Scientific Annals, School of Geology, Aristotle University of Thessaloniki Proceedings of the XIX CBGA Congress, Thessaloniki, Greece	Special volume 100	63-69	Thessaloniki 2010

ASSESSMENT OF HEAVY METALS CONCENTRATIONS IN SEDIMENTS OF BOGDANAS RIVER AT THE ASSIROS-LAGADAS AREA, NORTHERN GREECE

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Abstract: Bogdanas river flows east of Thessaloniki, in Northern Greece. Its sources are found at the western part of the Vertiskos mountain and flows along the Assiros and Lagada plane towards Koronia lake. In this study, variations of the heavy metal concentrations in Bogdanas river sediments has been evaluated. Sediment samples were collected at 8 representative sampling sites along the river, during two sampling periods. Chemical analysis indicated that the sediment samples show variable concentrations of heavy metals. Sediment quality assessment according to the limits determined by the European Community's legislation indicated that the river sediments were not contaminated, apart from 3 samples and 1 sample concerning Zn and Cu, respectively. On the other hand, sediment quality assessment according to the US EPA Sediment Quality Guidelines (SQG), revealed that there was heavy metal pollution with respect to especially Zn, Cu and Ni. Concerning Zn, only 1 sample is close to the EPA's moderately polluted level, while 10 samples surpass it and 5 samples exceed the EPA's heavily polluted level. Concerning Cu, 7 samples are classified as moderately polluted and 9 samples as heavily polluted. Finally, no pollution is defined for Ni, apart from 2 samples which are classified as moderately polluted. In conclusion, the research showed that the revealed heavy metal pollution is more attributed to the lithology of the area and less to human activity.

Keywords: Bogdanas river, Koronia lake, heavy metals, sediments, Assiros, Lagadas, Northern Greece

1. Introduction

The contamination of the surface water bodies with heavy metals has been attracting considerable public attention over the past few decades. Heavy metals can be added to an aquatic system either by natural or anthropogenic sources.

Heavy metals released to aquatic systems are generally bound to particulate matter, which are eventually incorporated into sediments (Suthar et al., 2009). Thus, sediments are an efficient mean of accumulation and downstream transport of inorganic contaminants, like heavy metals (Espinosa et al., 2009). It is a proven fact that heavy metals induce toxic effects on living organisms, therefore they can pose a high risk when found in high concentrations in sediments (Förster and Salomons, 1991). For this reason limit values for heavy metals have been proposed for the protection of these endangered habitats (Zehl and Einax, 2005).

An example of an aquatic system which is constantly downgrading is that of Koronia lake in central Macedonia, Greece. The water of the lake has been extensively polluted by agricultural and cattle livestock activities as well as by industrial wastes. According to Tzimopoulos et al. (2006) and Gantidis et al. (2006) the quality of the water has worsened–due to the bio-accumulation of the heavy metals and the concentration of toxic algal blooms in the lake.

The pollution of Koronia's water body has increased by the torrents which discharge at the catchment basin of the area and flow into the lake. One of these torrents is Bogdanas river which springs from the western slopes of the Vertiskos Mountain. Bogdanas river flows with a W-SW direction towards Assiros town and then turns to the south. Following that, it passes west of Lagadas

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town and finally flows into the northwestern part of the Koronia lake (Fig. 1).

During the field surveys along Bogdanas river various injurious human activities were observed, such as the discharge of untreated urban waste liquids from Assiros and Lagadas towns into the river and the existence of uncontrolled landfills and cultivated fields, which may have played a significant role in the Bogdanas river pollution.

The aim of this study is to determine the concentrations of toxic heavy metals such as Pb, Cd, Zn, As, Cu and Ni in the Bogdanas's sediments, in order to evaluate, firstly, the degree of the river's environmental pollution and secondly to investigate if there is any possible pollution that is caused to the Koronia lake by the river.

