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TRACE METALS IN THE ATMOSPHERE AND ATMOSPHERIC DEPOSITION IN THE VICINITY OF A COAL-FIRED POWER PLANT AND A COPPER SMELTER

Airborne measurements were carried out for trace metals-bearing dusts emitted by a copper smelter and a power plant. The samples were analysed statistically for interspecies relations. Enrichment factors relative to aluminium and deposition fluxes were calculated. Cadmium, arsenic and copper are among those trace elements that identify a copper smelter as an emission source. The identifying trace metals for a power plant are manganese and cobalt.

INTRODUCTION

The growth of industrial activity throughout the world, as well as the related enhance in energy production have resulted in an ever-increasing release of environmental pollutants. Fly ash, which is produced by a wide variety of high-temperature processes, is one of the major solid waste products generated within the world. Coals and ores contain numerous impurities, and the exhaust plume generally introduces into the atmosphere a variety of trace elements creating serious environmental hazards which have become recently a problem of great concern.

Among the largest sources of high-temperature anthropogenic emissions copper smelters and power plants are of prime importance [1]–[4].

In this paper a small part of an extensive study is reported. Its aim and scope are to assess:

1) the concentrations of SO_2 , NO_x , and particulate matter S (IV), sulphates, heavy metals, and radionuclides in the atmosphere,

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- 2) the formation of sulphates and nitrates in the presence of solid particles bearing heavy metals,
- 3) the changes that occur in the natural composition of atmospheric air at various distance from the emission source,
- 4) the washdown of pollutants under various atmospheric conditions,
- 5) the migration of pollutants through the individual components of the environment, i.e. water, soil and vegetation.

The investigations reported here include two objects: a copper smelter and a coal-fired power plant.

2. EXPERIMENTAL

The copper smelter under study has been operated since 1971 to extract copper from ore. The ore is concentrated in a flotation process prior to smelting. The concentrate is smelted in reverberatory furnaces to separate copper and iron sulphide from siliceous slag. The temperature and the oxidizing conditions in the furnace account for the conversion of some part of the iron and sulphur to oxides, whereas copper and some part of iron remain in the sulphide form. The copper matte obtained in this procedure is transported to convertory furnaces in which sulphide reacts with high-pressured air to form SO_2 , metal oxides and some SO_3 , and produces 99% copper. In both kinds of furnaces SO_2 and particulates containing various heavy metals are expelled and emitted into the atmosphere through stacks.

The power station of interest is a 2000 MW unit fired with pulverized lignite. The gas stream passes through electrostatic precipitators with an efficiency of 94 to above 99%, which depends on the particle size.

For the copper smelter the investigations were begun in April 1983, and are being continued. The investigation of the power plant was started in April 1982, and is also underway. Determinations were performed for the elemental composition of both the power-plant stack ash and the ash from reverberatory furnaces of the copper smelter. Samples were collected at four measuring sites located along the pathway of a normal plume flow, at a distance varying from 300 m to 5.0 km from the emission source. The measurements carried out at each site included concentrations of SO_2 , NO_x , and total particulate matter, as well as dust fallout deposition, the amount of precipitation received in this area, and the influence of some other meteorological factors. Particulate samples were analyzed for elemental concentrations. The atmospheric aerosol was sampled with the use of a high-volume air sampler. The chemical composition of the emitted dust was determined by the X-ray fluorescence method. The shape and size of the emitted dust particles, as well as the development of their surface area were examined under a scanning

microscope. The ASA method was used to determine the total concentrations of heavy metals. Prior to this procedure, the elements contained in the particulates were mineralized.

Aerosol and dust samples were also analyzed for the composition of major ions. A portion of the exposed air filter or deposited dust was immersed in distilled water. The water-soluble compounds were extracted and after filtering, the solutions were analyzed for pH and for the following components: SO_4^{-2} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Mg^{+2} , and Ca^{+2} , using conventional methods [5].

