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Significance evaluation of factors controlling river water composition

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Abstract In the present paper the factors controlling river water chemistry are described and their significance is evaluated, including: climate, petrography, soils/sediments, geomorphology of the catchment area, hydrography, pollution, biological activity of rivers, and rainwater composition. The results of this study indicate that the dominant factors influencing riverwater chemistry are the climate and the petrography of the catchment area. In the case of heavily polluted rivers, pollution appears to be the dominant factor.

Key words River water chemistry — Petrography — Geomorphology — Climate — Pollution

Introduction

Thirteen major Greek rivers and tributaries, which yield 80 percent of the total surface discharges in the Mediterranean, were surveyed, from their sources or state boundaries down to their mouths, four times seasonally, during one hydrological cycle (September 1983–June 1984). The rivers and tributaries are as follows: Evros–Ardas, Nestos–Arkudoremma, Strymon–Angitis, Gallikos, Axios, Aliakmon, Pinios, Sperchios, Acheloos, and Louros. A total of 160 samples were collected from 42 river sites (Fig. 1) and analyzed with respect to the following parameters: temperature, pH, conductivity, dissolved oxygen, total hardness, alkalinity, chlorine (in situ), calcium, magnesium, sodium, potassium, sulfate, nitrate, phosphate, silicate, dissolved organic carbon (DOC), total suspended solids (TSS), particulate organic carbon (POC), nitrogen, copper, lead, and zinc as well as the mineralogy of suspended matter (laboratory analysis). Table 1 shows the average composition of the waters in the examined rivers.

The approach followed is based on the watershed information, e.g., climatic, geomorphological, petrographical (percentage distribution of geochemical important petrographic units), soil/sediment composition, rainwater composition, as well as the hydrographic and the hydrochemical data of the rivers.

In order to achieve a better understanding of the nature of the factors influencing river water composition as well as to specify them quantitatively, multivariate statistical analyses (factor and cluster analyses) were performed on the rain-corrected hydrochemical and petrographic information of the watersheds.

Results and discussion

According to a cluster analysis (Q-mode) performed on the hydrochemical data, three main river groups with characteristic compositions were distinguished (Fig. 2a):

First hydrochemical group

Rivers in northern Greece: Ardas, Nestos, Strymon, and Axios.

Second hydrochemical group

Rivers in northern-middle Greece: Aliakmon, Pinios, and Sperchios. To this group belong also the rivers Angitis and Gallikos (northern Greece).

Third hydrochemical group

Rivers in western Greece: Acheloos and Luros.

The rivers Evros and Arkudoremma constitute separate hydrochemical units.

In order to identify characteristic factors regulating hydrochemical similarities of rivers belonging to the same group, as well as the hydrochemical differences of the different river groups, a factor analysis (R-mode) on hydro-

