

BOHDAN GŁOWIAK*, ANNA ZWOŹDZIAK*, JERZY ZWOŹDZIAK*

STUDIES ON ATMOSPHERIC POLLUTION CONTRIBUTED BY AIR-BORNE COPPER AND ZINC PARTICULATES AROUND A COPPER SMELTER

Measurements were carried for copper- and zinc-bearing dusts emitted by a copper smelter. The concentrations of these metals in atmospheric particulates, dust fallout deposits and total particulate load were determined and the results obtained are discussed. The copper and zinc levels were found to be high — especially those in the rainwater — creating a serious hazard both to soil and to water resources.

1. INTRODUCTION

The development of the copper industry brings about an increase of heavy metals accumulation in the environment. It is expected that the environmental hazard will also increase in the future due to the ever increasing demand for non-ferrous metals.

The mechanisms involved in the biochemical transformation of heavy metals, their combinations in the atmosphere, soil and water, as well as their pathways in the ecological chain, are still insufficiently known. Most of the information on heavy metals behaviour reported in the literature deals with transformation of mercury. However, the literature data published so far for copper and zinc transfer in the environment are poor and incomplete.

It is commonly known that copper and zinc are amongst those microelements which exert a considerable influence on the proper functioning of a living organism. They are contained in the soil and from there on they pass and move through different food chains. The natural concentrations of these elements are very low and create no contamination hazard to the environment. But the environmental contamination becomes a serious problem in the immediate vicinity of a copper smelter.

* Institute of Environment Protection Engineering, Technical University of Wrocław, Wrocław, Poland.

2. EXPERIMENTAL PROCEDURES

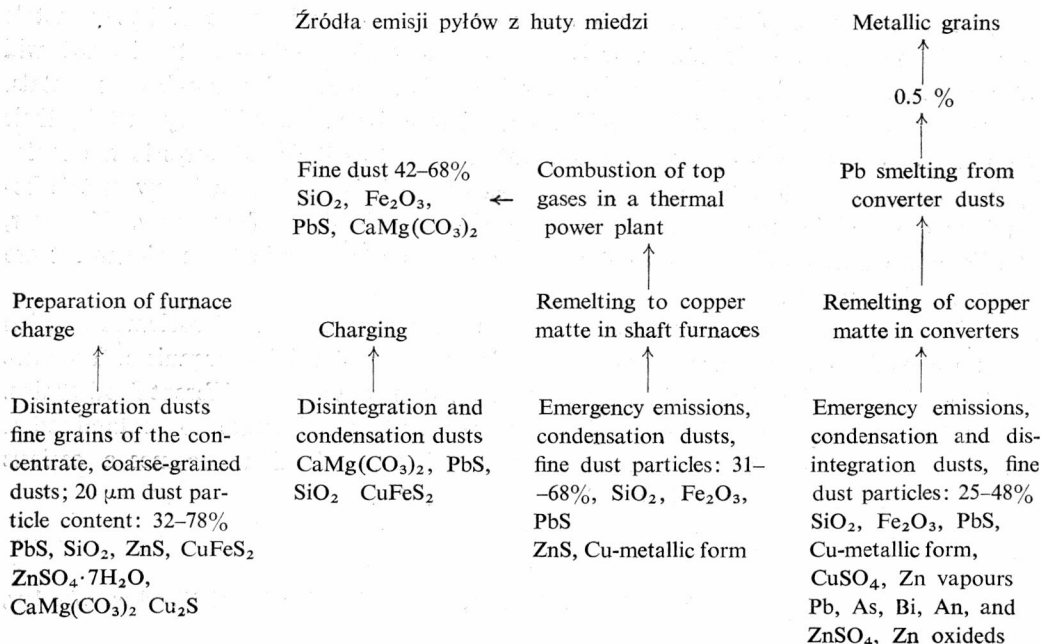
The studies were carried out on dust samples collected in the vicinity of a copper smelter. Total concentrations of copper and zinc were measured by atomic absorption spectroscopy using an atomic spectrophotometer. Prior to this procedure, the elements contained in the particulates had been taken into solution. The samples were treated with a mixture of nitric and hydrochloric acids p.a. and 30% hydrogen peroxide solution. X-ray fluorescence method was employed to determine the heavy metals composition of the sample. For this purpose an X-ray apparatus with a diffractometer and typical equipment for impulse recording and analysis was used. Cobalt lamp radiation was employed because of the presence of iron in the analysed samples. The reflection angles and interplanar distances were determined and the intensity of the particular lines estimated. The dusts generated by two emission sources — Emitter II and Emitter III — were analysed by fluorimetry.

