

The Geochemical Characterization of Mine Effluents from the Phosphorite Processing Plant of Kpémé (Southern Togo)

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Abstract Sedimentary phosphorites are being exploited in southern Togo. The ore is processed to high-grade purified commercial phosphorite by wet sieving, using water pumped directly from the sea. The resultant muddy tailings are dumped directly into the sea without any pre-treatment. We have separated the solid and liquid phases of the muddy tailings and characterized their metal contents. Leaching tests were conducted with weak acid and saline water to evaluate the solubility and the potential bioavailability of various metals. The results show that the purification process leads to the enrichment of certain metals (Cr, Cu, Ni, V, Zn, Ba, Sr, Fe, and Al) in the tailings due to their association with the clay minerals, whereas Cd, Th, and U are enriched in the purified apatite-rich phase. The leaching tests showed that the solubility of metals generally increases when salinity increases or when pH decreases. Thus, the processing of phosphorites with sea water and the dumping of phosphorite tailings into the sea represent a serious potential risk for the marine ecosystem and for human health through the food chain.

Keywords Phosphorite mine tailings · Trace metals · Toxicity · Salinity · Coastal pollution · Togo

Introduction

The worldwide increase in demand for metals in industrial societies has intensified ore exploitation. Most of these ore deposits are low grade, so large quantities of mine waste material are generated (Allan 1995; Garci'a-Meza et al. 2006). Phosphorites have been exploited since 1959 in the areas of Hahotoé and Kpogamé (southern Togo). These marine sedimentary phosphate deposits, like those elsewhere in the world, are highly enriched with numerous heavy metals, such as Cd, Cr, Cu, Ni, V, Zn, Pb, U, Th, Mo, Ag, F, Y, and rare earths (Altschuler 1980; Johnson 1987; Kunkel 1990; Piper 1994). The main phosphorite mineral in Togo phosphorite is a carbonate fluorapatite (francolite; Johnson 1987; Kunkel 1990). The chemical composition of francolite is very variable because its crystal structure allows a variety of substitutions (McArthur 1990; McClellan 1980; McClellan and Van Kauwenbergh 1990; McConnell and Lehr 1969).

The Hahotoé-Kpogamé phosphorite ore is processed with seawater to commercial grade using sieves and hydrocyclones in a factory situated 25 km from the mines, close to the Kpémé beach. Two principal types of mine waste are produced during this processing: fine-grained clayey muddy tailings and a coarse-grained waste, both representing 40% of the raw ore. About 2.5 million tons of the muddy phosphorite tailings are rejected annually into the coastal waters of Togo without any pre-treatment (Fig. 1), contaminating the coastal waters and sediments (Gnandi et al. 2006; Gnandi and Tobschall 1999a, b, 2003).

Metals are present in the environment in different chemical forms, which influence their reactivity, and therefore, their mobility and bioavailability (Abollino et al. 2002; Morgan and Stumm 1995). Some environmental, physical, and chemical factors such as pH, salinity, redox

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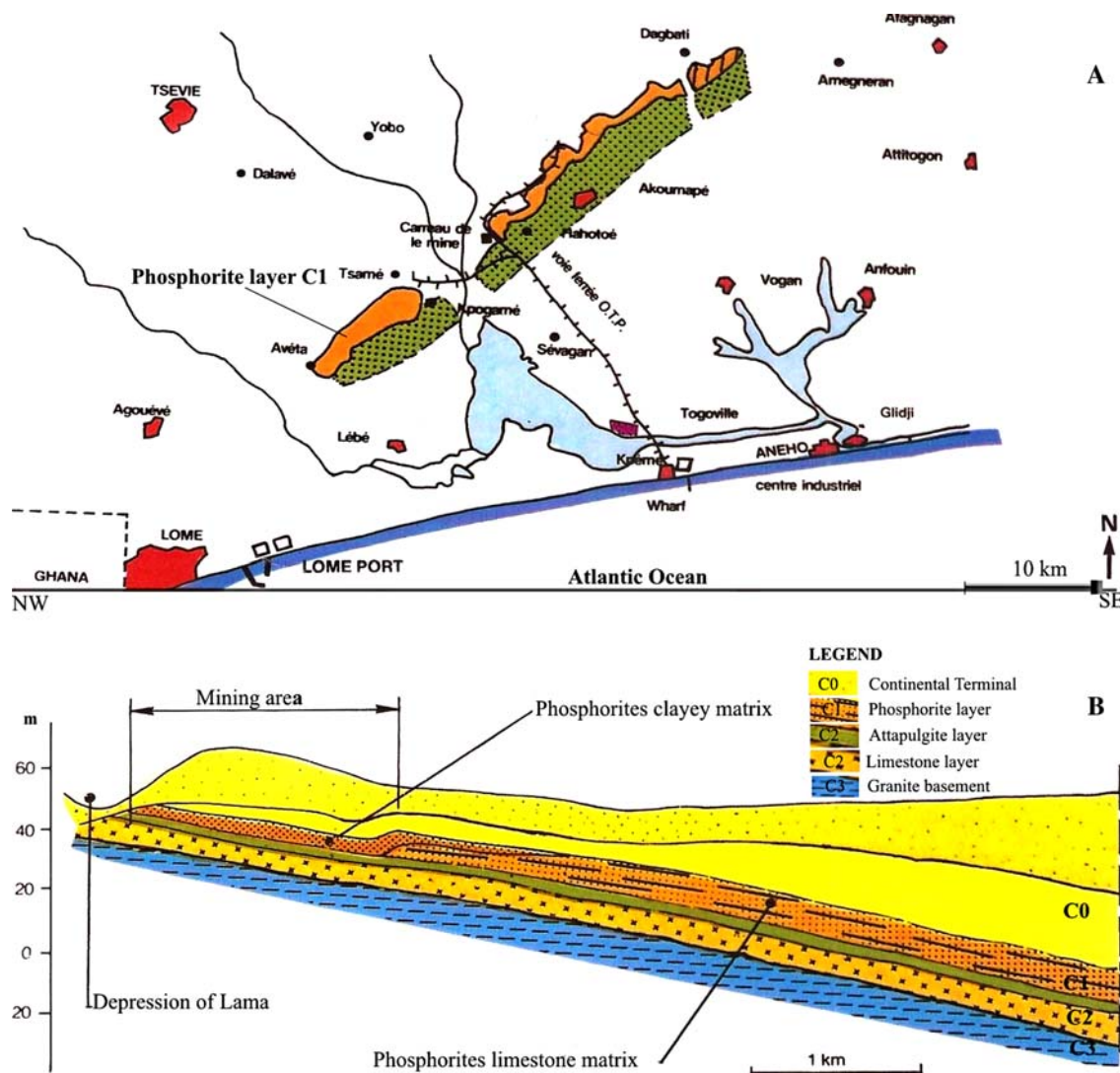
Fig. 1 The dumping of muddy phosphorite mine tailings into the coastal waters of Togo by Kpémé

