A CORRELATION STUDY OF MAJOR AND TRACE ELEMENTS IN SEDIMENTS OF RIVER NESTOS, NORTHERN GREECE AND COMPARISON WITH OTHER FLUVIAL SYSTEMS

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ABSTRACT

Fourteen sediment samples from the banks of River Nestos, Northern Greece, were collected, extracted with HNO_3 and analyzed for their content in 10 major and 32 trace elements. The analytical techniques used were ICP-OES and ICP-MS. The calculation of the Pearson Correlation Coefficient amongst the analyzed elements has revealed that among the majority of the elements exist positive correlations, which explains why most of them have a similar distribution along the river course. A comparison between the results acquired for the River Nestos and other fluvial systems, national and international, has shown the similarity of the geochemical identity of the River Nestos sediments with these systems.

Keywords: Trace elements, correlation, sediment, River Nestos, Greece.

INTRODUCTION

Sediments and soils may be regarded as important sinks or sources, depending on their physicochemical properties, for trace elements, especially sediments in aquatic environments. Elevated concentrations of Potentially Toxic Trace Elements (PTTE), particularly heavy metals, in sediments may be mobilized and accumulated in microorganisms, aquatic flora and fauna, which, in turn, may enter into the human food chain and result in health problems. A variety of human activities, but mainly industry and agriculture, have contributed to increase the concentrations of environmentally important trace elements through many ways such as waste disposal, atmospheric deposition, fertilizer and pesticide use, and other means (Fernandez-Turiel et al. 1995, Hesterberg 1998, Kabata-Pendias and Pendias 2001, Sin et al. 2001, Sarkar et al. 2004, Papastergios 2008).

During the past years, River Nestos, which is called Mesta in Bulgaria, has been monitored for his monthly flow, water and air temperature, redox potential, dissolved oxygen, chemical content of its water for some elements and Hg in fish tissues and several other parameters (Darakas 2002, Petalas et al. 2005, Psilovikos et al. 2006, Christoforides et al. 2008), while at the same time, several studies have been published regarding water management problems and transboundary river basin management (Diadovski et al. 2007, Mimides et al. 2007, Mylopoulos et al. 2008). Additionally, recent research has contributed to the study of the elemental content and distribution of the river sediment load (Papastergios et al. 2008).

The aim of the present work was to further contribute to the assessing of the geochemistry of major and, especially, trace elements in the Nestos River sediments, as well as, exploring their interrelationships. This research is regarded as a contribution to the environmental monitoring of the River Nestos and its hydrological basin, a major concern in northern Greece due to the occurrence of areas of great ecological interest as well as the development of important economic activities in this region.

STUDY AREA

Nestos, is regarded as one of the most important transboundary rivers in the Balkan Peninsula. Its delta is one of the most sensitive wetlands in Greece, if not in Europe. Because of its biodiversity the delta of River Nestos accommodates a variety of habitat types and flora and fauna species that are not found anywhere else in Europe, which has resulted in the protection of the area by the RAMSAR treaty as an internationally important wetland complex (Darakas 2002, Efthimiou et al. 2003, Kallioras et al. 2006, Psilovikos et al. 2006) (Fig. 1).

The wetlands which are located within the river delta are influenced, to a great extent, by the operation of two Greek large dams that are constructed upstream (Papastergios et al. 2008), namely Thisavros and Platanovrisi (Fig. 1). The construction of these dams by DEH (Public Power Corporation of Greece S.A.) in the early 90s, has aroused great concern about their impact on the river downstream (Darakas 2002, Efthimiou et al. 2003, Petalas et al. 2005, Kallioras et al. 2006, Psilovikos et al. 2006). On the Bulgarian part of the river operates the dam of Despat which was constructed and operated before the dams of the Greek side. As a result of the human activities taking place in both the Bulgarian and Greek part of the river, several types of contaminants are introduced into the river flow (i.e., wastewater, either treated or untreated, pesticides or fertilizers residues and others) (Darakas 2002, Papastergios et al. 2008).

GEOLOGICAL SETTING

The study area (Fig. 1) is a part of the Rhodope massif, which mainly consists of: a) gneisses, schists and amphibolites (Permian-Eocene), b) marbles (Permian-Eocene), c) granitic and granodioritic rocks (Eocene-Miocene), d) acid-intermediate volcanic rocks (Eocene-Miocene) and e) sedimentary deposits (Miocene-Holocene). The intense plutonism of the Rhodope is represented by granites, granodiorites, monzonites, quartz monzonites and diorites while its volcanic activity is represented by basalts to rhyolites (Kilias et al. 1999, Christofides et al. 2001, Zagorchev 2007). Furthermore, inside the Greek part of the river Nestos catchments' area several ore occurrences of PBG sulfides, Mn and other elements can be found (Epitropou and Chatzipanagis 1989, Nimfopoulos and Pattrick 1989, Filippidis et al. 1996, Vavelidis et al. 1996, 1997).