Quantitative analyses were made for dust fallout deposit, dusts emitted by Emitter I, Emitter II and Emitter III. From January to July 1978 a Staplex aspirator with Whatman No. 4 filter paper was operated to measure the atmospheric particulate matter near the copper smelter. This sampling period has been selected for our studies, as the winter and spring seasons are characterized by the most adverse meteorological conditions. The sampling site has been located 350 m west of the emission source, in the direction

Table 1

Dust emission sources in the area of a copper smelter

Źródła emisji pyłów z huty miedzi



of prevailing winds. The measurements were performed 2.5 m above ground level to prevent secondary pollution. Samples were collected twice monthly.

The filters were dried and weighed under standard conditions in the laboratory. The dust residue was calculated from the differences in the filter mass before and after measurement. Heavy metals concentrations were determined with the use of an atomic absorption spectrophotometer in the way described above. To compare the Cu and Zn concentrations recorded in the immediate vicinity of the copper smelter with those measured in the adjacent residential area (5 km apart), the measurement-results obtained by the Epidemiological Station in 1977–1978 have been used.

The analyses for heavy metals were also carried out on rain water samples collected in plastic tanks. The deposition collection was first filtered and then some parts of the filtrate were used for the determination of heavy metals dissolved in the filtrate. The residue was subjected to further treatment consisting of two steps — drying at 378 K and weighing. Cu and Zn concentrations were measured by spectrophotometry. The average concentrations of these metals were compared with the results recorded in North America, in the United Kingdom, and in Australia. The organic matter content in the samples was measured by ashing in a muffle furnace, until a constant weight was achieved.

3. DISCUSSION OF RESULTS

The dust emission sources are characterized in table 1. The total yearly copper and zinc mass emitted by the copper smelter approaches 3500 Mg and 43 Mg, respectively. The dusts from this smelter are characterized by a high content of heavy metals with copper, lead and zinc each accounting for approx. 20%, 12% and 2%, respectively. The measurement results are listed in table 2. Organic matter contained in the dust samples (dark bituminous substances, graphite, as well as sintered carbon and iron Fe_3C) varies from 12 to 14%.

Table 2

Heavy metal concentrations in the dust samples mg/kg
Zawartość metali ciężkich w próbkach pyłu, mg/kg

Dust	Fe	Zn	Cu	Cd	Pb
Fallout dust	27,700	16,000	19,5000	107	1,580
Emitter I	25,000	11,260	18,900	95	1,180
Dust generated at the cyclones battery					
Emitter II	—	21,000	13,3000	233	11,830
Dust emitted from the emergency stacks of the shaft furnace					
Emitter III	26,300	15,700	20,1800	123	1,710
Concentrate bedding tank					

The identification of phases in the diffractograms has revealed that the most intensive lines corresponding to quartz, SiO_2 , graphite, PbS , PbSO_4 , CuAl_2 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{Zn}(\text{PO}_3)_2$ occurred for those samples which had been collected in the vicinity of Emitter III (table 3). Samples from Emitter II consist chiefly of $< 20 \mu\text{m}$ dust particles and contain predominantly PbS (galena) and ZnS (sphalerite). The dusts emitted from Emitter

Table 3

Lines on the diffractogram for Emitter III
Dane na podstawie dyfraktogramu z emitera III

Angular position of the reflection Q rad	Intensity of the lines I	Interplamar distance d nm	Phases
0.265	vs	0.341	PbS $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{PO}_3)_2$
0.270	vs	0.334	SiO_2 , C, PbSO_4
0.290	es	0.303	CuFeS_2 , PbSO_4 , CuAl_2 , $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$
0.305	vs	0.297	PbS $\text{Zn}(\text{PO}_3)_2$
0.315	av	0.288	$\text{Zn}(\text{PO}_3)_2$
0.440	w	0.208	C, PbS , PbSO_4 , CuAl_2 , $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ $\text{Zn}(\text{PO}_3)_2$
0.472	w	0.196	PbSO_4 $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ $\text{Zn}(\text{PO}_3)_2$
0.479	w	0.194	CuAl_2 , $\text{ZnSO}_3 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{PO}_3)_2$
0.523	av	0.178	PbS , PbSO_4 , $\text{Zn}(\text{PO}_3)_2$
0.617	w	0.154	SiO_2 , C, $\text{Zn}(\text{PO}_3)_2$
0.737	w	0.133	CuFeS_2 , PbS $\text{Zn}(\text{PO}_3)_2$
0.831	w	0.121	SiO_2 , PbS , CuFeS_2 , $\text{Zn}(\text{PO}_3)_2$

