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METAL INTOXICATION OF ATMOSPHERIC PRECIPITATIONS NEAR COAL POWER STATIONS

Intoxication of atmospheric precipitation near coal power stations is presented. The migration of some metals in air is described by intoxication coefficient, which in 1981 for Pb changed from 2.25 to 2.96, for Cd from 1.92 to 3.0, for Cu from 2.31 to 4.44, for Fe from 2.78 to 3.95, and for Mn from 1.77 to 3.76. The coefficient value defines potential ecotoxicity of a given metal in the region investigated. Rain or snow intoxication by Pb, Cd, Cu, Fe and Mn, depending on their amount, is described by equation $y = a \cdot x^b$.

1. INTRODUCTION

In recent years town and country planning and environmental chemistry arouse tremendous interest. The most important reason of such a state of affairs is environment protection against negative influence of microelements. The concentrations of metals introduced to environment by industrial dusts and atmospheric precipitations in most cases exceed permissible concentrations ensuring natural equilibrium of self-purification processes. Any change of chemical equilibrium of environment causes not only disturbances of growth and development of animals and plants, but may also influence human health.

Precipitation intoxication, which is the main source of secondary changes in chemical characteristics of the soil, water and plants, causes serious problems because the emission of some metals in Poland has one of the highest values in the world, similar to those in USSR and West Germany.

According to Salbioni the value of total emission of Cd, Ni, Pb and Zn in dusts, not exceeding currently 1.5, in 1990 will be equal to 0.94, 12.4, 93.8, and 119, respectively. The above calculations were made in order to estimate human health protection [1].

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Further ecological research concerning metal migration in environment is established. Quantitative determination of the mass of metals eliminated from the atmosphere during precipitations such as rainfalls, snowfalls, falling fog, gravitational and turbulent dustfall to the ground enables calculation of the equation which comprises elements of air layer close to the ground and the soil. Rainfalls on the areas near coal power stations eliminate 45–65% of dust contaminations from the atmosphere [2]. The co-occurrence of metals in precipitations may be distinctive for the given area [3].

2. METHODS

Falling water was collected by the means of devices, the active surface of which was 2.5 m^2, exposed in the open areas to the height of 1 m above the ground for one month. The falls were collected in 13 points in industrial areas, 3 points on three dam reservoirs, and 1 point in the mountains (913 m a.s.l.). For determination of the insoluble elements samples were filtrated, dried, and digested in HNO_3 and H_2O_2 mixture according to BRIX [4]. The metal content was determined by means of the absorption atomic spectrometry method (Varian Techtron apparatus, the model AA-6DA, with corrector). The water collected was filtered through the filter paper No. 0.45. The limits of detection of the method used were as follows:

Cu – 0.1 ng/cm^3,
Cd – 0.5 ng/dm^3,
Mn – 2.5 ng/dm^3,
Co – 2.5 ng/dm^3,
Zn – 0.02 μg/cm^3,
Cu – 2.5 ng/cm^3,
Mg – 0.25 ng/cm^3,
Sr – 5.0 ng/dm^3,
Mg – 0.01 μg/cm^3,
Fe – 5 ng/cm^3,
Ni – 2.5 ng/dm^3,
Al – 50 ng/dm^3.

3. RESULTS

The research on the occurrence of the selected metals was conducted in the period ranging from 1979 to 1983. The total mean contents of metals investigated were the following:

26.0 – 766 μg/dm^3, average 173 μg/dm^3 (Pb),
1.6 – 34.2 μg/dm^3, average 10.35 μg/dm^3 (Cd),
2.5 – 109.2 μg/dm^3, average 25.78 μg/dm^3 (Cu),
346 – 22918 μg/dm^3, average 3079 μg/dm^3 (Mg),
87 – 3934 μg/dm^3, average 712,5 μg/dm^3 (Fe),
22.5 – 812.9 μg/dm^3, average 155.51 μg/dm^3 (Mn),
0.0 – 67.0 μg/dm^3, average 9.36 μg/dm^3 (Ni),
0.0 – 21.1 μg/dm^3, average 2.79 μg/dm^3 (Co),
114 – 2753 μg/dm^3, average 702.14 μg/dm^3 (Zn),
19 – 2086 μg/dm^3, average 167.29 μg/dm^3 (Sr),
3.49 – 95.71 μg/dm^3, average 13.83 μg/dm^3 (Ca),
69.0 – 5847 μg/dm^3, average 941.9 μg/dm^3 (Al).