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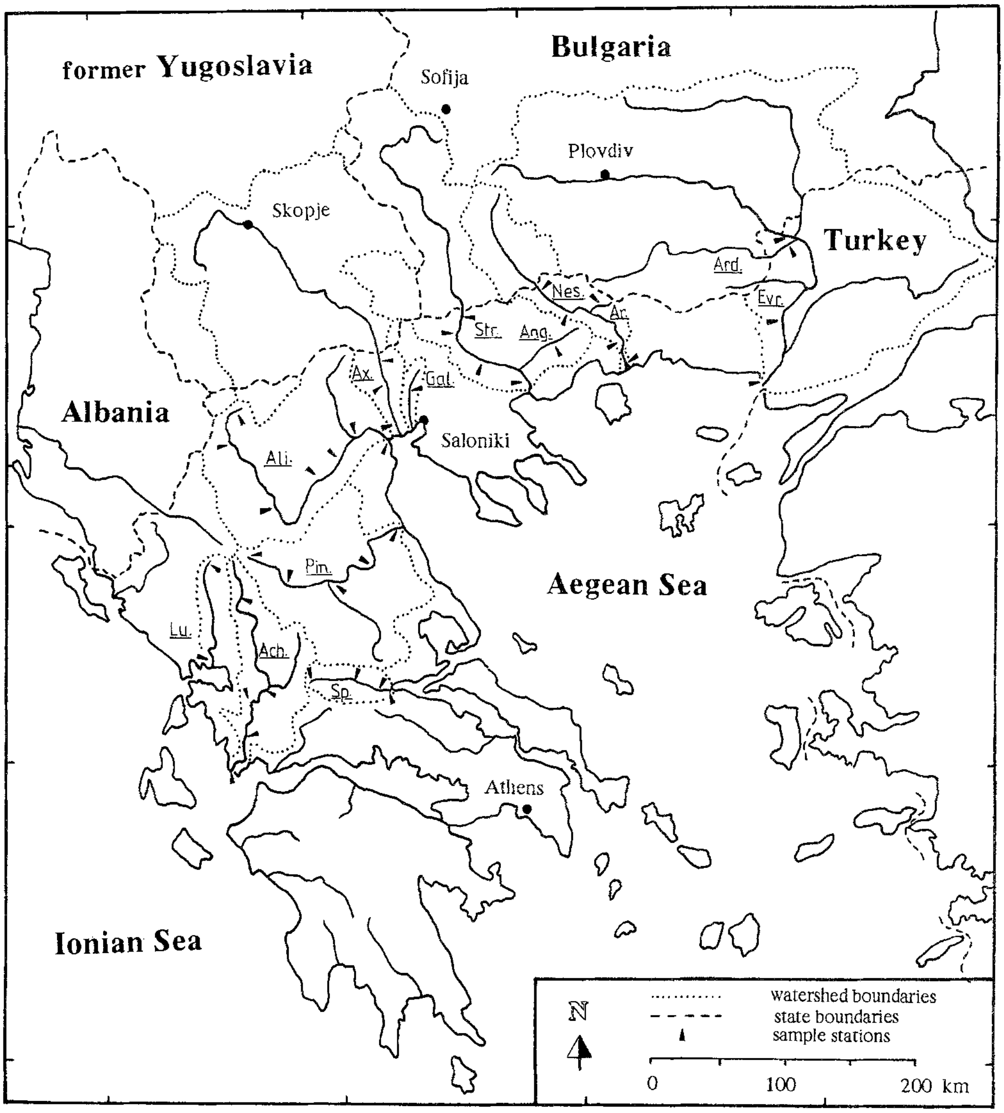

Fig. 1. The river catchments and sample stations

chemical data was done (Table 2), which distinguishes four main factors with 86 percent of the total variance: carbonate and mafic silicate rock weathering (48 percent of the total variance); pollution (18 percent of the total variance); biological activity (12 percent of the total variance); and weathering of acid silicate rocks (9 percent of the total variance).

In the following section, the influence of several factors on the river water composition will be discussed.

Precipitation

The mean percentage contribution of rain water on river water chemistry is given in Table 3. The high sodium and chlorine rainwater contribution to the rivers is due to marine spray.

Petrography and weathering

Table 4 presents the percentage distribution of geochemically important petrographic rocks within the studied river catchments. To illustrate the influence of petrography on river water composition, a factor analysis (R-mode) on hydrochemical and petrographic data (Table 5) as well as a cluster analysis on petrographic data (Fig. 2b) were performed. From the factor analysis results, the influence of the different petrographic features and their weathering on river water solute concentration were determined: The calcium, magnesium, hydrogen carbonate, and chlorine content of the rivers originate mainly from the weathering of young sediments. A significant part of riverine magnesium results from mafic rock weathering. The total silicate content of river water originates from the weathering of mafic and acid rocks. Only a part of the potassium content of river water results from weathering of acid rocks. The extension of carbonates and flysch-molasse within the catchments is not significant for the river water chemistry. The hydrochemical similarities of the rivers of the second hydrochemical group is due to their high carbonate content. The hydrochemical similarities of the rivers of the third hydrochemical group is due to the absence of magmatic and metamorphic rocks in their catchments.

