Heavy metals distribution of soils around mining sites of cadmium-rich marine sedimentary phosphorites of Kpogamé and Hahotoé (southern Togo)

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Abstract Metal concentrations of 37 soil samples taken from mining areas (abandoned mine pits and transport routes) in Kpogamé and Hahotoé (southern Togo) range from 0.2–43 ppm for Cd, 15–115 ppm for Pb, 182–1,029 ppm for Cr, 18–356 ppm for Cu, 15–432 ppm for Ni, 90–513 ppm for V, 35–563 ppm for Zn, 80–469 ppm for Zr and 266–3,161 ppm for Sr. The tropical alteration of the ore waste plays an important role in the distribution of trace elements in the studied soils. Because the alteration affects the element mobility, generally old abandoned mining areas are less polluted with trace metals Cd, Cr, Ni and Zn compared with fresh abandoned mining areas, which, together with soils near the transport routes, show a higher degree of contamination. Under low pH and oxidising conditions in studied soils Cd, Ni and Zn are generally easily mobilised and are thus available to the environment.

Keywords Heavy metals · Mining · Phosphorites · Soil pollution · Southern Togo

Introduction

Soils, as part of the terrestrial ecosystem, play a significant ecological role in element cycling. Heavy metal content of soils are influenced by several factors including mineralogical and geochemical composition of parent rock, organic matter content, particle size distribution, soil horization, age, drainage, vegetation, anthropogenic and aerosol input (Kabata-Pendias 1993). Anthropogenic soil pollution by trace metals such as Cd, Zn, Pb, Cu, Ni, As and Hg has been recognised in many countries (e.g. Japan, USA and Germany). In recent years, it has become one of the most important environmental problems in the developed countries. Mining activities and the application of soil fertilisers and pesticides are known as the main factors of soil pollution. The present study deals with soil pollution caused by mining activities. Generally, marine offshore sedimentary phosphorites in the world are well known to be enriched with numerous trace and rare earth elements (Altschuler 1980; Slansky 1980; Piper 1991). This is also the case for the phosphorite deposits of Hahotoé and Kpogamé, which have been exploited in the Tertiary coastal basin of southern Togo since 1962. These deposits are of Lower to Middle Tertiary age (Upper Ypresian–Lower Luthetian) and contain trace metals such as Cd, Cr, Cu, Ni, Sr, V, U and Zn, and trivalent rare earth elements in high concentrations (Gnandi and Tobschall 1999). The enrichment of those elements in marine sedimentary phosphorites is principally caused by the structure of the main apatite mineral, a carbonate fluorapatite (francolite), which has a hexagonal open crystal structure that allows various isomorphic ionic substitutions into its lattices (Slansky 1980). The incorporation of trace elements in the apatite lattice occurs during sediment diagenesis by substitution with various ions, e.g. Ca^{2+} , PO_4^{3-} and F^- (Nathan 1984). The primary source of trace elements in phosphorites is the organic matter of dead plankton, which initiates phosphorite genesis in the environment by sedimentation. The decomposition of organic matter in such an environment leads to the release of phosphorus and various trace elements. It is generally recognised that the formation of sedimentary marine phosphorites is coupled with upwelling currents of the oceans, in which increased biological productivity is prominent (Kazakov 1937; Baturin

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et al. 1970; Lucas and Prévôt 1997). Thus, phosphorites as raw materials for fertilisers can be a source of soil pollution by heavy metals.

The aim of the present work was to study the geochemical impact of phosphate mining on the pollution of soils with trace metals in the regions of Hahotoé and Kpogamé. This study is of great ecological importance because phosphorite mining is taking place within an area that possesses important groundwater aquifers in the coastal region of Togo. Additionally, soils in this region are also used intensively for agricultural purposes.