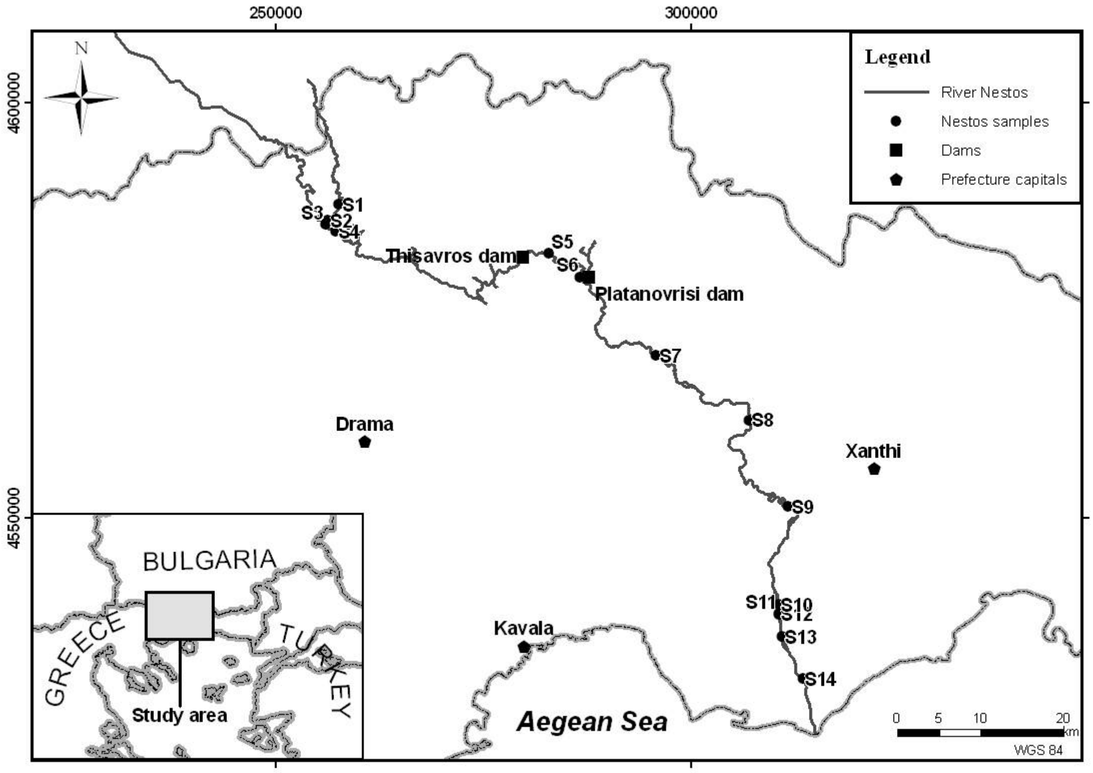

Figure 1. Map showing the course of River Nestos in Greece, the sample sites and the locations of Thisavros and Platanovrisi dams.

MATERIALS AND METHODS

Fourteen samples from the banks of River Nestos were collected between December 2002 and January 2003. The samples are distributed through the whole Greek part of the river (Fig. 1). All samples were dried in an oven at 40^{o}C and the <200 μm fraction was used due to the fact that the environmentally available trace elements mainly remain in this fraction (Fernandez-Turiel et al. 1995, Kabata-Pendias and Pendias 2001)

Ten major (Al, Ca, Cl, Fe, K, Mg, Na, P, S and Si), and 32 trace element (Ag, As, B, Ba, Cd, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hg, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Th, Ti, U, V, W, Y, Zn and Zr) concentrations were determined in all samples by ICP-OES and ICP–MS. The analyzed elements were extracted by using analytical grade nitric acid. The HNO_3 extraction procedure is a very strong acid digestion that puts in solution almost all elements that could become "environmentally available" (Sastre et al. 2002, Papastergios et al. 2006, Papastergios 2008). Analytical grade HNO_3 has been selected in order to work with extreme conditions and maintain, at the same time, the compatibility of the leachate with the input solution for chemical analysis (direct determination after dilution). The analyses were performed at the SCT – UB (Scientific Technical Services of the University of Barcelona), Barcelona (Spain). Details regarding the ICP-MS analysis can be found in Fernandez-Turiel et al. (2000) and regarding the extraction procedure in Papastergios (2008) and Papastergios et al. (2008).

RESULTS AND DISCUSSION

The Pearson Correlation Coefficient (r) measures the strength and direction of linear relationships between two or more random variables and ranges from −1 to 1 (Howarth and Sinding-Larsen 1983, Paine 1998, Bluman 2003). In the present study r is used to describe the interrelationships between the elements analyzed at a significance level (p) of < 0.01.