Table 1. Average river water composition

	Evros	Ardas	Nestos	Arkudoremma	Strymon	Angitis	Axios	Gallikos	Aliakmon	Pinios	Sperchios	Sperchios springs	Acheloos	Luros
Temperature (°C)	16.90	17.88	16.06	13.38	15.75	16.75	13.58	19.00	14.12	15.19	15.00	8.75	15.83	12.80
pH	8.39	8.43	8.28	8.14	8.33	7.88	8.28	8.07	8.49	8.28	8.31	7.00	8.25	7.82
Total hardn. (mval/l)	3.61	2.33	2.42	1.16	3.44	4.91	3.49	4.16	3.95	4.56	4.95	1.06	2.83	3.04
Conductivity (mS/cm)	0.54	0.33	0.28	0.14	0.40	0.51	0.44	0.53	0.41	0.47	0.62	0.13	0.33	0.34
Ca (mval/l)	2.84	1.93	2.11	1.06	2.71	3.92	2.69	3.12	2.69	3.06	3.89	0.78	2.47	2.72
Mg (mval/l)	0.77	0.40	0.31	0.10	0.73	0.99	0.80	1.04	1.27	1.50	1.10	0.29	0.36	0.32
Na (mval/l)	1.53	0.48	0.34	0.19	0.57	0.40	0.81	1.45	0.24	0.31	0.57	0.19	0.53	0.49
K (mval/l)	0.16	0.08	0.07	0.05	0.09	0.05	0.10	0.09	0.05	0.05	0.07	0.02	0.04	0.02
HCO_3 (mval/l)	2.93	1.86	2.25	1.09	3.15	4.55	3.18	4.40	3.71	4.33	4.18	1.03	2.68	2.87
SO_4 (mval/l)	1.54	0.48	0.33	0.15	0.56	0.46	0.67	0.64	0.32	0.34	0.73	0.12	0.23	0.33
Cl (mval/l)	0.62	0.37	0.18	0.13	0.32	0.27	0.43	0.64	0.17	0.27	1.12	0.13	0.46	0.35
NO_3 (mg/l)	10.93	4.48	3.76	1.28	3.92	5.61	4.88	3.69	3.05	4.33	4.13	1.00	2.64	3.54
PO_4 (mg/l)	1.23	1.27	0.37	0.14	0.27	0.21	1.57	0.13	0.15	0.25	0.20	0.16	0.04	0.06
TDS (mg/l)	394.41	213.01	220.13	108.46	314.27	416.61	333.91	437.56	327.61	383.12	441.12	98.64	261.05	277.27
SiO_2 (mg/l)	11.54	11.19	11.09	11.94	11.21	8.55	10.05	10.29	10.25	13.05	9.98	11.91	4.10	4.78
PCO_2 (ppmv)	812.10	359.00	652.71	495.25	805.20	2965.25	800.33	2348.50	585.31	1616.17	1023.63	5061.00	759.25	2100.00
Slcal[a]	0.68	0.47	0.38	−0.36	0.68	0.57	0.61	0.61	0.87	0.79	0.95	−1.68	0.53	0.15
Sldol[a]	0.43	0.16	−0.01	−0.87	0.41	0.31	0.35	0.43	0.72	0.67	0.68	−1.91	0.13	−0.30
TSS	32.41	9.47	17.92	4.60	17.90	5.14	15.60	3.11	16.41	19.98	13.19	1.66	3.48	3.86
O_2 sat. (%)	107.80	115.75	104.15	113.00	99.23	96.45	98.66	114.30	104.87	99.68	100.61	84.15	118.52	101.00
DOC (mg/l)	2.77		2.39	1.81	2.07	1.09	1.39	2.30	1.59	1.54	0.99		0.74	
POC (mg/l)	1.68		2.73		1.10	0.28	0.49	0.09	0.46	1.08	0.36		0.29	
PN (mg/l)	0.27		0.38		0.21	0.11	0.19	0.06	0.10	0.26	0.07		0.06	
TOC (mg/l)	4.45		5.12		3.17	1.37	1.88	2.39	2.05	2.62	1.35		1.03	
Cu (ppb)	7.90	4.70	8.30	4.40	4.20		4.80		9.30			5.90		4.30
Pb (ppb)	5.00	2.00			6.00	2.00	4.50	4.00	2.00	2.50	9.00	2.50	5.60	3.00
Ni (ppb)	23.00	26.00	26.00	15.00	41.20	23.00	20.00	17.0	18.30	18.50	73.60	17.00	43.50	24.00

[a] Slacl = saturation index of calcite; Sldol = saturation index of dolomite.