Regional setting of the study area

The area of this study is the Tertiary coastal basin of Togo, which extends from the south-eastern corner of Ghana through to Togo Benin into Nigeria (the Togo-Benin basin). It is composed of marine formations of the Mesozoic and the Tertiary systems, which rest in discordance on the Precambrian Dahomean basement (Slansky 1962). These formations are covered by a 7- to 30-m-thick ferruginous lateritised top soil ('barren soils') from the Quaternary (Fig. 1). The exploited phosphatic layer known as 'couche-1' is 3 to 6 m thick and extends in a SW-NE direction between Aveta and Dagbati over a length of 30 km, whereas the width does not exceed 3 km (Fig. 2). It overlies an attapulgitic clay and an phosphatic limestone of 'couche 2-3' (Kilinc and Cötlön 1977). The phosphatic layer is of marine off-shore sedimentary origin. It has a yellowish brown colour

because of its high iron oxide content. The texture of the deposit is sandy-clayey with a pseudo-oolithic appearance.

From a morphological point of view, this basin is composed of a number of plateaus of red soil cut in a SW-NE direction by a depression called the Depression of Lama. The climate is subtropical, hot and humid with an annual average rain fall of between 800 and 1,000 mm. The average temperatures range from 25 to 27 °C.

Materials and methods

Soil samples were taken from the old and newly abandoned exploitation areas (inside and outside of mine pits), and along the transport routes (Fig. 3). Soils in abandoned mining pits are very inhomogeneous and are composed of a mixture of overburden and ore waste. The overburdens are composed of Quaternary red barren soil layers and Tertiary sand and clay layers. The soil material along the transport routes is mixed with raw material that falls during the transport of the ore from the mine to the processing factory in Kpémé, located at 30 km from the coast. Samples from the surface soil were taken at depths of 0-20 cm using a shovel. The chemical and mineralogical composition of phosphorites were studied using phosphorite samples taken from the exploited phosphate layer in Hahotoé and Kpogamé (Fig. 2). All samples were collected during the dry seasons in March to April 1996. The background was de-

Fig. 1
Geological map of the Tertiary coastal basin of Togo (modified after Slansky 1962)

Fig. 2

Phosphorite deposits of Kpogamé and Hahotoé showing phosphorite sample locations (modified after Kilinc and Cotillon 1977)

fined using a soil sample taken far (3 km northerly) from the source of pollution in an area that has a similar lithology, soil horizons (red barren soils) and vegetation as that of the soil covering the whole basin of exploitation.

The mineralogical composition of soil was investigated using selected samples, which were fine powdered ($<20\ \mu\text{m}$) and prepared on a sample carrier for X-ray

analysis. The XRD analysis were performed using a Siemens D5000 diffractometer (Cu tube, 35 mA, step size $0.02^\circ 2\ \theta$, counting time up to 60 s/step, illuminated sample length of 20 cm, graphite diffracted beam monochromator, scintillation detector, rotating sample). Redox potential and pH values of samples were determined using the method given by Ulrichs et al. (1984): about 10 g dried soil material were introduced into a laboratory glass containing 25 ml KCl solution (normality 1). The sample was rested for 2 h and was shaken occasionally during this time. After, the redox potential and pH values of soil solutions were measured using a WTW-Instrument, type pH-96-B.

For the determination of element abundances, the size fraction of $<63\ \mu\text{m}$ was separated using plastic sieves and deionised water. It is usual in the geochemistry of soil and sediment to use the $<63\ \mu\text{m}$ fraction because it is representative for chemical analysis and it contains high amounts of clay and iron and manganese oxide, which accumulate numerous heavy metals by adsorption (Tosiani and Tapia 1993). After drying the sieved fractions at 40°C $\sim 100\ \text{mg}$ soil material were digested using the acids $\text{HF-HNO}_3\text{-HCl}$ suprapure (Merck). The contents of the major elements Ca, K, Na, Ti, Fe, Al, Mg and Mn as well as those of the trace elements Cd, Cr, Cu, Ni, Pb, V, Sr, Zr and Zn were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) in the laboratory of the Institute of Geology and Mineralogy of University of Erlangen (Germany). Phosphorus was determined using the molybdenum blue method given by Gaudette et al. (1974). Organic carbon of the samples was determined using a titration method given by Morphy and Riley (1962). The accuracy of the analysis were checked using the reference material SARM 51 (South African Bureau of Standards, stream