Numerous physico-chemical processes, which occur in the atmosphere, are of crucial importance for the natural environment. Precipitation intoxication is the result of adsorption on the aerosal drops and both electrostatic and gravitational coagulation. This process is aided by turbulent whirl. The changes of metal contents in air are described by intoxication coefficient B:

$$B = \frac{\ln(C_i/C_o)}{\ln h} \ (\mathrm{cm}^{-1})$$

where:

C_i – average monthly metal concentration in air,
C_o – average monthly metal concentration in precipitations,
h – total precipitations in a month, cm.

The estimated values of the parameter B show differences in metal precipitation. In 1981, the values of the parameter B for Pb, Cd, Cu, Fe, and Mn had changed within the ranges 2.25–2.96, 1.92–3.0, 2.31–4.44, 2.78–3.95, and 1.77–3.76, respectively. When emission of power stations was constant, intoxication coefficients changed in the same way. The highest values of parameter B for Pb, Cd, Cu, Fe were observed in February and March, and the lowest, in June. Intoxication coefficient B estimated in subsequent years is a relatively good indicator of air pollution observed. Comparison of intoxication coefficients is presented in tab. 1.

Table 1

Comparison of intoxication coefficients (B) in two localities in the period of 1979–1983

Locality	Year	Pb	Cd	Cu	Fe	Mn	Ni	Zn	Total	Average
Katowice-Załęże	1979	2.24	2.10	2.60	2.16	2.06	2.15	1.86	15.17	16.91
	1980	2.35	2.30	2.93	2.49	2.30	2.38	1.97	16.72	
	1981	2.29	2.15	2.86	2.27	2.13	2.22	2.01	15.93	
	1982	2.77	2.69	3.46	2.92	2.52	2.61	2.19	19.16	
	1983	2.46	2.36	3.15	2.63	2.43	2.41	2.11	17.55	
Goczałkowice	1979	1.94	1.93	2.20	2.00	1.64	1.77	1.82	13.30	13.48
	1980	2.05	1.96	2.35	2.12	1.78	1.87	1.87	14.0	
	1981	1.88	1.86	1.98	1.69	1.51	1.60	1.70	12.22	
	1982	2.25	2.12	2.45	2.20	1.85	2.03	2.10	15.0	
	1983	1.90	1.91	2.08	1.93	1.58	1.73	1.76	12.89	

The sum of each intoxication coefficient referring to a given metal may be a representative indicator of relative changes of air quality because it provides some information about changes of an element concentration in time (tab. 2). Except for Pb, Cu, Mn, Co, and Sr, the values of the parameter B are higher for atmospheric precipitations in heating period.

Table 2

Intoxication coefficients in summer and winter for whole investigated region

Period	Pb	Cd	Cu	Mg	Fe	Mn	Ni	Co	Zn	Sr	Ca	Al
Average for summer 1979–1983	2.38	2.11	2.85	1.75	2.43	2.24	2.22	2.30	2.03	1.96	1.59	2.39
Average for winter 1979–1983	2.21	2.29	2.85	1.88	2.49	2.15	2.52	2.13	2.06	1.84	1.66	2.65

Table 3

Intoxication of rain in industrial area

Element	Locality	Load Me^{+n} (mg/m^2· month)	Metal concentration in rain		Average metal content in dust fall (mg/m^2·year	Average metal content in air (ng/m^3)	Washout coefficient		
			Soluble forms (mg/m^2· month)	Insoluble forms (mg/m^2· month)			B_R	B_N	B_C
Pb	Katowice-Załęże	6.59	1.76	4.83	73.76	1230	2.43	2.76	2.87
	Chorzów-Planetarium	13.44	5.25	8.19	161.3	975	3.09	3.27	3.45
	Kozłowa Góra	3.61	1.33	2.28	43.32	550	2.77	2.96	3.13
	Goczałkowice	4.30	1.42	2.88	51.60	350	3.00	3.12	3.40
	Jaworzno	5.26	1.62	3.64	63.12	1120	2.88	3.20	3.34
Cd	Katowice-Załęże	0.42	0.22	0.20	4.72	48	2.82	2.79	3.03
	Chorzów-Planetarium	0.68	0.38	0.30	8.16	31	3.39	3.30	3.59
	Kozłowa Góra	0.18	0.13	0.05	2.16	17	3.17	2.84	3.29
	Goczałkowice	0.18	0.12	0.06	2.16	13	3.31	3.06	3.45
	Jaworzno	0.39	0.24	0.15	4.68	32	3.53	3.34	3.72
Cu	Katowice-Załęże	1.15	0.84	0.41	12.19	580	2.14	1.81	2.25
	Chorzów-Planetarium	1.22	0.71	0.51	14.64	285	2.81	2.64	3.01
	Kozłowa Góra	0.35	0.25	0.10	4.20	188	2.56	2.24	2.68
	Goczałkowice	0.71	0.44	0.27	8.52	104	3.01	2.84	3.13
	Jaworzno	0.95	0.72	0.23	11.40	326	3.04	2.59	3.15

