The pollution of marine sediments by trace elements in the coastal region of Togo caused by dumping of cadmium-rich phosphorite tailing into the sea

K. Gnandi · H. J. Tobschall

Abstract The marine coastal sediments from Togo have been analysed for the trace elements Cd, Cr, Cu, Ni, Pb, Sr, V, Zn and Zr to ascertain the geo-ecological impact of dumping of phosphorite tailings into the sea. Trace element concentrations ranged from 2–44 ppm for Cd, 22–184 ppm for Cu, 19–281 ppm for Ni, 22–176 ppm for Pb, 179–643 ppm for Sr, 38–329 ppm for V, 60–632 ppm for Zn and 18–8928 ppm for Zr. Regional distribution of trace elements in the marine environment indicates that the concentrations of Cr, Cu, Ni, Pb, V, Sr and Zn increase seawards and along the coastal line outwards of the tailing outfall, whereas Cd and Zr showed reversed spatial patterns. Sorting and transport of phosphorite particles by coastal currents are the main factors controlling the distribution of particle-bound trace metals in the coastal environment. The Cd, Sr and Zn concentrations decrease with decreasing grain size in marine coastal sediments, whereas Cr, Cu, Ni and Zn concentrations increase with decreasing grain size. Percolation and shaking experiments were carried out in laboratory using raw phosphate material and artificial sea water. Enhanced mobilization of Cd from phosphorites by contact with the sea water was observed.

Key words Marine pollution · Trace elements · Phosphorite tailings · Togo

Introduction

Phosphorites are being mined in the coastal basin of Togo in the region of Hahotoé and Kpogamé. The exploited phosphate layer known as *couche 1* is of Middle-Eocene (Lutetian) age and extends in a SW–NE band between Aveta and Dagbati over a length of 30 km, whereas the width does not exceed 3 km. The thickness of the economic layer varies between 1–10 m. It overlies an attapulgite clay and phosphatic limestone of *couche 2–3* and it is covered with red barren soils 7–30 m thick. The phosphatic layer is yellowish coloured and looks like a sandy-clay with pseudoolithic appearance (Killing and Cotillon 1977). The exploited materials are transported to the Kpémé beach where the ore is enriched and purified using sea water. The processing site is located approximately 40 m from the shore line. During this process phosphorite tailings (about 40% of the primary ore; Arégba 1989), are discarded into the adjacent sea. The treatment of the ore consists of a sieving process (for particles >1 mm) using sea water and a decaying process (for silt and clay particles <45 µm) using a hydrocyclone system with sea water. The marketable phosphate is obtained by rinsing with fresh water. After the drying process, the iron oxides are eliminated by means of a magnetic separator. The exploitation and marketing of the ore are executed by O.T.P (Office Togolais des Phosphates) which produces about 3.5 million tons of commercial phosphate annually.

Because of the various isomorphic substitutions in the apatite lattice, it is known that the marine phosphorites are enriched in numerous trace metals such as Cd, Cr, Zn, Ni, Cu, Sr, Zr, U and REE (e.g. Tooms and others 1969; Nathan 1984; MacArthur 1985). This is also the case for the phosphorite ores in Hahotoé-Kpogamé of South Togo. Previous work by Kunkel (1990) has shown that Cd concentrations in these phosphorites are high, with values ranging from 5 to 267 mg/kg and an average of 66 mg/kg. Our own analyses on the same phosphorites show Cd values ranging from 2 to 109 mg/kg with an average of 43 mg/kg. The aim of the present work is to study the geo-chemical impact of the processing on the nearby marine environment. For this purpose the con-

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K. Gnandi (✉) · J. Tobschall
University of Erlangen-Nürnberg, Institute of Geology and Mineralogy, Chair of Applied Geology, Schlossgarten 5,
D-91054 Erlangen, Germany,
e-mail: kissao.gnandi@geo.stud.uni-erlangen.de

tents of the trace metals Cd, Cr, Cu, Ni, Pb, V, Sr, Zn and Zr were determined in 61 coastal sediment samples, collected in the offshore area of the site where the phosphorite processing is now taking place.