conditions, and temperature influence the solubility and thus the mobility of heavy metal in aqueous environment (Salomons and Förstner 1980). The aim of this study was to

geochemically characterize the phosphorite mine tailings and to assess the effects of salinity and pH on the solubility and bioavailability of phosphorus and associated metals in the Hahotoé-Kpogamé phosphorites.

Geology

The Togo phosphorite deposits occur in a paleogeographical Tertiary coastal basin that extends from the south-eastern corner of Ghana through Togo and Benin into Nigeria. The exploited phosphatic layer (C1) extends SW-NE between the villages of Avéta and Dagbati over a length of 30 km; its width does not exceed 3 km. The thickness of the economic layer varies from 1 to 10 m. It overlies attapulgite clay and phosphatic limestone strata (C2–3; Fig. 2) and is covered with 2–20 m of red barren soil (Killinc and Cotillon 1977). A geological cross-section



of this basin shows marine formations of Mesozoic and Cenozoic Eras, resting in discordance on the Precambrian Dahomeyan basement. The phosphatic formations are of Lower–Middle Eocene age (Upper Ypresian–Lower Lutetian; Van Kauwenbergh and McClellan 1990), and dip gently towards the southeast. The Eocene formations are overlain by a continental sequence of sand, gravel, and clay; the entire “Continental Terminal” is covered by a barren ferruginous lateritized top soil.

Materials and Methods

Sixteen samples were collected to geochemically characterize the Hahotoe-Kpogame phosphorite deposits being exploited at Kpogame in August, 2006. Samples were taken in the middle of the phosphatic layer C1 along a length of about 1.5 km, where this layer (normally 30 m underground) was accessible after the overburden had been removed. The samples were kept in ciprox sachets for transport to the laboratory.

In the same month, 15 wet phosphorite tailings samples were collected at 10 min time intervals at the Kpémé tailings outfall. The muddy tailing samples were collected in clean 1.5 volumetric polyethylene bottles and kept cool during transport to the laboratory. The raw phosphorite samples and, after decantation and filtration, the muddy tailings, were dried at 70°C for several days in an electric oven and crushed in a silicon mortar. Crushed samples were prepared as pressed powder tablets (for trace element analysis) and as glass tablets (for major element analysis) by fusing the sediment with lithium tetraborate at high temperature. The total chemical composition of the phosphorite and the mine wastes was determined by X-ray fluorescence at the Institute of Geology and Mineralogy, University of Mainz, Germany.

The pollution of seawater by trace metals caused by the dumping of these mine tailings was previously studied using seawater samples taken along the coastline in the area influenced by the tailings (Gnandi et al. 2006). To assess the solubility of phosphorus and trace elements in saline water, about 10 g of the raw phosphorite material were reacted for several hours with 100 mL of artificial seawater in a 250 mL volumetric closed beaker (ratio 1/10, according to German standard procedures (DIN 38414 1984). Artificial saline water with various salt concentrations (10, 17, and 33 g/L) was prepared using NaCl (Prolabo Normapur, 99.5% purity) and distilled water. The experiment was carried out under agitation for time intervals of 4, 12, and 24 h, and 1, 2, 3, and 4 weeks.

