

Witold Lenart, Ewa Malinowska-Miros

STUDIES OF THE CHEMICAL COMPOSITION OF THE SOIL COVER AS A METHOD OF DETERMINING THE SPATIAL RANGE OF THE INFLUENCE OF LARGE URBAN-INDUSTRIAL COMPLEX ON THE ENVIRONMENT

With the increasing anthropopressure, the problem of determining the spatial range of influence of anthropogeneous substance sources is of particular importance. Especially those sources are important which are a serious threat to the natural environment.

The imperfection of the research methodology and measuring systems in this domain is widely known. Hence, within the past several years these problems have been analysed and investigated. However, a method of quick and precise determination of threats and changes of the environment, as well as the spatial range of emission especially in the zone effected by large urban-industrial complexes, has not been developed yet.

The helpfulness of widely applied diffusive models (Sutton's and Pasquille) of pollutant propagation seems problematical. These models are particularly sensitive to incorrectly determined meteorological parameters and rate of emission (it changes in time i.a. due to manufacturing processes). They do not include incidental emission or topographical conditions which modify air motion in the lower layer. And thus determined diffusion coefficients can have a significant error. All this leads to a spatial distribution of the anthropogeneous substance which in many cases differs from the results of immission measurements made at the same time. Therefore, the model in the hitherto existing form loses its physical sense and is not confirmed by measurements performed in the field. The model has to include several additional parameters. Methods of conducting spatial studies useful in the complex determination of the influence range of urban-industrial should aim at the spatial analysis of measurements of pollution immission. Such an analysis should include a detailed recognition of the environment system, its ability of anthropogeneous substance assimilation, transport and accumulation, and qualitative changes in its particular components.

From among components of the natural environment the soil is the main accumulation medium of many chemical substances. Soils are an extremely

significant element in the migration process of pollutants in the environment system. Owing to the sorption process and intensive mass and energy exchange with other components, soils can assimilate and stop chemical substances which migrate in the water or air. Therefore, they usually are a good determinant of the chemical environment. At the same time, they are a stable medium and do not require a continual recording of their chemical composition.

The direct surroundings of the Refining and Petrochemical Plant and the town of Płock (to so-called Płock Urban-Industrial Complex) are a typical area affected by a large industrial centre. This region is under detailed observation of the Mazovian Geographical Observatory of the Faculty of Geography and Regional Studies of the University of Warsaw. These observations are expected to result in a spatial description of changes of the environment, and particularly in the determination of the content increase of chosen chemical compounds (mainly heavy metals), their accumulation dynamics and determination of concentration zones. They should produce a full, complex anthropogeneous image of the chemism conversion of the environment.

Studies of the soil chemism will be reliable only when results of laboratory analysis are confronted with a detailed and precisely recognised structure of the soil environment. Thus, these studies are an example of complex environmental studies and thus they can take advantage of methods widely applied by complex physical geography. These methods are based on an assumption that chosen components of the environment and features are recognised in detail and then they are systemized in a system of typological units. The latter system is then the object of further studies. Typological problems are of such great importance, because any environmental studies, which are to give us effects, have to treat the environment as a system of related elements. However, the application of the above-mentioned units allows us to assume that their mutual relations and interactions are to a certain extent similar. On this basis point investigations can be extrapolated onto the surface of the whole unit and onto units of the same type. This is especially useful when we do not have enough measurements and information. In this paper the above procedure is reduced to the determination of soil units with definite types of accumulation of chemical compounds. These soil units will be a reference in further research on their resistance and degree of contamination threat.

Studies were carried out within an area of approximately 400 km² around the Petrochemical Plant. This area is characterized by the frequent occurrence of situations in which the concentration of dust and gas pollutants exceeds standard values. The atmospheric delivery of anthropogeneous substance is quite substantial. The following types of soil are most widespread in this area: brown leached soils and brown soils formed from clays and agrillaceous sands, podzolized lessive soils formed on sands, black

earth and degraded black earth, numerous hydrogeneous soils-mainly sandy alluvial soils, bog and peat soils (low peat-bog) and peat mucky soils. All these types of soils have low or average sorptive power with relation to chemical compounds, which creates a serious threat of including the anthropogeneous substance into the cycle. Soils characterized by high sorptive power occur only occasionally and cover small areas.