Notation: vs = very strong
es = extremely strong
av = average
w = weak

III are in the most part dolomite grains, clay substances, bitumen, single quartz grains, and sulphate minerals: Cu_2S , $\text{Cu}_2\text{S}(\text{Fe}, \text{Cu})\text{S}$, CuFeS_2 , PbS , ZnS , of a grain diameter below $60 \mu\text{m}$, but larger grains — up to $100 \mu\text{m}$ — can also be found. Yearly dust fallout deposits containing copper and zinc collected at a distance above 5 km of the smelter along the direction of prevailing winds are shown in fig. 1 for the years 1977–1978.

The fallout deposits of copper and zinc-bearing dusts measured in the sampling period are comparable with those found in other countries (table 4). Fig. 2 illustrates the variability of the atmospheric Cu and Zn concentrations for the first six months of 1978. The values are very high and several times exceed those reported in the literature (table 5) [3,5–9]. This is possibly due to the distance of the sampling sites from the emission sources studied; the concentrations represented in fig. 2 had been measured 350 m from the pollution source where the maximum values are recorded. The difference between the litera-

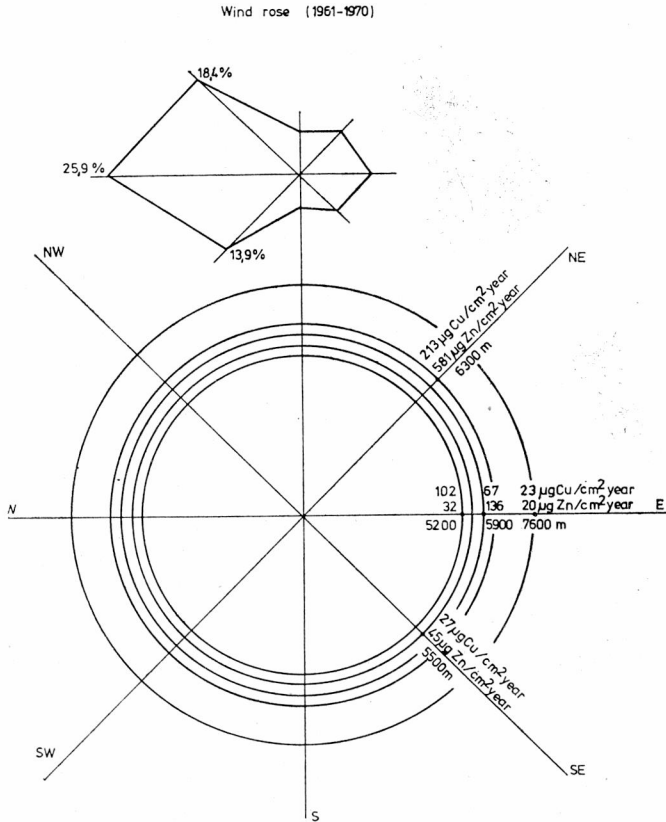


Fig. 1. Yearly dusts fallout deposits containing copper and zinc collected at a distance more than 5000 m from the smelter; 1977-1978

Rys. 1. Roczny opad pyłów zawierających Cu i Zn w odległości ponad 5000 m od huty; 1977-1978

Table 4

Fallout depositions of Cu- and Zn- bearing dusts in various countries
Opad pyłów zawierających Cu i Zn w różnych krajach

Reference	Dust fallout, g/cm/year				Country
	Area with no industrial emission source		Industrialized area		
	Cu	Zn	Cu	Zn	
VOLCHOK [10]			9.8	32.0	USA, New York
CAWSE [3]	1.3	5.8	1.1-5.3	3.5-21.0	United Kingdom
LAGERWERF [8]				52.0-288.0*	USA, Kansas
HUTCHINSON [7]	2.6	7.0	266.5**	9.0**	Canada, Sudbury
BEAVINGTON [2]	1.9	5.7	59.0-307.0	25.0-126.0	Australia, Wollongong

