

Natural and anthropogenic effects on the sediment geochemistry of Nestos river, Northern Greece

Georgios Papastergios · Jose-Luis Fernández-Turiel ·
Andreas Georgakopoulos · Domingo Gimeno

Received: 7 August 2008 / Accepted: 28 October 2008 / Published online: 13 November 2008
© Springer-Verlag 2008

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 methods used were ICP-OES and ICP-MS. The results indicate that the sediments in the northern Greek part of the river have the highest elemental concentrations partly because of human activities, but mainly due to natural processes. The two dams that have been constructed in the middle course play a buffering role on the elemental content, for all the elements analyzed, of the river sediments, decreasing downstream concentrations and sediment load. An increase of concentrations is newly observed in the low course and delta because of the mobilization of fine sediments by natural processes and agricultural practices. The comparison of the river sediment contents with contaminated land guidelines has not revealed any potentially dangerous concentrations for the elements analyzed.

Keywords Trace elements · Sediments · Geochemistry · River Nestos · Greece

Introduction

Trace elements, especially heavy metals, in sediments may lead to irreversible health diseases while, at the same time, playing an important role on the ecological quality of an ecosystem. It is certain that a variety of human activities often mobilize and redistribute the natural content of trace elements in the environment so much that they, in some cases, can cause adverse effects. High levels of heavy metals in sediments and soils 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 (Kabata-Pendias and Pendias 2001; Sin et al. 2001; Sastre et al. 2002; Cui et al. 2005; Papastergios 2008). Both 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 (Hesterberg 1998; Kabata-Pendias and Pendias 2001; Cui et al. 2005; Papastergios 2008).

Sediment is mainly composed of inorganic and organic particles and can be considered as a relatively heterogeneous media matrix, in terms of its biological, chemical and physical properties. Sediments and soils may be regarded as important sources, depending on their physicochemical properties, for trace elements, especially sediments in aquatic environments (Fernández-Turiel et al. 1995). Trace elements are introduced in such environments through many ways, such as atmospheric deposition, erosion of geological materials or through anthropogenic activities (Sin et al. 2001; Sarkar et al. 2004).

G. Papastergios (✉) · A. Georgakopoulos
Department of Mineralogy-Petrology-Economic Geology,
School of Geology, Aristotle University of Thessaloniki,
54124 Thessaloniki, Greece
e-mail: gpapaste@geo.auth.gr

J.-L. Fernández-Turiel
Institute of Earth Sciences “Jaume Almera”,
Consejo Superior de Investigaciones Científicas (CSIC),
Lluís Solé i Sabarís, s/n 08028, Barcelona, Spain
e-mail: jlfernandez@ija.csic.es

D. Gimeno
Department of Geochemistry,
Petrology and Geological Exploration,
University of Barcelona, Zona Universitària de Pedralbes,
Martí i Franquès, s/n 08028, Barcelona, Spain
e-mail: domingo@natura.geo.ub.es

The chemical analysis of river sediments is a useful method for studying metal contamination in an area (Dalmacija et al. 2006; Papastergios 2008). Furthermore, sediments not only act as the carrier of contaminant substances, but also may contribute, as a potentially secondary source, to the deterioration of the aquatic system by releasing trace elements found in their surface, into the water phase, through various processes (Kabata-Pendias and Pendias 2001; Sin et al. 2001; Sarkar et al. 2004).

River Nestos has been monitored during the past years for several parameters, such as water level, water and air temperature, water conductivity, monthly flow, redox potential, dissolved oxygen, chemical content of its water for some elements and Hg in fish tissues (Darakas 2002; Petalas et al. 2005; Psilovikos et al. 2006; Christoforides et al. 2008). Moreover, several studies have been published regarding water management problems and transboundary river basin management, from both Greek and Bulgarian sides (Diadovski et al. 2007; Kampragou et al. 2007; Mimides et al. 2007; Eleftheriadou and Mylopoulos 2008; Mylopoulos et al. 2008). However, to the knowledge of the authors, no research has been available until now, regarding the elemental content and distribution of the river sediment load. The present paper aims to do so and to further contribute to assess the distribution of major and, especially, trace elements in the Nestos river sediments. This research is 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, which is called Mesta in Bulgaria, is one of the most important transboundary rivers in the Balkan Peninsula. Its source is located at Mt Rila, in central Bulgaria, and discharges into the Thracian Sea (North Aegean Sea), where it forms its delta, which is one of the most sensitive wetlands in Greece, if not in Europe. The total area of the river basin is around 5,750 km², lying about 60% of this area in Bulgaria. The length of the river course is about 230 km, around 135 km of which are within Greece. The Greek part of Nestos river flows through the prefectures of Drama, Xanthi and Kavala and contributes to the recharge of karstic springs which are a significant source for the irrigation and water supply needs for these prefectures (Darakas 2002; Kallioras et al. 2006) (Fig. 1).

Nestos river forms an extensive deltaic plain (about 600 km²) in the boundaries between Kavala and Xanthi prefectures. Because of its biodiversity the delta of Nestos river 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 (Efthimiou et al. 2003; Emmanouloudis et al. 2006; Kallioras et al. 2006; Psilovikos et al. 2006).

Fig. 1 Map showing the course and the basin of river Nestos



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 (Emmanouloudis et al. 2006), namely Thisavros (height: 175 m, capacity: $7.05 \times 10^8 \text{ m}^3$) and Platanovrisi (height: 95 m, capacity: $8.4 \times 10^7 \text{ m}^3$) (Fig. 2). These dams were constructed during the early 1990s (1990–1998) by DEH (Public Power Corporation of Greece S.A.) in a mountainous region and provide hydroelectric power and water supply for irrigation. The construction of these dams has aroused great concern about their impact on the river downstream (Darakas 2002; Efthimiou et al. 2003; Petalas et al. 2005; Emmanouloudis et al. 2006; 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 parts of the river, several types of contaminants are introduced into the river flow. These contaminants are wastewater, either treated or untreated, from small towns and industrial areas in the Bulgarian part of the river and wastewater, either treated or untreated, from small towns, industrial areas and agricultural drainage ditches which receive residues of pesticides and fertilizers in the Greek part (Darakas 2002).