Fig. 3

Map of the mining areas in Kpogamé and Hahotoé showing soil sample locations

Table 1

Chemical composition of studied soil samples (trace elements in ppm, major elements in wt%, fraction <63 µm)

No.	Cr	Cu	Ni	V	Zn	Zr	Sr	Cd	Pb	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Corg.
1	435	83	250	368	434	95	430	15	87	0.28	26.60	1.13	0.03	1.31	0.53	0.00	0.44	7.46	0.24
2	745	116	432	383	563	86	383	28	21	0.54	11.48	4.95	0.04	0.87	24.69	0.24	0.27	12.38	0.062
3	890	287	106	357	227	135	3,161	15	110	0.70	16.14	13.93	0.02	0.29	16.51	0.29	0.23	15.71	0.18
4	682	105	85	242	126	97	499	18	39	0.64	13.56	5.12	0.01	0.43	24.64	0.23	0.23	18.39	0.33
5	637	176	256	336	324	184	2,840	15	103	0.96	16.81	13.06	0.04	0.38	14.73	0.28	0.19	12.12	0.63
6	240	73	61	153	161	236	620	5	60	1.35	18.93	6.15	0.06	0.29	7.62	0.29	0.14	6.04	0.85
7	253	48	58	174	129	235	521	3	52	1.38	19.83	5.95	0.04	0.23	8.29	0.22	0.16	6.64	0.87
8	217	46	58	192	125	234	528	6	68	1.20	16.17	7.60	0.03	0.34	6.73	0.30	0.15	2.47	n.a.
9	916	134	216	383	308	80	526	38	56	0.66	12.09	7.14	0.05	0.66	23.81	0.38	0.38	21.78	0.06
10	694	130	201	355	333	99	429	28	67	0.93	12.70	5.55	0.02	0.84	17.27	0.26	0.27	14.69	0.58
11	668	94	215	333	295	167	361	16	27	1.06	15.93	7.27	0.05	0.60	18.59	0.27	0.20	10.49	0.14
12	1028	138	327	503	417	130	493	32	80	0.81	9.74	7.50	0.01	0.82	29.10	0.28	0.34	18.47	0.46
13	529	114	142	300	235	177	495	20	54	0.69	12.88	6.41	0.03	0.85	29.89	0.40	0.31	12.39	0.89
14	606	105	227	336	366	93	561	43	48	1.61	18.99	6.88	0.02	0.26	12.52	0.13	0.21	22.15	0.4
15	464	146	185	281	245	339	1,298	17	69	1.59	19.57	4.42	0.02	0.33	5.52	0.12	0.33	0.38	1.14
16	703	124	249	577	337	130	517	32	54	0.87	15.64	8.25	0.04	0.88	21.20	0.33	0.29	19.26	0.48
17	396	130	70	194	123	269	1,673	11	57	1.34	20.38	6.66	0.02	0.13	14.32	0.26	0.11	10.48	0.42