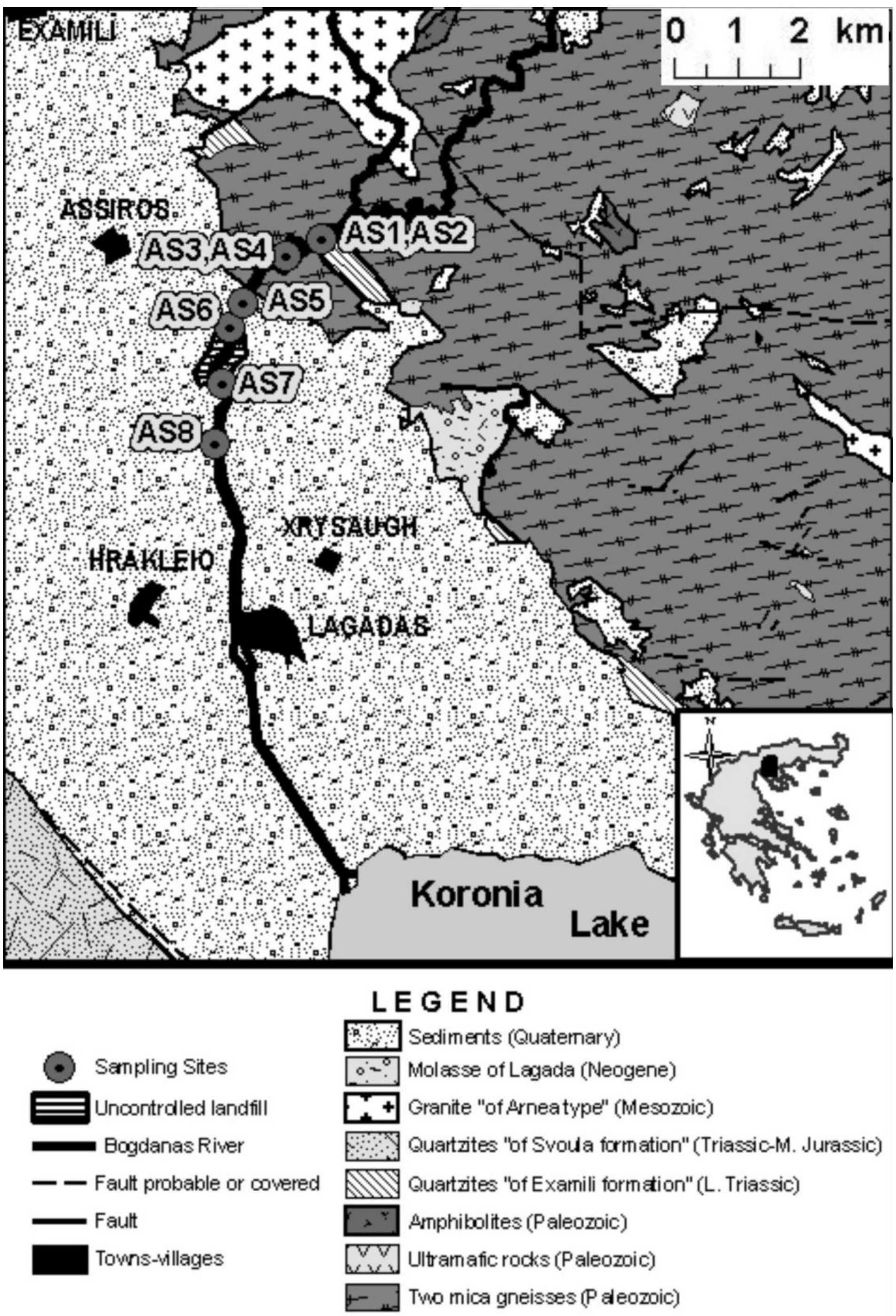

Fig. 1. Geological map of the western part of the Mygdonian basin with the Bogdanas river and the sampling sites (according to Kockel et al., 1978, 1979, with modifications).

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2. Geological Setting

The studied area belongs to the boundary between the Serbomacedonian massif and the Circum Rhodope belt, at the western part of the Mygdonian basin, which comprises a tectonic graben (Fig. 1).