Metals that are potentially available to organisms can be leached from the particle surface. Therefore, although there is no defined protocol to measure bioavailable metals

associated with sediment (Luoma 1989), typically the amount of metals extracted from sediment samples following relatively mild acid treatment (i.e., leachable metals) is used as an approximate measure of bioavailable metals (Deheyne et al. 2005; Snape et al. 2004). The mild acid treatment extracts the leachable metals, including metals associated with the organic matter and adsorbed to the sediment particles, but not constituent metals from the mineral structure (Cook et al. 1997; Katz and Kaplan 1981). In this study, 45% nitric acid (7 N HNO₃) in distilled water was used for metal extraction. About 0.1 g of tailings samples was digested with 0.5 mL HNO₃ at 80°C in a microwave digester for 1 h. After digestion, 10 mL of distilled water was added to the sample solution, which was then allowed to settle for 24 h before a sample of the solution was taken for analysis. The filtered mine waters and test solutions were analyzed by atomic absorption spectrometry (Thermo Orion Solaar S2) at the University of Lomé.

Results and Discussion

Table 1 summarizes the chemical composition of the raw phosphorite from Hahotoé-Kpogamé. The results show that the phosphorite deposits of Hahotoe-Kpogame are enriched in Cd, V, Cr, Cu, Ni, Cd, Zn, Sr, Ba, and U. Cadmium values in the phosphorite range from 43 to 102 mg/kg, Sr from 210 to 718, Ba from 74 to 274, U from 78 to 108, V from 101 to 317, Cr from 177 to 796, and Zn from 161 to 471. Compared to shale values (Wedepohl 1991), the enrichment factors are: 237 (Ni), 236 (Cd), 25 (U), 9 (Zr), 6 (Cr), 4 (Sr), 2 (V), and 1.5 (Zn and Cu). Compared to similar phosphorite deposits elsewhere in the world (Altschuler 1980), the phosphorite studied contains four times as much Cd and Cr, three times as much Cu, twice as much V and Zn, and 1.5 times as much Ni. Zirconium, U, and Pb are depleted in the Togo phosphorite, with factors of 0.9, 0.8, and 0.2, respectively.

Heavy metal contents for the mine tailings range from 339 to 396 for V, 835–993 for Cr, 45–79 for Cd, 574–642 for Zn, 499–1293 for Sr, and 187–205 for Ni (Table 2). Compared to phosphorite elsewhere in the world, the enrichment factors are 3.3 (Cd), 7.4 (Cr), 4 (Cu), 3.7 (Ni and V), 3 (Zn), 0.4 (Sr), 0.3 (Pb), and 0.4 (U). Thus, the phosphorite mine tailings are too contaminated with potentially toxic heavy metals to be disposed of in the sea. Furthermore, with a residual P₂O₅ mean value of 14.6% in the tailings (vs. 31.3% in the raw phosphorite), the processing method is neither ecologically nor economically appropriate.

The metal contents of the raw phosphorite and mine tailings are compared in Fig. 3, which shows that some

Table 1 Chemical composition of raw Hahotoé-Kpogamé phosphorite (P) (minor elements in mg/kg, oxides in %)

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Sum
P1	11.31	0.23	4.98	3.76	0.02	0.32	41.19	0.01	0.15	29.00	29.00	98.17
P2	11.30	0.20	4.50	3.01	0.02	0.26	42.43	0.01	0.13	30.31	6.00	98.24
P3	9.86	0.20	4.43	3.37	0.02	0.28	42.97	0.01	0.13	30.49	6.70	98.52
P4	9.70	0.19	4.22	3.42	0.03	0.26	43.41	0.01	0.12	30.79	6.56	98.76
P5	11.60	0.22	4.75	3.33	0.07	0.24	41.73	0.03	0.14	29.95	6.33	98.43
P6	10.40	0.20	4.38	3.21	0.02	0.25	42.87	0.01	0.12	30.50	6.53	98.55
P7	11.40	0.23	5.22	3.47	0.02	0.26	41.06	0.03	0.14	29.66	6.82	98.28
P8	4.10	0.08	1.56	2.18	0.02	0.10	49.82	0.11	0.05	34.96	5.33	98.33
P9	9.59	0.19	4.31	2.70	0.02	0.19	43.97	0.01	0.11	31.57	5.66	98.35
P10	10.20	0.21	4.42	2.97	0.02	0.25	42.98	0.01	0.12	30.62	6.26	98.07
P11	9.89	0.20	4.52	4.29	0.03	0.21	42.50	–	0.11	30.40	5.84	98.05
P12	11.00	0.22	4.20	3.09	0.06	0.30	42.25	0.02	0.14	30.11	6.39	98.37
P13	11.20	0.24	5.62	0.72	–	0.19	43.79	0.12	0.15	31.67	5.12	98.62
P14	4.27	0.11	2.60	2.16	0.01	0.05	49.53	0.10	0.07	35.78	4.00	98.53
P15	11.70	0.26	5.68	3.26	0.02	0.26	40.60	0.10	0.14	29.32	6.72	98.07
P16	4.85	0.12	2.86	2.43	0.01	0.06	48.77	0.10	0.08	35.16	6.53	100.83
Min	4.10	0.08	1.56	0.72	–	0.05	40.60	0.12	0.05	29.04	4.00	98.05
Max	11.70	0.26	5.68	4.29	0.07	0.32	49.82	0.11	0.15	35.78	7.11	100.83
Mean	9.50	0.19	4.30	2.96	0.02	0.22	43.74	0.02	0.12	31.27	6.12	98.51
	V	Cr	Cd	Ni	Cu	Zn	Sr	Zr	Ba	Pb	Th	U
P1	238	454	43	96	69	422	495	74	139	8	19	89
P2	237	456	66	103	71	462	485	79	155	8	20	94
P3	241	436	70	97	71	434	514	67	144	8	21	90
P4	228	426	67	99	71	435	522	70	146	10	23	93
P5	233	492	69	97	75	433	546	72	194	10	25	98
P6	227	449	63	93	68	423	518	67	155	8	21	94
P7	101	177	70	43	58	304	492	56	125	12	22	108
P8	230	493	90	90	66	373	515	79	158	11	21	92
P9	282	672	81	104	70	402	718	91	274	12	21	95
P10	229	428	98	102	70	448	512	70	121	11	21	92
P11	267	573	55	117	73	424	542	77	190	13	21	90
P12	242	461	61	102	69	471	483	81	158	11	19	89
P13	102	631	71	20	39	161	210	60	82	6	18	78
P14	262	706	65	46	63	233	277	42	77	12	21	104
P15	209	654	102	30	50	209	276	46	89	7	23	104
P16	317	796	64	50	63	243	270	42	74	7	21	97
Min	101	177	43	20	39	161	210	42	74	6	18	78
Max	317	796	102	117	75	471	718	91	274	13	25	108
Mean	228	519	71	80	65	367	461	67	143	10	21	94