Geological setting

The study area (Fig. 2) is a part of the Rhodope massif, which mainly consists of (a) gneisses, schists and amphibolites

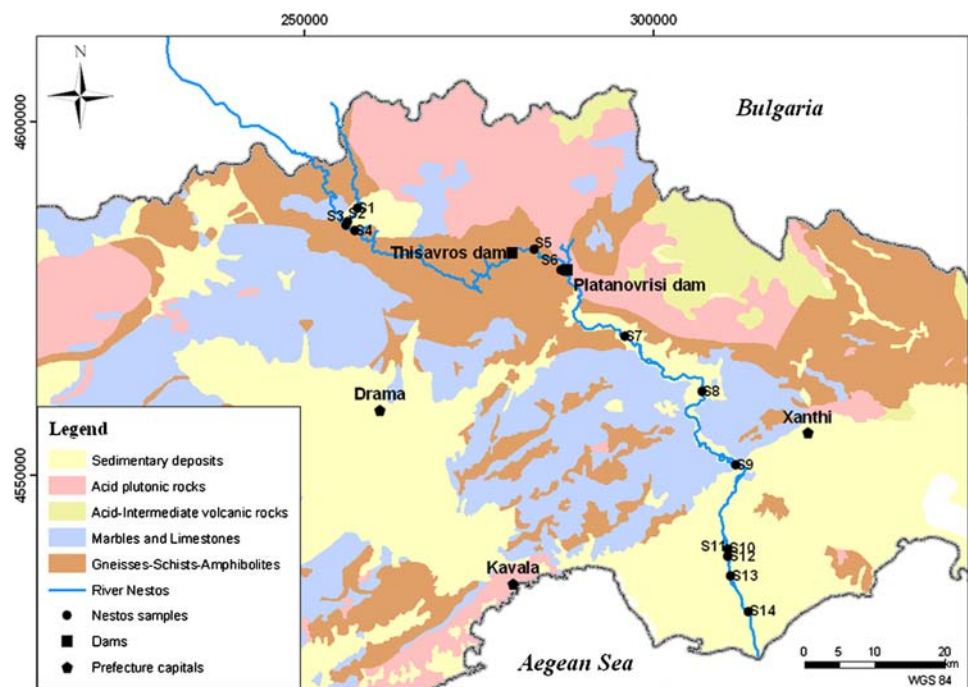
(Permian–Eocene); (b) marbles (Permian–Eocene); (c) granitic and granodioritic rocks (Eocene–Miocene); (d) acid-intermediate volcanic rocks (Eocene–Miocene) and (e) sedimentary deposits (Miocene–Holocene). The intense plutonism of the Rhodope is represented by granites, granodiorites, monzonites, quartz monzonites and diorites while its volcanic activity is represented by rhyolites to basalts (Kilias and Mountrakis 1998; Kilias et al. 1999; Christofides et al. 1998, 2001; Pe-Piper and Piper 2002; Rondoyanni et al. 2004; 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 Patrick 1989; Filippidis et al. 1996; Vavelidis et al. 1996, 1997; Nimfopoulos et al. 2000).

Materials and methods

Sampling

The sampling took place between December 2002 and January 2003. Fourteen samples from the banks of river Nestos were collected. Sample S1 was collected from river Despatis about 2 km before it meets with river Nestos. Sample S2 was collected at the crosspoint of Nestos and Despatis rivers. The rest of the samples are distributed through the whole Greek part of the river. A G.P.S. was used to locate the sampling points. Geographical, geological, and geochemical information was implemented in a GIS project using ArcGIS 9.0 software (Fig. 2).

Fig. 2 Simplified geological map showing the major geological units in the study area, the sample sites and the locations of Thisavros and Platanovrisi dams (modified, after IGME 1983)



Sample preparation

The river sediments were dried in an oven at 40°C (Fernández-Turiel et al. 1995, 2001; Papastergios et al. 2006; Papastergios 2008). The <200 µm fraction was used due to the fact that the environmentally available trace elements mainly remain in this fraction (Fernández-Turiel et al. 2001; Kabata-Pendias and Pendias 2001; Lucho-Constantino et al. 2005). Fine grain particles may act as effective carriers of dissolved metals from the water column to the sediments and thus originate elevated concentrations of heavy metals in the fine-grained sediments. Because of their larger specific area, the fine-grained fraction usually contains higher concentrations of trace elements (Lu et al. 2005).

The elements of interest were extracted using analytical grade nitric acid (Papastergios et al. 2006; Dalmacija et al. 2006; Papastergios 2008). The HNO₃ extraction procedure is a very strong acid digestion that puts in solution almost all elements that could become “environmentally available” (Pickering 1986; Walsh et al. 1997; USEPA 1998; Quevauviller 2002; Sastre et al. 2002). Analytical grade HNO₃ 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).

A split of 0.1 g of each sample was placed into 14 mm diameter polyethylene tubes. Then, 2 ml of HNO₃ was added. All samples were placed in a rotary shaker for 24 h. After the extraction procedure, the solution was filtered (Schleicher and Schmell 5892 white ribbon, ash-less, filter paper circles of 125 mm diameter) in 100 ml volume flasks. The volume flasks were made up volume with Milli-Q type deionized water of 18.2 MΩ/cm. The final solution was placed in HDPE (high-density polyethylene) bottles, labeled, and stored in dark at 4°C until analysis (Papastergios et al. 2006; Papastergios 2008).

Analytical methods

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 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). A Perkin Elmer Optima 3200RL with a Perkin Elmer Autosampler AS-90+ was used for the ICP-OES analysis, while a Perkin Elmer Sciex Elan 6000 with a Perkin Elmer AS-91 automatic sampler was used for the ICP-MS analysis. The analyses were performed at the SCT-UB (Scientific Technical Services of the University of Barcelona), Barcelona (Spain).