Methodology

All samples were collected during the dry season of March to April 1996 (Fig. 1). Sediment samples were taken using an Ekman grab sampler. In the studied coastal region sampling was done in 20 profiles perpendicular to the coastline. Three sediment samples, rarely two, were taken for each profile. The first samples are located near the coastline, the second and the third ones were taken in an offshore area. The sampling points were determined using theodolites located on the beach. The sampler was tied to a graduated rope which allowed the

measurement of the water depth of the sampling point which lies between 6 and 20 m. For the determination of the geochemical background values, two samples, one from the coast and the second from offshore were taken far away from the source of pollution. The geochemistry of the phosphorites of southern Togo was studied using 17 phosphorite samples taken in three profiles from the exploited phosphorite layer C1 in Hahotoé and Kpogamé. Selected samples were split into various size fractions using plastic sieves and Atterberg tubes. The phosphorite samples were separated into five fractions (1–0.2, 0.2–0.1, 0.1–0.063, 0.063–0.002 and <0.002 mm), whereas four fractions (63–20, 20–6.3, 6.3–2 and <2 μm) were selected

Fig. 1
Location of the phosphorite deposits of southern Togo (A), coastal sediment sampling sites (B) and phosphorite sampling locations (C)

to study the grain size dependence of metal concentrations in coastal sediments.

For the determination of the total content of major and trace elements, about 100-mg sediment sample were digested using analytical grade HF, HNO₃ and HCl. The major elements Ca, K, Na, Ti, Fe, Mg and Mn, and the trace elements Cd, Cr, Cu, Ni, Pb, V, Sr, Zn and Zr were measured by ICP-AES. Phosphorus was determined colorimetrically using the molybdenum blue method given by Morphy and Riley (1962). Organic carbon of the samples was determined by titration method according to Gaudette and others (1974).

Shaking and percolation experiments were carried out in the laboratory using raw phosphate and artificial sea water at a ratio 1:10, according to German industrial norms (DIN 38414 - Teil 4 1984). Then, 100 ml of artificial sea water was added to 10 g of phosphorites in a shaking bottle. The bottles were shaken for 24 h using a mechanical shaker. For the elution experiment 10 g of raw phosphorite were percolated for 4, 8, 16, 24 and 32 h, respectively, with 100 ml of artificial sea water. After shaking and each percolation period, the residual solution was filtered through a membrane filter of 0.45 µm opening and acidified with HNO₃. Cadmium was analysed by a graphite furnace AAS. Artificial sea water was prepared using industrial sea salt (Sera-Salz) having a chemical composition identical to sea water composition (pH = 8.3; salinity 33‰).

Results and discussions

Geochemistry of the phosphorite deposits of Hahotoé-Kpogamé

Major and trace element contents of phosphorites. The statistical values of the chemical composition of the

phosphorite deposits of Hahotoé-Kpogamé are listed in Table 1. The frequency of the major and trace element contents in analysed phosphorites are given in Fig. 2a, b. The distributions of the major elements show unimodal diagrams (Fig. 2a) where the frequent measured concentrations lie by 0.19 wt.% for TiO₂, 2 wt.% by Al₂O₃, 5 wt.% for Fe₂O₃, 0.12 wt.% for MnO, 0.13 and 0.19 wt.% for MgO, 35 wt.% for CaO, 30 wt.% for P₂O₅ and 0.050 and 0.50 wt.% for C_{org}. The results show that trace elements such as Cd, Cr, Cu, Ni, V, Sr and Zn are highly enriched in the phosphorites. Trace metal contents range between 2–109 ppm for Cd, 126–707 ppm for Cr, 55–511 ppm for Cu, 38–363 ppm for Ni, 207–18004 ppm for Sr, 92–339 ppm for V, 116–1869 ppm for Zn, and 19–93 ppm for Zr. The Cd contents found in the phosphorites lie lower in comparison to values given by Kunkel (1990) on the same phosphorites which ranged from 5 to 267 ppm Cd. The distribution of trace metals show (Fig. 2b) maximal values by 40 ppm for Cd, 300 ppm for Cr, 50 ppm for Cu, 100 ppm for Ni, 150 ppm for V, 200 ppm for Zn, 400 ppm for Sr and 30 ppm for Zr. The enrichment factors are calculated by dividing the median values of trace metals in these phosphorites by the concentrations of the same elements in world phosphorites (Altschuler 1980) or in shales (Wedepohl 1991). The calculated enrichment factors for the analysed trace metals are high for all elements except Zr (Table 1). The phosphorites are weathered and numerous trace metals including Cd are released from the Francolite and sorbed onto other phases in phosphorites such as crandallite, iron and manganese oxides, clay minerals and calcite. The highest Cd value is found in an oxidated altered horizon of the profile P4b. In the intensive weathered crandallite and kaolinite rich upper part of the profiles Cd is depleted (e.g. P1a). Released Cd is sorbed on the calcite minerals of the underlying limestone layer (e.g. 116 ppm in P4d), whereas in the attapulgite clays from the same strati-

