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Contamination of the Xiropotamos stream sediments (Drama district, Western Rhodope massif, Northern Greece) by mining and manganese ore processing activities

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Замърсяване на седименти на река Ксиропотамос (район Драма, Западнородопски масив, Северна Гърция) в резултат на миннодобивна дейност и обогатяване на манганови руди

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Резюме. Мангановите находища в района на гр. Драма, Северна Гърция, са експлоатирани активно в периода 1950–1994 г. От миннодобивната и обогатителната дейност са останали огромни количества рудни отпадъци, съдържащи дребнозърнести руди, и насипи от обогатена руда, изоставени в района на неработещия рудник и обогатителната фабрика на Като Неврокопи. Вследствие на дългогодишното изветряне и транспорт на тези отпадъци, седиментите на река Ксиропотамос са замърсени с тежки метали. Извършените изследвания на седиментите с помощта на прахова рентгенография, оптична микроскопия, сканираща електронна микроскопия и електронносондов микроанализ показват, че главните прозрачни минерали са кварц, калцит, слюди и фелдшпат, а от непрозрачните в най-големи количества се намират тодорокит, пиролузит, бирнесит, коронадит и гьотит. Химичният анализ на седиментите установява следните съдържания за някои тежки метали (в ppm): Mn – 131863, Zn – 3302, Pb – 1612, Ba – 542, Cu – 158, Sr – 991 и Ni – 74. Тези стойности значително надвишават средните съдържания на тези елементи за почвите в света, а някои от тях и международните стандарти за безопасни почви. Особено това се отнася до концентрациите на Mn, Pb, Zn и отчасти на Cu, които са много над допустимите фитотоксични нива. Микросондовият анализ на мангановите минерали установява повишени съдържания на тези метали: 33,34 тегл.% PbO, 4,28 тегл.% ZnO, 1,99 тегл.% CuO в коронадита, 14,61 тегл.% ZnO в бирнесита, 2,00 тегл.% PbO, 3,51 тегл.% ZnO, 0,90 тегл.% CuO и 0,72 тегл.% BaO в тодорокита, 1,28 тегл.% ZnO в пиролузита. Тези резултати показват, че главният източник на тежки метали в речните седименти са мангановите минерали, идващи от рудните отпадъци – резултат от миннодобивната и обогатителната дейности в Като Неврокопи. Еоличната ерозия на рудните отпадъци и излужването на тези замърсители, както и възможно наводнение, могат да засегнат земеделските земи и водните екосистеми в целия район. Необходимо е да се вземат предпазни мерки, за да се спре пренасянето на рудни отпадъци от изоставения рудник чрез река Ксиропотамос до река Ангитис и заобикалящите ги земеделски земи.

Ключови думи: Драма, замърсяване, тежки метали, минна дейност, замърсители.

Abstract. An extensive exploitation of Mn-ore took place during the period 1950 to 1994 in the Drama district, Northern Greece. Mining and ore processing has created a vast amount of wastes including tailings, low grade ore and heaps of concentrated ore, which were deposited around the central establishment of Kato Nevrokopi. A long time transportation of these wastes by fluvial processes has affected the Xiropotamos stream sediments by a serious contamination with some toxic heavy metals. X-ray powder diffraction, optical microscopy, SEM and EPMA studies of the Xiropotamos stream sediments showed that quartz, calcite, micas and feldspars are the prevailing gangue minerals, while goethite and the Mn-oxide minerals todorokite, pyrolusite, birnessite and coronadite are the widely present opaques. Bulk chemical analyses of the sediments revealed the following average contents for some heavy metals: Mn – 131863, Zn – 3302, Pb – 1612, Ba – 542, Cu – 158, Sr – 991, and Ni – 74 (all values in ppm). These values significantly exceed the average soil composition worldwide, and some of them the international safety standards for soils. Specifically, the concentrations of Mn, Pb, Zn, and partly of Cu are far in excess of the stipulated phytotoxic levels. Electron probe microanalyses of the Mn-minerals revealed metal contents, as high as: 33.34 wt.% PbO, 4.28 wt.% ZnO, and 1.99 wt.% CuO in coronadite, 14.61 wt.% ZnO in birnessite, 2.00 wt.% PbO, 3.51 wt.% ZnO, 0.90 wt.% CuO and 0.72 wt.% BaO in todorokite, and 1.28 wt.% ZnO in pyrolusite. These results suggest that the prime cause of stream sediments contamination are the manganese minerals introduced to the sediments by the run-off of mining and ore processing wastes of Kato Nevrokopi. A wind erosion of these wastes, or a leaching of their pollutants as well as a possible land flooding process may influence the agricultural fields of the surrounding area and the aquatic ecosystem. Thus, some protective measurements have to be taken in order to stop the transportation of wastes from the disused establishment, through the Xiropotamos stream to the Angitis river and the surrounding plain.