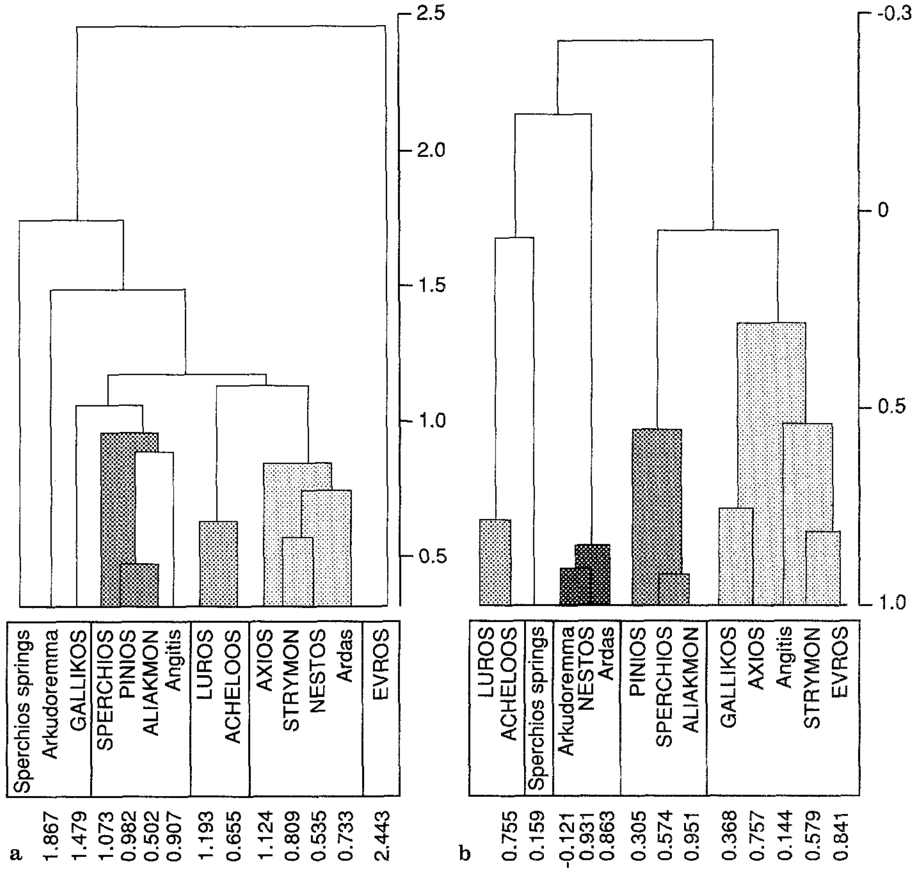

Fig. 2a,b. a Cluster analysis (Q-mode) of the river hydrochemistry, **b** Cluster analysis (Q-mode) of the river catchment petrography

The cluster analysis distinguishes five river catchment groups:

First petrographic group

The catchments of the northern Greek rivers: Nestos, Ardas (first hydrochemical group) and Arkudoremma, with the highest percentage of acid silicate rocks.

Second petrographic group

The catchments of the northern Greek rivers: Strymon (first hydrochemical group), Angitis (second hydrochemical group), and Evros.

Third petrographic group

The catchments of the northern Greek rivers: Axios (first hydrochemical group) and Gallikos (second hydrochemical group).

Fourth petrographic group

The catchments from the northern-middle rivers (second hydrochemical group): Aliakmon, Pinios, and Sperchios, characterized by a high percentage of mafic rocks and flysch-molasse sediments.

Fifth petrographic group

The catchments from the western Greek rivers (third hydrochemical group): Acheloos and Luros, consisting only by three petrographic units (flysch-molasse, carbonates, young sediments).