Table 1
Major and trace element contents in phosphorites of

southern Togo (total sample): major elements are in wt.%, trace elements are in ppm, F = Enrichment factor

N = 17	Cd	Cr	Cu	Ni	V	Zn	Zr	Sr
Min	2	126	38	55	92	116	19	207
Max	109	707	363	511	339	1869	93	18004
Average	44	356	109	158	173	465	46	1429
Median	43	314	85	113	147	276	44	364
Shales ^a	0.3	90	45	68	130	95	160	300
World phosphorites ^b	18	125	75	53	100	195	70	750
F1 (shales)	143.33	3.49	1.89	1.66	1.13	2.90	0.27	1.21
F2 (world phosphorite)	2.39	2.51	1.13	2.13	1.47	1.41	0.62	0.49
N = 17	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	P ₂ O ₅	C _{org}
Min	0.05	0.90	0.56	0.002	0.09	6.89	4.96	0.02
Max	0.42	30.86	16.04	0.09	0.57	48.32	40.89	0.22
Average	0.19	5.27	3.87	0.02	0.23	34.12	28.37	0.10
Median	0.18	3.36	2.12	0.02	0.18	36.04	29.90	0.07

^a Wedepohl (1991)

^b Altschuler (1980)

Fig. 2

a Frequency of major elements distribution in total sediment of phosphorite

graphical level Cd contents are very low. The other trace metals are preferentially bound to clay minerals and to iron and manganese oxides.

Distribution of trace metals in grain size fractions. The grain size is an important factor for the distribution of the trace elements in phosphorites. Cd concentrations decrease by decreasing grain size and show linearity with the P₂O₅ contents. Highest Cd values are found in the fractions 1–0.1 mm, whereas the concentrations of Cr, Cu, Ni, V, Sr, Zn and Zr increase by decreasing grain size. The highest concentrations of these trace elements are found in the clay fractions (Table 2).

Inter-elemental correlations. The correlation of Cd with apatite is moderately positive in the bulk sediment of phosphorite ($r=0.63$) but increases to $r=0.91$ in the fraction 1–0.2 mm in which the highest P₂O₅ concentrations occur. There are significant positive correlations between Cd and iron or manganese oxides. Cr, Cu, Ni, V, Sr, Zn, Zr show also positive significant correlations with alumi-

nium or iron oxides. Numerous trace elements exhibit positive inter-elemental correlations which point to their common enrichment processes in phosphorites. The significant positive correlations in bulk sediment and in various grain size fractions are listed in Table 3.

Metal distributions in coastal sediments

Mineralogy and grain size distribution of coastal sediments. The X-ray diffraction analyses reveal that the polluted coastal sediments have mineralogical composition similar to the phosphorites. Fluoroapatite is the main mineral of the marine coastal sediments dealt with. In addition, goethite, calcite, quartz, kaolinite and montmorillonite occur. Samples taken from the unpolluted zone of the coast did not contain fluoroapatite. The grain size distribution of these coastal sediments show a sorting of particles by density and transport by coastal currents. Sediments taken close to the coastline are enriched with coarser particles (up to 50%), whereas offshore sediments contain higher percentages of silt and clay particles (up to 40%). The cumulative grain size curves of the coastal sediments are shown in Fig. 3.