In accordance with assumptions of the applied method, before the soil cover can be classified in terms of its ability of cummulating chemical substances, these features which influence the sorptive power of soils have to be analysed in detail. The following features were determined: mechanical composition (especially silty fraction content), depth of the humus level and percentage of organic substance, pH, oxidation-reduction potential, infiltration time, direction and intensity of the superficial and underground motion of the substance.

Each of the above-mentioned features highly influences the capacity accumulating chemical compounds by the soil cover. The factor analysis of the particular features with respect to their role in the circulation of chemical elements proves that the mechanical composition (including the content of the silty fraction from the montmorillonite and illite group), percentage of organic substance and topographic position which determines the direction and intensity of substance flow, have the greatest influence on the sorption process. Other elements are usually derivatives of those features.

The image of the soil sorption power obtained as a result of the above-mentioned procedure made it possible to create a map of soil resistance to pollutants.

Soil resistance is understood here as the soil capacity of stable accumulation of large amounts of chemical elements which makes it impossible to lixiviate these elements to underground waters or absorb them by plants. In accordance with this, all soils containing many sily minerals (especially from the montmorillonite and illite group) and a large organic substance content, with neutral or alkaline reaction and with a high ferrous mineral content, especially in the hydrogenerated amorphous form, have great binding power and ability of retaining chemical elements mainly in surface layers. Hence, they are resistant soils.

Sour sandy soils are their contradiction. However, the process of chemical element accumulation in colloids and organic complexes occurring in soils is not a constant effect. Each (e. g. seasonal) change of conditions, such as a decrease of organic substance content or an increase of acidification, can cause a change in the chemical element content. So maybe the term "soil resistance" should be substituted by the term "soil neutral" to population or to permeability of pollutants.

The map of soil resistance on the scale of 1:50,000 was constructed on the basis of spatial distribution of areas with similar types of sorption of chemical compounds.

These areas determined separately for lithogeneous and hydrogeneous soils were obtained from a confrontation of information on these soil cover features which condition sorption processes (silty fraction and organic substance content, position in the field). Thus, a network of units with non-explicit and non-homogeneous rank was obtained. Their limits were verified (taking into consideration secondary features which condition sorption) in the subsequent stage of studies. Thus new units with similar taxonomic rank, with an approximately homogeneous similarity of distinguished features, were created.

Then the resistance to anthropogeneous substances of distinguished units was determined. Each unit was separately evaluated from the point of view of the quality of features which are decisive to soil cover resistance in given limits. The soil valuation method was applied at diversified ranks of individual components in the process of chemical substance sorption. Main factors were given values from 10 to 50 points and secondary factors 5—25 points.

Depending on the characteristics of the particular factors, units can have point value from 45 to 225 points. This value expresses resistance of units to substances under investigation. On this basis individual fields have been classified to various resistance classes (Table 1).

Despite its subjectivity, related with the soil valuation method, the charted map of soil cover resistance gives a sufficiently reliable image of the soil sorptive power and constitutes a basis for further studies of the threat of dust and gas emission to soils. It also makes it possible to determine most representative places for soil sampling for chemical analysis.

On the basis of information on spatial diversification of soil cover resistance and on the volume of annual delivery of chosen pollutants (heavy metals) to the substrate (Fig. 1) degraded areas and areas potentially subject to degradation were delimited. The detailed classification of these areas into five classes is presented in Table 2.