* Re-counted by the authors from $\text{g}/\text{cm}^2/\text{day}$

** Re-counted by the authors from $\text{g}/\text{m}^2/28$ days

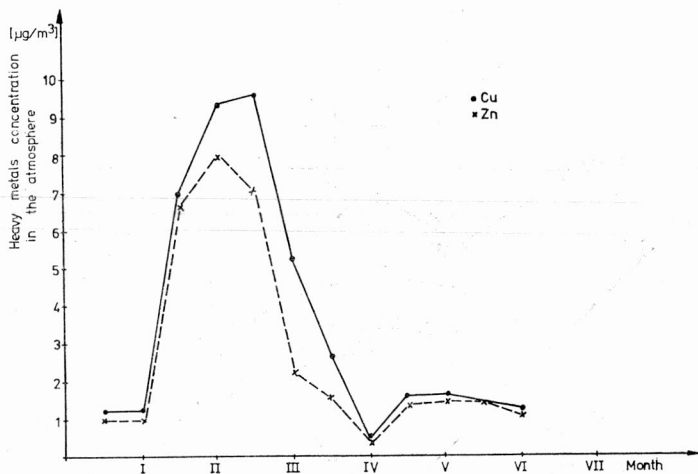


Fig. 2. The variability of the atmospheric Cu and Zn concentrations for the first six months of 1978
Rys. 2. Stężenia Cu i Zn w powietrzu w pobliżu huty w okresie pierwszego półrocza 1978

Table 5

Cu and Zn concentrations in the atmosphere over various countries
Stężenie Cu i Zn w różnych krajach

Reference	Concentration, ng/m ³				Country
	Area with no industrial emission source		Industrialized area		
	Cu	Zn	Cu	Zn	
RAHN [9]	2.4	8.76	208.8	2760.0	Belgium, Liège
HETTICHE [6]	—	—	100.0 ÷ 940.0	300.0 ÷ 222.0	West Germany
ALEXANDER [1]	—	—	50.0 ÷ 900.0	100.0 ÷ 1700.0	USA
CAWSE [3]	6.0	30.0	37.2	224.0	United Kingdom
DORN [4]	9.5	70.8	19.4	174.6	USA, New Lead Belt
GOODMAN [5]	—	—	70.0	810	Australia, Hobart

ture data and our sampling results may also result from the variable duration of the sampling periods employed by other workers [6], [8], [3], covering 3 weeks, 14 weeks, 36 weeks and one year, respectively.

There exists a strong correlation ($r = +0.810$; significance level = 0.05) between zinc and copper concentrations, which indicates that these metals originate from the same emission source. Copper and zinc make up some 20% of the total atmospheric aerosol in this area (fig. 3).

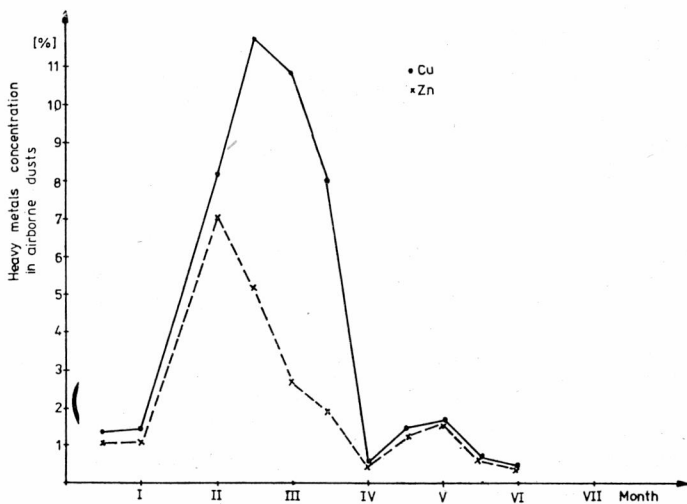


Fig. 3. The variability of Cu and Zn concentrations in airborne dusts for the first six months of 1978
 Rys. 3. Stężenie Cu i Zn w pyłach tworzących aerozol atmosferyczny w okresie pierwszego półrocza 1978