The calculation of *r* revealed that no negative linear relations exist among the major elements, or the trace elements, or even between major and trace elements. Among the major elements, Al, Fe, K and Mg are positively correlated with correlation factors between 0.86 and 0.99, indicating a highly positive relation which explains the similar distribution that these elements show throughout the Nestos River (Papastergios et al. 2008). A high positive correlation (*r*: 0.98) is, also noted between Na and Cl which, again explains the similar distribution of these elements in the sediments of the river. Silicon has no significant correlation with any major element or with any trace element. However, this behavior could be attributed to the extraction method applied to this research. Although, Ca, P and S also, do not have any significant correlation between them or with any other major element, if the significance level is changed to $p<0.05$ instead of $p<0.01$ some positive relations among them and the rest of the major elements are revealed, explaining with they follow the same pattern as the rest of the elements, but not with the same degree of similarity (Papastergios et al. 2008).

The most important observation that arises from the calculation of the *r* for the trace elements is that elements such as Cd, Pb and Zn do not have any positive relations with none of the elements analyzed, both major and trace. Because of the presence of PBG occurrences in the study area, one would expect that elements such as these would be genetically associated and, thus, have positive correlation among them or with other elements such as S, As and others. The lack of this correlation could be attributed to the influence of the distribution of these elements by the anthropogenic activities taking place along the river course. Another element with no significant *r* is Zr, but the reason for this, probably, is the same as for Si.

Regarding the rest of the elements, a series of positive correlations among them is noted. Elements such as As, As, Ce, Co, Cr, Cs, Ge, Hg, La, Li, Ni, Rb, Sb, Th, V, W and Y show positive correlations between them and with many of the analyzed elements, explaining their similar behavior in the river sediments. From the remaining elements, B is correlated only to Sn (*r*: 0.89), Ti to Li (*r*: 0.82) and U to Ce (*r*: 0.80).

A comparison of the River Nestos average concentrations, for some of the most environmentally important elements (i.e., Cd, Cu, Pb, Zn), with other fluvial systems in Greece (Table 1) and Europe (Table 2) has revealed that these elements have similar or lower concentrations to the fluvial systems used for comparison.

Table 1. Comparison between the average concentrations (mg kg^{-1}) for seven elements of the River Nestos and other fluvial systems in Greece.

Element	Nestos[1]	Evros[2]	Acheloos[3]	Strimon[4]	Axios[4]	Aliakmon[4]	Pinios[4]
Cd	0.3	0.4	-	1.1	3.3	1.1	1.8
Cr	22.5	77.3	54.7	-	-	-	-
Cu	19.1	43.0	24.1	25.0	27.3	19.5	27.6
Mn	477.8	-	552.0	1006.0	553.0	425.0	424.0
Ni	18.1	39.4	87.8	43.8	95.0	232.0	154.0
Pb	22.3	60.1	-	20.0	20.5	10.4	6.5
Zn	77.8	115.0	54.7	82.5	95.0	42.5	50.0

[1] Papastergios et al. 2008, [2] Kanellopoulos et al. 2006, [3] Dassenakis et al. 1995, [4] Sawides et al. 1995

Table 2. Comparison between the average concentrations (mg kg^{-1}) for several trace elements of the River Nestos and other fluvial systems in Europe.

Element	Nestos[1]	Belgium-Luxemburg[5]	Spain[6] (Manzanares)	Bulgaria (Danube)[7]
Ag	0.1	-	4.1	-
As	2.7	18.0	23.0	-
Ba	101.5	393.0	303.0	-
Cd	0.3	2.0	-	0.6
Co	7.8	12.0	6.0	-
Cr	25.5	116.0	38.0	117.0
Cs	2.7	6.0	-	-
Cu	19.1	34.0	71.0	52.6
Hg	0.1	-	0.5	0.2
Mn	477.8	-	481.0	-
Ni	20.3	26.0	19.0	47.7
Pb	18.6	79.0	118.0	183.0
Rb	35.8	68.0	-	-
Sr	17.2	73.0	-	-
Th	8.3	10.0	-	-
V	28.5	64.0	31.0	-
Zn	66.8	231.0	130.0	130.0

[1] Papastergios et al. 2008, [5] Swennen et al. 1998, [6] de Miguel et al. 2005, [7] Ricking and Terytze 1999

CONCLUSIONS

No negative linear relations exist among the major elements, or the trace elements, or even between major and trace elements. Elements such as Cd, Pb and Zn do not have any positive relations with none of the elements analyzed. The luck of this correlation could be attributed to the influence of the distribution of these elements by the anthropogenic activities. Among the majority of the rest of the elements exist high positive correlations, which explain why they have similar distributions throughout the river course. The environmental quality of the river sediments seems to be similar to those of other fluvial systems, both national and international.

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