– Not determined

elements are more abundant in the tailings than in the raw phosphorite; this was shown to be the case for V, Cr, Ni, Cu, Sr, Zr, and Ba. Other metals, such as Cd, U, and Th are more highly enriched in the raw phosphorite. Most of the major elements (e.g., Fe, Al, Ti, Mn, Na, and K) are abundant in the

tailings; the exceptions are elements that are associated with the apatite structure, such as P, Ca, and Mg. Thus, the processing of phosphorite by wet sieving not only concentrates the apatite-rich phase, but also redistributes the potential environmental contaminants. The clayey phase rejected as

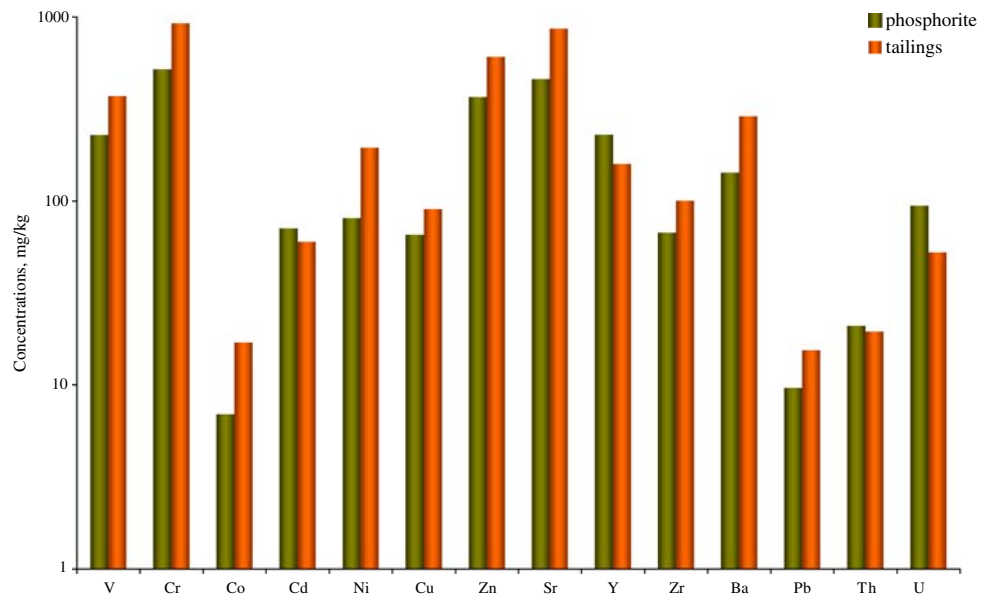
Table 2 Chemical composition of mine tailings (T) of the Kpémé phosphorite processing plant (minor elements in mg/kg, oxides in %)