Key words: Drama, contamination, heavy metals, mining activities, pollutants.

Introduction

Heavy metals are a notable source of pollution both in the aquatic and the soil environments. Many heavy metals (e.g. Co, Cu, Mn, Zn, Sr etc) are essential in small amounts for biological viability. However, all of them when present in high concentrations may cause toxic effects on biota and may constitute long term health risk to ecosystem and humans (Ewers, 1988, 1991; Adriano et al., 2005). Soil contamination by heavy metals affect the flora and fauna, the water aquifers and through them the human food chain (Lacatusu et al., 1996; Stojanov, 1999; Urzelai et al., 2000; Samsoe-Peterson et al., 2002; Turkdogan et al., 2002; Nicholson et al., 2006). Thus, determination of the concentration of these elements in the polluted environment is important in assessing their potential environmental impact.

The introduction and concentration of heavy metals into soils and sediments has been the subject of increasing study in recent decades (Alloway, 1990; Forstner, 1995; Stojanov, 1999; Sirotkin et al., 2000; Kabata-Pendias, Pendias, 2001).

Soil enrichment in heavy metals may be caused by both natural factors (geogenic) and anthropogenic pollution.

Mining, ore processing or smelting activities and waste disposals constitute the major anthropogenic sources inducing heavy metals in the environment (Demetriades et al., 1996; Siegel, 2002; Weber, Karczewska, 2004).

Drama region was one of the most extensively mined areas in Greece during the period 1950 to 1994 with more than 7 Mt total concentrate production of Mn-oxide of dry-cell battery type (Nimfopoulos et al., 1997a). The main center of mining and the establishment of ore processing are located adjacent to the Drama-Kato Nevrokopi main road, 25 km from Drama town (41°15'19'' N – 23°58'23'' E).

Mining and Mn-ore processing discarded vast amounts of wastes including tailings, low grade ore and waste waters. However, mining activities in the area ceased in 1994, and the wastes as well as large heaps of concentrated ore stay around the Kato-Nevrokopi establishment. All these materials are dry and uncovered and emission of dust from them by the winds may impact the surrounding area. Besides, leaching of pollutants from the mine tailings by the drainage water may affect the surface water and groundwater, and hence the aquatic ecosystem.

The Xiropotamos stream, a tributary of Angitis river, passes through the Kato Nevrokopi area, erodes the mining wastes and transports them towards the alluvial river terrace (Fig. 1). During winter months the stream sediments can be discharged onto the agricultural fields and meadows via a possible land flooding process and therefore can influence the surface layers of the soils.

River sediments constitute a significant sink of metals in the river environment. For this reason pollutant contents in sediments are used as a sensitive and reliable indicator for geochemical impact assessment.

The present research examines the prospective contamination of the Xiropotamos stream sediments by some heavy metals as byproducts of the manganese mining activities in the Kato Nevrokopi area.

Study area

The study area geologically belongs to the western part of the Rhodope massif. The Mn-mineralization of the Drama district is scattered in an area of approximately 170 km^2 near the Greek-Bulgarian border, but the main mines are the 25th km and Mavro Xylo (Fig. 1) known as the Kato Nevrokopi mining and ore-processing center. The mineralization is hosted by a thick sequence of Paleozoic marbles (Upper carbonate Sequence) which has been thrust over a sequence of alternating gneisses, mica schists, amphibolites and marbles (Lower Gneiss Sequence). These two sequences form the Rhodope Massif basement (Dimadis, Zachos, 1989). The Mn-mineralization is confined to the intersection of the northeast -and northwest- trending faults (Fig. 1) and the thrust zone forming the junction between the Upper Carbonate and the Lower Gneissic unit. The mineralization contains supergene ores predominantly composed of Mn-oxides and has developed by weathering of continental hypogene rhodochrosite-sulphide veins (Nimfopoulos, 1988; Nimfopoulos, Pattrick, 1991; Michailidis et al., 1995, 1997; Nimfopoulos et al., 1997a, 1997b).