Details on ICP-MS analysis are in Fernández-Turiel et al. (2000). In order to check the quality of the results, the same methods were applied to the reference material NIST SRM 2704, as well as to four duplicates of a randomly selected sample.

Results and discussion

Major elements

Table 1 shows the descriptive statistics for the major element concentrations of sediments (mean, median, minimum, maximum and standard deviation). Iron has the largest, median¹ (10.01 g kg⁻¹) and is followed by Al which has the second largest one (6.37 g kg⁻¹). Calcium has a median of 6.23 g kg⁻¹, Mg of 3.85 g kg⁻¹ and K of 2.83 g kg⁻¹. The rest of the major elements shows medians below 1 g kg⁻¹. The low Si values are due to the HNO₃ extraction procedure that is not designed to attack aluminosilicate matrices.

Aluminum, Ca, Fe, Mg and K have a very similar pattern in their geographical distribution (Fig. 3a). Concentrations in sample S1 are close to their median values. Sample S2 shows a first peak, which is the maximum value for Al and K. Then, a decrease is noted for samples S3 and S4 and the concentration of the elements reaches near their median values again. For samples S5 and S6, a second increase is noted and the maximum values for Al, Fe and Mg are observed in sample S6 and in sample S5 for Ca and K. From there on (sample S7), until sample S9, which has the minimum values for all five elements of this group, a second decrease is noted. Finally, for the rest of the samples (S10–S14) an increase is observed once more and the concentrations of the elements reach near their median values again (Table 1). The remaining group of elements (Cl, Na, P and S) seems to follow this pattern, but not with the same degree of similarity. Their common characteristic is that they have their largest values in either sample S5 or S6 (Fig. 3b). These observations are in agreement with Darakas (2002) which cited similar results regarding the water quality of the river. Silicon shows a rather constant behavior throughout the whole river as a consequence of the extraction method (Table 1).

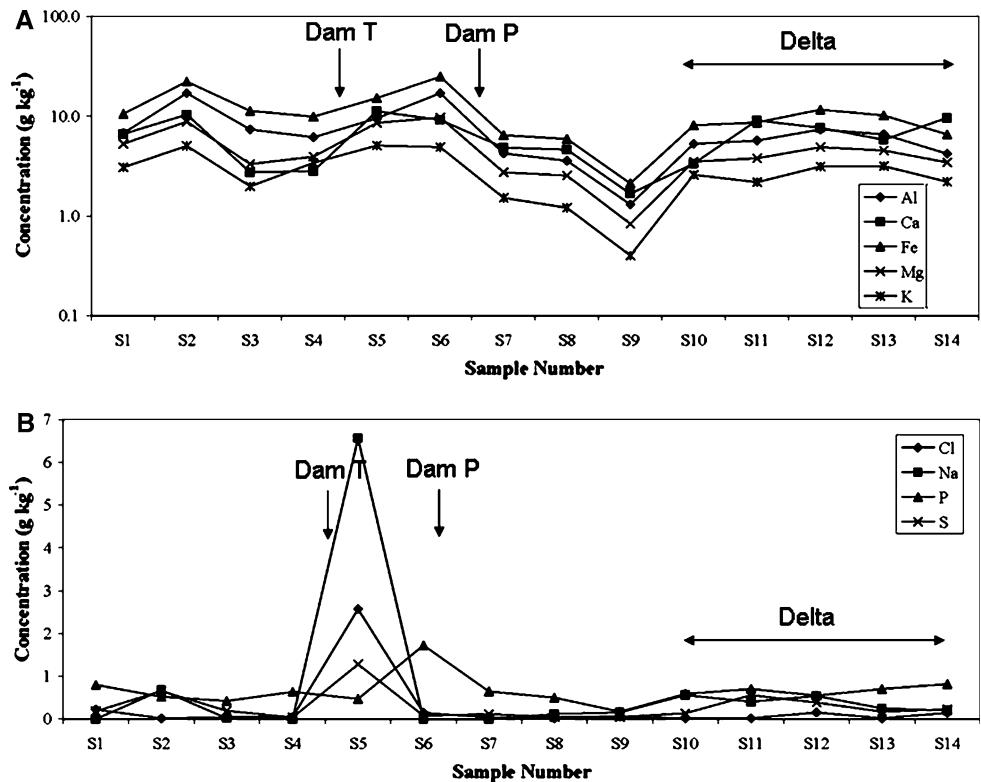
Aluminum, Ca, Cl, Fe, K and Mg have larger median values in the first group (S1–S6), whereas Na, P and S have larger median values in the third group (S10–S14), which is near the river's delta. This distribution could be attributed to the surrounding rocks that the river crosses in its northern part and that could contribute to the elevated

¹ Because the mean is more influenced by extreme values than the median, the latter is chosen for discussion in the text.

Table 1 Concentration values (in g kg^{-1}) for the major elements of the present study and their descriptive statistics

