

Kind of dust	Ca	Mg	Fe	Mn	Zn	Pb	Cd	Cu	As	Sb	Bi	Se	Te	Mo	Co	Ni	Cr	Mn	Other
Illite	0.01	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Chamosite	0.01	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10

Alina KABATA-PENDIAS<sup>x</sup>

HEAVY METALS SORPTION BY CLAY MINERALS AND OXIDES  
OF IRON AND MANGANESE<sup>xx</sup>

UKD 632.122.1:541.183.5.03:546.815+546.47:549.623:552.52+546.71/.72-31:669.162.252.8

**A b s t r a c t:** Sorption characteristics of soil components are the most important in governing fixation, transport and bioavailability of heavy metal pollutants in soils. Solubility of metals from dusts of a copper smelter and their fixation by different minerals were studied as a function of pH. Pb and Zn were the most readily soluble from the dusts, while Pb was much more strongly fixed than Zn and Cd by all the minerals. The metals were sorbed on minerals in the decreasing order: Mn-oxides > montmorillonite > kaolinite > Fe-oxides > illite. Amorphous hydrous oxides of Mn and Fe had the highest affinity for Pb.

INTRODUCTION

Clay minerals, amorphous hydrous oxides and organic matter play an important role in controlling the concentration and behaviour of metallic pollutants in soil. In general, oxides of iron and manganese are more significant than those of aluminum and silicon because the former have greater sorption capacities and are less stable under variable oxidation conditions of the soil environment.

The present research focused upon the solubility of heavy metals from dusts emitted from a copper smelter, and upon their sorption by some soil-forming minerals as pH-dependent process. The factor of pH is of special interest in the studies of the behaviour of metallic pollutants in soil because industrial emission also contains a high proportion of sulphur compounds compared with that of metals (Table 1/.

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<sup>xx</sup>The paper was presented at the Fourth Meeting of the European Clay Groups in Freising, GFR, September 1980.



Therefore the decrease in the soil pH is one of the most common phenomena in contaminated soils.

Table 1  
Chemical composition of dusts emitted from a copper smelter (%)

Kind of dust	Ca	Mg	K	Na	Fe	Mn	Cu	Pb	Zn	Cd	S-total
Flue	0.02	0.10	1.50	0.10	0.15	0.005	0.69	54.0	9.60	0.09	nd
Chimney	0.06	2.05	0.60	2.55	0.73	0.007	0.85	33.0	11.40	0.32	10 <sup>x</sup>

The term "sorption" used in this paper refers to all phenomena at the solid-solution boundary including adsorption, precipitation and other concentrating processes.

#### MATERIALS AND METHODS

The fraction < 2 μm was separated from possibly pure mineral specimens: kaolinite, illite /from weathered muscovite layers/ and montmorillonite. Manganese oxides were obtained from a manganese ore of sedimentary origin. Iron oxide /goethite/ was fractionated from meadow ore. X-ray diffraction patterns of the separated fractions of the minerals show that neither iron oxides nor manganese oxides are well crystallized /Fig. 1/. Amorphous material predominates in the two kinds of oxides.

The sample of manganese ore contains 10% Mn and the sample of meadow ore 20% Fe.

Manganese oxides are associated with calcareous rocks and presumably represent a continuous series of composition from MnO/OH/ to MnO<sub>2</sub>/OH/ without distinct reflections in the X-ray diffraction pattern, where the strongest peak is that of calcite  $d = 3.03$  /Fig. 1/.

The suspensions composed of 5g mineral /1g of montmorillonite/ in 50 ml H<sub>2</sub>O with 1g of smelter dusts were shaken for 5 min. and adjusted to the desired pH /3,4,5,6 and 7/ with diluted HNO<sub>3</sub> or NaOH. The suspension with adjusted pH were shaken for 5 min., incubated at 20°C for 24 hours and shaken again for 5 min.