Sampling and analytical methods

Sampling

A total of twelve sampling sites were chosen along the course of the Xiropotamos stream, starting from the Kato Nevrokopi mining and ore processing center up to the Angitis main river. Besides, one side located at about 3 km to the east of the stream was sampled and was considered as unpolluted background refer-

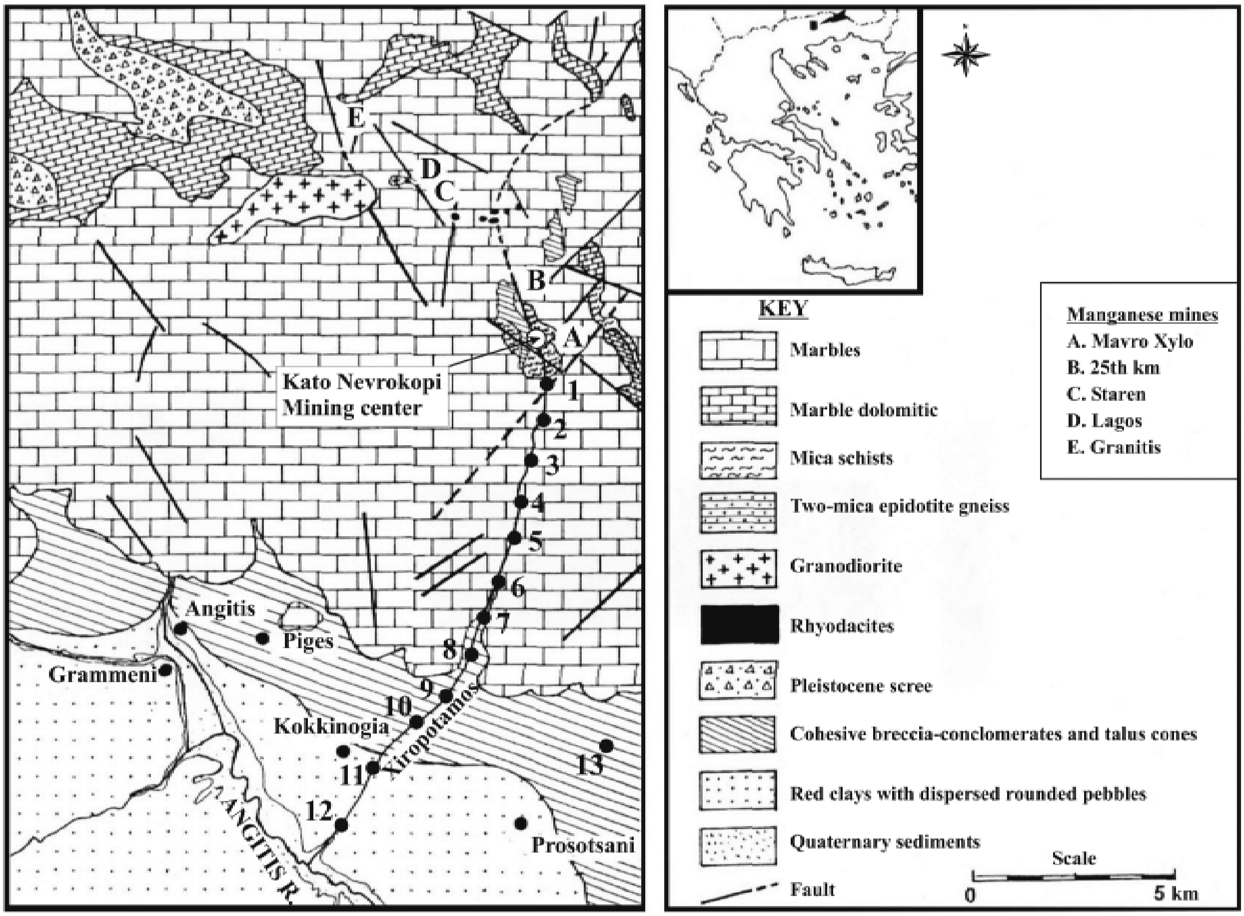

Fig. 1. Simplified geological map and manganese mineralization at Kato Nevrokopi, Drama. Sampling sites (1–12) along the course of the Xiropotamos stream and the reference sample (13) are also depicted.

Фиг. 1. Схематична геоложка карта на района Като Неврокопи, Драма с местата на манганови минерализации. Представени са и местата на опробване (1–12) по протежение на р. Ксиропотамос както и на фоновата проба (13).

ence (Fig. 1). Samples were collected at 0–20 cm depths. For each side, a composite sample was taken using material from at least three different places. Plastic and wooden tools were used for sampling, and samples were stored in clean plastic bags. After removing organic material and rock fragments the samples were ground using an unglazed porcelain mortar and pestle and then sieved by hand through a 2 mm sieve. Then, they were pulverized in an agate planetary mill to a grain size < 0.063 mm for further analytical work.

Analytical methods

The pH values of the sediment samples were measured in the leachates of distilled water and sediment in a ratio 30 g sediment: 30 ml H_2O, at room temperature (22 ± 2°). A pH meter Corning model Checkmate II, equipped with a temperature sensor was used.

