negative connection between Cr content in soil and Cr content in plants may mean that chromium can bind manganese (or vice versa) that leads to deficiency of manganese in plants. Low correlation between Cr and Mn concentrations in plant seems to prove it.

Iron content in plants was very high. Possibly, Cr, Co, Cu, Zn, Cd, Pb were conductive to the processes of Fe absorption by plant from soil: there were high coefficients of correlation between them and Fe. Excesses of Zn, Pb, Al, Ca and Na in soil resulted in excess of Cu in plants, and excess of Cu in soil resulted in excess of Zn in plants.

There was often a contradiction in the results obtained. The study of the relationships between elements in plants and soil is a very difficult problem that needs further investigation.

## 4. Conclusions

The quantities and spectra of air pollutants determined the concentrations and spectra of plant contamination.

High level of air, soil and plants pollution is the result of various economic activities, of which industry is the most important. The spectra of pollutants depended mainly upon the kind of industry.

The negative impact of industry leads to changes in chemical composition of the biosphere, accumulation of pollutants in air, soils, and plants.

The atmosphere of the Southeast Ukraine is heavily polluted. On average, more than 15% of total volume of Ukrainian emissions take place here [6]. The air basin of large industrial cities is extremely polluted in spite of the permanent convection and inter-boundary transferring. The high level of atmospheric pollution is the result of various economic activities, of which industry and transportation are the most polluting.

## References

[1] U. Slavin, Atomic absorption spectroscopy, Chimia (Leningrad) (1971) 236, (Rus.).
[2] A.S. Radov, I.V. Pustovoy, A.V. Korolkov, Manual on Agrochemistry, Agropromizdat, Moscow, 1985, p. 312, (Rus.).
[3] L.A. Khazemova, T.L. Radovskaya, A.V. Selezneva, Pochvovedenie 1 (1979) 148–151, (Rus.).
[4] N.P. Gritsan, G.W. Miller, G.G. Shmatkov, Fluoride 28 (4) (1995) 180–188.
[5] A. Kabata-Pendias, H. Pendias, Trace Elements in Soils and Plants, 2nd edn., Levis Publ., Boca Raton, FL, 1992, p. 365.
[6] N.P. Gritsan, N.V. Shpak, G.G. Shmatkov, A.G. Shapar, A.P. Babiy, T.I. Dolgova, V.L. Nesterenko, V.V. Fedotov, Ecological Fundamentals of Nature Management, National Academy of Sciences of Ukraine, Dnepropetrovsk, 1998, p. 413, (Rus.).