The supernatant liquid obtained after the centrifugating of the mineral suspensions was analyzed for Fe, Mn, Cu, Pb, Zn, Cd by atomic absorption spectroscopic method on a Perkin-Elmer 403 spectrometer. Adopting the same procedure, the solubility of heavy metals from the smelter dusts and minerals was measured at various pH of the suspensions /Tables 2 and 3/.

Fig. 1. Smoothed X-ray diffraction patterns for the minerals used in the experiment, using Cu K<sub>α</sub> radiation. The figures given at the peaks are  $d_{hkl}$  values in Å

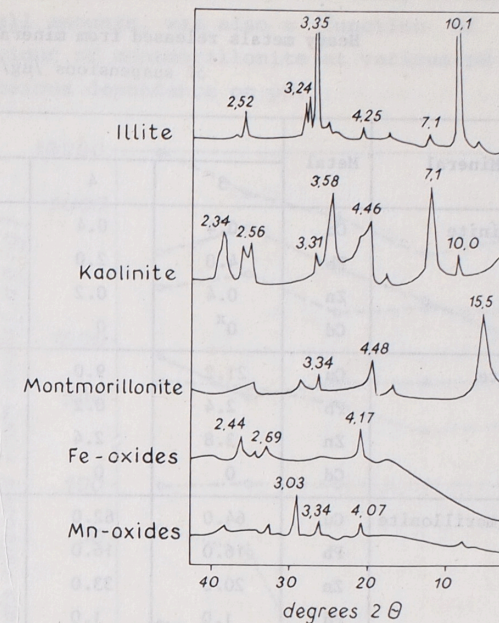


Table 2  
Heavy metals released from the smelter dusts at various pH of suspensions /in % of total content/

Metal	Flue dust, at pH					Chimney dust, at pH				
	3	4	5	6	7	3	4	5	6	7
Lead	0.73	0.74	0.44	0.32	0.14	0.25	0.15	0.18	0.18	0.18
Zinc	1.87	2.34	1.64	1.68	1.59	9.67	5.32	3.90	2.36	3.15
Cadmium	11.11	12.55	11.11	12.55	12.55	19.53	17.18	14.06	10.15	11.71
Manganese	36.00	32.00	30.00	30.00	30.00	10.00	7.14	7.14	7.14	7.14
Iron	4.13	2.93	0.40	0.13	0	0	0	0	0	0



Table 3

Heavy metals released from minerals at various pH  
of suspensions / $\mu\text{g}/\text{g}$ /

Mineral	Metal	pH				
		3	4	5	6	7
Kaolinite	Cu	0.4	0.4	0.2	0	0
	Pb	4.0	2.0	1.6	1.2	0
	Zn	0.4	0.2	0.2	0.2	0.2
	Cd	0 <sup>x</sup>	0	0	0	0
Illite	Cu	21.2	9.0	2.2	1.2	0
	Pb	2.4	0.2	0.2	1.6	0
	Zn	3.8	2.4	1.4	1.0	0.2
	Cd	0	0	0	0	0
Montmorillonite	Cu	64.0	82.0	74.0	45.0	57.0
	Pb	16.0	16.0	30.0	14.0	32.0
	Zn	20.0	33.0	32.0	24.0	29.0
	Cd	1.0	1.0	1.0	1.0	0
Fe-oxides	Cu	0	0	0	0	0
	Pb	0	0	1.1	1.6	1.6
	Zn	180.0	24.0	6.4	30.0	0.2
	Cd	0	0	0	0	0.1
Mn-oxides	Cu	0.4	0.2	0.2	0.2	0
	Pb	8.0	4.0	4.0	3.0	7.0
	Zn	0	0	0	0	0
	Cd	0	0	0	0	0

<sup>x</sup>Zero of metal released into the water phase means the content below detectability limits.