We therefore conclude that petrography is a significant factor influencing river water composition. Petrography must be a controlling factor for the rivers of northern-middle and western Greece, as they have identical hydrochemical and petrographic characteristics. Nevertheless rivers of the same hydrochemical group are classified in different petrographic groups and vice versa (see Fig. 2). The result is that, besides petrography, there are other significant factors controlling river water composition.

Human influence

Pollution

The pollution factor (Table 2) also includes sodium as well as nitrate, phosphate, sulfate, and potassium. Riverine nitrate, phosphate, sulfate, and potassium originate mainly from fertilizers, while chlorine is mainly from sewage.

If one uses the ratio $SiO_2/Na^+ + K^+$, polluted rivers are marked by a much lower ratio compared to those which would theoretically originate from pure silicate weathering to illite or kaolonite (the main weathering residuals trans-

Table 2. Factor analysis (R-mode) on river water chemistry

	Rotated factor matrix			
	Factor 1, petrography (carbonates–mafic rocks)	Factor 2, pollution	Factor 3, biological activity	Factor 4, petrography (acid silicate rocks)
Variance (%)	47.5	18	12	9
Temperature (°C)		0.42	−0.65	
pH			−0.89	
Total hardness	0.98			
Conductivity	0.88	0.45		
Ca	0.93			
Mg	0.90			
Na		0.89		
K		0.83		−0.43
HCO_3	0.97			
SO_4		0.88		
Cl		0.53		
NO_3		0.78		
PO_4		0.60		
SiO_2				−0.85
DOC			−0.47	−0.51
PCO_2			0.92	
SIcal[a]	0.73		−0.64	
SIdol[a]	0.78		−0.56	
TSS				−0.75
% O_2 saturation			−0.84	
Si/(Na + K-Cl)		−0.75		
	Varimax factor scores			
Evros	−0.12	2.61	0.01	−1.19
Ardas	−0.90	0.22	−1.14	−0.13
Nestos	−0.74	−0.26	−0.76	−0.62
Arkudoremma	−1.58	−0.73	−0.77	−0.10
Strymon	0.12	0.02	−0.34	−0.58
Angitis	1.22	−0.12	0.82	0.63
Axios	0.02	0.74	0.12	−0.45
Gallikos	0.59	1.00	−0.07	1.02
Aliakmon	0.81	−1.53	−0.60	−1.00
Pinios	1.25	−1.10	0.12	−1.29
Sperchios	1.48	0.16	0.29	0.49
Sperchios springs	−1.47	−0.56	2.84	−0.27
Acheloos	−0.14	−0.38	−0.98	1.92

[a] SIcal: saturation index of calcite; SIdol: saturation index of dolomite

Table 3. Mean percentage distribution of rainwater on river water chemistry

	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-
Average rainwater composition (mval/l)	0.136	0.044	0.077	0.005	0.160	0.047	0.052
Average river water composition (mval/l)	2.708	0.745	0.600	0.069	3.170	0.520	0.350
Contribution of precipitation (%)	5	5.9	12.8	7.2	5	9	14.8

ported by the examined rivers), which are 3 and 2, respectively (Stallard 1985). As the average potassium content of river water corresponds to only 11 percent of the mean alkali concentration, the low ratio values are mainly caused by increased sodium inputs from sources other than rock weathering (Skoulikidis 1988). A major source of sodium is municipal wastewaters, containing urea, detergents, etc., which are enriched with sodium.

Taking into account the factor analysis (Table 2, varimax factor scores) as well as the pollution series of the examined rivers (Table 6), by using the concentrations of pollution parameters (nitrate, phosphate, sulfate, heavy metals, oxygen saturation index, and the ratio $SiO_2/Na^+ + K^+$), one realizes that the Evros and Arkudoremma exhibit a significantly different pollution pattern, showing maximum and minimum pollution, respectively.