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Sum
T1	21.53	0.50	12.16	6.56	0.02	0.95	21.07	3.05	0.39	15.20	18.94	100.52
T2	26.87	0.63	13.83	6.01	0.03	0.91	20.76	1.24	0.39	14.58	12.58	97.97
T3	25.85	0.60	13.28	5.79	0.03	0.98	20.17	2.23	0.41	14.09	14.39	97.96
T4	24.84	0.58	12.77	5.57	0.02	0.99	20.39	2.50	0.4	14.29	15.32	97.82
T5	26.55	0.62	13.59	6.03	0.03	0.86	21.91	0.87	0.37	15.26	11.61	97.85
T6	25.79	0.60	13.22	5.53	0.02	1.17	17.94	3.31	0.44	12.58	17.23	97.95
T7	26.71	0.63	13.68	6.03	0.03	0.87	21.27	0.9	0.38	14.87	11.73	97.24
T8	21.45	0.50	12.01	6.51	0.02	1.00	21.13	3.55	0.41	15.30	12.70	94.72
T9	22.24	0.50	12.43	6.39	0.03	1.09	19.76	4.07	0.43	14.40	15.59	97.05
T10	27.05	0.64	13.87	6.06	0.03	0.86	21.35	0.66	0.38	14.85	15.51	101.41
T11	21.99	0.50	12.40	6.25	0.02	1.13	18.85	4.27	0.43	13.80	17.28	97.07
T12	21.50	0.49	12.13	6.61	0.03	0.93	21.78	3.02	0.39	15.79	14.41	97.22
T13	21.16	0.49	12.08	6.59	0.03	0.93	22.30	2.95	0.38	16.19	14.42	97.65
T14	22.64	0.52	12.81	6.69	0.03	1.00	20.79	2.98	0.40	15.19	13.32	96.49
T15	20.68	0.48	11.89	6.48	0.03	0.90	22.87	3.00	0.37	16.66	14.23	97.73
Min	20.68	0.48	11.89	5.53	0.02	0.86	17.94	0.66	0.37	12.58	11.61	94.72
Max	27.05	0.64	13.87	6.69	0.03	1.17	22.87	4.27	0.44	16.66	18.94	101.41
Mean	23.79	0.55	12.81	6.21	0.03	0.97	20.82	2.57	0.40	14.87	14.62	97.78
	V	Cr	Cd	Ni	Cu	Zn	Sr	Zr	Ba	Pb	Th	U
T1	363	906	79	191	95	593	1144	92	319	14	19	58
T2	393	970	52	205	86	628	514	113	242	17	20	47
T3	370	922	50	196	85	611	510	111	229	16	18	45
T4	356	880	52	190	83	607	499	107	223	15	20	45
T5	396	967	48	197	86	633	517	113	233	14	19	48
T6	339	835	45	188	81	599	546	109	235	19	20	41
T7	395	983	53	204	88	636	522	115	236	16	20	48
T8	389	978	73	201	87	642	518	113	243	18	21	46
T9	370	935	54	187	93	586	1068	90	312	12	20	58
T10	351	861	50	192	92	574	1111	92	310	14	19	55
T11	360	889	75	201	94	587	1165	92	334	17	18	54
T12	375	943	72	189	94	601	1158	90	341	15	19	60
T13	375	931	75	189	97	595	1172	89	330	13	20	60
T14	370	907	53	193	95	594	1293	88	372	16	21	63
T15	386	949	74	200	98	610	1250	93	370	16	21	60
Min	339	835	45	187	81	574	499	88	223	12	18	41
Max	396	983	79	205	98	642	1293	115	372	19	21	63
Mean	373	924	60	195	90	606	866	100	289	15	20	52

tailings is rich in Cr, Cu, Ni, V, Zn, Sr, Ba, Fe, Al, Ti, and Mn whereas the industrial grade apatite-rich phase was shown to contain more U, Cd, and Th. The distribution patterns showed a grain size dependence of trace element partition: the concentration of Cd, Th, and U decreased with decreasing grain size whereas the concentrations of Cr, Cu, Ni, V, Sr, Zn, etc. increased with decreasing grain size (Gnandi and Tobschall 1999a, b, 2003).

The metal extraction test showed that many of the elements of concern that occur in the phosphorite are highly leachable. Compared to their total content in the analyzed phosphorite samples, the average extracted values ranged up to 72% for Pb, 66% for Sr, 42% for Mn, 38% for Cd, 34% for Cr, 32% for Cu and Zn, 31% for V, 27% for Ni, 18% for Fe, 15% for Al, and 1% for Ti (Table 3). This high extractability indicates that several of

Fig. 3 Comparison of the trace element contents (mg/kg) between the raw phosphorite (P) and the muddy phosphorite tailings (T)



the trace elements in the phosphorites are bioavailable, even some of those that have been considered as structural constituent elements.

The filtered mine waters have elevated concentrations of Cd, Ni, Zn, Al, and Fe (Table 4). Compared to normal seawater values, the tailing waters are too polluted to be disposed of without any pretreatment. The amounts of cadmium, in particular, pose a serious threat to the marine ecosystem and to man, through the food chain.

As discussed in Gnandi et al. (2006), after the tailings are dumped into the coastal waters, littoral currents (littoral drift and rip currents) transport them and disperse them over large areas of the coastal zone. Because of dilution, the metal concentrations in seawater decrease with increasing distance from the tailings outfall. Table 5 compares sampled values with those of normal seawater. Site 1 corresponds to seawater sampled very close to the outfall. Thereafter, seawater parameters improve both eastward (Sites 2 and 3) and westward (Sites 4 and 5). Thus, the dumping of mining effluent into the sea was shown to contaminate and acidify the seawater.

Salinity can enhance the release of these elements (Bopp and Biggs 1981; Petit 2006; Salomons and Förstner 1984). In order to better understand the effect of salinity on their solubility, laboratory tests were carried out using raw phosphorite and artificial seawater (ratio 1/10). The results for some selected metals and phosphorus are shown in Fig. 4, which indicates that when salinity increases (from 10 to 17, and to 33 g/L), the solubility of phosphorus and trace metals also increased. A salinity of 33 g/L was chosen to simulate natural conditions, as average seawater salinity is ca. 33‰. Contact time further increased metal solubility in seawater. Figure 4 indicates

that initially (from 4 h to 2 weeks), the solubility is very low for cadmium compared to phosphorus, iron, and copper. Later (2–4 weeks), the solubility increases rapidly for all elements, suggesting that the contact time between phosphorite tailings and the saline water is very important.