Such a detailed recognition of the physical and chemical state of the soil cover, its resistance and degree of potential anthropogeneous threat has created an adequate background for finding points most representative from

Table 1
Classification of soil resistance according to valuation values

Resistance class of the area.	Valuation value
Resistant	185
Moderately resistant	150—185
Low resistance	115—150
Sensitive	80—115
Very sensitive	45— 80

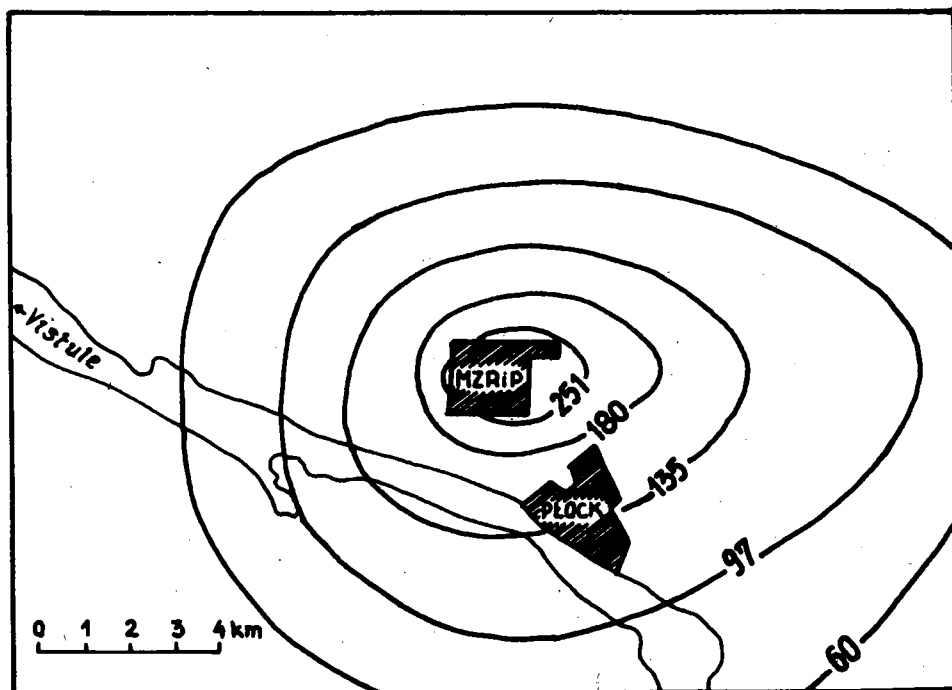


Fig. 1. Delivery of heavy metals ($\text{kg}/\text{km}^2/\text{year}$) to the soil in the zone affected by the Plock Urban-Industrial Complex

Table 2

The threat of heavy metal contamination in the zone affected by the Plock Urban-Industrial Complex

Degree of threat	Delivery $\text{kg}/\text{km}^2/\text{year}$	Resistance type
Very high	251—180	very sensitive
High	251—180	sensitive, low resistance
	135—180	very sensitive, sensitive
	97—135	very sensitive
Average	251—180	moderately resistant, resistant
	180—135	low resistance, moderately resistant, resistant
	97—135	sensitive, low resistance, moderately resistant
	60—97	very sensitive, sensitive, low resistance
	<60	very sensitive, sensitive
Low	97—135	resistant
	60—97	moderately resistant
	<60	low resistance, moderately resistant
Very low	<60	resistant

the point of view of the range of the soil environment contamination with industrial emission for sampling for purposes of chemical analysis. These studies are additionally aimed at grasping differences in chemical composition due to various criteria of sampling. The analysis of the directional wind rose, developed for the 1978—1983 period, has proved that the area in the NW direction from the Petrochemical Plant and town is a convenient place for the localisation of our studies, because of a significant contribution of winds from the SE direction. About 25 points were chosen in this area. Soil material was sampled from the full genetic profile (a total of 104 samples) in these points. The *pH* (with the electrometric method) was determined in the samples as well as the content of heavy metals (*Cd*, *Cr*, *Cu*, *Ni*, *Zn*, *Pb* — with the application of atomic absorption spectrophotometry) from a group of elements active and not very active in an oxidizing medium and inert in a reducing medium.

Chemical analysis results of chosen soil profiles are presented in Table 4, while Figure 2 shows their graphic illustration. Data obtained was systemized in accordance with the particular sampling criteria and subjected to the statistical analysis.