The mineralogical composition of the stream sediment samples was determined by the X-ray powder diffraction method using a Philips PW 1710 diffractometer. The XRD patterns were recorded at $1° \ 2\theta \times min^{-1}$ with Ni-filtered Cu-Kα radiation.

Polished sections of selected samples were also examined by transmitted and reflected light microscopy in order to characterize opaque mineral phases and gangue mineral associations.

Electron probe microanalyses (EPMA) on opaque minerals were carried out with a JEOL JSM-840 Scanning Electron Microscope (SEM) equipped with a LINK system energy-dispersion analyzer. Operating conditions were: accelerating voltage 15 kV, beam current 3 nA, beam diameter 1 μm and counting time 100 seconds. Natural minerals or pure metals were used as standards. Element concentrations have been calculated with a ZAF-4/FLS software provided by LINK.

Chemical analyses for major, minor elements and heavy metals were assessed on bulk, unfractionated sediment samples by atomic absorption spectroscopy using a Perkin Elmer 901A instrument. An aqua regia extraction method for heavy metals was used.

Results and discussion

pH values and mineral constituents of the sediments

The pH values measured on the stream sediments were neutral to slightly alkaline (7.00–7.96) with an average value of 7.52. The highest pH value was shown by the samples far from the Kato Nevrokopi site. The pH of the background reference sample was 7.50.

The color of the stream sediments was dark grey to black due to the presence of Mn-oxide minerals, while the reference sample has a brown to reddish one.

X-ray diffraction and microscopy studies of the Xiropotamos stream sediment samples showed that the prevailing gangue minerals are quartz, calcite, mica and feldspars. Thus, the mineral composition of the sediments is comparable to the mineralogy of the rocks hosting the Mn-mineralization (mainly marbles, gneisses and mica schists).

Reflected light microscopy and SEM studies revealed also the presence of goethite and the manganese-oxides todorokite, pyrolusite, birnessite and coronadite as the opaque mineral phases in the sediments. Identification of the Mn-minerals was based on the microprobe analyses and SEM images as well as on the detailed work of Michailidis et al., (1997) who additionally used the X-ray powder diffraction method for this purpose. These Mn-minerals are among the main constituents of the secondary manganese ore deposits of the broader Drama area (Nimfopoulos, 1988; Micahilidis et al., 1997).

Bulk chemical composition of the sediments

Major and minor elements

Bulk chemical analyses showed that SiO_2, CaO and MnO contents (Table 1) vary in a broad range, designating the main mineral constituents (silicates, carbonates and manganese-oxide minerals) of the sediments and their quantitative variation.

The loss on ignition (LOI) is high reflecting the content of CO_2 and fixed water in minerals.

Heavy metals

Several countries have defined classes of soil quality criteria (no restriction on land use) and cut-off criteria (any contact with the soil should be omitted), or otherwise maximum allowable limits (MAL) of concentration of heavy metals in soils (Kloke, 1980; Ewers, 1991; Kabada-Pendias, 1995; Urzelai et al., 2000; Kabada-Pendias, Pendias, 2001). However, some of these thresholds were changed and there was no general agreement concerning the maximum allowable concentrations of heavy metals in contaminated (or polluted) soils and river sediments.

The concentration of metallic elements in the stream sediments can be compared with the soil composition for understanding the possible presence of a pollution process induced by human activity (Bianchini et al., 2002).

The heavy metal (Mn, Pb, Zn, Cu, Ni, Sr and Ba) concentrations in the Xiropotamos stream sediments and the reference sample are presented in Table 2. Besides, in Table 3 the mean and minimum to maximum values of metal concentrations are compared with the average soil composition (Siegel, 1974), the minimum, average, and maximum contents in surface soils worldwide (Kabada-Pendias, Pendias, 2001), the maximum allowable limits (MAL) of concentration of heavy metals in soils as quoted by Kloke (1980), Ewers (1991), Kabata-Pendias (1995), the maximum phytotoxic levels (Kabata-Pendias, Pendias, 2001) and the limits of concentration levels for toxic elements and heavy metals as quoted by the EU Council Directive 1991 and the Greek Government law 1995 for soils with pH > 7. An enrichment factor (EF) or pollution index (PI) was also calculated (as the