The series of decreasing rain intoxication in winter (heating period) and for summer (tab. 2) are following:

Cu > Al > Ni > Fe > Cd > Pb > Mn > Co > Zn > Mg > Sr > Ca,
Cu > Fe > Al > Pb > Co > Mn > Ni > Cd > Zn > Sr > Mg > Ca.

These significant differences justify further research on estimation of air pollution by means of intoxication coefficient, the value of which defines potential ecotoxicity of a given metal. The importance of the parameter B is of local range. Table 1 confirms the statement that the sum of intoxication coefficients for the metals in question is a representative indicator of relative changes of air quality in various places.

The sequence of individual elements is characteristics of the given place, i.e.,

1. Near power stations (500 m): Cu > Pb > Cd > Mn > Zn > Fe > Ni.
2. At the distance of 6 km, according to the characteristic wind rose: Cu > Fe > Pb > Ni > Cd > Mn > Zn.
3. At the distance of 50 km: Cu > Pb, Fe, Cd > Zn > Ni > Mn.

This is the reason why there exist some territorial differences in man's exposition to the action of metals in a given area. The contamination of rain in industrial region can be expressed by the following parameters: load of metal, concentration of soluble and insoluble elements, average dust fall, washout coefficient (tab. 3).

Intoxication level depends not only on dust fractional composition and various sources of dust emission, but also on soluble forms of metals (tab. 3). Columns 3, 4 and 5 in tab. 3 present the amount of metals which pass from air to precipitations in both soluble and insoluble forms, as well as their total amount. The participation of soluble and insoluble forms in precipitation intoxication varies depending on the metal and the place. Erosion efficiency of those metals is characterized by washout coefficients of their soluble forms (B_R), insoluble forms (B_N), and total sample (B_C).

Lead fallout is slower than that of cadmium, manganese, nickel, and zinc which can be explained by chemical composition of fine-dispersive dusts. The values of the coefficient B, characterizing generally the harmfulness of air, in connection with those concerning the other elements of the environment, such as water (B_R), soil and plant (B_N), are of great ecotoxical importance, because they provide information about real possibilities of migration of a given load of selected metal. Values of washout coefficients evidence the potential toxicity of a metal.

Precipitation intoxication is determined by complex processes influenced by amount of precipitations, mineralization, pH, metal concentration in air and in precipitations, dustfall and dust concentration.

The processes of precipitation intoxication are presented in fig. 1. The parameter B decreases with the increase of precipitation, which means that even small volume of precipitation can considerably intoxicate the areas with metal. Subsequent rainfalls enable migrations of the metals in a drainage basin and thus environment intoxication.

Precipitation intoxication with Pb, Cd, Cu, Fe, and Mn, depending on their amount, is described by the equation $y = a \cdot x^b$, where y denotes the metal content (in μg/dm^3), and x is the rainfall (in mm).

$y = 5.12\,x^{-0.19}$, $r = 0.86$, $d = 0.75$ (Pb),
$y = 5.98\,x^{-0.25}$, $r = 0.90$, $d = 0.81$ (Cd),

$y = 7.33\,x^{-0.23}$, $r = 0.88$ $d = 0.78$ (Cu),
$y = 6.34\,x^{-0.23}$, $r = 0.94$, $d = 0.87$ (Fe),
$y = 5.35\,x^{-0.22}$, $r = 0.86$, $d = 0.73$ (Mn).