#### RESULTS AND DISCUSSION

Heavy metals occurring in the smelter dusts mainly as sulphides and oxides show relatively low solubility in water suspensions. The highest solubility was observed for Mn /up to 36%/ and Cd /up to 19%/ , while the solubility of Pb did not exceed 1% of their content in the smelter dusts /Table 2, Fig. 2/. Copper present in the smelter dusts in a relatively small amount /Table 1/ was not dissolved in the water suspension. Apparently the smelter dusts should be considered as a source of readily soluble Pb, Zn, and to a lesser extent, of Cd. The solubility

of metals decreased with increasing pH. The release of heavy metals by the minerals, although in small amounts, was also a function of pH /Table 3/. However, the behaviour of montmorillonite at various pH was different and did not show obvious dependence on pH.

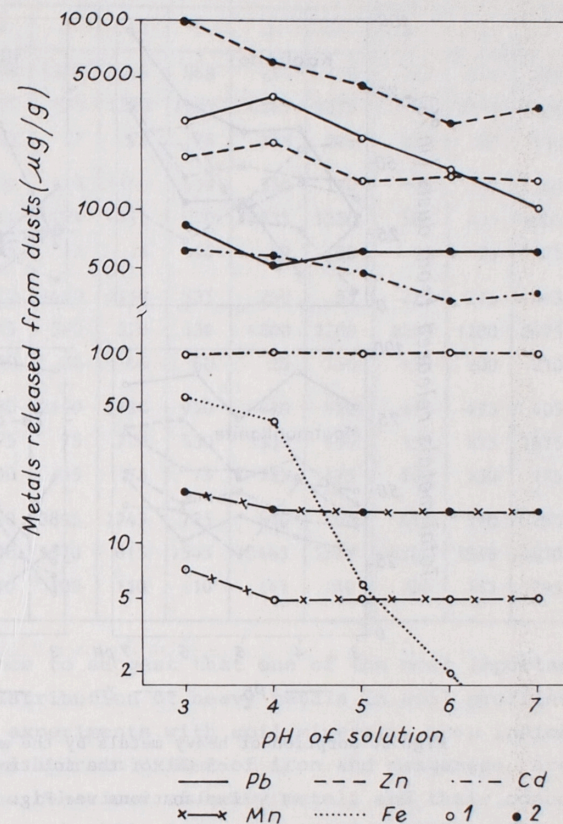


Fig. 2. Metals released from smelter dusts plotted as a function of pH of the solution  
1 - flue dust, 2 - chimney dust

The solubility of heavy metals from two different kinds of dusts was variable, and while Pb, Mn and Fe were released more easily from the flue dust, Zn and Cd were released more readily from the chimney dust. Also the solubility of Zn and Cd from the chimney dust was less pH-dependent than it was observed for other metals and other dusts /Fig. 2/.

The effect of pH on heavy metals sorption on kaolinite, plotted as the percentage of total metals released from the dusts is shown in Figure 3. Besides the effects of pH, the equilibrium concentration of metal cations in the solution was also a factor influencing the sorption. The sorption capacity of kaolinite increased steadily with the increa-



sing pH. In the case of Zn released from the flue dust, the decreasing sorption reflected presumably much higher affinity for kaolinite than other metals. The pronounced dependence of Pb sorption on kaolinite on pH and Pb concentration was also reported by Griffin *et al.* /1977/.