18	591	88	75	240	113	140	613	15	49	0.88	16.97	5.82	0.01	0.41	17.63	0.27	0.20	12.35	0.29
19	237	27	31	175	84	391	953	0.18	53	1.88	27.55	4.29	0.01	0.25	0.89	0.20	0.20	2.68	0.48
20	289	57	22	214	78	354	1,597	0.58	29	1.62	26.36	3.12	0.01	0.21	1.26	0.16	0.21	1.18	0.48
21	235	44	46	182	164	256	1,307	3	15	1.44	18.56	5.25	0.03	0.37	1.24	0.14	0.22	0.5	0.87
22	199	356	25	189	67	467	266	3	83	1.30	17.62	7.70	0.01	0.68	3.18	0.28	0.22	3.24	0.24
23	254	52	56	214	138	372	720	6	95	2.12	18.15	8.33	0.05	0.37	1.33	0.28	0.20	1.57	0.48
24	199	356	25	189	67	467	266	1	83	0.52	10.48	4.57	0.02	0.62	31.24	0.13	0.23	0.45	0.42
25	278	39	55	201	113	351	755	1	84	2.20	22.80	7.29	0.02	0.16	0.33	0.27	0.13	1.98	0.56
26	304	31	75	217	131	292	798	2	114	1.31	20.25	5.38	0.00	0.47	1.84	0.23	0.25	1.63	0.18
27	205	38	39	200	74	469	481	1	111	1.18	16.11	6.76	0.01	0.75	1.81	0.23	0.27	0.46	0.33
28	269	21	20	90	50	262	515	4	52	1.52	19.38	9.03	0.02	0.47	3.30	0.48	0.13	0.35	0.09
29	475	90	168	404	192	161	390	1	116	1.46	21.06	6.50	0.01	1.00	6.12	0.25	0.27	5.85	0.43
30	182	18	16	157	35	414	653	1	31	0.91	13.39	10.96	0.01	1.03	6.12	0.30	0.40	0.72	0.21
31	544	73	225	320	282	154	435	14	67	0.94	17.09	6.63	0.02	1.37	14.15	0.30	0.41	7.51	0.11
32	280	30	15	263	61	453	372	2	137	1.92	17.46	4.18	0.01	0.16	0.42	0.19	0.11	2	0.2
33	500	80	125	297	203	190	1,033	13	83	0.81	9.74	7.53	0.03	0.90	29.09	0.28	0.34	11.62	0.71
34	353	51	108	262	192	230	878	3	140	1.99	17.69	5.61	0.01	0.35	0.67	0.27	0.18	3.45	0.52
35	1,029	114	293	513	380	121	412	25	48	2.00	21.88	9.80	0.05	0.25	1.31	0.27	0.15	13.41	0.2
36	657	185	311	345	333	170	2,000	16	134	1.67	14.65	5.91	0.01	0.37	1.40	0.12	0.23	7.29	0.13
37	714	117	222	401	301	151	737	21	75	0.80	15.00	6.56	0.01	1.31	21.13	0.34	0.44	15.42	0.6