Conclusions

The phosphorite deposits of Hahotoé-Kpogamé (southern Togo) contain relatively high levels of potentially toxic metals such as Cd, Cr, Cu, Ni, V, U, and Zn. Some of the elements (Cd, U, Th, and F) are incorporated into the francolite lattices by isomorphic substitutions (Jarvis et al. 1994; Nathan 1984); the rest are adsorbed on sediments phases such as clay, calcite, iron and manganese minerals, and organic matter. During post-depositional alteration of francolite, some metals have been totally or partially (depending on the degree of alteration) released from the lattices, and can be transported into ground water or adsorbed on mineral phases, as indicated above (Cook 1972). Metals that are adsorbed on particle surfaces may be available; this is expressed by the high leacheability of these metals in dilute nitric acid and saline water. When seawater is in contact with phosphorite, metals are released through breakdown of organic matter and increased ionic competition on particle surfaces, which leads to exchange of adsorbed metals with seawater cations such as Ca, Mg, K, and Na. After that, the released metals become complexed with inorganic ligands, such as chloride, that renders them more mobile and consequently more toxic (Bopp and Biggs 1981; Salomons and Förstner 1980).

Table 3 Trace element distribution of mine tailing samples T (Ct = total concentration in mg/kg) and the amounts of extractable metal (Extr = amounts extractable in mg/kg and in %) using dilute nitric acid

	V			Cr			Cd			Ni			Cu			Zn		
	Ct.	Extr.	%	Ct.	Extr.	%	Ct.	Extr.	%	Ct.	Extr.	%	Ct.	Extr.	%	Ct.	Extr.	%
T1	363	68	19	906	195	22	79	20	26	191	24	12	95	18	19	593	151	25
T2	393	68	17	970	188	19	52	21	41	205	29	14	86	23	26	628	184	29
T3	370	86	23	922	243	26	50	21	42	196	40	20	85	26	30	611	190	31
T4	356	75	21	880	209	24	52	21	41	190	33	17	83	23	28	607	195	32
T5	396	113	29	967	327	34	48	23	49	197	61	31	86	38	45	633	259	41
T6	339	110	32	835	302	36	45	20	44	188	61	33	81	39	48	599	262	44
T7	395	105	27	983	314	32	53	23	43	204	55	27	88	34	38	636	241	38
T8	389	188	48	978	492	50	73	23	32	201	99	49	87	58	67	642	418	65
T9	370	141	38	935	401	43	54	23	42	187	62	33	93	46	50	586	262	45
T10	351	182	52	861	468	54	50	22	44	192	89	47	92	57	62	574	337	59
T11	360	115	32	889	320	36	75	21	27	201	47	24	94	37	39	587	223	38
T12	375	119	32	943	349	37	72	23	32	189	41	22	94	37	40	601	230	38
T13	375	127	34	931	360	39	75	24	32	189	52	27	97	40	42	595	241	41
T14	370	104	28	907	275	30	53	17	31	193	45	23	95	31	32	594	191	32
	Sr			Pb			Ti			Al			Fe			Mn		
	Ct.	Extr.	%	Ct.	Extr.	%	Ct.	Extr.	%	Ct.	Extr.	%	Ct.	Extr.	%	Ct.	Extr.	%
T1	1,144	531	46	14	5	35	5,000	7	0.1	121,600	11835	10	65,600	4,217	6	200	80	40
T2	514	267	52	17	6	35	6,300	8	0.1	138,300	12971	9	60,100	4,685	8	300	105	35
T3	510	305	60	16	10	61	6,000	11	0.2	132,800	16015	12	57,900	6,324	11	300	106	35
T4	499	273	55	15	6	43	5,800	10	0.2	127,700	13581	11	55,700	5,318	10	200	112	56
T5	517	388	75	14	10	71	6,200	30	0.5	135,900	19672	14	60,300	10,880	18	300	123	41
T6	546	386	71	19	13	69	6,000	28	0.5	132,200	19000	14	55,300	11,720	21	200	110	55
T7	522	390	75	16	11	68	6,300	23	0.4	136,800	20250	15	60,300	9,580	16	300	124	41
T8	518	443	86	18	21	119	5,000	82	1.6	120,100	30654	26	65,100	21,979	34	200	138	69
T9	1,068	799	75	12	14	118	5,000	46	0.9	124,300	20887	17	63,900	15,786	25	300	102	34
T10	1,111	879	79	14	17	122	6,400	73	1.1	138,700	23893	17	60,600	22,197	37	300	109	36
T11	1,165	708	61	17	8	45	5,000	36	0.7	124,000	17547	14	62,500	11,898	19	200	96	48
T12	1,158	762	66	15	13	88	4,900	36	0.7	121,300	19586	16	66,100	11,654	18	300	101	34
T13	1,172	808	69	13	11	82	4,900	43	0.9	120,800	20221	17	65,900	13,104	20	300	106	35
T14	1,293	663	51	16	9	56	5,200	37	0.7	128,100	15436	12	66,900	11,385	17	300	77	26