Major elements contents in coastal sediments. Changes of the chemical composition of coastal sediments due to the dumping of phosphorite tailing can be documented by

Fig. 2

b Frequency of trace elements distribution in total sediment of phosphorite

major element concentrations of coastal sediments (Table 4). The histogram representation of major element distributions in coastal sediments is drawn in Fig. 4a which shows maximum values of 1 wt.% for TiO_2 , 9 wt.% for Al_2O_3 , 6 wt.% for Fe_2O_3 , 0.05 wt.% for MnO , 1.4 wt.% for MgO , 7.5 wt.% for CaO , 2 wt.% for P_2O_5 and 0.24 wt.% for C_{org} . The enrichment factors of major elements in coastal sediment, calculated by dividing the median values of each element in sediments by the averages of the background concentrations of the same element show high values for P_2O_5 ($\text{EF}=14.07$), CaO ($\text{EF}=8.00$) and Al_2O_3 ($\text{EF}=2.92$) and low values for Fe_2O_3 ($\text{EF}=1.38$), MgO ($\text{EF}=1.32$), K_2O ($\text{EF}=1.19$) and Na_2O ($\text{EF}=0.39$). Natural coastal sediments are richer with TiO_2 ($\text{EF}=0.26$), MnO ($\text{EF}=0.35$) and C_{org} ($\text{EF}=0.34$) than the contaminated coastal sediments.

Trace metals distribution in coastal sediments. The trace metal contents of studied coastal sediments are very high with values ranging between 2–44 ppm for Cd, 22–176 ppm for Pb, 115–753 ppm for Cr, 22–184 ppm for Cu,

19–281 ppm for Ni, 38–329 ppm for V, 60–632 ppm for Zn, 179–643 ppm for Sr and 18–8928 ppm for Zr (Table 4). The frequency of the distribution of trace metal contents in coastal sediments shows (Fig. 4b) maximums of 5 ppm for Cd, 250 ppm for Cr, 70 and 90 ppm for Cu, 220 ppm for Ni, 200 ppm for V, 300 ppm for Zn, 60 ppm for Pb, 450 and 500 ppm for Sr, 97 ppm for Zr. The enrichment factors of 100 for Cd, 4.4 for Cr, 2.7 for Zn, 2.4 for Ni, 2.8 for Pb, 1.7 for Cu, 1.4 for V, 1.5 for Sr and 0.7 for Zr indicate that the coastal sediments are highly contaminated with mine tailings. For the calculation of enrichment factors the shale values were taken because the background value of Cd (3 ppm) of the coastal sediments of Togo seems to be too high. Probably the dumping of communal waste of the capital Lomé into the sea and the discharge of stream sediment of the river Volta from the western side in Ghana contribute to the observed metal enrichments in background sediments.

The concentration isolines for the selected metals in analysed sediments are represented in Fig. 5. The regional distribution of trace metals in studied sediments indicate that the contents of Cr, Cu, Ni, Pb, Sr, V and Zn increase seawards and outwards from the point source of the mine tailing, whereas Cd contents decrease seawards and also along the coastal line outwards from the source of pollution. The higher contents of Cd were found very

Table 2
Trace metal concentrations (ppm) in various grain size fractions of phosphorites

<i>Fraction 0.2–1 mm</i>								
N = 17	Cd	Cr	Cu	Ni	V	Zn	Zr	Sr
Minimum	5	101	22	14	30	123	14	241
Maximum	132	601	6492	396	375	791	116	13 092
Average	53	175	460	67	107	261	41	1135
Median	52	136	65	39	79	204	27	392
<i>Fraction 0.1–0.2 mm</i>								
N = 17	Cd	Cr	Cu	Ni	V	Zn	Zr	Sr
Minimum	1	79	16	9	36	104	11	247
Maximum	142	405	205	361	258	403	134	14 063
Average	53	155	70	67	88	179	40	1175
Median	52	140	55	30	65	148	32	364
<i>Fraction 0.06–0.1 mm</i>								
N = 17	Cd	Cr	Cu	Ni	V	Zn	Zr	Sr
Minimum	2	75	22	9	31	106	9	211
Maximum	130	597	695	684	333	1513	125	1207
Average	52	178	123	98	107	303	43	433
Median	50	140	76	29	66	192	40	370
<i>Fraction 0.002–0.06 mm</i>								
N = 13	Cd	Cr	Cu	Ni	V	Zn	Zr	Sr
Minimum	14	305	62	52	188	133	46	242
Maximum	54	1009	475	393	545	776	251	1158
Average	33	637	147	156	308	301	102	609
Median	29	616	119	123	300	244	88	585
<i>Fraction < 0.002 mm</i>								
N = 13	Cd	Cr	Cu	Ni	V	Zn	Zr	Sr
Minimum	1	520	52	14	282	66	84	267
Maximum	29	1986	763	367	874	1234	239	8597
Average	15	1175	221	191	487	454	117	1312
Median	12	1089	143	190	484	344	104	661