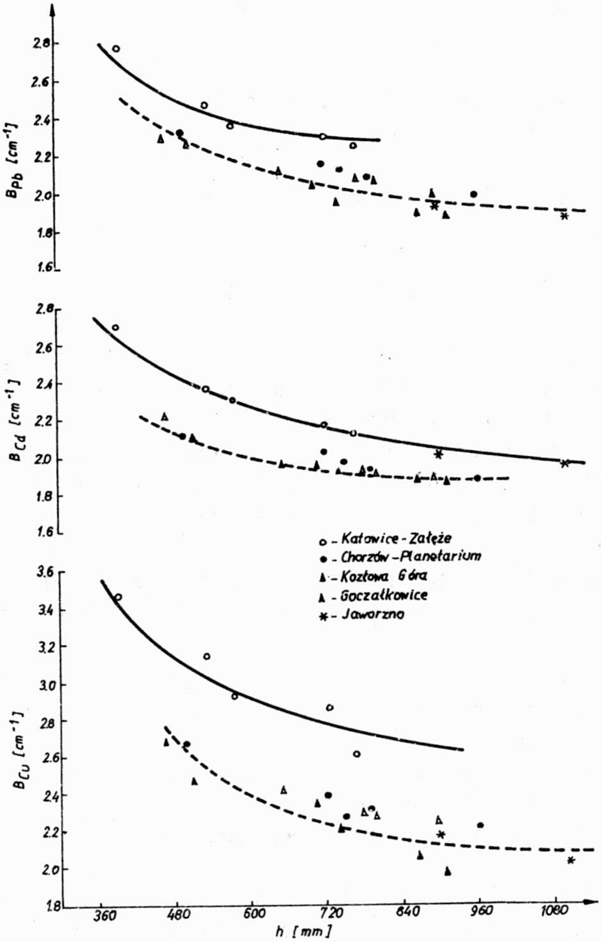

Fig. 1. Intoxication of rain by Pb, Cd, Cu in relation to precipitation

Between these parameters there is a distinct relationship, characterized by the correlation coefficient r and the determination coefficient d. About 80% of all the results reflects well the laws of nature. The change in the harmfulness is calculated within 20–30 mm range of precipitations. Extrapolated values express relative participation in "chemopression". Relatively higher values of the intoxication coefficient obtained by extrapolation at the same precipitation volume in a given month indicate and define ecotoxicological importance of the metals in reference