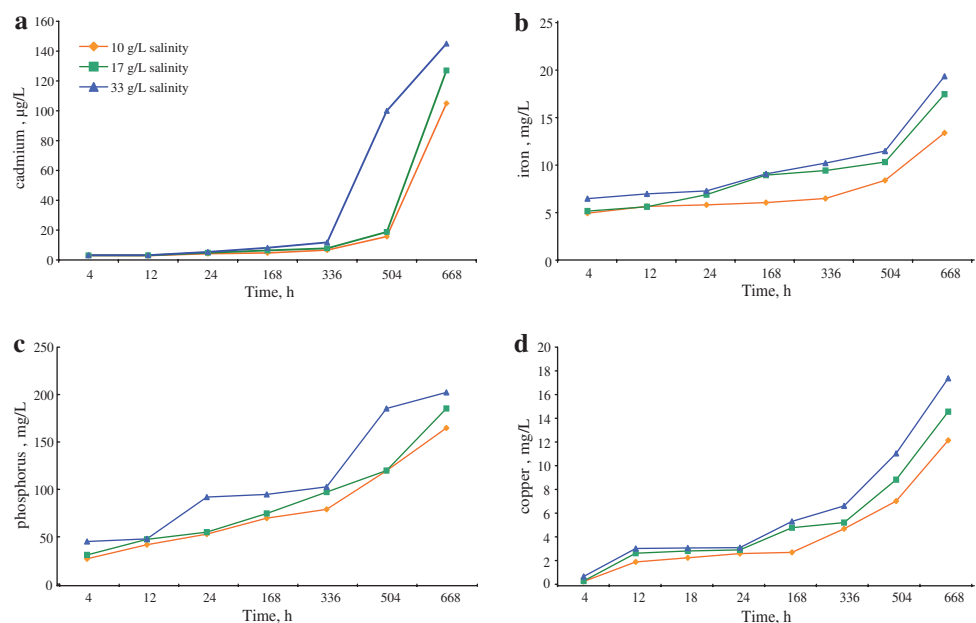
Table 4 Trace metal contents (ppb) of water filtered from the muddy phosphorite tailings

	Cd	Ni	Zn	Al	Fe
W1	49.5	34.0	58.5	83.8	130.1
W2	54.1	48.9	24.4	110.2	360.6
W3	24.0	56.6	43.1	24.6	41.6
W4	36.2	44.6	36.3	67.8	68.7
W5	40.8	36.3	35.3	69.9	53.2
Normal seawater	10	20	10	70	120

Because of the high metal concentrations in the mine tailings, the wet sieving using sea water and the disposal of the mine tailings into the sea are a major source of pollution of the coastal waters of Togo. The discharge of the mine tailings elevates seawater acidity, conductivity, and the concentrations of certain metals. Acidification and salinity enhances metal dissolution in the aquatic environment. Thus, the current practices represent a serious threat to the regional marine ecosystem and to human health (through the food chain).

Table 5 Chemical characterization of seawater influenced by mine tailings along the coastal zone of Togo (Total metals)

	Effluent	Agbodrafo, Site 5	Entry of the factory, Site 4	Wharf Site 1	Goumou-Kopé, Site 2	Aného Site 3	Seawater values
Distance from fall	0	2 km	500 m	2 m	1 km	2 km	Background
T (°C)	27.1	30.0	31.4	31.5	27.0	28.3	29.0
pH	7.32	7.52	7.66	6.50	8.28	8.21	8.30
Electr. cond.	4,260	46,400	46,600	46,700	46,800	47,000	48,500
Cd (µg/L)	41.0	5.6	8.3	12.0	7.0	3.5	0.01
Pb (µg/L)	9.0	6.7	10.0	7.0	8.5	3.7	0.003
Fe (µg/L)	360	152	210	265	300	102	2
F (µg/L)	1,310	1,600	852	558	1,360	435	–
Al (µg/L)	198	260	250	300	260	230	230
Zn (µg/L)	982	3110	343	417	78	791	100

Fig. 4 Mobilization of cadmium (a), iron (b), phosphorus (c) and copper (d) in phosphorites by artificial seawater (ratio 1:10); seawater salinity 10, 17 and 33 g/L

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References

- Abollino O, Aceto M, Malandrino M, Mentasti E, Sarzanini C, Petrella F (2002) Heavy metals in agricultural soil from Piedmont, Italy: distribution, speciation and chemometric data treatment. *Chemosphere* 49:545–557
- Allan RJ (1995) Impact of mining activities on the terrestrial and aquatic environment. In: Salomons W, Förstner U, Mader P (eds) *Heavy metals, problems and solutions*. Springer, Berlin, p 412
- Altschuler ZS (1980) The geochemistry of trace elements in marine phosphorites, Part I: characteristic abundances and enrichment. In: Bendor YK (ed) *Marine phosphorites*. Soc of Economic Paleontologists and Mineralogists Special Publ 575–B, pp 19–30
- Bopp F, Biggs RB (1981) Metals in estuarine sediments, factor analysis and its environmental significance. *Science* 214:441
- Cook PJ (1972) Petrology and geochemistry of the phosphorite deposits of Northwest Queensland, Australia. *Econ Geol* 67:1193–1213
- Cook JM, Gardner MJ, Griffiths AH, Jessep MA, Ravenscroft JE, Yates R (1997) The comparability of sample digestion techniques for the determination of metals in sediments. *Mar Pollut Bull* 34:37–644
- Deheyn DD, Gendreau P, Baldwin R, Latz MI (2005) Evidence for enhanced bioavailability of trace elements in the marine ecosystem of Deception Island, a volcano in Antarctica. *Mar Environ Res* 60:1–33
- DIN (Deutsche Industrie Normen) 38414–Teil 4 (1984) *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Schlamm und Sediment Gruppe S*. Beuth Verlag, Berlin, Germany
- García-Meza JV, Carrillo-Chávez A, Morton-Bermea O (2006) Sequential extractions on mine tailings samples after and before