Sample number	Al	Ca	Cl	Fe	K	Mg	Na	P	S	Si
S1	6.76	6.63	0.22	10.54	3.09	5.29	0.00	0.80	0.18	0.17
S2	17.08	10.34	0.02	22.21	5.06	8.84	0.67	0.52	0.65	0.22
S3	7.40	2.74	0.04	11.28	1.98	3.33	0.02	0.42	0.20	0.32
S4	6.15	2.82	0.05	9.87	3.43	3.93	0.00	0.64	0.04	0.25
S5	9.54	11.21	2.57	15.22	5.07	8.61	6.57	0.47	1.28	0.21
S6	17.06	9.17	0.14	25.02	4.88	9.74	0.00	1.73	0.08	0.38
S7	4.26	4.83	0.04	6.48	1.52	2.73	0.00	0.65	0.12	0.17
S8	3.59	4.64	0.02	5.90	1.21	2.55	0.12	0.50	0.05	0.38
S9	1.30	1.67	0.06	2.13	0.40	0.84	0.16	0.18	0.04	0.23
S10	5.30	3.33	0.02	8.10	2.58	3.51	0.56	0.59	0.14	0.16
S11	5.72	9.09	0.02	8.69	2.18	3.77	0.41	0.70	0.56	0.24
S12	7.40	7.65	0.16	11.60	3.14	4.92	0.54	0.55	0.39	0.31
S13	6.60	5.84	0.02	10.14	3.17	4.55	0.25	0.70	0.18	0.22
S14	4.19	9.61	0.14	6.60	2.20	3.44	0.20	0.82	0.23	0.18
Mean	7.31	6.40	0.25	10.98	2.85	4.72	0.68	0.66	0.29	0.25
Median	6.37	6.23	0.05	10.01	2.83	3.85	0.18	0.61	0.18	0.23
Minimum	1.30	1.67	0.02	2.13	0.40	0.84	0.00	0.18	0.04	0.16
Maximum	17.08	11.21	2.57	25.02	5.07	9.74	6.57	1.73	1.28	0.38
SD	4.58	3.16	0.67	6.21	1.43	2.60	1.71	0.35	0.34	0.07
S1–S6 (median)	8.47	7.90	0.09	13.25	4.16	6.95	0.01	0.58	0.19	0.24
S7–S9 (median)	3.59	4.64	0.04	5.90	1.21	2.55	0.12	0.50	0.05	0.23
S10–S14 (median)	5.72	7.65	0.02	8.69	2.58	3.77	0.41	0.70	0.23	0.22

Fig. 3 Diagrams showing the variation in the concentrations of Al, Ca, Fe, K and Mg and the concentrations of Cl, Na, P and S from samples S1 to S14. Locations of the Thisavros (*T*) and Platanovrisi (*P*) dams are indicated



concentrations of these elements. Nestos river, at its northern part, crosses through a series of metamorphic rocks (i.e. gneisses, schists, amphibolites) which could be the natural sources of these elements (Fig. 2). However, the possibility of some kind of contamination, as a result of the human activities taking place at that part of the river, or before, cannot be excluded. In addition, the two dams of Thisavros and Platanovrisi must play some kind of buffering role to the further extension of the contamination downstream. In fact, the dams regulate the Nestos flow and improve the water quality and, consequently, also the ecological quality. They operate as large-scale sedimentation cells (Emmanouloudis et al. 2006), decreasing the content of suspended sediment and the concentrations of associated elements (samples S7–S9). This feature has also been observed in other Mediterranean basins (Fernández-Turiel et al. 2003).

The partly elevated concentrations that are noted in the southern part of the river reflect the geological setting and the anthropogenic activities. After sample S9, the Nestos river flows through its extensive deltaic plain where cultivation of several agricultural species is intensive (Fig. 2) hence, the increased concentrations of elements (e.g. P) associated with the overuse of phosphoric fertilizers were expected. Samples S10–S14 are in the river delta and also show these effects. In addition, the delta sediments are fine and can be easily eroded naturally and by agricultural practices.

Trace elements

The descriptive statistics for trace element concentrations of Nestos basin sediments (mean, median, minimum, maximum and standard deviation) are shown in Table 2. Selenium is not included in this table because all values were below the detection limit (0.01 mg kg^{-1}).

Trace elements with median values above 100 mg kg^{-1} are Mn and Ti while Ba and Zn have medians between 100 and 50 mg kg^{-1} . Median concentrations between 50 and 1 mg kg^{-1} have Rb, V, Ce, Cr, Ni, Cu, Pb, Sr, La, Li, Y, Th, Co, B, Ga, Cs, As, U and Zr. The rest of the elements (Sn, Cd, Mo, Ag, W, Sb, Hg and Ge) have medians below 1 mg kg^{-1} .

The geographical distribution pattern, for the majority of the trace elements, is similar to the one described for the major elements (Table 2). All trace elements show their largest values in the first six samples (S1–S6) which are above the dam of Platanovrisi (Fig. 4a–d), except for Cd and Zn that have their largest values in samples S11 and S14, respectively (Fig. 4b, d). Almost all elements show either one or two peaks in samples S2 and S5 or S6. From sample S7 until S9 they show a decrease in their concentrations, with sample S9 having the lowest concentrations

for all trace elements apart from As and Cd (Table 2). From sample S10 until S14 all elements show an increase in their concentrations, which in some cases form another pick (i.e. Zn for sample S14 and Mn for sample S12) (Fig. 4a–d).

The trace elements allow to classify the samples into three groups, such as the major elements, according to the spatial distribution of their concentrations (Table 2). Almost all of the trace elements have larger median values for the first group of samples (S1–S6) than for the second (S7–S9) and the third (S10–S14). Exceptions are As, Cd and Mo, which have larger medians for the third group and Hg, Mn, Ni and W which have, approximately, the same medians for the first and third groups (Table 2). These elements are associated with phosphoric fertilizers and their increased concentrations in the southern part of the river could be attributed to the overuse of such agricultural products. In general, the distribution of the trace elements content is similar to that of the major elements, and we might attribute it to the same reasons, which are a combination of natural and anthropogenic activities for the northern part of the river, dam sedimentation effect in the middle course and natural and agricultural processes in the delta river, especially since elements such as Cd and Zn that have their maximum values in that part, have been associated with such contamination sources (Hesterberg 1998; Kabata-Pendias and Pendias 2001; Cui et al. 2005).

According to the new Dutch List for contaminated land (Dalmacija et al. 2006; Leung et al. 2006; Contaminated Land 2006) no studied sample has values larger than the target value proposed for the elements included in the list (i.e. As, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb). However, sample S2 exceeds the optimum limits for Ba, Cu, and Ni, sample S5 for Cu and Ni, and sample S14 for Zn. A further comparison with other international directives, such as the ICRCCL 59-83 (Interdepartmental Committee on the Redevelopment of Contaminated Land) (Contaminated Land 2006) shows similar results. No element has concentrations larger than the proposed action values. Only As has larger than threshold value for sample S2 and Cr for samples S2, S5, S6 and S12. The above observations are in agreement with Christoforides et al. (2008) who found that Hg (and organochlorine) in fresh water fish from the river Nestos did not exceed WHO and USEPA health guidelines.