The bedrock of the Bogdana's river water catchment basin consists of Alpine and Pre-alpine metamorphic rocks, such as gneisses, amphibolites, quartzites and ultrabasic rocks (Kockel et al., 1978; Kockel et al., 1979). Significant is the presence of a two-mica and biotite granite, of Arnea type, that intrudes these rocks (De Wet, 1989; Kostopoulos et al., 2001). The Mygdonian basin contains Oligocene to Quaternary sedimentary deposits with a thickness of 50 to 450 m. They consist of clays, sands and gravels (Psilovikos, 1977; Tranos et al., 1999). Normal neotectonic faults cut the basement rocks as well as the younger sediments which overlie them (Chatzipetros and Pavlides, 1998).

Numerous restricted ore mineralizations are found in the broader area. According to Vavelidis et al. (1999) and Melfos et al. (2001) mineralized quartz veins are located in Drakontio and Stefania areas, at the northern part of the region. They relate to Cu, Fe, Pb, Zn, As, Bi, Au, Ag, Co, Ni. A small occurrence of a copper mineralization with a old underground excavation is also located east of Assiros town, by the Bogdanas river (Giouri, 2008).

3. Materials and Methods

3.1. Sampling

For the purposes of the present study, 8 sites (AS1 to AS8) were sampled for their sediments downstream Bogdanas river, between Assiros town and Koronia lake (Fig. 1). It should be mentioned that sites AS1 and AS3 are close to AS2 and AS4, respectively, with the first two being at the river banks and the two latter being at the river bed. Sixteen sediment samples were collected at the top of the riverbed and its banks, avoiding the input of ground materials.

Sampling was carried out during July 2006 corresponding to the dry season of the summer. In the meantime, the public authorities of the region tried to apply measures in order to eliminate any human activities in the wider area. Sampling was repeated in February 2009, corresponding after the rainy season, so as to ascertain the measures' adjustment.

3.2. Laboratory treatment of the sediments

All samples were collected with a plastic shovel and were put in plastic bags. At the laboratory, after the removal of organic material, samples were dried in an oven at 60˚C. They were gently ground with rolling pin to disaggregate the samples but not break down the grains themselves, and sieved to collect less than 0.063 mm grain sizes.

The sediment portion with particle size <0.063mm was used to determine the heavy metal concentrations. Contaminants accumulate mainly in the finest particles of sediments (<0.063 mm) due to the larger surface area and the presence of reactive sites. So the environmental available trace elements remain mainly in this fraction (Fernandez-Turiel et al., 2001; Kabata-Pendias and Pendias, 2001). For this reason, fine sediments have been used to investigate river pollution around the world (Salomons, 1995; Murray et al., 1999).

The metals in the sediment samples were extracted using the aqua regia digestion while heated at 120˚C for 12 hours. The samples were centrifugated during 10 min at 2500 rpm. All the extracts were diluted to 50 ml with deionized water in volumetric flasks and stored in polyethylene bottles until analysis.

3.3. Analysis of heavy metals

The sediment samples were analyzed for their concentration in Pb, Cd, Zn, As, Cu and Ni. The concentrations of Pb, Cd and Ni were determined by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS), with a Perkin Elmer AA400 atomic absorption spectrophotometer, equipped with an HGA 900 furnace programmer. The concentrations of Zn and Cu were determined by Flame Atomic Absorption Spectrophotometry (FAAS) using the same instrument (AA400). Total Arsenic concentration was measured using the hydride generation technique applied with a FIAS apparatus. The heavy metal analyses were carried out by the Environmental Pollution Control Laboratory at the Department of Chemistry in Aristotle University of Thessaloniki.

4. Results and Discussion

The results of the chemical analysis that was carried out in the finest fraction of sediment samples collected in Bogdanas river, are presented in table 1.

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Table 1. Heavy metal concentrations at every sampling site of the studied area in mg/g of dry weight.