Table 2
Statistical values of metal contents (major elements in wt%, trace elements in ppm, fraction of <63 µm) in phosphorites and in different zones of studied soils, BG Background, F enrichment factors

	Cr	Cu	Ni	V	Zn	Zr	Sr	Cd	Pb	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Corg.
Phosphorite bulk sediment (n=17)	Min.	126	55	38	92	116	19	207	2	13	0.05	0.90	0.36	0.09	6.89	0.19	0.04	4.96	0.02
	Max.	707	511	363	339	1,869	93	18,004	109	160	0.42	30.86	16.04	0.57	48.32	0.52	0.25	40.89	0.22
	Mean	356	158	109	173	465	46	1,429	44	67	0.17	5.21	3.62	0.25	33.86	0.30	0.10	29.55	0.10
	Median	314	85	113	147	276	44	364	43	63	0.18	3.36	2.12	0.18	36.04	0.26	0.10	29.90	0.07
All soil samples, fraction <63 µm (n=37)	Min.	182	18	15	90	35	80	266	0.18	15	0.28	9.74	1.13	0.005	0.13	0.00	0.11	0.35	0.06
	Max.	1,029	356	432	513	563	469	3,161	43	140	2.20	27.55	13.93	0.66	31.24	0.48	0.44	22.15	1.14
	Mean	484	106	138	279	211	234	825	13	72	1.22	17.29	6.74	0.62	11.24	0.25	0.24	8.24	0.42
	Median	464	90	106	263	192	190	528	13	67	1.20	17.09	6.56	0.62	7.62	0.27	0.22	7.29	0.42
Transport routes (n=9)	BG	173	63	46	178	73	343	146	0.39	104	2.01	24.01	8.57	0.1	0.3	0.82	0.58	0.16	0.43
	F	2.7	1.4	2.3	1.5	2.6	0.6	3.6	32.4	0.6	0.6	0.7	0.8	0.2	1.4	0.5	1.4	17.0	-
	Min.	217	46	58	192	125	80	361	3	27	0.66	9.74	5.55	0.007	0.25	0.26	0.15	2.47	0.06
	Max.	1,029	138	327	513	417	234	1,033	38	140	2.00	21.88	9.80	0.05	0.90	0.38	0.38	21.78	0.71
Newly abandoned exploitation areas (n=8)	Mean	679	101	199	357	288	153	575	21	69	1.15	14.62	7.36	0.03	0.63	0.29	0.26	12.85	0.39
	Median	694	114	215	355	308	130	517	25	67	0.93	15.64	7.50	0.03	0.66	0.28	0.27	13.41	0.47
	BG	173	63	46	178	73	343	146	0.39	104	2.01	24.01	8.57	0.1	0.3	0.82	0.58	0.16	0.43
	F	4.0	1.8	4.7	2.0	4.2	0.4	3.5	63.7	0.6	0.5	0.7	0.9	0.3	2.2	0.5	1.7	31.2	-
Old abandoned exploitation areas (n=15)	Min.	182	18	16	90	35	86	383	1	21	0.28	11.48	1.13	0.006	0.29	0.53	0.00	0.35	0.06
	Max.	890	287	432	404	563	414	3,161	28	116	1.52	26.60	13.93	0.04	1.37	0.48	0.44	18.39	0.43
	Mean	528	99	163	290	239	175	808	12	65	0.87	17.34	7.28	0.02	0.85	0.26	0.30	8.55	0.21
	Median	509	86	137	338	210	145	467	14	60	0.80	16.61	6.56	0.02	0.94	0.27	0.27	7.49	0.20
	BG	173	63	46	178	73	343	146	0.39	104	2.01	24.01	8.57	0.10	0.30	0.82	0.58	0.16	0.43
	F	2.9	1.4	3.0	1.9	2.9	0.4	3.2	36.4	0.6	0.4	0.7	0.8	0.2	3.1	0.5	1.7	17.4	-
	Min.	199	27	22	174	67	140	266	0.2	15	0.52	10.48	3.12	0.005	0.13	0.33	0.12	0.11	0.45
	Max.	714	356	311	401	333	469	2,000	21	134	2.20	27.55	8.33	0.05	1.31	0.34	0.44	15.42	0.87
	Mean	335	108	78	222	136	308	881	6	73	1.39	18.73	6.08	0.02	0.44	0.23	0.21	4.56	0.45
	Median	254	52	56	200	123	292	737	3	75	1.34	18.15	5.95	0.01	0.37	0.23	0.21	2.47	0.45
	BG	173	63	46	178	73	343	146	0.39	104	2.01	24.01	8.57	0.10	0.30	0.82	0.58	0.16	0.43
	F	1.5	0.8	1.2	1.1	1.7	0.9	5.0	7.7	0.7	0.7	0.8	0.7	0.1	1.2	0.4	1.3	5.7	-

Fig. 4

Distribution of cadmium in the soil fraction of $<63 \mu\text{m}$ around the mining areas in Kpogamé and Hahotoé

Fig. 5

Distribution of Cr, Zn, Ni (A) and Cu and Sr, V, Zr and Pb (B) in soil fraction of $<63 \mu\text{m}$ around the mining areas in Kpogamé and Hahotoé

sinks for all metals (Gnandi 1998). Released Cd is preferentially adsorbed onto the calcite and iron oxide phases. This fact is concordant with the research results given by some authors who found that, although numerous trace metals in sedimentary phosphorites show a high affinity with the phosphatic phase (Gilinskaya et al. 1993), some of them are also present by adsorption on other mineral and organic phases in the ore (Jarvis et al.