3. RESULTS AND DISCUSSION

3.1. COMPOSITION OF PRIMARY EMISSIONS

Fly ash from a copper smelter and a power plant is a complex solid material difficult to characterize. Both types of fly ash appear mostly amorphous in X-ray analyses, colourless, and have a low refractive index. Microscopic examinations prove that they are predominantly fine particles of a diameter below 20 μm , spherical in shape or rounded. However, there have also been distinguished a number of non-spherical particles with sharp edges, unfused mineral particles – mostly quartz, as well as large amounts of amorphous carbon and soot, because the furnaces used for copper smelting are fired with coal.

Microscopic examinations also reveal fine-grained deposits on the surface of many individual spheres. Unlike the power plant fly ash, the ash particle samples from the smelter show many agglomerates of spheres having a diameter less than 3 μm ; cenospheres are absent. The identification of phases in the diffractograms shows that the lines corresponding to SiO_2 , C, PbS, PbSO_4 , ZnS, and ZnSO_4 are the most intensive for copper smelter fly ash; for the fly ash from the power plant the most intensive are the lines corresponding to SiO_2 , Al_2SiO_4 , and Fe_2O_3 .

The chemical composition of the primary emissions in the particulate matter is given in fig. 1. As shown by this figure, copper smelter fly ash exhibits significantly higher contents of trace elements and lower concentrations of aluminosilicate compounds, as compared to the fly ash from the power plant.

3.2. COMPOSITION OF AIRBORNE PARTICLES AND ATMOSPHERIC DEPOSITION

Figure 2 gives the average elemental composition of atmospheric aerosol in the vicinity of both the copper smelter and the power plant 5.0 km from the emitters. From this figure it is easily seen that there occurs only a slight difference in the concentrations of the most important components between the two aerosols, so that a more detailed analysis of trace element concentrations was needed in order to identify the emission source. The analytical results indicate that in air samples

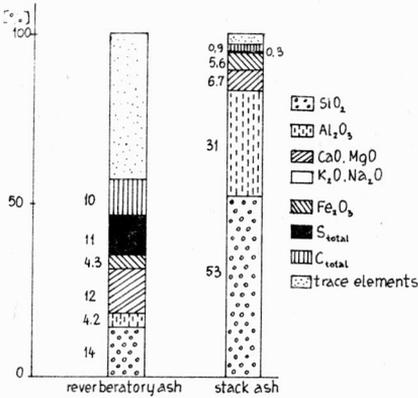


Fig. 1. Chemical composition of the primary emissions in the particulate matter

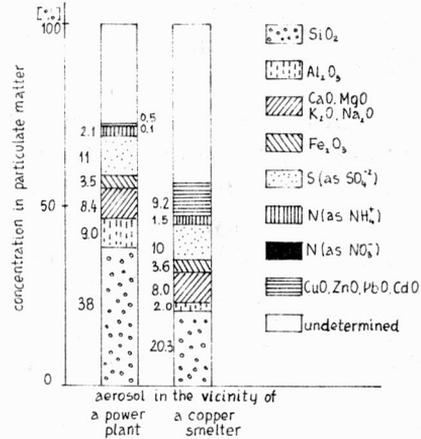


Fig. 2. Average elemental composition of atmospheric aerosol in the vicinity of the copper smelter and the power plant

collected 5.0 km downwind the copper smelter they were cadmium, arsenic, lead, copper, and zinc that occurred at high concentrations, whereas in the vicinity of the power plant higher concentrations were measured for manganese and cobalt. There are, however, significant variations in the trace element composition of airborne particles. Some of these differences can be attributed to the variability of the components in the emitted plume, as well as to the influence of some meteorological factors, measurement errors not excluded.

For this reason, the enrichment factor (EF) is defined as the ratio of a given element to a reference element in the suspended particulate material divided by the same ratio for soil material. In our study aluminium has been chosen as the reference element because of its favourable features: it occurs at high concentrations both in the soil and in the ambient aerosols, the variability of its concentration is insignificant, and the volatility of this metal is small.

