Baltic Coastal Zone No. 3	
(11-20) 1999	Institute of Biology and Environmental Protection University of Education of Słupsk

ENRICHMENT FRACTIONS OF TRACE METALS IN THE FINE SLUDGE'S COLLECTED FROM POMERANIA

Henryk Janukowicz[1], Jerzy Wira[2]

[1]*Department of Geology and Paleogeography, Szczecin University*
[2]*Department of Water environment Engineering, Technical University of Szczecin*

Abstract

Fine sludge's were collected from five filtration plants, and the partitioning of ten metals (Ag, Cd, Mn, Zn, Pb, Cu, Sn, Co, Ni and Fe) anthem was determined by selective leaching techniques.

1. The available amounts, which shows the total of each metal leached between 1 M. CH_3COONH_4 and 30 percent H_2O_2, for Ag, Cd. and Mn, ranged from 51 to 98 percent for five sludge's.
2. The available amounts for Zn, Pb, Cu and Sn were 47 - 92 percent for five sludge's.
3. The most important fraction for Co, Ni and Fe, except the Ueckermünde sludge, which is markedly polluted by organic matter, was the crystalline particle.
4. Therefore, the above metals, except Co, Ni and Fe, are thought to be enriched on ion exchangeable sites, organic matter, hydrous Fe/Mn oxides and sulphides in fine sludges.

INTRODUCTION

In the analysis of natural water, is would be interesting to determine quantities of trace metals in potable water sludges, since these trace metals, derived from yearly averages of suspended solids from the river, not only influence the environment for men and animals, but will also help in investigating the mechanism of enrichment of trace metals on solids suspended in river water.

Teraoka and Kobayashi, (1980) reported that markedly higher concentrations of trace metals such as Pb, Zn, Cu, Ni, Mn and Co were found in the suspended solids collected from 166 principal rivers and three lakes in Japan than in unpolluted solids or in the continental crust (Taylor, 1964). It was also found that (1) a positive correlation exists between the amount of suspended solids in river water and the size of particles tested by a scanning electron microscopic method, and (2) a positive correlation exists at P = 0,1 percent between loss on ignition and the concentrations of the trace metals Pb, Zn, Cu and Ni, which are abundant in suspended solids. Furthermore, it was found that the finer the particles of suspended solids, the greater the quantity of loss on ignition and the Pb, Zn, Cu, Ni and Mn that they contain (Taroka and Ogawa, 1984).

The rivers of northern-western Germany and Poland are generally clear, although the concentration of suspended solids in river water is greatly influenced by discharge (Janukowicz, 1998). It is difficult to obtain enough suspended solids when the mechanism of enrichment of trace metals on suspended solids is investigated. Therefore, as a means of studying the mechanism of enrichment of trace metals, the authors determined the partitioning of ten metals into five fractions of potable water sludge's by selective chemical leaching techniques (Janukowicz, 1998; Kitano et al., 1980; Nakashima, 1982).

EXPERIMENTAL METHODS

Sample collection

In the filtration plant, the suspended solids flowing into the plant are removed from river water by adding about 10 mg/l of aluminium sulphate or polyaluminium chloride and concentrated to about 6 w/v percent. The precipitated and thickened sludge's were collected in May-August 1997 from the five plants shown in Table 1. The samples were dried under vacuum freezing conditions, and chemical analyses were carried out on the powdered samples. The water was removed from the sludge during drying. As the contamination derived from trace metals contained in the aluminium flocculates seemed to be partitioned into two fractions of the water and the sludge sample, it was difficult to measure quantitatively the partitioning ratio of their concentrations. The loss on ignition was measured by asking the dried sample at 450^{o}C.