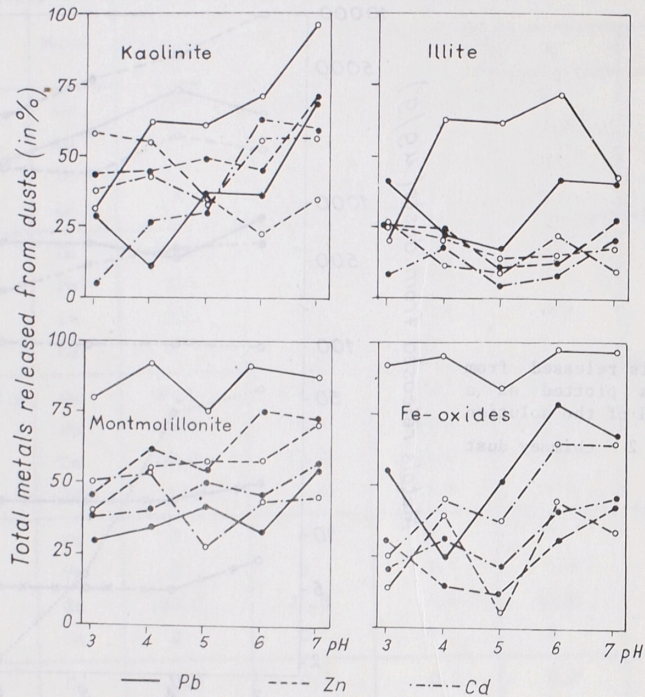


Fig. 3. Sorption of heavy metals by the minerals as a function of pH of the solution  
Explanations see Fig. 2

The adsorption of heavy metals on illite was evidently smaller than on kaolinite /Fig. 3/, but also lead was fixed in the highest proportion. The influence of pH on the sorption capacity of illite was less pronounced than for kaolinite.

Montmorillonite is well known to have the highest sorption capacity for various cations. It is evident that sorption of heavy metals by montmorillonite was in general the highest and less pH-dependent than by the other clay minerals /Fig. 3, Table 4/. This mineral also released the highest amount of metals into the water phase /Table 3/. The small effect of pH on the sorption capacity of montmorillonite was apparently due to high buffer properties of that mineral.

Table 4

Sorption of Pb, Zn and Cd released from the smelter dusts by minerals at various pH of suspension  $\sim \mu\text{g/g}$

Mineral and metal	Flue dust, at pH					Chimney dust, at pH					
	3	4	5	6	7	3	4	5	6	7	
Montmorillonite	Pb	2350	3700	1800	1606	868	250	170	252	230	336
	Zn	825	1385	875	1220	1105	4365	3375	2620	1575	2650
	Cd	50	63	27	75	75	238	225	225	150	212
Illite	Pb	600	2500	450	1250	400	350	110	100	250	240
	Zn	450	400	225	245	270	2835	1350	500	405	1005
	Cd	25	15	15	25	15	50	100	25	25	75
Kaolinite	Pb	950	2450	1450	1150	535	250	55	220	215	415
	Zn	1035	1215	540	370	530	4800	2700	2260	1200	2475
	Cd	35	50	30	60	60	25	150	135	200	210
Fe-oxide	Pb	2715	3880	2150	1700	950	470	120	310	475	405
	Zn	225	675	75	720	530	3330	990	550	855	1575
	Cd	25	50	35	75	75	125	175	100	130	175
Mn-oxide	Pb	2940	3900	3895	1745	775	810	480	580	590	755
	Zn	1240	750	1570	615	1545	10465	5575	4305	2580	4830
	Cd	95	110	100	110	110	145	110	230	185	295

There is strong evidence to suggest that one of the most important factors controlling the distribution of heavy metals in soil profiles is the clay fraction. All experiments with soil minerals, have indicated however, that amorphous hydrous oxides of iron and manganese are largely responsible for the behaviour of heavy metals and their concentration in soils /Forbers *et al.* 1976; Gadde and Laitinen 1973, 1974; Jenne 1977; McKenzie 1977; Norrish 1975; Stuanes 1976/.

Hydrous oxides of iron and manganese play apparently a more important role in soil where heavy metals occur as pollutants. Presumably when these metals are inherited from the parent soil material, they are related more to aluminosilicate clays since hydrous oxides are formed later during soil-forming processes. When metallic pollutants are added to soils, hydrous oxides of iron and manganese are capable of fixing a very high proportion of trace metals.