The results are given in fig. 3. As shown by this diagram, some of the elements

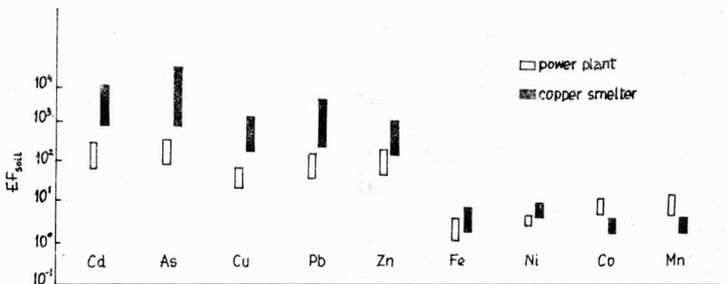


Fig. 3. A comparison of enrichment factors from the copper smelter and the power plant

under study have a much greater contribution to the enrichment in the vicinity of the copper smelter than in the adjacent area of the coal-fired power plant. This holds for cadmium, arsenic, copper, lead and zinc. However, manganese and cobalt enrichment of airborne particles near the power plant is much more pronounced than in the vicinity of the copper smelter.

Aerosol samples were also analyzed for the composition of major ions. The results are listed in tab. 1. The data given there indicate that the difference in the

Table 1

Water soluble species in atmospheric aerosols near the copper smelter and the power plant

Emitter	Concentration, %							pH of extract	
	K ⁺	Na ⁺	Mg ⁺²	Ca ⁺²	NH ₄ ⁺	SO ₄ ⁻²	Cl ⁻		NO ₃ ⁻
Copper smelter	1.10±0.32		0.25±0.10		0.92±0.45		1.71±0.08		6.5±7.3
Power plant	0.97±0.03	4.60±0.41	0.27±0.08	1.81±0.05	0.95±0.56	7.6±2.6	1.23±0.61	0.40±0.25	5.9-7.2
		5.1 ±1.2		1.90±0.24		8.2±4.1		0.30±0.05	

mean percentage of the water-soluble fractions between airborne particulates measured near the copper smelter and those determined near the power plant is insignificant. The high concentration of SO₄⁻² in the vicinity of the emission sources is neutralized by the presence of Ca⁺², Mg⁺², Na⁺, and K⁺ ions. The results also suggest that sulphates are primarily associated with the cations of the metals emitted from both sources.

Detailed investigations of the atmospheric aerosol in the vicinity of the power plant covered a longer period of time than did the investigations of the copper smelter, so the number of samples is more representative.

Table 2 gives the mean concentrations of the species in question with standard deviation in the atmosphere over the power plant at a distance of 5.0 km from the emitter for one-year samples.

As can be seen from these data, all of the trace elements under study occur at very high concentrations which markedly exceed those measured in the reference semi-rural area [6], [7].

Examined were also the interspecies relations which exist in the region. These relationships have been evaluated to date by linear least-square regression analysis. Table 3 presents the linear correlation coefficients for the data collected at the sampling site 5.0 km downwind the stacks. From this table the following features may be noted: aluminium, iron, sodium, calcium, magnesium, and manganese all are correlated with each other. Copper is highly correlated with aluminium, sodium, manganese, iron, lead, and zinc. Cadmium shows apparent relationships to zinc and reduced correlation with iron. Zinc is related to lead and copper and

shows only weak or no correlation to the other chemical parameters examined in this study.

One of the most interesting and significant results, evident from tab. 3, is the high negative aluminium-iron correlation. This means that in particles which exhibit high concentrations of aluminium, the concentrations of iron are low. The

Table 2

Concentration of species in the atmosphere near the power plant, $\mu\text{g}/\text{m}^3$

Species	Mean concentration	Standard deviation
Dust	320.0	62.0
Al	46.0	2.5
K	13.5	5.1
Na	57.6	7.9
Ca	8.2	6.0
Mg	3.2	0.1
Fe	11.5	0.2
Mn	0.27	0.16
Ni	0.097	0.032
Co	0.20	0.11
Pb	1.02	0.61
Zn	6.4	3.4
Cu	0.56	0.23
Cd	0.016	0.010

Table 3

Linear correlation coefficients for samples collected 5.0 km downwind the coal-fired power plant