Table 1

Water systems of filtration plants in Poland, and loss ignition and Al content in sludge's

No.	Filtration Plant	Water system (river)	Loss on ignition (%)	Al. (%, dry basis
1	Ueckermünde	Uecker	37,8	12,0
2	Pasewalk	Uecker	37,4	12,0
3	Anklam	Peene	22,1	11,0
4	Białogard	Parsęta	26,0	11,0
5	Darłowo	Wieprza	16,3	11,0

Determination of Partitioning

For determination of the partitioning of Ag, Cd, Mn, Zn, Pb, Cu, Sn, Co, Ni, and Fe, the selective chemical leaching techniques used in this study are described in the flow in Figure 1; the details of the leaching techniques have been reported already by Nakashima, (1982). The determination of heavy metals, except for Sn, was carried out by electrothermal atomic absorption spectrometry after wet digestion following the extraction by DDTC-$CHCl_3$. Tin was determined by atomic absorption spektrophotometry following stagnate generation (Nakashima, 1979).

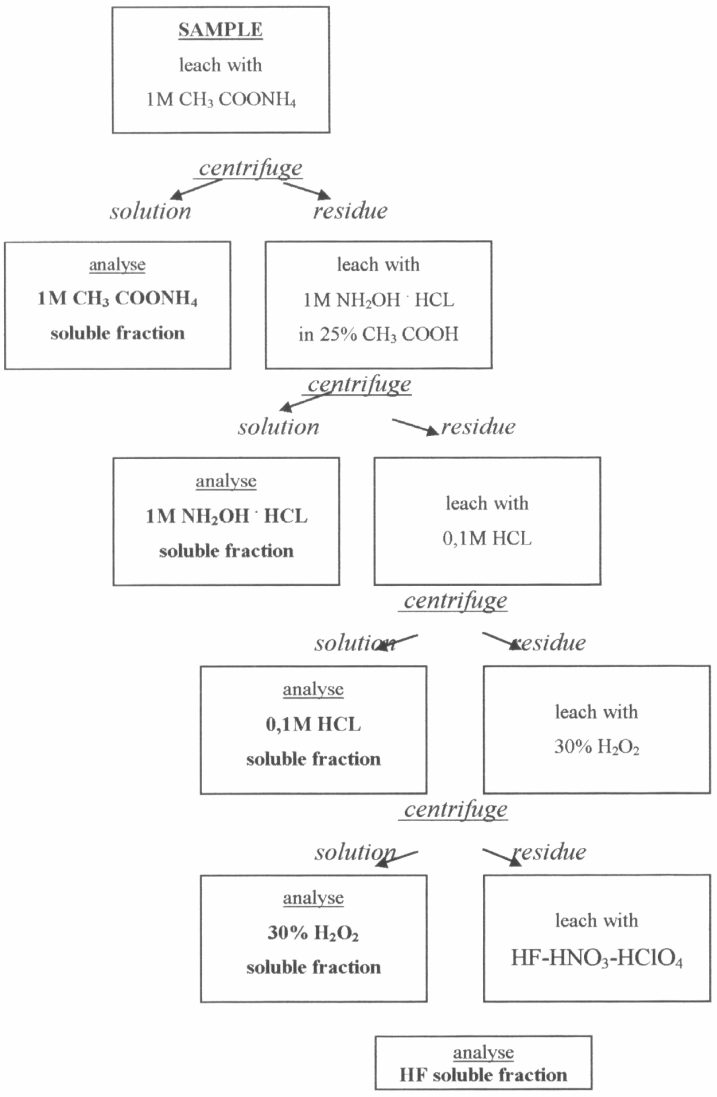

Fig. 1. Flow diagram of selective chemical leaching techniques

RESULTS AND DISCUSSION

Contents of Loss on Ignition and Aluminium

Table 1 shows the water system of each filtration plant, the loss on ignition at 450^{o}C, and the aluminium content. The highest value of loss on ignition was 37,8 percent in the Ueckermünde, followed by 37,4 percent in the Pasewalk. This may be due to the

pollution by organic materials caused from the waste water from big cites and industries. Its content in the other sludge's, which are slightly polluted, was similar to or lower than the average value (25 percent) in suspended solids from rivers and lakes on the northern Poland (Janukowicz, 1998).