The following conclusions can be formulated on the basis of a complex analysis of information on the chemical composition of soils influenced by the Płock Urban-Industrial Complex:

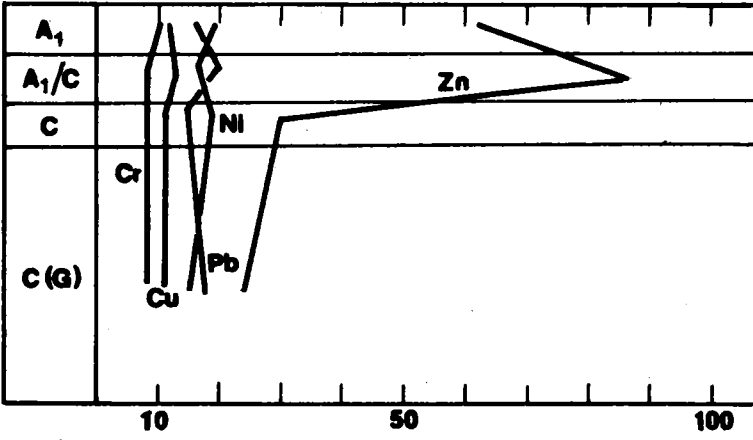
1. A comparison between data concerning the chemical composition of studied soils with data concerning the natural range of elements occurring in similar types of soils found in Poland (Table 3) proves that there is no great divergence between these quantities. However, this statement may only be treated as an estimate, because in most papers the problem of the heavy metal content in soils was not given sufficient attention. These papers do not give a full soil documentation (concerning the morphometric composition, organic substance content, size of the sorptive complex etc.) The localisation of soils outside the probable range of emitters is the main criterion of "naturalness".

Table 3

Average content of trace elements in natural soils (according to A. Kabata-Pendias) (ppm)

Soil type	<i>Cu</i>	<i>Zn</i>	<i>Cd</i>	<i>Pb</i>	<i>Cr</i>	<i>Mn</i>	<i>Ni</i>
Sandy	1—26	5—220	0.01—0.04		30—91	15—1535	1—52
Dust	8—54	17—127			21—38	110—1060	7—70
Loamy	17—36	13—362	0.09—1.8		35—81	45—820	10—104
Peat	1—113	13—250		18—85		20—2200	0,2—50
Black earth	3.53				27—100	220—890	
Podsol					30—91	320—910	
Podzolized lessive						50—650	
Brown					35—81	320—690	

1B



2B

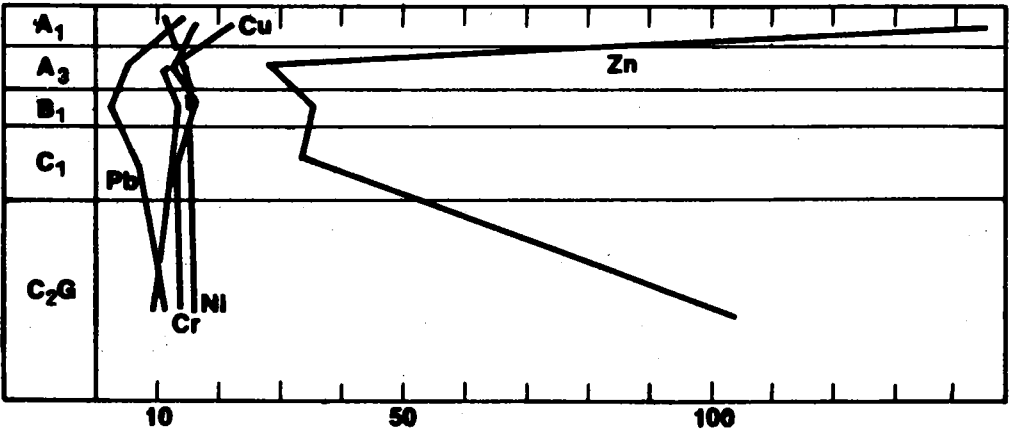
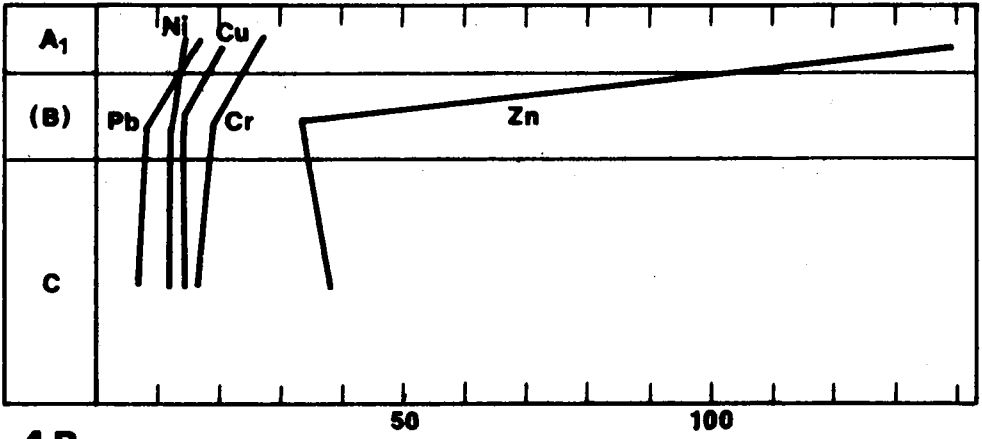