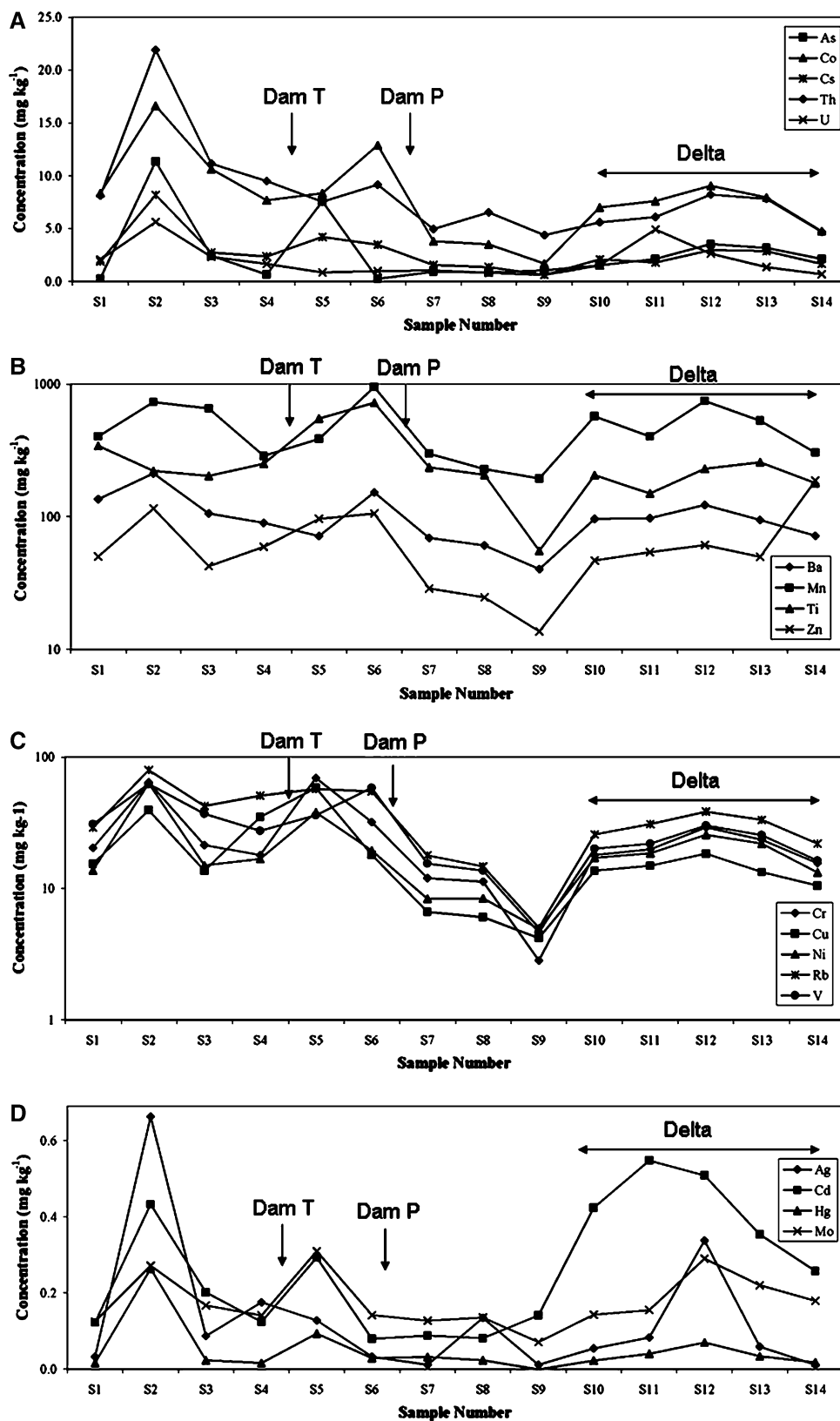
Conclusions

Both major and trace elements have similar geographical distribution patterns throughout the sediments of Nestos river. They have their largest values in the northern part of the river, above the dams of Thisavros and Platanovrisi, as a consequence of natural processes and human activities.

Table 2 Concentration values (in mg kg⁻¹) for the trace elements of the present study and their descriptive statistics