The Al content was similar in sludge's from the five filtration plants, but its content for all sludge's was higher than the Poland average (7,5 percent; Janukowicz, 1998), owing to the addition of aluminium sulphate or polyaluminium chloride to coagulate suspended solids.

Partitioning of Metals

The partitioning of metals into 1 M CH_3COONH_4 - soluble, 1 M $NH_2OH \cdot HCl$ - soluble, 0,1 M HCl - soluble, 30 percent H_2O_2 - soluble, and HF - soluble fractions in the sludge's is shown in Tables 2 - 11, which summarise the results of the chemical analyses on the basis of dry samples. Metals leached with the 1 M CH_3COONH_4 treatment are chiefly absorbed on ion-exchangeable sites of clay minerals, organic matter, and hydrous Fe/Mn oxides or loosely bound to their materials. The 1 M $NH_2OH \cdot HCl$ - soluble, 0,1 M HCl - soluble, and 30 percent H_2O_2 - soluble fractions are intended to dissolve metals enriched in by hydrous Fe/Mn oxides, sulphides, and organic matter, respectively. Finally, metals dissolved in the HF - soluble fraction are regarded as chiefly from the crystalline particles. The results are discussed after being classified in three groups (Table 2 - 11) in order of the available amount, which shows the sum total of each metal leached between 1 M CH_3COONH_4 and 30 percent H_2O_2, on the assumption that metal in the crystalline particles is unavailable to any normal environmental process.

Silver. The total content of Ag was markedly higher in sludge's collected from Ueckermünde (13,25 mg/kg) and Pasewalk (6,23 mg/kg). This must be due to the fact that Ag is enriched in suspended solids after being released into the river as wastewater from big cites, because the two filtration plants are downstream of the Uecker River, which originates from Lake Oberuecker-see and Lake Unteruecker-see and through large cites.

Of the total Ag (Table 2), 80,0 percent from Ueckermünde and 57,1 percent from Pasewalk are enriched by coating with hydrous Fe/Mn oxides. The next important means of enriching Ag is represented by the adsorption on ion-exchangeable sites in the Ueckermünde sample and by the accumulation in organic matter in the Pasewalk sample. Ultimately, the available amount of the total Ag accounts for 97,2 percent in the Ueckermünde and 92,9 percent in the Pasewalk samples. For the other three sludge's, collected from the Anklam, Białogard and Darłowo filtration plants, the total content of Ag was 2,95; 1,65 and 1,53 mg/kg respectively. In addition, of the total Ag, 60,3 percent in the Anklam sludge's, 93,9 percent in the Białogard sludge's, and 88,9 percent in the Darłowo sludge's are enriched in the available fraction.

Table 2

Partitioning of Ag into five selective chemical fractions of sludge's from five filtration plants (mg/kg, dry basis)

Filtration plant	Chemical fractions of sludge's				
	1M CH_3COONH_4	1M $NH_2OH{\cdot}HCl$	0,1M HCI	30% H_2O_2	HF
Ueckermünde	1,06	10,61	0,61	0,60	0,37
Pasewalk	0,00	3,56	0,27	1,96	0,44
Anklam	0,00	1,21	0,14	0,43	1,17
Białogard	0,92	0,33	0,00	0,30	0,10
Darłowo	0,00	0,85	0,00	0,51	0,17

Table 3

Partitioning of Cd into five selective chemical fractions of sludge's from five filtration plants (mg/kg, dry basis).