Metal	Linear correlation coefficient										
	Al	Ca	K	Na	Fe	Mn	Ni	Pb	Zn	Cu	Cd
Al	1.00										
Ca	0.47	1.00									
K	0.65	0.54	1.00								
Na	0.47	0.17	0.84	1.00							
Fe	-0.74	0.57	-0.19	-0.42	1.00						
Mn	0.58	0.31	0.14	0.40	0.79	1.00					
Ni	-0.74	0.13	0.22	0.22	0.92	0.61	1.00				
Pb	0.02	-0.20	0.25	0.22	-0.58	0.83	0.20	1.00			
Zn	0.37	0.46	0.31	0.18	0.32	0.39	0.04	-0.52	1.00		
Cu	0.88	-0.36	0.87	0.42	-0.60	0.92	-0.02	0.65	-0.69	1.00	
Cd	-0.34	0.29	0.21	0.19	0.50	0.36	0.25	-0.15	0.91	-0.08	1.00

same type of relationship exists between aluminium and nickel and between lead, copper and zinc, iron. High correlations between the species are a reflection of similarities in the particle size distribution, identical sources or identical behaviour during coal combustion. Thus, aluminium, iron, sodium, calcium, magnesium, and manganese are classified as lithophilic components, and they constitute a part of the alumino-silicate dominated matrix. HULLET and co-workers [8] show that the magnetic spinel phase is enriched in many trace elements, particularly first-row transition metals. Their finding suggests a similar behaviour of iron, manganese, and nickel and a different behaviour of aluminium. On the other hand, lead, cadmium and zinc appear to be volatilized during combustion and by the time the combustion gases have cooled, they could deposit by heterogeneous condensation of fine particles. Copper displays an intermediate behaviour; it may condense from the gases to form a layer of oxides on the persisting particles or may condense simultaneously with other substances, such as silica, to form a slag layer.

The results of investigations on air pollution in general, and the environmental impact of trace metals as air pollutants in particular, lead to the conclusion that the contamination of human organisms, animals and vegetation from trace metals in the vicinity of the emitters is more adequately characterized by the data of deposition measurements than by the results of suspended-particulate-matter measurements. The typical total dust deposition, along with the contribution of various constituents of the rain water and dust fallout deposition samples (dry and wet) are listed in tab. 4. The data given in this table were obtained from chemical analyses of monthly samples collected at all measuring sites in the radius of 5.0 km from the emission sources. Considering the dust fallout deposition in the vicinity of the smelter and the power plant, as well as the concentrations of the species under study, it becomes evident that the contamination values from the deposition of iron, lead, and zinc measured near the two emitters are comparable. However, the remaining metals behave in a different manner. While copper and cadmium are deposited in larger quantities near the copper smelter, manganese and cobalt deposition values are found to be higher in the vicinity of the power plant.

Furthermore, the analysis of dust fallout deposition substantiates the environmental impact of stack plumes released by the two types of emitters. This impact consists of the following factors: increasing concentrations of trace metals in soluble forms, increasing concentrations of sulphates and decreasing pH at a distance greater than 2.5 km from the source which becomes especially pronounced when comparing these values with those measured at a distance of 0 to 1.0 km.

Table 5 gives the solubility values of the metals measured in the vicinity of the power plant. As shown by these data, the solubility of iron, calcium, zinc, and manganese has a particular tendency to increase with distance. Thus, the occurrence of iron in soluble form at a distance of 5.0 km is over 10 times as high as at the distance of 1.0 km from the source. For calcium, zinc, and manganese the increase

Table 4

Total dust deposition and heavy metal contents measured in the vicinity of the smelter and the power plant

Emitter	Distance from the source, km	Total dust deposition kg/m ² month	Concentration, ‰							
			Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Copper smelter	2.5	16.5 × 10 ⁻³	0.0167	0.0026	0.920	3.25	0.0110	0.0150	0.44	0.25
	5.0	9.7 × 10 ⁻³	0.0080	0.0032	0.250	3.22	0.0066	0.0040	0.26	0.13
Power plant	2.5	48.0 × 10 ⁻³	0.0040	0.0083	0.012	1.70	0.0196	0.0040	0.11	0.19
	5.0	10.2 × 10 ⁻³	0.0022	0.0024	0.009	1.64	0.0197	0.0047	0.07	0.13