Sample number	Ag	As	B	Ba	Cd	Ce	Co	Cr	Cs	Cu	Ga	Ge	Hg	La	Li	Mn
S1	0.04	0.25	1.79	135.69	0.13	20.86	8.35	20.28	1.87	15.37	3.58	0.04	0.03	11.36	11.86	403.91
S2	0.67	11.33	7.18	211.82	0.44	67.48	16.63	64.28	8.17	39.25	8.35	0.08	0.27	32.63	28.07	731.81
S3	0.10	2.42	4.69	105.67	0.21	38.49	10.62	21.38	2.73	13.62	3.77	0.05	0.03	18.04	10.82	653.22
S4	0.19	0.64	2.55	89.84	0.13	38.98	7.66	18.00	2.36	35.00	3.69	0.05	0.03	19.29	11.67	288.87
S5	0.14	7.57	15.69	71.41	0.30	25.57	8.36	69.43	4.19	58.26	4.99	0.06	0.10	10.67	24.32	385.69
S6	0.04	0.25	10.97	153.01	0.09	30.75	12.88	31.95	3.47	18.04	11.88	0.09	0.04	17.91	35.32	949.52
S7	0.02	0.90	4.57	69.34	0.10	16.22	3.79	11.94	1.56	6.61	2.53	0.03	0.04	8.82	8.05	299.03
S8	0.14	0.84	3.24	60.77	0.09	14.33	3.50	11.23	1.33	6.04	2.05	0.02	0.03	6.64	6.76	229.25
S9	0.02	1.03	0.68	40.24	0.15	9.33	1.70	2.82	0.61	4.18	0.71	0.01	0.01	4.94	2.50	194.41
S10	0.06	1.51	2.73	96.20	0.43	23.11	7.00	17.99	2.09	13.69	2.87	0.04	0.03	11.45	9.29	570.24
S11	0.09	2.11	1.41	97.46	0.56	32.80	7.59	19.83	1.77	14.92	2.95	0.05	0.05	14.35	9.32	402.57
S12	0.35	3.52	2.78	122.53	0.52	33.87	9.04	29.11	2.97	18.39	4.09	0.06	0.08	16.80	13.48	746.65
S13	0.07	3.15	4.15	94.42	0.36	25.56	7.95	23.47	2.87	13.33	3.61	0.04	0.04	12.96	13.32	530.11
S14	0.02	2.11	5.27	71.99	0.27	16.19	4.75	15.55	1.66	10.53	2.19	0.02	0.03	8.20	7.89	304.29
Mean	0.14	2.69	4.83	101.46	0.27	28.11	7.84	25.52	2.69	19.09	4.09	0.05	0.06	13.86	13.76	477.82
Median	0.08	1.81	3.69	95.31	0.24	25.56	7.80	20.05	2.22	14.31	3.59	0.04	0.04	12.21	11.25	403.24
Minimum	0.02	0.25	0.68	40.24	0.09	9.33	1.70	2.82	0.61	4.18	0.71	0.01	0.01	4.94	2.50	194.41
Maximum	0.67	11.33	15.69	211.82	0.56	67.48	16.63	69.43	8.17	58.26	11.88	0.09	0.27	32.63	35.32	949.52
SD	0.18	3.13	4.08	43.77	0.17	14.56	3.88	18.98	1.83	15.04	2.84	0.02	0.07	7.00	9.12	225.46
S1–S6 (median)	0.12	1.53	5.93	120.68	0.17	34.62	9.49	26.66	3.10	26.52	4.38	0.05	0.04	17.98	18.09	528.56
S7–S9 (median)	0.02	0.90	3.24	60.77	0.10	14.33	3.50	11.23	1.33	6.04	2.05	0.02	0.03	6.64	6.76	229.25
S10–S14 (median)	0.07	2.11	2.78	96.20	0.43	25.56	7.59	19.83	2.09	13.69	2.95	0.04	0.04	12.96	9.32	530.11
Sample number	Mo	Ni	Pb	Rb	Sb	Sn	Sr	Th	Ti	U	V	W	Y	Zn	Zr	
S1	0.13	13.75	16.59	28.92	0.02	0.26	17.83	8.10	343.23	2.04	30.77	0.07	7.11	49.99	0.89	
S2	0.28	62.93	9.51	79.27	0.54	0.58	32.46	21.91	221.74	5.61	62.45	0.38	21.18	115.11	8.12	
S3	0.18	14.96	56.36	42.49	0.06	0.29	12.32	11.15	202.85	2.31	36.90	0.14	11.21	42.44	10.36	
S4	0.15	16.72	38.41	50.61	0.05	0.25	11.53	9.48	250.81	1.65	27.38	0.08	9.81	59.30	1.26	
S5	0.32	37.97	28.04	57.29	0.34	1.33	29.83	7.53	549.55	0.83	36.03	0.23	7.17	96.25	2.99	
S6	0.15	19.40	8.22	54.60	0.11	0.49	29.74	9.16	721.80	0.98	58.04	0.11	23.42	105.45	0.73	
S7	0.14	8.35	5.67	17.83	0.06	0.23	10.47	4.94	235.76	1.04	15.44	0.11	7.87	28.81	0.95	
S8	0.15	8.42	5.42	14.73	0.05	0.19	9.43	6.54	207.67	0.80	13.66	0.06	5.51	24.69	0.87	
S9	0.08	4.91	4.54	5.01	0.02	0.17	4.16	4.38	55.25	0.61	4.61	0.05	2.14	13.63	0.42	
S10	0.15	17.13	21.20	25.71	0.05	0.25	9.73	5.59	205.78	1.50	20.03	0.09	7.66	46.76	1.31	
S11	0.17	18.47	24.79	30.75	0.12	0.26	22.94	6.08	149.65	4.91	21.97	0.16	9.82	54.11	2.14	
S12	0.30	25.65	18.88	38.24	0.15	0.31	19.77	8.22	229.93	2.64	30.03	0.22	9.90	60.98	2.25	
S13	0.23	21.86	13.48	33.27	0.07	0.25	14.88	7.81	256.93	1.35	25.44	0.13	8.05	49.78	1.23	
S14	0.19	13.26	9.03	21.91	0.05	0.20	15.67	4.69	179.93	0.68	16.30	0.09	6.06	187.35	1.27	
Mean	0.19	20.27	18.58	35.76	0.12	0.36	17.20	8.25	272.21	1.93	28.50	0.14	9.78	66.76	2.48	
Median	0.16	16.92	15.03	32.01	0.06	0.25	15.27	7.67	225.84	1.43	26.41	0.11	7.96	52.05	1.26	
Minimum	0.08	4.91	4.54	5.01	0.02	0.17	4.16	4.38	55.25	0.61	4.61	0.05	2.14	13.63	0.42	
Maximum	0.32	62.93	56.36	79.27	0.54	1.33	32.46	21.91	721.80	5.61	62.45	0.38	23.42	187.35	10.36	
SD	0.07	14.75	14.68	19.74	0.14	0.30	8.70	4.40	169.72	1.55	16.16	0.09	5.78	45.65	2.97	
S1–S6 (median)	0.16	18.06	22.31	52.61	0.08	0.39	23.79	9.32	297.02	1.85	36.46	0.13	10.51	77.78	2.13	
S7–S9 (median)	0.14	8.35	5.42	14.73	0.05	0.19	9.43	4.94	207.67	0.80	13.66	0.06	5.51	24.69	0.87	
S10–S14 (median)	0.19	18.47	18.88	30.75	0.07	0.25	15.67	6.08	205.78	1.50	21.97	0.13	8.05	54.11	1.31	

Fig. 4 Diagrams showing the variation in the concentrations of trace elements for all samples of the present study



The two dams of Thisavros and Platanovrisi act as large sedimentation cells and do not permit the sediments with the high concentrations to reach the southern part of the

river. However, since an increase is observed in the sediments of the river, as we reach the river delta, another pattern source of concentrations is identified. This is due to

natural and agricultural mobilization of fine particles and associated elements. What is important to point out is that the general quality of the river sediments is not above reference thresholds for contaminated land and, hence, it is not posing an immediate threat for the plants, animals and humans in the area.