Filtration plant	Chemical fractions of sludge's				
	1M CH_3COONH_4	1m. $NH_2OH{\cdot}HCl$	0,1M HCI	30% H_2O_2	HF
Ueckermünde	0,52	1,10	0,07	0,06	0,05
Pasewalk	0,23	0,29	0,21	0,12	0,04
Anklam	0,17	0,19	0,02	0,07	0,03
Białogard	0,14	0,39	0,12	0,20	0,04
Darłowo	0,13	0,28	0,09	0,15	0,03

Cadmium. The total content of Cd was 1,80 mg/kg in the Ueckermünde, 0,89 mg/kg in the Pasewalk, 0,78 mg/kg in the Anklam, 0,89 mg/kg in the Białogard, and 0,68 mg/kg in the Darłowo sludge's. There are two dominant fractions of enriching Cd, i.e., coating with hydrous Fe/Mn oxides and adsorption on ionexchangeable sites (Table 3). The total Cd in the Ueckermünde sludge is enriched 61,1 percent by coating with hydrous Fe/Mn oxides and 28,9 percent by adsorption on ion-exchangeable sites. Similarly for the other sludge's, Cd was enriched significantly by the above two means. In addition, the other two means of enriching Cd, fixation as sulphides and accumulation in organic matter, are also notable. Ultimately, the available amount of the total Cd accounts for 95,5-97,2 percent for all of the five sludge's. Its content in the crystalline particles is markedly low and is similar among all of five sludge's, i.e., range 0,029-0,044 mg/kg.

Manganese. The total content of Mn was 3878,7 mg/kg in the Ueckermünde sludge, 2469,5 mg/kg in the Pasewalk, 1635,5 mg/kg in the Anklam, 1123,0 mg/kg in the Białogard, and 1911,5 mg/kg in the Darłowo. As shown in Table 4, the two important means of enriched Mn, like Cd, were represented, i.e., coating with hydrous Fe/Mn oxides and adsorption on ion-exchangeable sites. For example, for the Ueckermünde sludge, 83,1 percent of the total Mn was enriched in the former way, followed by 7,8 percent in the latter. The Pasewalk sludge also enriched 45,2 percent of the total Mn by coating with hydrous Fe/Mn oxides and 40,5 percent by adsorp-

tion on ion-exchangeable sites. The Mn content in the crystalline particles occupied only 1,8 and 5,7 percent for the Ueckermünde and the Pasewalk sludge's, respectively. The distribution of Mn among the five soluble fractions for the residual three sludge's is similar to the above two sludge's, except for the crystalline particles fraction from the Darłowo.

Table 4

Partitioning of Mn into five selective chemical fractions of sludge's from five filtration plants (mg/kg, dry basis).

Filtration plant	Chemical fractions of sludge's				
	1M CH_3COONH_4	1M $NH_2OH \cdot HCl$	0,1M HCI	30% H_2O_2	HF
Ueckermünde	326,4	3224,1	207,3	51,8	69,1
Pasewalk	1000,5	1116,0	141,2	70,7	141,1
Anklam	369,5	914,6	140,6	70,3	140,5
Białogard	315,0	408,0	95,0	105,0	200,0
Darłowo	313,8	340,8	360,3	123,0	773,6

Table 5

Partitioning of Zn into five selective chemical fractions of sludge's from five filtration plants(mg/kg, dry basis).

Filtration plant	Chemical fractions of sludge's				
	1M CH_3COONH_4	1M $NH_2OH \cdot HCl$	0,1M HCI	30% H_2O_2	HF
Ueckermünde	6,9	172,8	21,7	21,8	26,4
Pasewalk	3,5	93,8	34,3	27,5	37,3
Anklam	3,5	35,3	13,5	14,6	47,1
Białogard	2,3	25,6	13,3	24,1	47,9
Darłowo	4,8	56,8	14,1	30,6	59,3

Zinc. The total content of Zn was 249,6 mg/kg in the Ueckermünde sludge, 196,4 mg/kg in the Pasewalk, 114,0 mg/kg in the Anklam, 113,2 mg/kg in the Białogard, and 165,6 mg/kg in the Darłowo. As shown in Table 5, the higher the concentration the total Zn, the greater its quantity occupied by coating with hydrous Fe/Mn oxides. It is thus understood that coating with hydrous Fe/Mn oxides is the most important means for enriching Zn. In addition, the other three fractions for enriching Zn, i.e., fixation as sulphides, accumulation in organic matter, and adsorption on ion-exchangeable sites, are comparatively important. However, unlike Ag, Cd and Mn mentioned above, the Zn content in the crystalline particles ranged from 26,4 mg/kg to 59,3 mg/kg for all five sludge's and so it is a more important fraction than coating with hydrous Fe/Man oxides for the Anklam, Białogard, and Darłowo sludge's.