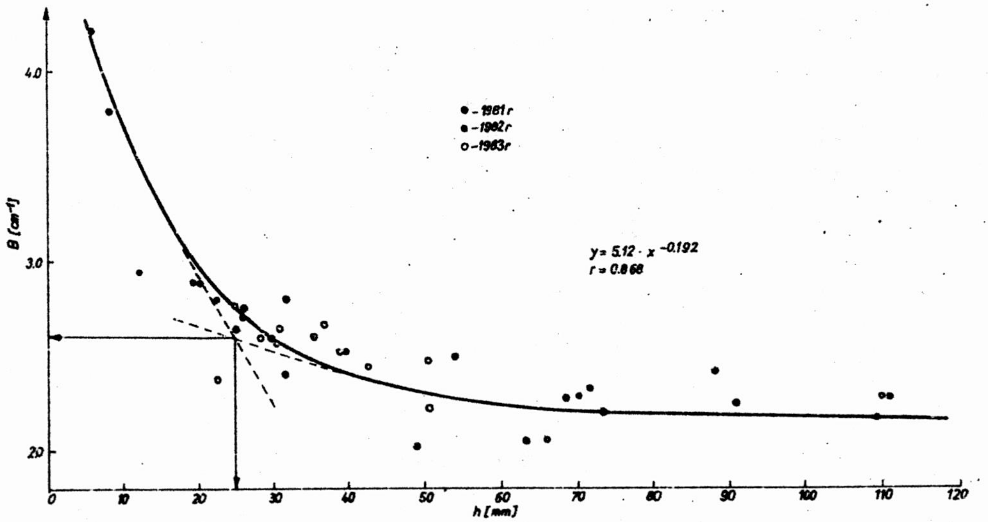

Fig. 2. Intoxication of rain by Pb in relation to monthly precipitation

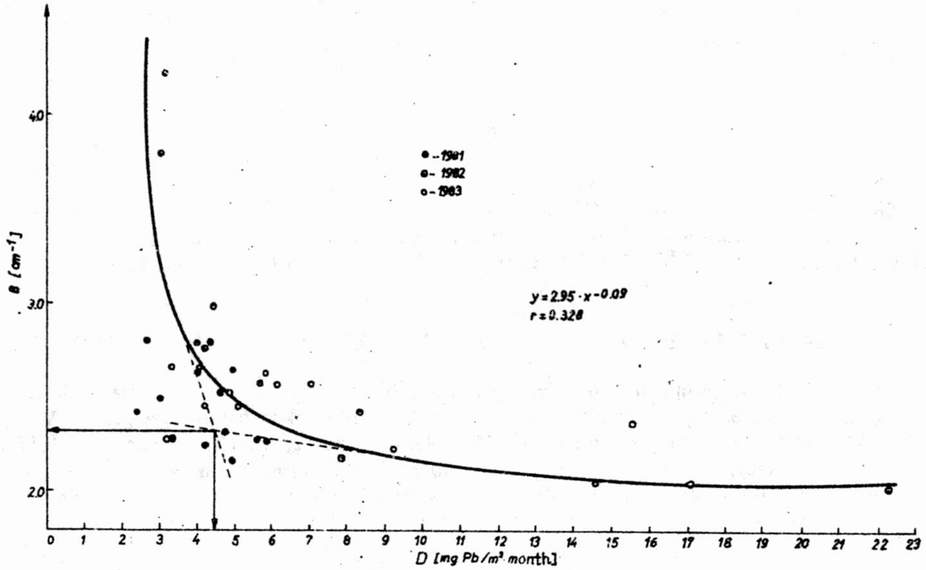

Fig. 3. Intoxication of rain by Pb in relation to concentration of Pb in the dustfall

to the environment. For example, manganese is described by $B = 2.2$ cm for statistical sum of precipitations equal to 28 mm, whereas the same value for copper is 3.0 for 24 mm precipitation.

Dependence of intoxication coefficients upon content of given metal in month's precipitation is expressed by atmospheric self-purification. Such a relation is described by equation $y = a \cdot x^b$, where coefficient b expresses an abatement of precipitation intoxication, and coefficient a may be interpreted as environmental background of precipitation intoxication with the given metal. The points specified on the inflexion of the curve designate the average values of precipitation intoxication with lead (fig. 3).

The participation of metals in total precipitation is given by the following equations:

$y = 2.95\,x^{-0.09}$, $r = 0.328$ (Pb),
$y = 1.92\,x^{-0.20}$, $r = 0.704$ (Cd),
$y = 2.97\,x^{-13}$, $r = 0.648$ (Cu),
$y = 5.54\,x^{0.24}$, $r = 0.658$ (Fe),
$y = 3.08\,x^{-0.17}$, $r = 0.751$ (Mn).

4. CONCLUSIONS

1. The analysed intoxication coefficient may be used for estimating the content of selected metals in rainfalls and snowfalls.

2. Intoxication coefficient is a relative measure of ecotoxicity of the given metal.

3. The general relative estimation of exposition of given places can be connected with the sum of intoxication coefficients of precipitations of given metals.

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INTOKSYKACJA METALAMI OPADÓW ATMOSFERYCZNYCH W POBLIŻU ELEKTROWNI

Przedstawiono intoksykację opadów atmosferycznych w pobliżu elektrowni. Przemieszczanie się metali w powietrzu jest opisane przez współczynnik intoksykacji, który w 1981 roku zmienił się w przypadku ołowiu z 2,25 do 2,96, kadmu z 1,92 do 3,0, miedzi z 2,31 do 4,44, żelaza z 2,78 do 3,95 i manganu z 1,77 do 3,76. Wartość tego współczynnika określa potencjalną ekotoksyczność danego metalu w badanym regionie. Intoksykacja deszczu lub śniegu przez ołów, kadm, miedź, żelazo i mangan, w zależności od ich ilości, jest opisana przez równanie $y = a \cdot x^b$.

ИНТОКСИКАЦИЯ МЕТАЛЛАМИ АТМОСФЕРНЫХ ОСАДКОВ ВБЛИЗИ ЭЛЕКТРОСТАНЦИЙ

Представлена интоксикация атмосферных осадков вблизи электростанций. Перемещение металлов в воздухе описано коэффициентом интоксикации, который в 1981 году изменился для свинца с 2,25 на 2,96, для кадмия с 1,92 на 3,0, для меди с 2,31 на 4,44, для железа с 2,78 на 3,95 и для марганца с 1,77 на 3,76. Значение этого коэффициента определяет токсичность данного металла в исследуемом районе. Интоксикация дождя или снега свинцом, кадмием, медью, железом и марганцем в зависимости от их количества описана уравнением $y = a \cdot x^b$.