Table 1
Bulk chemical analyses (wt.%) of the Xiropotamos stream sediment samples

Таблица 1
Валов химичен анализ (тегл.%) на седиментите от р. Ксиропотамос

Sample	SiO_2	Al_2O_3	TiO_3	MnO	Fe_2O_3*1	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI*2	Total
1	36.26	7.78	0.13	9.08	2.76	0.92	17.31	2.29	5.09	0.30	18.52	100.44
2	31.16	6.07	–	15.91	2.20	0.61	20.33	1.92	4.17	0.60	17.33	99.76
3	32.09	7.11	0.09	13.71	3.72	1.11	16.89	1.98	4.67	0.03	19.79	101.19
4	25.02	5.49	–	20.39	3.97	1.05	19.06	1.53	3.50	0.06	19.45	99.52
5	29.04	6.29	–	21.47	4.50	0.73	15.20	1.88	4.19	0.12	16.61	100.03
6	31.67	6.34	–	19.89	3.29	0.51	15.63	1.94	4.24	0.03	15.54	99.08
7	31.29	6.44	–	19.65	3.57	0.59	16.00	1.91	4.33	0.08	16.08	99.94
8	28.24	5.17	–	25.48	3.47	0.49	16.63	1.56	3.55	0.07	20.04	99.95
9	36.21	10.79	0.34	7.25	6.56	1.61	13.20	2.14	4.99	0.22	17.72	101.03
10	27.95	6.19	0.09	16.69	3.70	1.08	16.82	1.71	4.06	0.24	21.38	99.91
11	26.67	5.29	–	18.04	2.55	0.86	21.57	1.63	3.61	0.06	19.08	99.36
12	32.29	6.64	0.14	16.72	3.51	0.54	16.69	1.98	4.28	0.05	16.89	99.73

*1 Total iron as Fe_2O_3
*2 Loss on ignition

Table 2
Heavy metals (ppm) concentrations in the Xiropotamos stream sediments and the background reference sample

Таблица 2
Съдържание на тежки метали (ppm) в седиментите на р. Ксиропотамос и във фоновата проба

Sample	Ba	Co	Cr	Cu	Ni	Pb	Sr	Zn	Mn
1	331	<30	<20	50	86	430	775	1151	70334
2	536	<30	<20	114	62	1068	987	2809	123239
3	465	<30	<20	139	90	1310	987	2157	106198
4	651	<30	<20	231	74	3046	1140	5180	157941
5	740	<30	<20	153	76	1684	1136	4460	166307
6	677	<30	<20	308	54	2168	1126	4300	154068
7	564	<30	<20	292	88	2036	1113	4220	152209
8	676	<30	30	105	48	1422	1151	3990	197368
9	331	<30	<20	173	102	1830	461	3870	56159
10	516	<30	<20	123	62	1812	846	1655	129281
11	584	<30	<20	108	76	1518	1143	3420	139738
12	428	<30	<20	94	74	1020	1028	2412	129513
13*	520	–	21	24	25	61	640	152	1120

*Background reference sample

ratio of the element concentration in the stream sediment versus the average soil composition (after Kloke, 1980) to show the degree of pollution (Table 3).

In the uncontaminated soil sample (13) the concentrations of all elements were found within the normal range of surface soils as was quoted by Kabata-Pendias and Pendias (2001). The variations in concentration of the analyzed heavy metals along the course of the Xiropotamos stream are presented in Figure 2, along with the levels of average soil composition, the phyrotoxic and regulatory values.

The mean concentrations of the heavy metals were (values in ppm): Mn – 131 863, Zn – 3302, Pb – 1612, Sr – 990, Ba – 542, Cu – 158, and Ni – 74.

As results from Table 3 and Figure 2 the levels of Mn, Zn, and Pb measured in the Xiropotamos stream sediments are extremely higher than the maximum accepted by European and Greek legislation concentrations for soils with pH > 7 . These heavy metals will have immediate negative effects on plant growth and development (for they exceed the phytotoxic levels) or on other environmental components. So, the

Table 3
Heavy metal concentration (ppm) statistics for comparison with the Xiropotamos stream sediments

Таблица 3
Статистики за съдържание на тежки метали (ppm) за сравнение със седиментите на р. Ксиропотамос

Element	1	2	3	4	5	6	7
Mn	131863 70333–197368	850	155.13	500	558 80–1315	1500–3000	1000
Zn	3302 1151–5180	50	66.04	300	67 17–236	70–400	300
Pb	1612 430–3046	10	161.2	100	29 8–67	100–400	200
Cu	158 50–308	20	7.87	100	24 6–80	60–125	150
Ni	74 68–102	40	1.85	50	24 6–92	100	110
Ba	542 331–740	500	1.08	400	527 207–960	–	–
Sr	990 461–1151	240	4.13	–	190 15–675	–	–