Table 6.

Partitioning of Pb into five selective chemical fractions of sludge's from five filtration plants(mg/kg, dry basis).

Filtration plant	Chemical fractions of sludge's				
	1 M CH_3COONH_4	1M $NH_2OH{\cdot}HCl$	0,1M HCI	30% H_2O_2	HF
Ueckermünde	1,5	42,0	6,2	6,3	4,9
Pasewalk	2,4	21,9	4,7	6,5	7,0
Ankolam	3,4	15,0	3,7	4,1	8,3
Białogard	2,4	23,2	7,3	6,7	8,1
Darłowo	2,3	22,7	7,1	7,1	7,1

Table 7

Partitioning of Cu into five selective chemical fractions of sludge's from five filtration plants(mg/kg, dry basis).

Filtration plant	Chemical fractions of sludge's				
	1M CH_3COONH_4	1M $NH_2OH{\cdot}HCl$	0,1M HCI	30% H_2O_2	HF
Ueckermünde	3,0	34,2	22,5	18,6	17,1
Pasewalk	0,8	20,5	21,4	16,4	16,8
Anklam	1,1	15,1	11,3	9,2	13,2
Białogard	0,7	13,8	15,4	12,8	13,0
Darłowo	2,0	29,6	28,1	31,0	30,0

Table 8

Partitioning of Sn into five selective chemical fractions of sludge's from five filtration plants(mg/kg, dry basis).

Filtration plant	Chemical fractions of sludge's				
	1M CH_3COONH_4	1M $NH_2OH{\cdot}HCl$	0,1M HCI	30% H_2O_2	HF
Ueckermünde	0,0	75,5	5,9	0,7	89,7
Pasewalk	0,0	63,3	6,5	0,6	81,2
Anklam	0,0	10,1	6,4	0,5	28,3
Białogard	0,7	9,3	6,0	0,0	8,4
Darłowo	1,2	10,4	6,9	0,0	3,7

Lead. The total content of Pb was 60,9 mg/kg in the Ueckermünde sludge, 42,5 mg/kg in the Pasewalk, 65,1 mg/kg in the Anklam, 47,7 mg/kg in the Białogard, and 46,3 mg/kg in the Darłowo. Table 6 shows that the coating with Fe/Mn oxides is most important for enriching Pb. The other three fractions for enriching the metal are also significantly important. Ultimately, of the total Pb, the available amount accounts for 83-92 percent for all five sludge's. Its content in crystalline particles ranged between 4,9 and 8,3 mg/kg.

Copper. The total content of Cu was 95,4 mg/kg in the Ueckermünde sludge, 75,9 mg/kg in the Pasewalk, 49,9 mg/kg in the Anklam, 55,7 mg/kg in the Białogard, and 120,7 mg/kg in the Darłowo. As shown in Table 7, three are three important fractions for enriching Cu, i.e., coating with hydrous Fe/Mn oxides, fraction as sulphides, and accumulation in organic matter. Unlike all metals mentioned above, it is noticeable that the roles of the fixation as sulphides and the accumulation in organic matter for enriching the metal are as important as the coating with hydrous Fe/Mn oxides. Finally, the Cu content in the crystalline particles ranged from 24 to 36 mg/kg, except in the Darłowo sludge.