Sample	Sampling Period	Pb (mg/g)	Cd (mg/g)	Zn (mg/g)	As (mg/g)	Cu (mg/g)	Ni (mg/g)
AS1a	Jul-2006	17.2	bdl	354.1	1.6	104.2	15.4
AS2a		31.0	bdl	133.1	1.6	50.4	13.1
AS3a		22.5	bdl	148.2	1.6	62.4	14.1
AS4a		2.0	0.1	423.1	1.7	117.8	12.1
AS5a		12.2	bdl	178.4	1.5	48.6	0.3
AS6a		3.6	bdl	268.9	1.5	171.1	27.9
AS7a		0.1	bdl	99.6	2.1	72.8	bdl
AS8a		12.3	bdl	316.3	1.5	138.0	0.2
AS1b	Feb-2009	27.5	bdl	112.0	1.4	33.1	bdl
AS2b		33.5	0.1	71.1	1.5	34.1	bdl
AS3b		12.2	0.1	139.3	1.3	44.7	1.6
AS4b		11.7	0.1	102.7	1.4	44.7	21.7
AS5b		0.1	bdl	91.6	1.2	36.4	18.3
AS6b		1.8	0.1	139.6	0.8	69.5	bdl
AS7b		0.2	bdl	156.1	1.0	41.9	bdl
AS8b		0.8	0.2	229.2	1.3	50.4	0.3
Mean		11.8	<0.05	185.2	1.4	70.0	<8

bdl : below detection limit

According to the results, Pb varies from 0.1 to 33.5 mg/g dw with a mean of 11.8 mg/g dw. Cd is generally very low in all sampling sites, reaching 0.1 mg/g dw. Its mean content is <0.05 mg/g dw. Zn concentrations present significant variations in some sites and range from 71.1 mg/g dw to the extremely high value of 423.1 mg/g dw for the sample AS4a. The average content is 185.2 mg/g dw. Arsenic rises up to 2.1 mg/g dw with an average of 1.4 mg/g dw. Cu also shows significant variations at most of the sites, ranging from 33.1 mg/g dw to the elevated value of 171.1 mg/g dw (sample AS6a) with a mean content of 70.0 mg/g dw. Finally, Ni concentrations at some sites are below the detection limit and at the others they reach up to 27.9 mg/g dw for the sample AS6a. The average content for Ni is <8 mg/g dw.

Table 2 shows the maximum allowable concentrations of heavy metals as they are proposed in the directives of the European Community (EC), taken from Kabata-Pendias and Pendias (2001). Additionally, sediments were classified as non-polluted, moderately polluted and heavily polluted, based on the Sediment Quality Guidelines (SQG) of US Environmental Protection Agency (EPA) (Perin et al., 1997).

These limits were compared with the concentrations of the heavy metals measured in the sediments of the Bogdanas river, in order to evaluate the degree of the sediments contamination. The diagrams at figure 2 illustrate the heavy metals concentrations at every sampling site during the two sampling periods, in relation with the sediment quality guidelines.

All the samples contain Pb concentrations which are lower than the limits established by the European Community and EPA. Cd is very low and its concentrations are below the limits of EC and EPA. Zn concentrations show remarkable variations between the two sampling periods and most of them do not fulfill the established sediment quality guidelines. More particularly, samples AS1b, AS2a, AS3a and b, AS4, AS5a and b, AS6b

Table 2. Sediment Quality Guidelines determined by the EC and US EP.

Sediment Quality Guidelines	mg/g dw					
	Pb	Cd	Zn	As	Cu	Ni
EC [1]	300	3	300	20	150	75
EPA [2]						
Non Polluted	< 40	-	< 90	< 3	< 25	< 20
Moderately Polluted	40-60	-	90-200	3-8	25-50	20-50
Heavily Polluted	> 60	> 6	> 200	> 8	> 50	> 50

[1]: Maximum allowable heavy metals concentrations as they are determined by the legislation of the European Community (EC), taken from Kabata-Pendias and Pendias (2001).
[2]: Sediment Quality Guidelines as they are determined by the US Environmental Protection Agency (EPA) (Perin et al., 1997).