The sorption capacity of the two oxides was less pH-dependent than it was observed for clay minerals /Fig. 3/. There was clear evidence that lead was very easily fixed by Fe-oxides while all heavy metals were most easily fixed by Mn-oxides /Table 5/. There was also observed a



relatively broad pH range for high relative sorption /RS/ affinity<sup>x</sup> of Mn-oxides. All other minerals do not show any constant value of pH for the highest sorption of metals /Table 5/. The value of relative sorption /RS/ for all the metals was in the following order:

Mn-oxides > montmorillonite > kaolinite > Fe-oxides > illite.

In each case Mn-oxides show the highest and illite the lowest sorption affinity for heavy metals. As regards the other minerals lead was most readily fixed by Fe-oxides, while zinc and cadmium by montmorillonite /Table 5/.

T a b l e 5  
Relative sorption /RS<sup>x</sup>/ of Pb, Zn and Cd by various minerals at pH range 3-7

Mineral	Average RS value for all pH /%/			Highest RS value, at pH					
				Pb		Zn		Cd	
	Pb	Zn	Cd	%	pH	%	pH	%	pH
Montmorillonite	85	65	65	92	4	75	6	66	7
Illite	58	22	18	71	6	25	3	25	3
Kaolinite	81	47	55	95	7	57	3	56	7
Fe-oxides	94	25	48	97	4	44	6	66	6-7
Mn-oxides	99	88	97	99	5-7	99	5-7	99	5-7

<sup>x</sup>RS value means the total metals released from the flue dust into the solutions /in %/.

Although the relative sorption of metals /expressed in per cent of the amount released from the smelter dusts/ increased with the increasing value of pH /Fig. 3/, the total amount of the fixed metals increased with the decreasing pH of the suspension /Table 4/. This is apparently related to the higher proportion of metals released into more acid solutions.

#### FINAL REMARKS

Soils in the vicinity of a copper smelter are a collector for heavy metal pollutants. Their behaviour, transport and bioavailability are of great environmental concern. Smelter dusts in the investigated area were mainly a source of readily soluble lead and zinc. Their mobility

<sup>x</sup>"Affinity" is the name used to indicate that RS value is not related directly to CEC value.

in the dust-solution system was nearly equal /Fig. 2/. Copper emitted with the smelter dusts showed very low mobility in the dust-solution system. This is not the case in polluted soils, where copper is relatively readily soluble /Kabata-Pendias, Gondek 1978/.

The affinity of lead for the mineral soil components was much greater than that of other metals. The behaviour of lead was affected both by the kind of minerals and the source of polluting metals. It is evident that flue dust containing different compounds of lead and more polycyclic hydrocarbons than chimney dust released this metal in a higher proportion /Kabata-Pendias, Gondek 1978/. The observed increase in lead sorption in the case of flue dust, and the decrease in the case of chimney dust can be attributed to the tendency of lead to form metal-organic complexes the behaviour of which is highly influenced by pH. A significant role of organic complexes in the lead behaviour was also noticed by many other authors /Griffin *et al.* 1977; Mayer 1978; Riffaldi *et al.* 1976; Soldatini *et al.* 1976/.

The results of these studies show that amorphous hydrous oxides of iron and manganese may be of practical importance for solving the problems associated with the concentration of heavy metals by soils.