Table 5

Analytical results for water extracts from dust fallout deposition collections in the vicinity of the power plant

Distance from the source, km	Mass of collected dust, g	pH	Concentration, mg dm ⁻³												
			Al	Ca	Na	Mg	K	Fe	Zn	Cd	Cu	Co	Mn	Ni	SO ₄ ⁻²
1.0	1.468	5.86	0	20.1	14.1	39.6	7.8	0.47	0.16	0.008	0.03	0.08	0.16	0.32	13.2
2.5	0.959	4.53	5.5	30.1	10.5	7.65	6.6	3.73	0.83	0.000	0.06	0.05	0.40	0.20	153.5



was found to be 7.5, 8.5, and 4 times larger, respectively. The concentration of sulphates showed a 15 times larger increase with distance.

In general, there are two basic mechanisms governing the occurrence of trace metals in soluble form:

1. The long exposure of dust particles (one month) brings about an SO_2 absorption in aqueous solution and the oxidation of SO_2 to SO_4^{2-} ion, which is catalyzed by the presence of metal ions, predominantly iron, manganese, zinc, and copper. pH decreases to cause a further dissolution of metal oxides; increasing deposition of alkali metals in the vicinity of the power plant gives a partial neutralization of the forming sulphuric acid, and brings about an increase of pH in the solution, thus preventing some of the metal oxides to be dissolved.

2. The mechanisms described in (1) may also act in the air. At farther distances, heterogeneous nucleation of sulphuric acid vapour on the plume aerosols is believed to be a dominant mechanism responsible for the metal salts forming. The sulphate aerosol, which forms in the atmospheric air, is removed by washdown and by dry deposition.

At the present stage of our study, it seems to be the mechanism described in (1) that governs the occurrence of trace metals in soluble forms and contributes to the decrease of pH near the power plant. This mechanism is additionally substantiated by the composition of the atmospheric aerosol.

4. CONCLUSIONS

The study reported here will be continued in the nearest future and is intended to implement the factor analysis for the characterization of the atmospheric particulate composition. At present, the following generalizations can be made:

1. The environmental impact of power plants and smelters includes a) high concentrations of many trace elements in the atmospheric air and dust fallout deposition, b) the increase in the solubility of trace elements with distance, and c) the increase of sulphate concentration and decrease of pH with distance from the emitters.

2. Cadmium, arsenic and copper are amongst the trace metals that identify a copper smelter as an emission source. The identifying trace metals for a power plant are manganese and cobalt.

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METALE ŚLADOWE W ATMOSFERZE I OPADZIE PYŁU W POBLIŻU ELEKTROWNI WĘGLOWEJ I HUTY MIEDZI

Zmierzono stężenia metali śladowych w aerozolu atmosferycznym i opadzie pyłu w sąsiedztwie huty miedzi i elektrowni węglowej. Badano korelacje między stężeniami poszczególnych pierwiastków w atmosferze. Wyznaczono współczynniki wzbogacania w stosunku do glinu oraz określono skład opadu pyłu.

Okazało się, że kadm, arsen i miedź są pierwiastkami identyfikującymi hutę miedzi jako źródło emisji, mangan i kobalt natomiast elektrownię węglową.

МИКРОЭЛЕМЕНТЫ В АТМОСФЕРЕ И В ОСАДКАХ ПЫЛИ ВБЛИЗИ УГОЛЬНОЙ ЭЛЕКТРОСТАНЦИИ И МЕДЕПЛАВИЛЬНОГО ЗАВОДА

Измерены концентрации микроэлементов в атмосферном аэрозоле и в осадках пыли вблизи медеплавильного завода и угольной электростанции. Исследованы корреляции между концентрациями отдельных элементов в атмосфере. Определены коэффициенты обогащения по отношению к алюминию, а также состав осадков пыли.

Оказалось, что элементами, которые идентифицируют медеплавильный завод как источник эмиссии, являются кадмий, мышьяк и медь, тогда как угольную электростанцию идентифицируют марганец и кобальт.