Fig. 3
Cumulative grain size distribution for studied coastal sediments

close to the source of pollution since apatite particles have higher density and settle near to the coast, bearing in mind that apatite is the main carrier of Cd in phosphorites. The higher concentrations of Cr, Cu, Ni, Pb, V and Zn are found away from the coast line because the clay particles which act as carrier for these elements and substantial amount of Cd in phosphorites is transported far away and settle in off-shore. Thus, the regional dispersion of particles such as apatite and clay minerals control the contents of trace metals in coastal sediments as can be seen by the similarity of the contours of both the major and trace elements. For these distribution patterns physical transport by long-shore and wave currents, and the sorting of sediments according to the density of particles are the most important factors. Because of the yellowish coloration of the ore tailings, a visible pollution

Table 3
Some significant inter-elemental correlations in total samples and in various grain size fractions of phosphorites

Fraction d (mm)		Cd-P	Cd-Ca	Cd-Fe	Cd-Mn	Al-Cr	Al-V	Fe-Cu	Fe-Cr	Fe-V	Fe-Zr	Fe-Ni
Bulk sed.	(n = 16)	0.63	0.34	-0.07	0.20	0.12	0.59	0.87	0.69	0.78	0.75	0.04
1-0.2	(n = 16)	0.91	0.59	-0.51	-0.16	0.47	0.46	0.65	0.69	0.61	0.54	0.20
0.2-0.1	(n = 16)	0.16	-0.16	0.73	0.59	-0.29	-0.15	0.82	0.34	0.77	0.75	0.82
0.1-0.06	(n = 16)	-0.12	-0.55	0.68	0.61	0.93	0.93	0.18	0.88	0.81	0.89	0.96
0.06-0.002	(n = 12)	0.26	0.72	0.03	-0.49	0.37	0.75	0.78	0.09	0.31	0.61	0.81
<0.02	(n = 12)	0.47	0.41	0.09	0.13	-0.33	0.58	0.73	0.14	-0.48	0.38	-0.37

Table 4
Major and trace element contents in coastal sediments (fraction <63 μm). Major elements are in wt.%, trace elements are in ppm, EF = enrichment factor (median/shale), BG Background values of studied coastal sediments

N = 59	Cr	Cu	Ni	V	Zn	Zr	Sr	Cd	Pb
Minimum	115	22	19	38	60	18	179	2	22
Maximum	753	184	281	329	632	8928	643	44	176
Average	408	75	148	178	249	686	427	14	69
Median	398	78	160	181	253	107	443	13	62
Shales ^a	90	45	68	130	95	160	300	0.13	22
EF	4.4	1.7	2.4	1.4	2.7	0.7	1.5	100	2.8

N = 59	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Corg
Minimum	0.05	0.83	0.42	0.002	0.10	1.52	0.12	0.02	0.48	0.03
Maximum	9.36	17.35	11.93	0.34	5.52	35.87	21.85	1.37	24.24	3.09
Average	1.20	8.98	5.30	0.07	1.61	15.16	4.48	0.54	10.71	0.90
Median	0.59	9.11	5.04	0.04	1.34	14.88	1.69	0.49	12.24	0.58
BG	2.26	3.12	3.66	0.11	1.01	1.86	4.35	0.41	0.87	1.72
EF ^b	0.26	2.92	1.38	0.35	1.32	8.00	0.39	1.19	14.07	0.34

^a Wedepohl (1991)

^b EF = Enrichment factor (Median/BG)

can be observed in far distance from the outfall during the dumping. With this coloration one can draw the both important transport directions that are to the long-shore and to the onshore-offshore.