- bioassays: implications on the speciation of metals during microbial re-colonization. *Environ Geol* 49:437–448
- Gnandi K, Tobschall HJ (1999a) The pollution of marine sediments by trace elements in the coastal region of Togo caused by dumping of Cd rich phosphorite tailings into the sea. *Environ Geol* 38(1):13–24
- Gnandi K, Tobschall HJ (1999b) Heavy metal release from phosphorite tailings into sea water: a simulated laboratory study. *Sci Total Environ* 236(1–3):181–190
- Gnandi K, Tobschall HJ (2003) The distribution patterns of rare earth elements and uranium in Tertiary off/shore sedimentary phosphorite deposits of Hahotoé and Kpogamé (Togo). *J Afr Earth Sci* 37:1–10
- Gnandi K, Tchangbedji G, Baba G, Killi K, Abbe K (2006) The impact of phosphate mine tailings on the bioaccumulation of heavy metals in marine fish and crustaceans from the coastal zone of Togo. *Int J Mine Water Environ* 25(1):56–62
- Jarvis I, Burnett WC, Nathan J, Almbaydin FSM, Attia AKM, Castro LN, Flicoteau R, Hilmy ME, Husain V, Quitwanah AA, Serjani A, Zanin Y (1994) Phosphorite geochemistry: state-of-the-art and environmental concerns. *Ecol Geol Helv* 87(3):643–700
- Johnson AKC (1987) Le bassin côtier à phosphates du Togo: Thèse de doctorat, université de Dijon. France, unpubl 360 pp
- Katz A, Kaplan IR (1981) Heavy metal behavior in coastal sediments of southern California: a critical review and synthesis. *Mar Chem* 10:261–299
- Killinc M, Cotillon P (1977) Le gisement d'Hahotoé/Kpogamé (Terciaire du Sud Togo), exemple de piège sédimentaire à sables phosphatés. *Bull BRGM, Section II, 1*, pp 43–63
- Kunkel H (1990) Über die Cadmiumverteilung in den Phosphoritlagerstätten von Kpogamé/Hahotoé: Dissertation/Universität/Erlangen, unpubl, 149 p
- Luoma SN (1989) Can we determine the biological availability of sediment-bound trace elements? *Hydrobiologia* 176:379–396
- McArthur JM (1990) Fluorine-deficient apatite. *Min Mag* 54:508–510
- McClellan GH (1980) Mineralogy of carbonate fluorapatite. *J Geol Soc Lond* 137:675–681
- McClellan GH, Van Kauwenbergh SJ (1990) Mineralogy of sedimentary apatite. In: Notholt AJG, Jarvis I (eds) *Phosphorite research and development*. Geol Soc Spec Publ, vol 52, pp 23–31
- McConnell GH, Lehr JR (1969) Crystal chemical investigations of natural apatites. *Am Mineral* 54:1374–1391
- Morgan JJ, Stumm W (1995) Chemical processes in the environment, relevance of chemical speciation. In: Merian E (ed) *Metals and their compounds in the environment*. Verlag Chemie, Weinheim, pp 67–103
- Nathan Y (1984) The mineralogy and geochemistry of phosphorite. In: Nriagu JO, Moore PB (eds) *Phosphate minerals*, Chap. 8, Springer, Berlin, pp 275–291
- Petit CJ (2006) spéciation et biogéochimie des métaux dans les milieux estuariens (estuaire de l'Escaut). *Synthèse bibliographique*, Université Libre de Bruxelles, 17 pp
- Piper DZ (1994) Seawater as the source of minor elements in black shales, phosphorites and other sedimentary rocks. *Chem Geol* 114:95–114
- Salomons W, Förstner U (1980) Trace metal analysis on polluted sediments. II. Evaluation of environmental impact. *Environ Technol Lett* 1:506–517
- Salomons W, Förstner U (1984) *Metals in the hydrocycle*. Springer, Berlin, 349 p
- Snape I, Scouller RC, Stark SC, Stark J, Riddle MJ, Gore DB (2004) Characterization of the dilute HCl extraction method for the identification of metal contamination in Antarctic marine sediments. *Chemosphere* 57:491–504
- Van Kauwenbergh SJ, McClellan GH (1990) Comparative geology and mineralogy of southern United States and Togo phosphorites. In: Notholt AJG, Jarvis I (eds) *Phosphorite research and development*. Geological Society Special Publication No. 52, pp 139–155
- Wedepohl KH (1991) The composition of the upper earth's crust and the natural cycles of selected metals. In: Merian E (ed) *Metals and their compounds in the environment*. Verlag Chemie, Weinheim, pp p1–p10