Acknowledgments The authors would like to acknowledge the technical assistance provided by the personnel of the Faculty of Geology of the University of Barcelona, the SCT-UB and ICTJA-CSIC, Barcelona (Spain). The authors also wish to thank assistant professor of the Aristotle University of Thessaloniki, School of Geology, Department of Physical and Environmental Geography, K. Albanakis for supplying sample S2 and Ms. Evgenia Chonta for improving the English text. The constructive comments of an anonymous reviewer are greatly appreciated.

References

Christofides G, Soldatos T, Eleftheriadis G, Koroneos A (1998) Chemical and isotopic evidence for source contamination and crustal assimilation in the Hellenic Rhodope plutonic rocks. *Acta Vulcanol* 10(2):305–318

Christofides G, Koroneos A, Soldatos T, Eleftheriadis G, Kiliias A (2001) Eocene magmatism (Sithonia and Elatia plutons) in the Internal Hellenides and implications for Eocene–Miocene geological evolution of the Rhodope Massif (Northern Greece). *Acta Vulcanol* 13(1–2):73–89

Christoforides A, Stamatis N, Schmieder K, Tsachalidis E (2008) Organochlorine and mercury contamination in fish tissues from the River Nestos, Greece. *Chemosphere* 70:694–702

Cui Y-J, Zhai R-H, Huang Y-Z, Qiu Y, Liang J-Z (2005) Exposure to metal mixtures and human health impacts in a contaminated area in Nanning, China. *Environ Int* 31:784–790

Dalmacija B, Prica M, Ivancev-Tumbas I, van der Kooij A, Roncevic S, Krcmar D, Bikit I, Teodorovic I (2006) Pollution of the Begej Canal sediment—metals, radioactivity and toxicity assessment. *Environ Int* 32:600–615

Darakas E (2002) The transboundary River Nestos and its water quality assessment: cross-border cooperation between Greece and Bulgaria. *Environmentalist* 22:367–375

Diadovski KI, Atanassova PM, Ivanov SI (2007) Integral assessment of climate impact on the transboundary Mesta River flow formation in Bulgaria. *Environ Monit Assess* 127:383–388

Efthimiou G, Mertzanis A, Emmanouloudis D (2003) Direct and indirect human-made impact on the natural ecosystems of the River Nestos. In: Proceedings of the first international conference on environmental research and assessment, Bucharest, Romania, 23–27 March 2003

Eleftheriadou E, Mylopoulos Y (2008) A methodological framework supporting trans-boundary water agreements: the case of the Nestos/Mesta river basin. *Water Policy* 10(3):239–257

Emmanouloudis D, Myronidis D, Panilas S, Efthimiou G (2006) The role of sediments in the dynamics and preservation of the aquatic forest in the Nestos Delta (northern Greece). *IAHS-AISH Publication* (306), pp 214–222

Epitropou N, Chatzipanagis I (1989) Lithostratigraphic and tectonic controls of the iron–manganese, base and precious metal mineralizations in the west Rhodopes. *Geol Rhodopica* 1:381–388

Fernández-Turiel JL, López-Soler A, Llorens JF, Querol X, Aceñolaza P, Durand F, López JP, Medina ME, Rossi JN, Toselli AJ, Saavedra J (1995) Environmental monitoring using surface

water, river sediments, and vegetation: a case study in the Famatina range, La Rioja, NW Argentina. *Environ Int* 21:807–820

Fernández-Turiel JL, Llorens JF, López-Vera F, Gómez-Artola C, Morell I, Gimeno D (2000) Strategy for water analysis using ICP-MS. *Fresenius J Anal Chem* 368(6):601–606

Fernández-Turiel JL, Aceñolaza P, Medina ME, Llorens JF, Sardi F (2001) Assessment of a smelter impact area using surface soils and plants. *Environ Geochem Health* 23:65–78

Fernández-Turiel JL, Gimeno D, Rodríguez JJ, Carnicero M, Valero F (2003) Factors influencing the quality of a surface water supply system: the Ter River, northeastern Spain. *Fresenius Environ Bull* 12(1):67–75

Filippidis A, Georgakopoulos A, Kassoli-Fournaraki A, Misaelides P, Yiakkoupis P, Broussoulis J (1996) Trace element contents in composite samples of three lignite seams from the central part of the Drama lignite deposit, Macedonia, Greece. *Int J Coal Geol* 29:219–234

Hesterberg D (1998) Biogeochemical cycles and processes leading to changes in mobility of chemicals in soils. *Agric Ecosyst Environ* 67:121–133

Institute of Geology and Mineral Exploration (IGME) (1983) Geological map of Greece, scale: 1:500,000, 2nd edn. Athens, Greece

Kabata-Pendias A, Pendias H (2001) Trace elements in soils and plants, 3rd edn. CRC Press, Boca Raton, FL, p 413

Kallioras A, Pliakas F, Diamantis I (2006) The legislative framework and policy for the water resources management of transboundary rivers in Europe: the case of Nestos/Mesta River, between Greece and Bulgaria. *Environ Sci Policy* 9:291–301

Kampragou E, Eleftheriadou E, Mylopoulos Y (2007) Implementing equitable water allocation in transboundary catchments: the case of river Nestos/Mesta. *Water Resour Manage* 21:909–918