In the coast of Togo long-shore current plays an important role in the sediment transport, which is more pronounced in the east ward direction. The intensification of the long-shore transport in the eastward direction can be observed in the concentration contours of P₂O₅, Al₂O₃ and Cd which show a shifting to this direction. The littoral drift in the studied coastal area is generated by the oblique wave breaking. The angles of the wave breaking to the coastal line lies between 4° and 9° with an average of 6°–7° (Rossi 1989). Due to the active coastal erosion in the area of Gulf of Benin, the sediment transport by long-shore currents are increased.

Such a distribution of trace metals in marine sediments has been reported from other bays and estuaries, e.g. in Lawrance Bay and Estuary by Bopp and Biggs (1981) and have been attributed to the same factors. As found in this study, the highest trace metal contents have been found in areas with elevated compound of fine sediment (clay fraction), except for Cd. Although the contamination is of

anthropogenic origin, the distribution of trace metals in coastal sediments are controlled by natural factors. It is well known that these elements are incorporated into the apatite lattice by substituting other cations such as Ca (e.g. Nathan 1984). Weathering of phosphorites by ground- and rain-water in the ore itself has removed numerous trace elements from the apatite lattice (Cook 1972). These mobilized trace elements are adsorbed onto clay, calcite, newly crystallized apatite, iron and manganese oxide minerals. This distribution pattern in coastal sediments can also be explained by the grain size dependence of metal concentrations in phosphorites. The grain size dependence of trace metal concentrations in the polluted coastal sediments is similar as demonstrated for the phosphorites. The concentrations of Cr, Cu, Ni, Pb, V and Zn increase with decreasing grain size, whereas Cd, Sr and Zr behave in an opposite way (Fig. 6).

Inter-elemental correlations in coastal sediments. Cadmium shows significant positive correlations with P₂O₅ ($r=0.89$) and CaO ($r=0.82$) and negative correlations with organic carbon ($r=-0.55$). Cu, Ni, Sr and V correlate moderately with P₂O₅ ($r=0.63$, $r=0.61$, $r=0.65$,

Fig. 4

a Frequency of major element distribution in coastal sediments (fraction < 63 μm)

Table 5

Correlation matrix of various metals and organic carbon in coastal sediments (fraction < 63 μm)

	Al ₂ O ₃	CaO	Cd	Corg	Cr	Cu	Fe ₂ O ₃	MnO	Ni	P ₂ O ₅	Pb	Sr	V	Zn	Zr
Al ₂ O ₃	1														
CaO	0.05	1													
Cd	-0.27	0.82	1												
C _{org}	-0.11	-0.61	-0.56	1											
Cr	0.46	0.32	0.27	-0.29	1										
Cu	0.27	0.56	0.53	-0.44	0.52	1									
Fe ₂ O ₃	0.55	0.07	-0.21	-0.16	0.27	0.14	1								
MnO	-0.07	-0.49	-0.50	0.28	-0.25	-0.43	0.57	1							
Ni	0.50	0.60	0.50	-0.51	0.74	0.74	0.14	-0.59	1						
P ₂ O ₅	-0.09	0.88	0.90	-0.66	0.37	0.63	-0.12	-0.58	0.65	1					
Pb	0.09	-0.03	0.08	-0.22	0.40	0.12	0.39	0.29	0.11	-0.04	1				
Sr	0.23	0.66	0.59	-0.52	0.57	0.61	0.10	-0.46	0.66	0.63	0.44	1			
V	0.47	0.29	0.30	-0.28	0.88	0.49	0.32	-0.17	0.71	0.28	0.58	0.63	1		
Zn	0.05	0.36	0.60	-0.33	0.51	0.56	-0.13	-0.42	0.61	0.51	0.32	0.48	0.57	1	
Zr	-0.06	-0.36	-0.34	0.10	-0.09	-0.27	0.64	0.89	-0.41	-0.39	0.36	-0.32	-0.03	-0.28	1

Fig. 4
b Frequency of trace element distribution in coastal sediments
(fraction < 63 μm)