1. Mean, minimum-maximum values of the Xiropotamos stream sediments
2. Average soil composition (after Siegel, 1974)
3. Enrichment factor (E.F)
4. Maximum allowable limits (after Kloke, 1980; Ewers, 1991; Kabata-Pendias, 1995)
5. Mean, minimum-maximum values of surface soils (after Kabata-Pendias, Pendias, 2001)
6. Phytotoxic range levels (after Kabata-Pendias, Pendias, 2001)
7. Threshold values regulated by the E.C. and Greek legislation

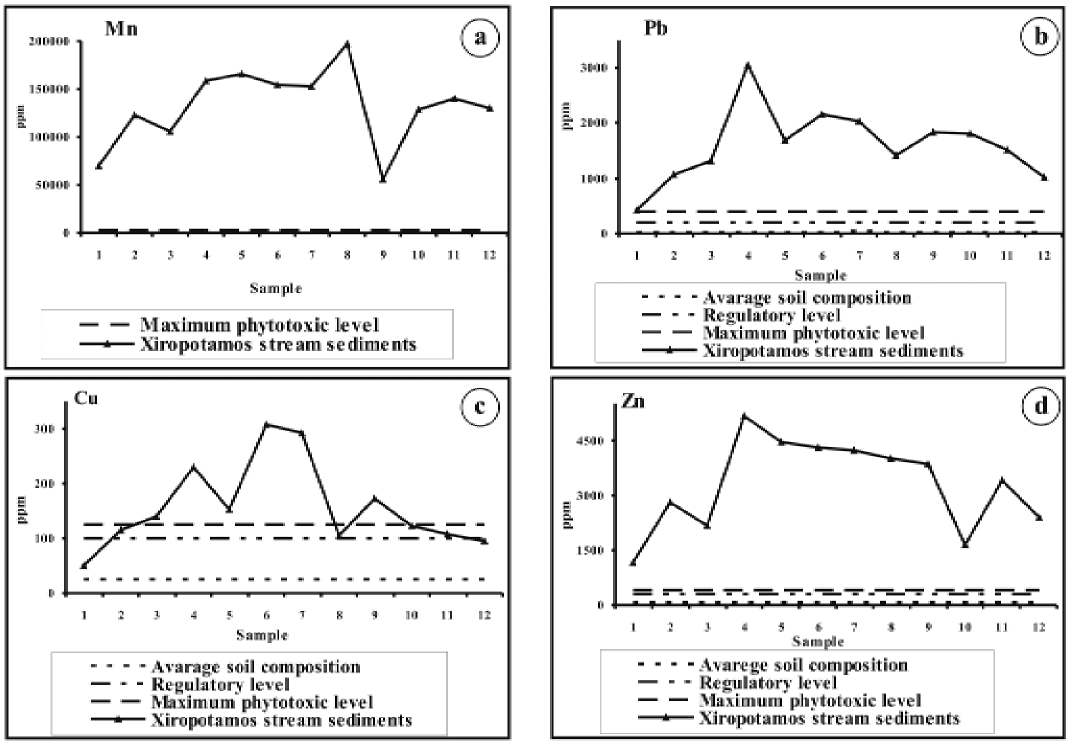

Fig. 2. Variation in concentrations of: a) Mn; b) Pb; c) Cu and d) Zn along the course of the Xiropotamos stream. Average soil composition and maximum phytotoxic levels after Kabada-Pendias and Pendias (2001), and maximum levels regulated by the E.C. and Greek legislations are also depicted.

Фиг. 2. Промяна в съдържанието на: a) Mn; b) Pb; c) Cu; d) Zn по протежение на р. Ксиропотамос. Посочени са и средният химичен състав и максималните фитотоксични нива според Kabada-Pendias и Pendias (2001) и максималните нива определени от ЕС и гръцкото законодателство.

stream sediments are characterized as strongly to extremely strongly polluted sediments in Mn, Zn and Pb.

The range of Cu (50–308 ppm) concentration showed that all samples exceed the average soil composition (Siegel, 1974; Kabada-Pendias, Pendias, 2001). Ten samples exceed the maximum allowable limit value (100 ppm) established by Kloke (1980) but only three the maximum accepted concentration (150 ppm) for soils with pH > 7. Six samples exceed the phytotoxic range (60–125 ppm) as quoted by Kabada-Pendias and Pendias (2001). Average Cu concentration (158 ppm), however, may pose a hazard to the environment and the studied sediments are characterized as medium polluted.

The range of Ni (68–102 ppm) concentrations exceed the average soil composition (Siegel, 1974), as well as the maximum accepted concentration (50 ppm) for soils (Kloke, 1980). However, only one sample exceed the phytotoxic level (100 ppm) and none the maximum accepted concentration (110 ppm) for soils with pH > 7. For these reasons the Xiropotamos stream sediments are considered as uncontaminated for Ni.