Kiliias AA, Mountrakis DM (1998) Tertiary extension of the Rhodope massif associated with granite emplacement (Northern Greece). *Acta Vulcanol* 10(2):331–337

Kiliias AA, Falalakis G, Mountrakis DM (1999) Cretaceous—tertiary structures and kinematics of the Serbomacedonian metamorphic rocks and their relation to the exhumation of the Hellenic hinterland (Macedonia, Greece). *Int J Earth Sci* 88:513–531

Contaminated Land (2006) Standards and guidelines. <http://www.contaminatedland.co.uk/std-guid.htm>. Cited 21 Oct 2006

Leung A, Wei Cai Z, Hung Wong M (2006) Environmental contamination from electronic waste recycling at Guiyu, south-east China. *J Mater Cycles Waste Manage* 8:21–33

Lu XQ, Werner I, Young TM (2005) Geochemistry and bioavailability of metals in sediments from northern San Francisco Bay. *Environ Int* 31:593–602

Lucho-Constantino CA, Álvarez-Suárez M, Beltrán-Hernández RI, Prieto-García F, Poggi-Varaldo HM (2005) A multivariate analysis of the accumulation and fractionation of major and trace elements in agricultural soils in Hidalgo State, Mexico irrigated with raw wastewater. *Environ Int* 31:313–323

Mimides Th, Kotsovinos N, Rizos S, Soulis C, Karakatsoulis P, Stavropoulos D (2007) Integrated runoff and balance analysis concerning Greek–Bulgarian transboundary hydrological basin of River Nestos/Mesta. *Desalination* 213:174–181

Mylopoulos Y, Kolokytha E, Kampragou E, Vagiona D (2008) A combined methodology for transboundary river basin management in Europe. Application in the Nestos–Mesta catchment area. *Water Resour Manage* 22:1101–1112

Nimfopoulos M, Patrick R (1989) Mineralogical evolution of the mineralization at K. Nevrokopi-Drama, Greece. *Geol Rhodopica* 1:444–452

Nimfopoulos MK, Arvanitidis N, Michailidis KM, Naden J, De Groot PA (2000) Fluid inclusion and isotopic investigation of the

- auriferous base metal mineralization in the Palia Kavala area, Macedonia, N. Greece. In: Proceedings of the 3rd international conference on the geology of the eastern Mediterranean, pp 211–220
- Papastergios G (2008) Environmental geochemical study of soils and sediments in coastal areas, east of Kavala (Macedonia, Greece) and production of geochemical maps via the use of GIS. PhD, Aristotle University of Thessaloniki, Greece (in Greek)
- Papastergios G, Georgakopoulos A, Fernández-Turiel JL, Gimeno D, Vouvalidis K, Kapetanios C (2006) The geomorphic control and the environmental impact of geochemical processes in the Pangeon Mountain area, Northern Greece. In: VIth international scientific conference, modern management of mine producing, geology and environmental protection (SGEM), Bulgaria, 12–16 June 2006
- Pe-Piper G, Piper DJW (2002) The igneous rocks of Greece, the anatomy of an orogen. Gebrüder Bornträger, Berlin, p 573
- Petalas C, Pliakas F, Diamantis F, Kallioras A (2005) Development of an integrated conceptual model for the rational management of the transboundary Nestos River, Greece. *Environ Geol* 48:941–954
- Pickering WF (1986) Metal ion speciation—soils and sediments (a review). *Ore Geol Rev* 1:83–146
- Psilovikos A, Margoni S, Psilovikos A (2006) Simulation and trend analysis of the water quality monitoring daily data in Nestos River delta. Contribution to the sustainable management and results for the years 2000–2002. *Environ Monit Assess* 116:543–562
- Quevauviller PH (2002) Operationally defined extraction procedures for soil and sediment analysis. Part 3. New CRMs for trace-element extractable contents. *Trends Anal Chem* 21(11):774–785
- Sarkar SK, Frančišković-Bilinski S, Bhattacharya A, Saha M, Bilinski H (2004) Levels of elements in the surficial estuarine sediments of the Hugli River, northeast India and their environmental implications. *Environ Int* 30:1089–1098
- Sastre J, Sahuquillo A, Vidal M, Rauret G (2002) Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. *Anal Chim Acta* 462:59–72
- Sin SN, Chua H, Lo W, Ng LM (2001) Assessments of heavy metal cations in sediments of Shing Mun River, Hong Kong. *Environ Int* 26:297–301
- Rondoyanni Th, Georgiou Ch, Galanakis D, Kourouzidis M (2004) Evidences of active faulting in Thrace region (north-eastern Greece). *Bull Geol Soc Greece*, vol XXXVI. In: Proceedings of the 10th international congress, Thessaloniki, Greece, April 2004
- USEPA (United States Environmental Protection Agency) (1998) Method 3051a, microwave assisted acid digestion of sediments, sludges, soils and oils, 24 pp
- Vavelidis M, Christofides G, Melfos V (1996) The Au–Ag bearing mineralization and placer gold of Palea Kavala (Macedonia, N. Greece). In: Knežević V, Krstić B (eds) Terranes of Serbia, the formation of the geologic framework of Serbia and the adjacent regions, Belgrade, pp 311–316
- Vavelidis M, Melfos V, Eleftheriadis G (1997) Mineralogy and microthermometric investigations in the Au-bearing sulfide mineralization of Palea Kavala (Macedonia, Greece). *Mineral deposits*, pp 343–346
- Walsh JN, Gill R, Thirwall MF (1997) Dissolution procedures for geochemical and environmental samples. In: Gill R (ed) Modern analytical geochemistry. An introduction to quantitative chemical analysis techniques for earth, environmental and materials scientists. Pearson Education Limited, England, p 329
- Zagorchev I (2007) Late Cenozoic development of the Strouma and Mesta fluviolacustrine systems, SW Bulgaria and northern Greece. *Quart Sci Rev* 26:2783–2800