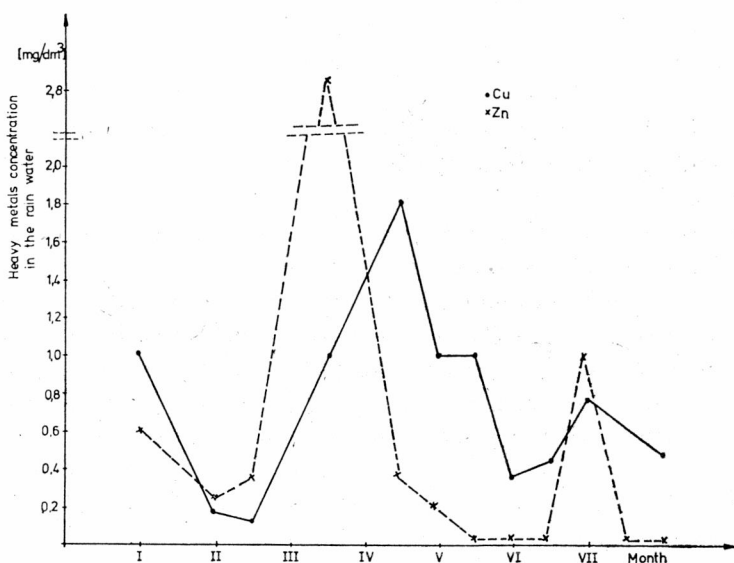


Fig. 4. Average concentration of Cu and Zn in the rainwater for the seven months of 1978
 Rys. 4. Zawartość Cu i Zn w wodach opadowych w okresie od stycznia do lipca 1978

The highest Cu and Zn concentrations both in the atmosphere and in dust fallout deposit are found in the winter and spring seasons (January–April 1978). This seasonal peak is attributable to the prevailing wind direction. Fig. 4 summarizes the average concentrations of copper and zinc in rainwater. Cu and Zn contained in the dust from the rainwater samples are presented in fig. 5. As shown by these figures, the spread of

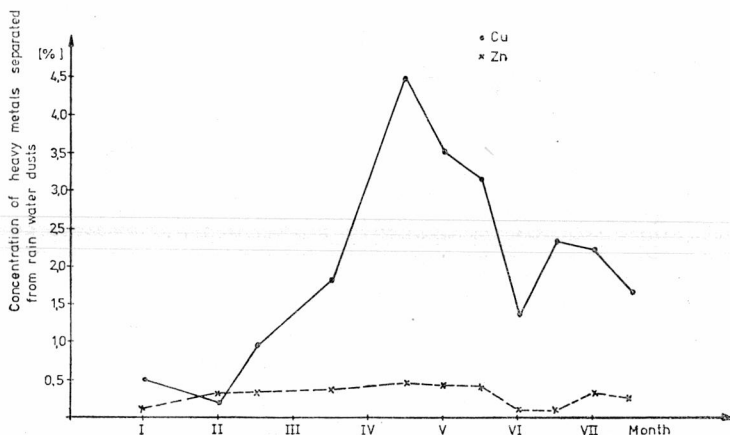


Fig. 5. Concentration of Cu and Zn separated from rainwater dusts for the first seven months of 1978

Rys. 5. Zawartość Cu i Zn w pyłe zebrany wraz z wodą opadową w okresie od stycznia do lipca 1978

the concentrations for the metals studied is high. This may be due to the variations both in precipitation intensity and in dust emissions for the individual sampling periods. The lowest precipitation rates were recorded in March and April, late May, mid June, and early July. For this same period the Cu and Zn concentrations measured in the rainwater samples were the highest.

The level of insoluble zinc compounds in the filtered dust (particulate) is below 0.5% and does not undergo serious variations (fig. 5). The same, however, is not true for soluble zinc (fig. 4).

There is a proportional relationship between Cu concentration in the rainwater and Cu concentration in the filtered dust (figs. 4 and 5).

In the dust emissions from Emitter II 0.9% of total particulate loading is contributed by soluble Cu compounds and 4.6% by soluble zinc compounds. In the dusts from other emitters the contents of these heavy metals are negligible. Thus, the Cu and Zn concentrations found in the rainwater samples depend first of all on the operation of Emitter II.

If the concentrations of heavy metals in the rainwater, as well as the precipitation rates and volumes are known, it is possible to estimate the contamination loads transferred with rainfall to the top soil. Thus, in the first six months of 1978 about 57 mg of soluble Cu compounds and approx. 8 mg of Zn compounds were absorbed by 1 m² of soil.

4. CONCLUSIONS

1. The concentration of copper and zinc in atmospheric particulates approaches 20% and 2%, respectively. Zinc concentrations in the atmospheric aerosol may reach as much as 7%. This is of importance with respect to the assessment of the environmental hazard created by the emission source.

2. The grain diameter of the dust particles is predominantly below 60 μm . It follows that heavy metal depositions are widely dispersed over a great area and distance from the emission source.

3. Fluorimetric analysis shows that zinc occurs most frequently as ZnS and ZnSO_4 ; copper is found to occur either in a metallic form or as CuFeS_2 , and less frequently as CuSO_4 .

4. Although copper and zinc contained in the particulate matter appear chiefly as insoluble compounds, the concentrations of these metals recorded in the precipitation water are high. These conditions can lead to high solubility of the heavy metals in the soil; they can increase their availability for plant intakes and create a serious contamination hazard to water systems and aquatic organisms.