The following results may be obtained: The hydrochemical differentiation of Evros and Arkudoremma from

Table 4. Percentage distribution of geochemical important petrographic units within river catchments

	Igneous–Metamorphic				
	Acid (%)	Mafic (%)	Carbonates (%)	Flysh-Molasse (%)	Neogene–Quaternary sediments (%)
Evros	37.8	0.9	10.0	9.4	41.9
Ardas	57.5	0.7	20.2	14.2	7.4
Nestos	68.3	0.0	12.6	1.1	18.0
Arkudoremma	91.5	0.0	6.4	2.1	0.0
Strymon	41.6	2.4	17.1	5.2	33.7
Angitis	9.3	0.0	31.3	0.0	59.4
Axios	43.5	7.7	11.3	5.6	31.9
Gallikos	53.1	4.4	1.0	0.0	41.5
Aliakmon	14.5	9.2	15.7	29.6	31.0
Pinios	17.5	6.2	14.7	15.8	45.8
Sperchios	0.0	12.1	16.4	47.9	23.6
Acheloos	0.0	0.0	41.6	48.4	10.0
Luros	0.0	0.0	62.8	0.0	37.2

Table 5. Factor analysis (R-mode) of rivers examined: Data on hydrochemistry, petrography, discharge, and catchment area[a]

	Rotated factor matrix			
	Factor 1	Factor 2	Factor 3	Factor 4
	petrography (carbonates–mafic rocks)	pollution	biological activity	petrography (igneous silicate rocks)
Variance (%)	40.5	20	11	9
Discharge		−0.70		
Catchment area		−0.80		
Temperature	0.40		−0.71	
pH			−0.77	
Total Hardness	0.97			
Conductivity	0.89			
Ca	0.89			
Mg	0.94			
Na		−0.76		
K		−0.87		
HCO_3	0.96			
SO_4		−0.91		
Cl	0.50			
NO_3		−0.87		
PO_4		−0.73		
SiO_2				0.95
DOC			−0.58	0.47
PCO_2			0.81	
Slcal[a]	0.73		−0.58	
Sldol[a]	0.80		−0.49	
TSS		−0.69		
O_2 saturation (%)			−0.82	
Si/(Na + K-Cl)		0.56		
Mafic rocks (%)[b]	0.73			
Acid rocks (%)[b]			−0.69	0.53
Mafic + Acidic (%)[b]			−0.70	0.58
Carbonates (%)[b]				−0.88
Flush + Molasse (%)[b]			0.78	
Sediments (%)[b,c]	0.76			

[a] Slcal = saturation index of calcite; Sidol = saturation index of dolomite
[b] % percentage distribution of geochemical important rock units
[c] Sediments = neogene and quatenary sediments

the other rivers examined is due to very high and insignificant pollution, respectively. The pollution factor in intermediate polluted rivers does not control their hydrochemical character, whereas in heavily polluted rivers, e.g., Evros, pollution may determine the hydrochemical profile.

Man-made lakes

Grate impoundments occur in the course of the Strymon, Aliakmon, and Acheloos rivers. In all cases, there is a clear downstream decrease of the nutrient levels, the car-

Table 6. Pollution series of rivers examined[a]

River	Pollution series	$Na^+ + K^+$ pollution (%)
Evros	8.0	93
Axios	4.9	84
Gallikos	4.4	87
Ardas	4.1	46
Strymon	3.6	67
Nestos	3.2	29
Sperchios	3.0	[b]
Angitis	2.7	8
Pinios	2.6	[b]
Luros	2.4	7
Aliakmon	2.3	[b]
Arkudoremma	1.9	0
Luros springs	1.9	[c]
Acheloos	1.8	[c]
Sperchios springs	1.0	0

[a] Percentage of riverine sodium and potassium originating from pollution

[b] These rivers are not included since their catchment areas contain mafic silicate rocks and a part of riverine silicate is originating additionaly from mafic rock weathering

[c] Suspended matter too low for XRD determinations

bonate concentration, and the suspended load, due to plankton assimilation, calcite precipitation, and sedimentation processes within the lakes (Skoulikidis 1991). However, the storage of grate river water masses within the lakes, for energy power production and agricultural purposes, causes an increase of sodium and chlorine concentration, down to the river mouths, reflecting soil and groundwater salinity rise.