Tin. The Sn content was 171,8 mg/kg in the Ueckermünde sludge, 151,6 mg/kg in the Pasewalk, 45,3 mg/kg in the Anklam, 24,4 mg/kg in the Białogard, and 22,2 mg/kg in the Darłowo. Its content coated with hydrous Fe/Mn oxides is high for the Ueckermünde and the Pasewalk sludge's composed of suspended solids from the Uecker River, which is polluted by sewage from „big" cites (Table 8). For the other three sludge's, coating with hydrous Fe/Mn oxides is also important for enriching the metal, but its accumulation in organic matter and adsorption on ion-exchangeable sites are almost negligible for all five sludge's. On the other hand, approximately half the total Sn, i.e., 52,2 percent (89,7 mg/kg) for the Ueckermünde and 53,6 percent (81,2 mg/kg) for the Pasewalk sludge's, is distributed in the crystalline particles. This may be due perhaps to the high concentration of the metal distributed geological in the Uecker River basin.

Cobalt. The total content of Co was 15,0 mg/kg in the Ueckermünde and Pasewalk sludge's, 21,0 mg/kg in the Anklam, 18,0 mg/kg in the Białogard, and 36,0 mg/kg in the Darłowo. The most important fraction, except in the Ueckermünde, is the crystalline particles followed by coating with hydrous Fe/Mn oxides and by accumulation in organic matter (Table 9). Fixation as sulphides is also as important as the above two fractions, except in the Ueckermünde.

Nickel. The total content of Ni was 45,0 mg/kg in the Ueckermünde sludge, 36,0 mg/kg in the Pasewalk, 34,0 mg/kg in the Anklam, 60,9 mg/kg in the Białogard, and 110,0 mg/kg in the Darłowo. The most important fraction, except in the Ueckermünde sludge, is the crystalline particles (Table 10). Of the total Ni, it attains 62,0 percent for the Darłowo sludge, 68,2 percent for the Anklam, 66,2 percent for the Białogard, 42,8 percent for the Pasewalk, and 32,9 percent for the Ueckermünde.

Iron. The total content of Fe was 2,97 percent in the Ueckermünde sludge, 3,57 percent in the Pasewalk, 4,74 percent in the Anklam, 3,36 percent in the Białogard, and 5,57 percent in the Darłowo. The most important fraction is the crystalline particles (Table 11). Of the total Fe, 84,2 percent for the Darłowo sludge is distributed in the crystalline particles, 75,6 percent for the Białogard, and 73,2 percent for the Anklam. However, for the Ueckermünde and Pasewalk sludge's, approximately half the total Fe was enriched by coating with hydrous Fe/Mn oxides, accumulation in organic matter, and fixation as sulphides. Adsorption on ion-exchangeable sites is negligible for all five sludge's. Markedly high concentrations of Fe in the Darłowo sludge, like Co and Ni, reflects a different rock type with higher concentrations of tees metals on the Wieprza river basin.

Table 9

Partitioning of Co into five selective chemical fractions of sludge's from five filtration plants (mg/kg, dry basis).

Filtration plant	Chemical fractions of sludge's				
	1M CH_3COONH_4	1M $NH_2OH{\cdot}HCl$	0,1 M HCI	30% H_2O_2	HF
Ueckermünde	0,0	6,6	0,9	3,3	4,2
Pasewalk	0,0	2,6	2,4	4,0	6,0
Anklam	0,0	6,1	2,6	3,7	8,6
Białogard	0,0	2,6	2,2	3,0	10,2
Darłowo	0,0	7,6	5,8	8,2	14,4

Table 10

Partitioning of Ni into five selective chemical fractions of sludge's from five filtration plants (mg/kg, dry basis).

Filtration plant	Chemical fractions of sludge's				
	1M CH_3COONH_4	1M $NH_2OH{\cdot}HCl$	0,1M HCI	30% H_2O_2	HF
Ueckermünde	1,3	17,2	3,9	7,8	14,8
Pasewalk	1,4	6,8	5,1	7,3	15,4
Anklam	1,0	5,3	0,9	3,6	23,2
Białogard	0,9	6,8	3,4	9,5	40,3
Darłowo	1,1	11,6	6,7	22,4	68,2

Table 11

Partitioning of Fe into five selective chemical fractions of sludge's from five filtration plants (percent, dry basis).