The range of Ba (331–740 ppm) concentration is within the normal range of surface soils (Kabada-Pendias, Pendias, 2001), while the mean value (542 ppm) is very close to the average soil composition quoted by Siegel (1974) and Kabada-Pendias, Pendias (2001) (500 and 527 ppm respectively).

Chaudry et al. (1977) (Kabada-Pendias, Pendias, 2001) reported more than 1 wt.% of Ba as toxic concentration in plants. However, Kloke (1980) considered as maximum allowable limit for Ba the 400 ppm content of soils.

The variation of Sr concentrations (461–1151 ppm) as well as the mean concentration (991 ppm) in the studied sediments exceed the values quoted by Siegel (1974) and Kabada-Pendias and Pendias (2001). However, there is no evidence that stable Sr at levels present in the biosphere may have any deleterious effects on man and animals.

SEM and EPMA studies

As stated by Nimfopoulos (1988), Michailidis et al. (1997) and Nimfopoulos et al. (1997a, 1997b) the Mn-oxide phases of the Kato Nevrokopi Mn-ores are the hosts of heavy metals as follows: nsutite for Zn, Pb, Ni, Ba, As, birnessite for Zn and Ba; todorokite for Zn±Cu±Ba and pyrolusite, chalcophanite and rancieite for Zn.

Scanning electron microscopy examination and electron microprobe analyses confirmed the presence

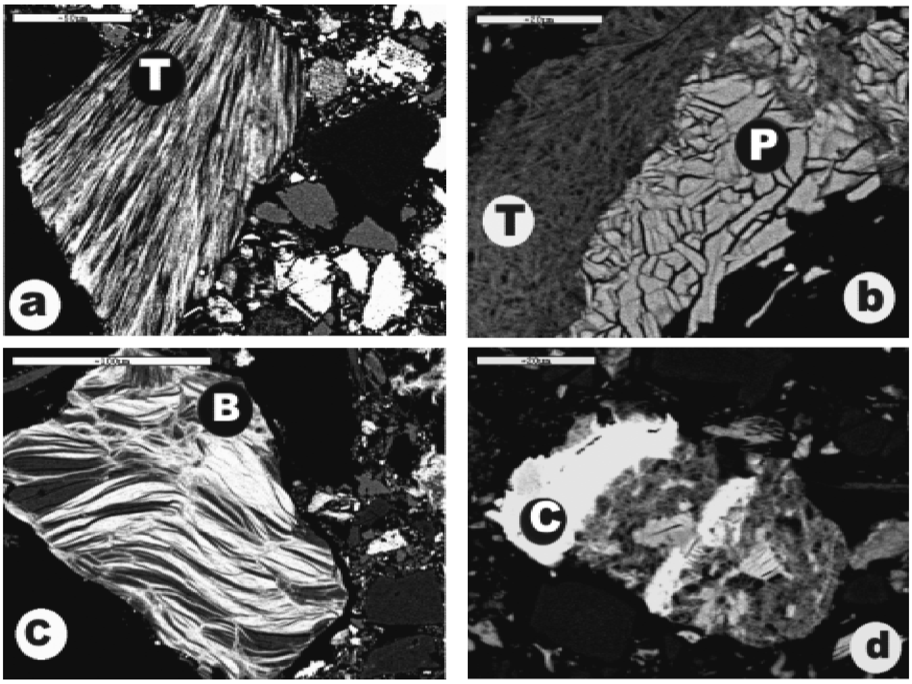

Fig. 3. SEM photomicrographs of Mn-minerals from the Xiropotamos stream sediments: a) fan-shaped todorokite grain (T); b) pyrolusite (P) replacing fibrous todorokite (T); c) flake birnessite grain (B); d) coronadite (C)

Фиг. 3. СЕМ снимки на мангановите минерали от седиментите на р. Ксиропотамос: a) тодорокит (T); b) пиролузит (P), заменящ тодорокитови фибри (T); c) бирнесит (B); d) коронадит (C)

Table 4
Representative electron probe microanalyses of Mn-oxide minerals and goethite from the Xiropotamos stream sediments

Таблица 4
Представителни микросондови анализи на мангановите минерали и на гьотит от седиментите на р. Ксиропотамос