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and AS7a and b are classified as moderately polluted, while samples AS1a, AS4a, AS6a and AS8a and b are classified as heavily polluted in relation to Zn. Concerning As, its concentrations are lower than the limits determined either by EC or EPA and their values remain relatively in the same level between the two sampling periods. Concerning Cu, most of the samples (AS1a, AS3a, AS4a, ASa and b, AS7a and AS8a and b) are classified as heavily polluted and all the rest as moderately polluted. Based on EC's limits, only one sample (AS6a) exceeds them reaching up to 171.1 mg/g dw. Finally, concentrations of Ni are in general below limits, with an exception of two samples (AS4b and AS6a) which exceed EPA's limit for moderately polluted sediments.

Considering all the data mentioned above, it is assumed that at most sites the concentrations of heavy metals in the sediments of 2006 sampling period are higher than the respective ones of 2009 (Fig. 2). There is no significant pollution detected concerning Pb, Cd and As. In spite of that, concentrations of Pb, Cd and As that were determined in some samples are mostly associated with the lithology of Bogdana's catchment basin than with the anthropogenic activities that were detected in the region. This is due to the fact that the sites in which Pb and Cd concentrations were determined are mainly in the northern part of the basin. In this area, according to Vavelidis et al. (1999) and Melfos et al. (2001) there are ore mineralizations at Drakontio and Stefania areas which contain small quantities of Pb related mainly to galena and of Cd found in the structure of sphalerite. Arsenic concentrations remain at the same level in every sample, indicating that it exists in the sediments along the river and doesn't derive from point pollution sources. Minerals such as cobaltite, gersdorffite and chalcopyrite contain As in the mentioned mineralization (Vavelidis et al., 1999; Melfos et al., 2001). Zn and Cu show almost similar behavior at