Filtration plant	Chemical fractions of sludge's				
	1M CH_3COONH_4	1M $NH_2OH{\cdot}HCl$	0,1M HCI	30% H_2O_2	HF
Ueckermünde	0,0	0,82	0,40	0,46	1,29
Pasewalk	0,0	0,77	0,45	0,52	1,83
Anklam	0,0	0,58	0,29	0,40	3,47
Białogard	0,0	0,36	0,17	0,29	2,54
Darłowo	0,0	0,30	0,17	0,41	4,69

CONCLUSION

The distributions of ten trace metals on the fine potable water sludge's collected from five filtration plants were found by selective leaching techniques.

The concentrations of Ag, Cd, and Sn were found to be markedly high in the amount available for an organism, which shows the sum total of each metal leached between 1 M CH_3COONH_4 and 30 percent H_2O_2. This fact will help use in managing

potable water sludge's and in studying the mechanism of enrichment of trace metals on solids suspended in the original river water.

REFERENCES

Janukowicz, H. 1998. *Mechanism of Trace Metals on Fine Sludge's Collected from Filtration Plants.* Marine Science., 243, 5, 135 - 147.

Kitano, Y., Sakata, M., Matsumoto, E. 1980. *Partitioning of Havy Metals into Mineral and Organic Fractions in a Sediment Core From Tokyo Bay*. Geochimica Cosmochimica Acta. 44,1279-1285.

Kobayashi, J. 1960. *A Chemical Study of the Average Quality and Characteristics of River Waters of Japan*. Berichte des Ohara Institutes für Landwirtschaftliche Biologie Okayama Univ., 11, 313-356.

Nakashima, S. 1979. *The Separation of Tin from Water and Sea-Water by Flotation and the Date Rumination of Tin by Atomic Absorption Spectrophotomery Following Atannane Generation*. Bulletin of the Chemical Society of Japan. 52, 1844-1849.

Nakashima, S. 1982. *Partitioning of Havy Metals (Mn, Fe, As, Cd, Pb, Cu, Zn, Co and Ni) into Selective Chemical Fractions in Sediment Cores from Lake Biwa*. Japanese J. of Limnology. 43, 2, 67-80.

Taylor, S. R. 1964. *Abundance of Chemical Elements in the Continental Crust, A New Table.* Geochimica Cosmochimica Acta. 28, 1273-1285.

Teraoka, H., Kobayashi, J. 1980. *Concentrations of 21 Metals in the Suspended Solids Collected from the Principal 166 Rivers and 3 Lakes in Japan.* Geochemical Journal. 14, 203-226.

Teraoka, H., Ogawa, M. 1984. *Behaviour of Elements in the Takahashi, Japanese River Basin:* Journal of Environmental Quality. 13, 3, 453-459.

WZBOGACANIE FRAKCJI METALI ŚLADOWYCH W OSADACH FILTRACYJNYCH POMORZA

Streszczenie

Osady filtracyjne pobrano z pięciu stacji filtracyjnych, określono w nich podział ilościowy dziesięciu metali (Ag, Cd, Mn, ZN, Pb, Cu, Sn, Co, Ni oraz Fe) za pomocą technik selektywnego ługowania. Stwierdzono, że:

1. Ilości dostępne, które pokazują całkowitą ilość każdego z metali wypłukanego pomiędzy 1M CH_3COONH_4 i 30 procentowym H_2O_2, dla Ag, Cd i Mn wynosiły od 34 do 96% w pięciu osadach;
2. Dostępne ilości dla Zn, Pb, Cu i Sn wynosiły od 38 do 95% na pięć osadów;
3. Najważniejszą frakcją dla Co, Ni i Fe z wyjątkiem osadu z Ueckermünde, znacznie zanieczyszczonego przez materię organiczną, była frakcja krystaliczna.

Dlatego uważa się, że powyższe metale, z wyjątkiem Co, Ni i Fe, są wzbogacane w miejscach wymiany jonowej, przez materię organiczną, uwodnione tlenki Fe/Mn oraz siarczki w osadach filtracyjnych.