Oxides wt. %	1	2	3	4	5	6	7	8	9	10	11	12
MnO_2	74.99	74.33	72.19	94.28	95.36	79.60	63.16	78.24	50.16	56.32	46.35	1.34
Fe_2O_3	0.49	0.13	1.21	0.10	0.42	bd	0.22	bd	3.86	0.62	8.60	53.90
SiO_2	0.27	0.22	0.25	0.42	0.60	0.10	bd	0.20	0.47	0.30	1.02	2.08
Al_2O_3	0.05	0.10	0.05	0.03	0.08	bd	bd	0.04	0.45	bd	0.99	4.66
CaO	2.94	3.00	2.21	0.48	0.64	1.86	0.39	0.86	0.43	0.75	0.32	0.46
MgO	3.00	2.26	0.56	0.04	0.06	bd	1.45	bd	0.69	0.50	0.96	2.12
Na_2O	0.92	1.22	3.40	0.06	bd	0.32	12.70	0.32	0.71	1.69	1.06	4.33
K_2O	1.22	1.06	0.06	0.04	bd	0.18	0.16	0.27	bd	0.16	0.27	bd
ZnO	1.37	1.96	3.51	1.28	1.14	5.47	14.61	5.86	1.68	4.28	3.16	4.27
NiO	0.18	0.05	0.18	0.04	0.05	bd	0.18	0.04	0.14	0.28	bd	bd
SrO	0.03	0.04	0.04	bd	bd	bd	bd	bd	0.04	0.07	0.66	bd
BaO	0.70	0.60	0.72	bd	bd	0.52	0.68	0.54	0.45	0.28	0.55	0.66
PbO	0.12	0.48	2.00	bd	bd	0.36	0.24	0.12	33.34	28.57	29.09	0.40
CuO	0.33	0.90	0.29	bd	bd	0.08	bd	bd	1.59	1.36	1.99	1.41
Total	86.61	86.35	86.67	98.35	98.35	88.49	93.79	86.49	94.01	95.18	95.06	75.63

bd, below detection limit
1–3, todorokite; 4–5, pyrolusite; 6–8, birnessite; 9–11, coronadite; 12, goethite

of goethite, todorokite, pyrolusite, birnessite and coronadite in the Xiropotamos stream sediments (Fig. 3).

Goethite (Table 3) was found with high contents of Zn (4.27 wt.% ZnO) and Cu (1.41 wt.% CuO).

The Mn-minerals were found containing variable amounts of the elements Pb, Zn, Cu, Ba, and Ni (Table 4). Zinc was detected in all Mn-minerals varying between 1.14 and 14.61 wt.% ZnO. Copper and Pb display the higher concentrations in coronadite with 1.99 wt.% and 33.34 wt.%, respectively. Barium is present in all mineral phases with a maximum content of 0.72 wt.% BaO in todorokite .

These results suggest that the principle sources of heavy metal inputs to the stream sediments are the Mn-minerals added to the sediments via the run-off of the mining and ore processing wastes.

Because of the low solubility of the Mn-compounds in oxidizing environment and alkaline pH levels the heavy metals migrate with the sediments and less in solution.

Conclusions

The Xiropotamos stream is the recipient of the solid wastes coming from the mining and manganese-ore processing activities at Kato Nevrokopi.

The color of the sediments was black indicating a possible enrichment in pollutants from the Mn-ore wastes.

The geochemical study showed that the stream sediments were severely contaminated (or polluted) by some heavy metals and toxic elements.

Continuous severe contamination of the stream sediments carry the possibility of pollution of the soil and aquatic environment in the broader area, via land flooding and leaching processes.

Mean values of Mn (131863), Pb (1612), Zn (3302), Sr (990), Cu (158) and Ni (74), (all contents in ppm) are significantly higher than the average soil composition.

The concentrations of Mn, Pb, Zn and partly Cu, are far in excess of the maximum stipulated phytotoxic levels and the levels regulated by E.C. and Greek legislations.

The Mn-oxide minerals present in the sediments are considered as the pollutants. Metal contents in their composition were found as high as: 33.34 wt.% PbO, 4.28 wt.% ZnO and 1.99 wt.% CuO in coronadite, 14.61 wt.% ZnO in birnessote, 2.00 wt.% PbO, 3.51 wt.% ZnO, 0.90 wt.% CuO and 0.72 wt.% BaO in todorokite and 1.28 wt.% ZnO in pyrolusite.

Pollutants migrate in the Xiropotamos stream with the sediments and less in solution because of the alkaline water pH and the aerobic conditions.

The heaps of mining wastes are the main source of metal pollution to the Xiropotamos stream, and may affect all elements of the surrounding area.

Preventing heavy metal pollution is critical because cleaning contaminated soil is extremely expensive and difficult.

Thus, some protective measurements have to be taken to stop the transportation of the heavy metal-rich solid wastes from Kato Nevrokopi through the Xiropotamos stream to the Angitis river and the surrounding alluvial terrace.

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