Fig. 2. Content of heavy metals (ppm) in chosen soil profiles

3B



4B

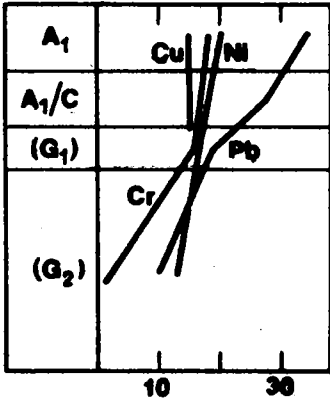


Fig. 2

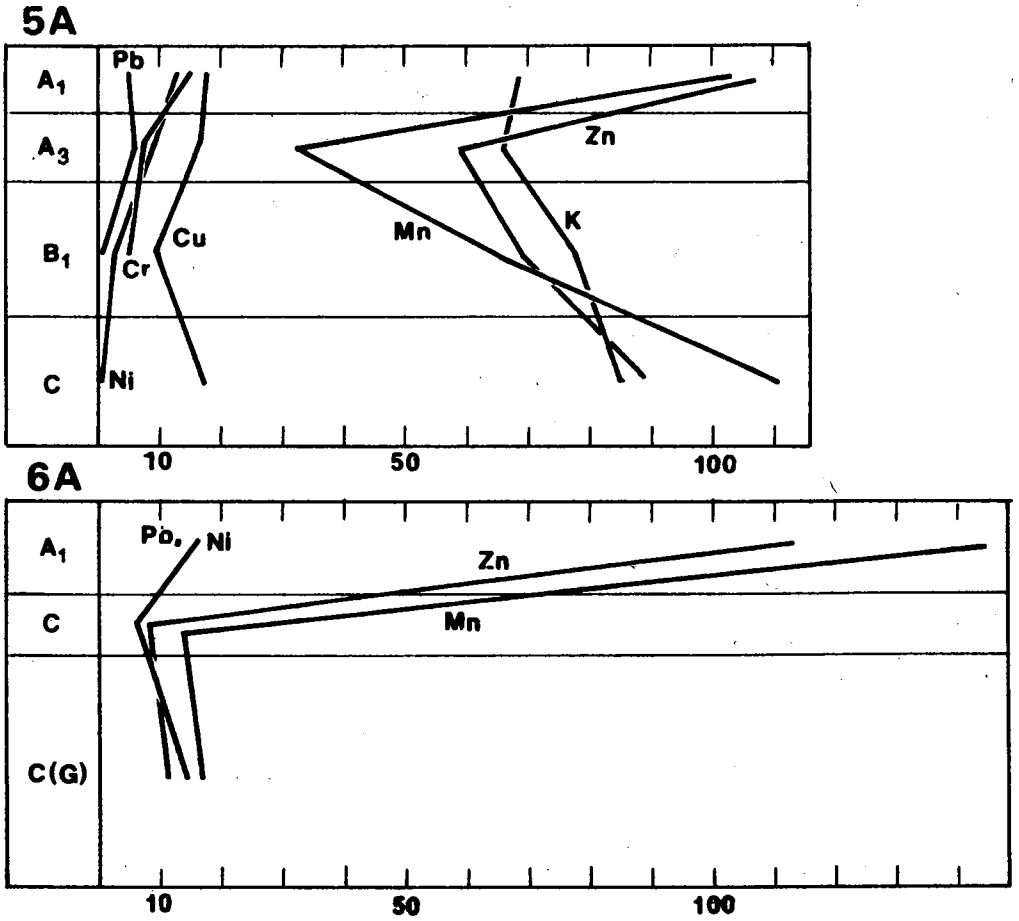


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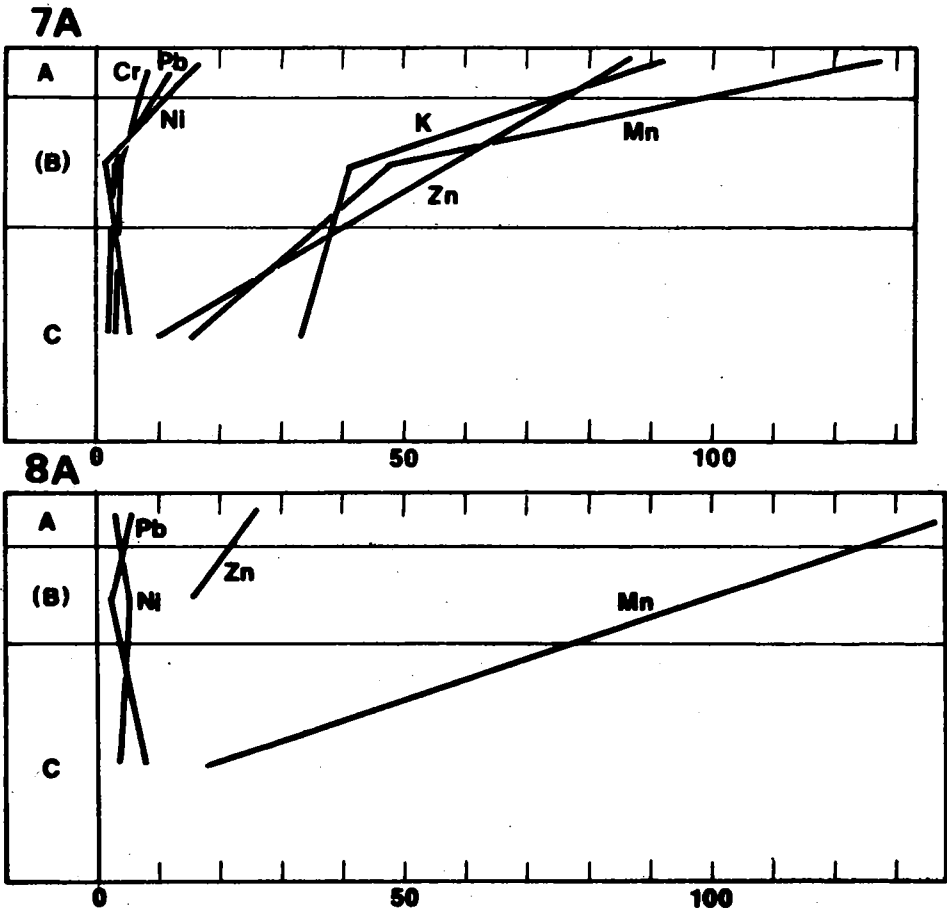


Fig. 2

2. Research performed shows that the Płock Urban-Industrial Complex influences mainly the zone neighbouring directly with the site of the Petrochemical Industrial Complex. A comparison between data on the chemical composition of soils (Table 4) and data concerning the composition of rocks from which these soils are formed shows that the concentration of such elements as: iron, nickel, lead, zinc, cadmium in soil levels (mainly A_1) is by far exceeded with relation to their natural content in the parent rock. This univocally points to their anthropogeneous origin.