Biological activity

In general, the contribution of biological activity on river water composition is not significant. Table 2 indicates that the high temperatures during the summer and the very low water levels favor photosynthesis, where CO_2 is consumed by algae and oxygen is released and as a result the DOC river content increase. The decrease of CO_2 drops the saturation indices of calcite and dolomite, and calcite precipitation takes place within the artificial lakes or at river mouths. During the winter, respiration dominates over photosynthesis, reversing the described processes.

Stream hydrography

Application of cluster analyses for each river examined, comparing seasonal hydrochemical variations with hydrochemical variations along the river course, show that river water composition is primarily a function of seasonal variations (see for example Fig. 3). Hydrochemical variations depend on discharge fluctuations and the origin of waters (surface runoff, interflow, base flow) that contribute to the river hydrography. In order to classify the rivers according to the seasonal relationship between water discharge and dissolved constituents, focusing especially on major ions, four river types were distinguished:

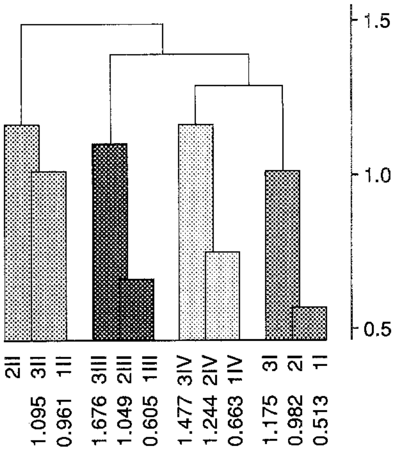

Fig. 3. Cluster analysis on hydrochemical data of the river Axios. 1, 2, 3: sample stations; I: automn (late summer), II: winter, III: spring, IV: early summer

Dilution-type rivers

This river type is marked by an inverse relationship between discharge and dissolved solid concentration, resulting from dilution of base flow, which is rich in solutes, by precipitation inputs, surface runoff, and interflow with shorter retention times. Small mountaineous rivers (Arkudoremma, Ardas and Gallikos) as well as the upstreams portions of Nestos and Sperchios belong to this river type.

Floodplain river type a

In this river type maximum solute concentrations occur during the summer accompanied by a second peak on the rising limb of the hydrograph in autumn, caused by an initial flushing of highly concentrated waters, accumulated in the soil pores during the dry period. With increasing discharge, the dilution effect dominates. Seasonal hydrochemical variations of this type occur in the major northern Greek rivers: Evros, Strymon, Axios, and the downstream portion of Nestos.

Floodplain river type b

This river type is characterized by higher solute content after initial flooding (flushing effect) than during base flow in summer. In spring, river water is diluted. Rivers of this type are Aliakmon, Pinios and Acheloos.

Karst water river type

Only the waters of the Angitis, mainly originating from carbonate karst, define this river type. The Angitis exhibits low seasonal discharge/hydrochemical fluctuations. Dilution and base flow effects are absent. High solute concentrations occur during the third quarter of the year and low concentrations during summer.

Classification of the rivers according to their seasonal hydrochemical variations results in the following: The hydrochemical similarities between the rivers Nestos, Strymon, and Axios (first hydrochemical group) could be explained by their similar seasonal discharge/solute concentration variations. Besides petrographic characteristics, the similar hydrographic characteristics of Aliakmon and Sperchios could contribute to their hydrochemical relationships.

Geomorphology

Highland rivers or river parts are marked by lower solute concentrations in comparison with lowland waters. This is caused by the following factors: The lower groundwater percentage of river water; the lower retention times of base flow, interflow, and surface flow waters; and the lower population concentration, industrial and agricultural activities, which are reflected on low pollution parameters concentrations. In contrast, the dissolved and particulate organic content of highland rivers or upstream river sites are higher, due to soil/climatic conditions (Schlessinger and Melack 1981).