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Alina KABATA-PENDIAS

#### SORPCJA METALI CIĘŻKICH PRZEZ MINERAŁY ILASTE ORAZ

#### TLENKI ŻELAZA I MANGANU

#### Streszczenie

Stopień zagrożenia środowiska glebowego przez metale ciężkie emitowane wraz z pyłami hutnictwa metali nieżelaznych zależy zarówno od ich rozpuszczalności jak i od sorpcyjnych właściwości minerałów oraz substancji organicznej. Badano rozpuszczalność metali występujących w pyłach huty miedzi oraz ich wiązanie przez następujące minerały: montmorillonit, kaolinit, illit i uwodnione tlenki żelaza oraz manganu. Do doświadczenia zastosowano suspensję minerałów i pyłów hutniczych z wodą o zróżnicowanym odczynie w zakresie pH 3-7. Stężenia metali ciężkich w fazie wodnej oznaczano metodami atomowej spektrometrii absorpcyjnej /ASA/. Oba rodzaje pyłów hutniczych, smolisty osad z filtrów /flue dust/ oraz pyły kominowe /chimney dust/ okazały się głównie źródłem łatwo rozpuszczalnych Pb i Zn. Rozpuszczalność Fe gwałtownie spadała w miarę wzrostu wartości pH suspensji, podczas gdy pozostałych metali - była mało zmienna. Wszystkie minerały wiązały najintensywniej Pb, ale największą zdolność do jego sorbowania wykazały uwodnione tlenki żelaza i manganu. Opierając się jednak na względnej pojemności sorpcyjnej, wyrażonej procentowym wiązaniem metali uwolnionych z pyłów hutniczych, ustalono następującą kolejność minerałów:

Mn-tlenki > montmorillonit > kaolinit > Fe-tlenki > illit.

Wykazano, że uwodnione tlenki żelaza i manganu mogą spełniać bardzo istotną rolę w procesach unieruchamiania metali ciężkich zanieczyszczających gleby.

#### OBJAŚNIENIA FIGUR

Fig. 1. Uprozczone dyfraktogramy rentgenowskie minerałów zastosowanych do doświadczenia

/promieniowanie  $\text{CuK}\alpha$ , przy pikach podano wartości  $d_{hkl}$  w Å/

Fig. 2. Rozpuszczalność metali z pyłów hutniczych w zależności od pH roztworu

1 - pył smolisty, 2 - pył kominowy

Fig. 3. Sorpcja metali ciężkich przez minerały w zależności od pH roztworu  
Objaśnienia przy fig. 2

Алина КАБАТА-ПЭНДЯС

#### СОРБЦИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ ГЛИНИСТЫМИ МИНЕРАЛАМИ,

#### А ТАКЖЕ ОКИСЛАМИ ЖЕЛЕЗА И МАРГАНЦА

#### Резюме

Степень засорения почвенной среды тяжелыми металлами, испускаемыми вместе с пылью цветной металлургии, зависит как от их растворимости так и от сорбционных свойств минералов, а также от органического вещества. Изучалась растворимость металлов, присутствующих в пыли медно-металлургического завода, а также их связывание такими минералами как монтмориллонит, каолинит, иллит, а также гидроокислами железа и марганца. В опытах применялась взвесь минералов и металлургической пыли в воде различной кислотности в диапазоне pH 3 - 7. Концентрация тяжелых металлов в водной фазе определялась методами атомноабсорбционной спектроскопии /MAAC/. Оба вида металлургической пыли - смолистый осадок фильтров /flue dust/ и дымоходная пыль /chimney dust/ - прежде всего оказались источником легко растворимых Pb и Zn. Растворимость Fe резко понижалась по мере увеличения pH взвеси, а для остальных металлов изменялась в небольшой степени. Все минералы наиболее интенсивно связывали Pb, но наибольшую способность к его сорбции обнаружили гидроокислы железа и марганца. Однако, основываясь на относительной сорбционной емкости, выраженной процентным связыванием освобожденных из металлургической пыли металлов, установлено следующий ряд минералов: окислы Mn > монтмориллонит > каолинит > окислы Fe > иллит.

Доказано, что гидроокислы железа и марганца могут исполнять весьма существенную роль в процессах фиксирования засоряющих почвы тяжелых металлов.

#### ОБЪЯСНЕНИЯ К ФИГУРАМ

Fig. 1. Упрощенные дифрактограммы применяемых в опытах минералов / $\text{C K}\alpha$  излучение, возле пиков указаны значения  $d_{hkl}$  в Å/

Fig. 2. Растворимость содержащихся в металлургической пыли металлов в зависимости от pH раствора

1 - смолистая пыль, 2 - дымоходная пыль

Fig. 3. Сорбция тяжелых металлов минералами в зависимости от pH раствора  
Объяснения см. фиг. 2