3. In accordance with expectations, the greatest accumulation of trace elements was stated in the top soil level A_1 . It was found out that the accumulation decreases while moving into the profile. This confirms an assumption concerning the influence of anthropogeneous activity (including air pollution) on the chemical composition of soils. Model studies carried out by the Institute of Cultivation, Fertilization and Soil Science indicate that the trace element content in soils not affected by pollutants containing trace elements increases while moving into the profile. Except for the humous level, an increase of element concentration can also be observed in the B_1 level of podzolized lessive soils and (B) level of brown leached soils. An increase of these elements in parent rock occurs only sporadically.

4. The greatest concentration of trace elements under investigation was recorded in soils of organic origin and in black earth, sporadically in alluvial soils. This regularity is true of all elements irrespectively of their origin. It confirms the important role of the sorptive complex in the process of element accumulation in soil. The concentration of chemical substances in the soil is significantly increased in the area directly adjoining the site of the Petrochemical Plant (0.5–5.0 km from the centre of the Płock Urban-Industrial Complex) in comparison with the area lying 10.0–16.0 km away from it. This concerns especially such elements as: nickel, chromium, cadmium, lead, zinc, and is a result of dust emission mainly from low emitters of from non-organised emission with relatively small range of influence.

5. On the basis of existing materials, zones of decreased influence of the Płock Urban-Industrial Complex can only be estimated. They were found at 2.5–3.5 km from its centre (*Cu* does not occur) and 12.0–13.5 km (*Ni* and *Cr* do not occur), while concentrations of other elements were reduced by 40–50%.

6. Significant differences in the content of trace elements in the soil were recorded in the case of various soil covers, because woodland and grassland soils accumulate much more trace elements than cultivable soil.

7. A linear correlation was developed and verified at significance levels of $\alpha=0.1\%$ and $\alpha=5\%$ in order to determine reasons for chemical element concentration in soils. The most significant correlation was found between the content of heavy metals and the silty fraction and organic substance content. This confirms initial results obtained from factor analysis.

Table 4
Mechanical and chemical composition of soil profiles in the zone affected by the Plock Urban-Industrial Complex

No Soil type and subtype	Depth of genetic level	Humus content	pH in KCL	P	Ni	Cr	Cd	Pb	Zn	Cu
1A Sandy alluvial	A ₁	0-35	6.90	4	2.21	8.52	0.18	4.45	121.30	3.02
	C	35-150	6.91	7	3.09	3.35	0.62	2.16	43.60	3.42
2A Brown leached soil	A ₁	0-20	5.30	12	12.66	34.70	0.60	8.34	134.56	12.61
	B	20-40	5.55	4	3.75	8.24	0.27	3.93	57.66	14.91
	C ₁	40-80	4.79	nw	8.72	0.045	9.24	149.80	11.14	
	C ₂	80-150	5.50	1	2.70	3.26	0.075	3.60	27.90	9.36
3A Black earth	A ₁	0-15	4.80	15	14.53	0.67	11.42	118.82	16.19	
	A ₁ /C	15-30	7.12	17	14.36	3.99	0.48	2.14	14.91	10.53
	C	30-100	7.32	27	16.79	5.94	nw	5.34	11.74	10.03
	C (G)	100-150	7.40	gls	27	13.57	0.21	3.93	12.19	10.35
4A Brown leached soil	A ₁	0-15	1.33	24	nw	nw	1.05	4.47	57.57	4.36
	B/C	15-60	7.20	28	0.27	3.45	nw	2.29	10.15	0.42
	C	60-150	7.40	33	0.53	nw	0.06	5.91	10.42	0.16
5A Podzolized soil	A ₁	0-25	1.15	16	11.88	11.30	0.24	4.83	100.39	14.89
	A ₃	25-50	4.75	17	nw	6.76	0.26	6.49	54.96	14.66
	B ₁	50-100	5.0	17	1.98	3.78	nw	3.36	67.29	8.93
	C	100-150	5.60	35	0.45	nw	0.65	nw	86.06	14.13
6A Degraded black earth	A ₁	0-40	4.59	25	13.90	nw	0.57	13.19	111.39	16.35
	C	40-60	7.33	29	6.09	nw	0.21	nw	10.69	10.54
	C/G	60-150	7.33	38	10.95	nw	0.63	nw	10.24	11.05
7A Brown leached soil	A ₁	0-20	2.45	28	13.57	10.56	0.42	8.19	87.78	14.79
	(B)	20-70	4.80	32	nw	2.98	0.30	4.03	53.05	4.23
	C	70-150	4.72	36	1.8	4.35	nw	2.70	10.59	2.19
8A Brown leached soil	A ₁	0-20	0.99	5	3.09	nw	0.19	4.89	22.66	0.49
	(B)	20-60	6.70	4	5.24	nw	nw	3.67	15.49	4.55
	C	60-150	7.42	2	4.65	nw	nw	6.36	nw	nw