Table 6
Results of shaking and percolation experiments: I Cd concentration in phosphorites (mg/kg); II Cd released ($\mu\text{g/l}$) by shaking (24 h); III total Cd released in mg for 1000 g Phosphorite material

Shaking experiment														
Samples	P1.b	P1.c	P1.d	P2.a	P2.b	P2.c	P3.a	P3.b	P3.d	P4.a	P4.b	P4.c	MM	MB
I	23	34	25	50	41	53	48	43	55	41	109	48	62	45
II	48.38	41.88	17.48	30.48	37.58	34.48	20.48	29.18	17.38	60.98	256.18	214.78	62.58	96.98
III	0.48	0.42	0.17	0.30	0.38	0.34	0.20	0.29	0.17	0.61	2.56	2.15	0.63	0.97

Percolation experiment						
Sample	4 h	8 h	16 h	24 h	32 h	Total Cd released after 32 h
P1.c	44.58	12.88	1.48	1.98	0.48	61.40
P3.b	37.68	12.58	2.48	6.98	0.48	60.01

Fig. 5 Distribution of P_2O_5 , Al_2O_3 , Cd, Cr, Zn, Pb, Ni, V and Cu in studied coastal sediments (Fraction < 63 μm)

$r=0.63$ and $r=0.51$, respectively, $n=59$). There are some positive significant correlations between trace elements themselves r (Cd vs. Zn)=0.59, r (Cr vs. Ni)=0.74, r (Cr vs. V)=0.88, for example which explain their common source of enrichment. Table 5 gives the correlation matrix of selected metals in coastal sediments.

Mobility of Cadmium

The results of shaking experiments show that high values of Cd between 17.4–256.1 $\mu g/l$ Cd are released from phosphorites to sea water (Fig. 7a). The release of Cd to sea water by percolation reveals that desorption processes of Cd are rapid in sea water and reach the maximum within 4 h. The release of Cd remains high for 8 h and decreases to low and constant values near to background concentrations of artificial sea water (Fig. 7b). The shaking experiment is quite similar to natural conditions which the tailing undergoes when it is dumped into the sea. But the percolation test is a good way to estimate the time factor of desorption processes. Among other factors such as pH and redox potential, salinity is also known to play an important role in the mobilization of particle bound trace metals by sea water (Förstner and Kersten 1987). The competition on sorption sites on solid surfaces and the

Fig. 6

Concentration of major and trace elements in various grain size fractions of coastal sediments

formation of soluble chloro-complexes of Cd might cause the substantial mobilization of Cd by the contact phosphorite-sea water. The release of trace metals such as Cd from suspended river particles and sediments in contact with sea water has been reported from several bays and estuaries, e.g. in Elbe and Weser estuaries in Northern Germany (Salomons and Förstner 1984). It was also demonstrated by Salomons and Mook (1980) that an increase of salinity increases the mobilisation of particle bound Cd. The same percolation test was performed with natural freshwater which gives negligible Cd concentrations in this kind of water. The mobility of other trace metals such as Cr, Cu, V and Pb is very lower than that of Cd which is quite similar to the study of Bourg (1983) showing that the effect of chloride on metal release follows the order of the $\log(K)$ values of the metal chloro-complexes: $\text{Cd} \gg \text{Cu} > \text{Ni}$.

Conclusion

The dumping of phosphorite mine waste into the sea is a source of coastal pollution with trace metals Cd, Cr, Cu, Ni, Pb, Sr, V and Zn. Instantaneous trace metal pollution of sea water occurs during the processing and dumping of mine tailing into the sea by the release of easily mobilizable Cd as demonstrated in the elution and shaking experiments. It is presumed that long-term release of Cd and other trace metals in sea water will occur, which can be enhanced by oxidation of the mine tailing on the sea floor as reported by Holmes (1986). Several million tons of mine tailing mixed to sediments lie on the sea floor which contains high concentrations of Cd and numerous other trace metals as seen by this study.

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Fig. 7

a Cd concentration (µg/l) in residual solution after shaking experiment using 10 g phosphorites and 100 ml artificial sea water for each sample, b temporal release of Cd (µg/l) into artificial sea water by elution experiment with phosphorites

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