REFERENCES

- [1] ALEXANDER P., *Trace metal pollution in the environment*, Poll. Control, Vol. 85 (1973).
- [2] BEAVINGTON F., *Trace elements in rainwater and dry deposition around a smelting complex*, Environ. Pollut., Vol. 13 (1977), pp. 127-131.
- [3] CAWSE P. A., *A survey of atmospheric trace elements in the U. R. 1972-73*, Env. and Medical Sciences Division AERE Harwell Oxfordshire, October 1974.
- [4] DORN C. R., PIERCE I. O., PHILIPS P. E., CHASE G. R., *Airborne Pb, Cd, Zn and Cu concentration by particle size near a Pb smelter*, Atm. Environ., Vol. 10 (1976), pp. 443-446.
- [5] GOODMAN H. S., NOLLER B. N., PEARMEN G. I., BLOOM H., *The heavy metal composition of atmospheric particulates in Hobart, Tasmania*, Clear Air, Vol. 3 (1976), pp. 38-41.
- [6] HETTICHE H. O., *Proceedings of the colloquium heavy metals as air pollutants*, Düsseldorf, 68, 1973.
- [7] HUTCHINSON T. C., *Proceeding of the first international symposium on acid precipitation and the forest ecosystem*, USPA Forest Service General Technical Report NE-23, 1976.
- [8] LAGERWERFF I. V., BROWER D. L., *Source determination of heavy metal contaminants in the soil of a mine and smelter area*, Trace Subst. Env. Health - IX 1975, A. symposium, D. D. Hemphile Ed.
- [9] RAHN K. A., *Study of national air pollution by combustion*, Progress Rept. Institut voor Nucleaire Wetenschappen, Ghent University of Liège.
- [10] VOLCHOK H. L., BOGEN D., *Trace metals - fallout in New York City*, H. A. S. L. Rept. No. 242, April 1971.

Z BADAŃ NAD ZANIECZYSZCZENIEM ATMOSFERY PYŁAMI MIEDZI I CYNKU EMITOWANYMI PRZEZ HUTĘ MIEDZI

W niniejszej pracy przedstawiono wyniki badań przeprowadzonych w pierwszej połowie 1978 r. w pobliżu huty miedzi. Badania dotyczą zanieczyszczenia atmosfery przez pyły miedzi i cynku.

Wyznaczono stężenia w atmosferze, stężenia w opadzie atmosferycznym, oraz udziały interesujących nas metali w całkowitej ilości zebranego pyłu. Stwierdzono, że poziomy tych metali są wysokie. Zanotowano duże stężenia miedzi i cynku w wodzie deszczowej, co może stanowić zagrożenie dla gleb i zbiorników wodnych.

ZUR LUFTVERSCHMUTZUNG MIT Cu- UND Zn-STÄUBEN DURCH KUPFERHÜTTENWERKE

Die hier dargestellten Ergebnisse von Untersuchungen der Luftverschmutzung durch Kupfer- und Zinkstäube in der unmittelbaren Nachbarschaft eines Kupferhüttenwerks beziehen sich auf die erste Hälfte des Jahres 1978.

Neben den Metallstaub-Konzentrationen in der Luft und im Niederschlag, wurden die erwähnten Metalle auch als Teil der gesamten Staubbiederschlagsmenge ermittelt. Die Metallkonzentrationen erwiesen sich in allen Fällen hoch. Hohe Konzentration von Kupfer und Zink sind auch im Regenabfluß nachgewiesen worden, was den Boden und die Wasserreservoirare gefährdern kann.

ИЗ ИССЛЕДОВАНИЙ ПО ЗАГРЯЗНЕНИЮ АТМОСФЕРЫ
ЭМИССИЯМИ МЕДНЫХ И ЦИНКОВЫХ ПЫЛЕЙ ИЗ МЕДНОПЛАВИЛЬНОГО ЗАВОДА

В настоящей работе приведены результаты исследований, проведённых вблизи медноплавильного завода первой половины 1978 г. Исследования касаются загрязнения атмосферы медными и цинковыми пылями.

Определены концентрации в атмосфере, концентрации в атмосферных осадках, а также доли интересующих нас металлов в полном количестве собранной пыли.

Выявлено, что уровни этих металлов являются высокими. Отмечены высокие концентрации меди и цинка в дождевой воде, что может представлять собой опасность для почв и водоёмов.