9A Peat soil	A ₁	0—10	nb	7.25	15.0	10.0	0.60	3.86	12.90	11.08
	A ₁	10—80		7.25	nw	19.0	nw	3.91	12.70	11.09
	T ₁	80—140		7.28	10.96	13.80	0.48	3.88	11.41	10.39
	T ₂	140—230		7.30	11.47	3.83	nw	5.23	12.70	10.39
	C ₂	230—280		7.42	14.99	nw	0.58	2.89	10.99	10.12
10A Peat mucky soil	AM ₁	0—50	nb	7.32	13.09	14.62	nw	1.56	10.85	10.76
	M ₂	50—100		7.79	11.78	nw	0.21	3.21	10.45	10.92
	M ₃	100—170		7.59	13.03	15.62	0.42	5.19	10.52	10.21
	T ₁	170—250		7.33	14.29	nw	0.82	1.87	10.39	10.18
1B Sandy alluvial soil	A ₁	0—20	0.85	7.45	19.3	11.55	nw	14.55	60.75	10.60
	A/C	20—30		7.10	19.15	10.50	nw	20.25	84.90	11.65
	C	30—50		7.10	19.75	9.15	nw	14.55	27.75	10.75
	C/G	50—150		7.0	17.65	9.30	nw	16.20	24.30	10.84
	A ₁	0—15	1.31	7.10	11.20	15.55	0.60	14.40	142.90	22.0
2B Podzolized lessive soil	A ₃	15—30		6.90	18	11.35	nw	5.10	28.80	13.0
	B ₁	30—45		7.43	16	11.95	0.30	3.45	34.65	14.50
	C ₁	45—70		7.20	27	nw	12.10	8.25	33.15	13.90
	C ₂ /G	70—150		7.60	26	12.70	0.45	11.40	104.40	10.80
	A ₁	0—25	1.58	7.10	15	11.95	0.30	13.50	148.30	17.20
3B Brown leached soil	(B)	25—60		6.90	6	10.60	0.90	9.60	32.25	13.45
	C	60—150		7.25	2	10.60	0.45	6.75	39.0	14.20
	A ₁	0—30	5.15	7.55	29	16.45	0.16	33.75	207.0	13.60
4B Black earth	A ₁ C	30—55		7.31	26	16.15	0.60	32.25	146.95	12.25
	(G ₁)	55—70		7.33	25	14.06	0.20	16.35	100.05	12.55
	(G ₂)	70—150		7.40	23	12.85	0.60	11.55	247.50	11.50
	A ₁	0—30	1.48	7.21	38	15.70	nw	21.45	178.45	13.90
5B Brown leached soil	(B)	30—70		6.92	34	16.45	nw	19.35	192.0	13.90
	C	70—150		7.05	31	13.15	nw	19.05	226.0	12.70

P — % particle size <0.02 mm, nb — without probe, nw — undetected.

8. Results of the chemical analysis of the soil material, systematized with relation to criteria of designating sampling points indicate that measuring errors reaching 400% result when similar conditions of the soil environment are not taken into consideration. It is impossible to draw samples in a geometrical network of points without a full pedological recognition (which unfortunately is generally done by the environment protection services).

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