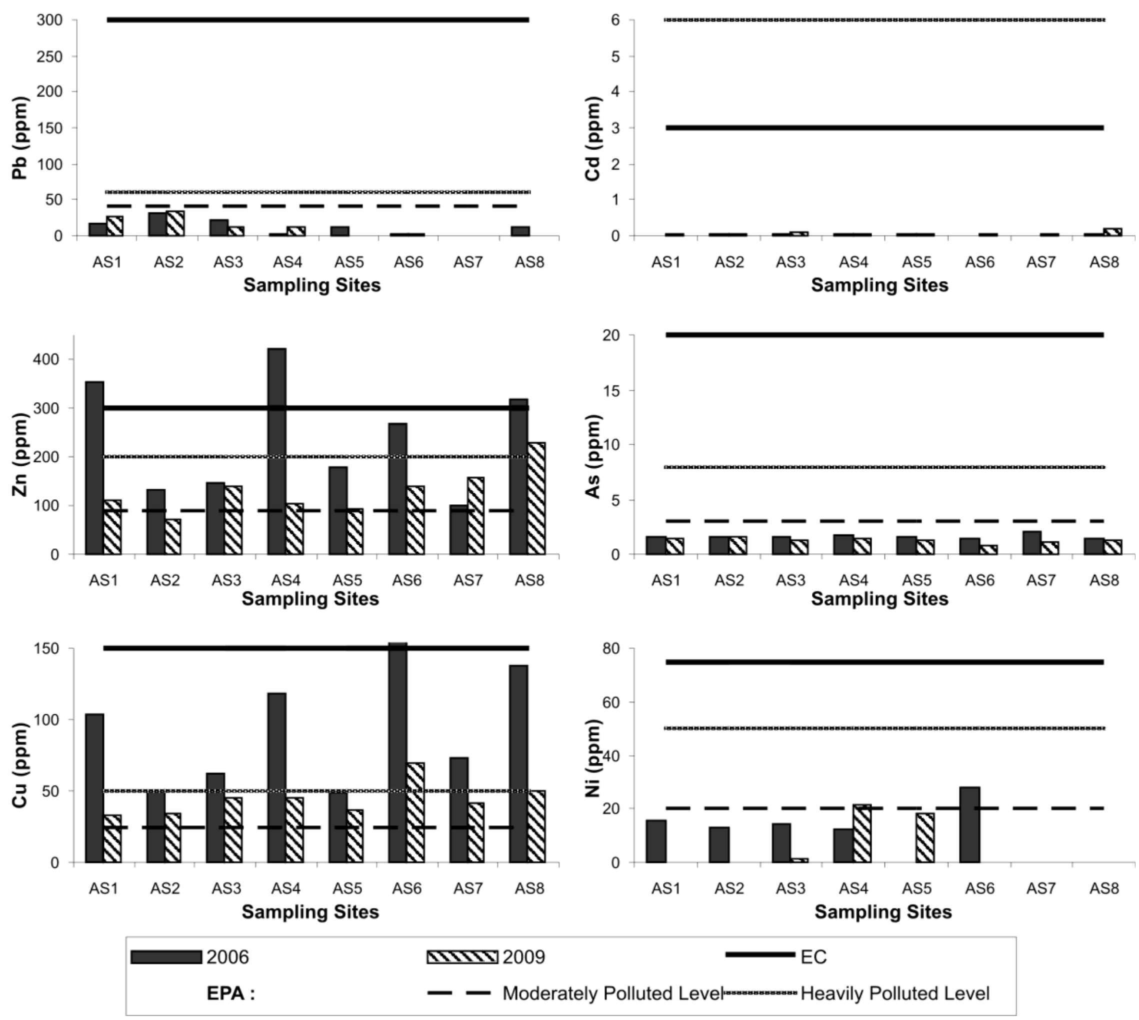

Fig. 2. Concentrations of Pb, Cd, Zn, As, Cu, and Ni in sediments collected from Bogdanas river, in comparison with EC and EPA Sediment Quality Standards.

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the Bogdanas sediments and their relatively elevated concentrations are connected probably with the weathering of the ore mineralizations in Drakontio, Stefania and Assiros (Vavelidis et al., 1999; Melfos et al., 2001; Giouri, 2008). This is emphasized by the fact that the higher Zn concentrations coexist at the same sites with the higher Cu concentrations. Similar behavior was observed for Ni, which is probably attributed also to the weathering of the ore mineralizations, which mainly contain gersdorffite and ultramafic rocks that exist in the region contributes to its concentrations. The elevated concentrations of Zn, Cu and Ni at sites AS5, AS6 and AS7, especially in the 2006 sampling period, may have also been affected by the presence of an extensive uncontrolled litter landfill, very close to Assiros town. So the presence of batteries for example, could contribute to the increasing of Ni and Zn concentrations. The fact that the area was evacuated by all the litters meantime, affected the chemical composition of the sediments in the 2008 sampling period, and the Zn, Cu and Ni concentrations were lower.

5. Conclusions

The results of the chemical analyses at the sediments of Bogdanas river showed very limited and insignificant heavy metal contamination. Comparing the concentrations of Pb, Cd, Zn, As, Cu and Ni, with the limits determined by the European Community's legislation it is concluded that sediments are polluted at a percentage of 19% for Zn and 6% for Cu. Comparing these concentrations with the US EPA Sediment Quality Guidelines (SQG) it is concluded that in relation to Zn, 62.5% of the sediments are classified as moderately polluted and 31% as heavily polluted. As for Cu, a percentage of 44% and 56% are classified as moderately and heavily polluted, respectively. In addition, only the 12.5% of the sediments are classified as moderately polluted concerning Ni. The heavy metal concentrations in the Bogdanas sediments are mainly related to the lithology of the broader area and especially to the copper mineralizations in Drakontio, Stefania and Assiros areas, than to human activities. Part of the contamination is possibly attributed to the human activities, and mainly the presence of an extensive uncontrolled litter land fill near Assiros town. This is supported by the differences of some heavy metal contents (Zn, Cu, Ni) between the first sampling period of 2006 and the second sampling period of 2008. The higher heavy metal concentrations in the first period indicate that especially at the sites close to the uncontrolled landfill, metal bearing materials (such as batteries) could contribute to the sediments of the river. The decrease of the heavy metal contents in 2008 show that the public authorities applied the appropriate environmental measures established by legislation.

Acknowledgements

The first author (Giouri A.) would like to thank the State Scholarships Foundation of Greece for the financial support during her post-graduate studies.

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