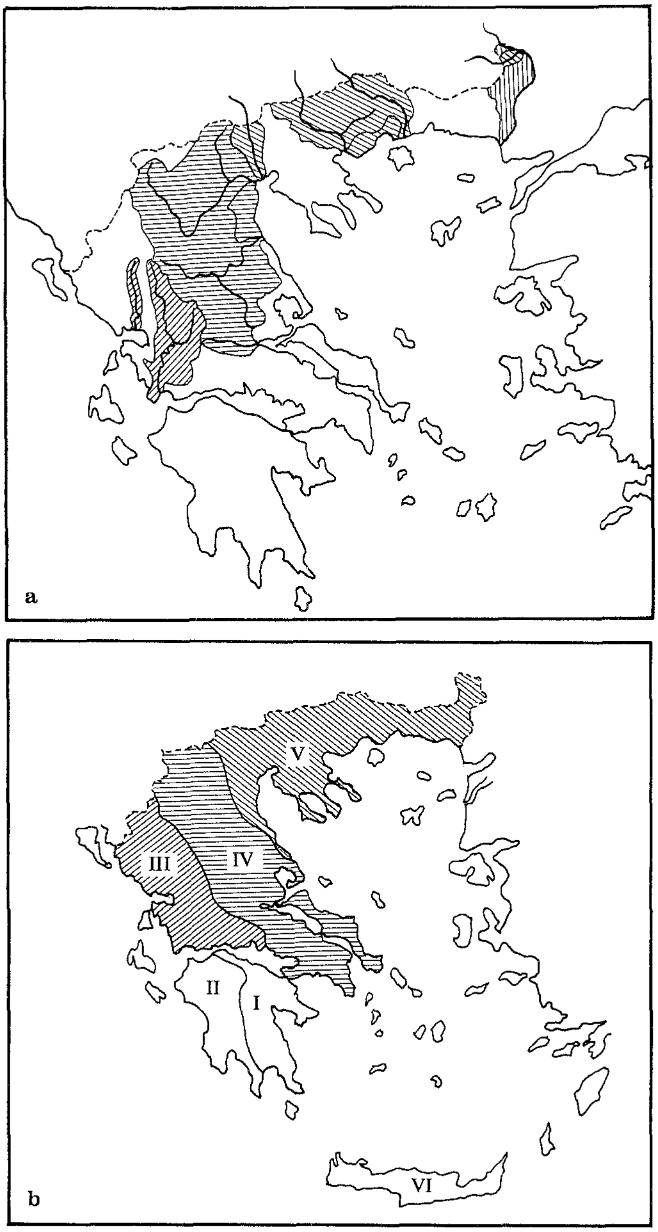

Fig. 4a,b. a Hydrochemical classification of the major Greek rivers, **b** climatic zones of Greece

Soils/sediments

The low ion, silicate, and DOC concentrations in the western Greek rivers is caused by the poor, leached soils of their watersheds (Nakos 1984). River suspended solids are derived by erosion and soil transport during flood events (Skoulikidis 1991). The positive correlation between river discharge and DOC concentration (see Table 2) indicates that the origin of DOC in river water is mainly terrestrial and is transported as a soil constituent during flood events. The correlation between DOC and river catchment area (Table 2) reflects the higher DOC concentrations in soils of the great northern Greek international river catchments (Evros, Nestos, Strymon, Axios).

Climate

Climate is relief dependent. It includes precipitation rates, and controls stream hydrography as well as the weathering intensity, soil/sediment formation/composition and the biological activity. By comparing the hydrochemical river classification with the climate zones of Greece (Katsiou and others 1989) (Fig. 4), one can see the great influence of climate on river water composition.

In conclusion, it is mainly climate and petrography of the catchment area and less aquatic pollution that control river water composition.

References

Katsiou K, Kontaxopoulos G, Petrou MF and Trezos CG (1989) Snow loading in Greece—a statistical analysis. Techn Chron 9(1):37–70

Nakos G (1984) Relationships of bio-climatic zones and lithology with various characteristics of forest soil in Greece. Plant Soil 79:101–121

Schlessinger Wand Melack (1981) Transport of organic carbon in the World's Rivers: Tellus, 33, p. 172–187.

Skoulikidis NT (1988) Biogeochemistry of the major Greek rivers. In: Astruc M and Lester JN (Eds) Heavy metals in the hydrological cycle. London: Selper Ltd., pp 687–694

Skoulikidis NT (1991) Overview on the hydrochemistry of the major Greek rivers. Ann Geol Pays Hell (accepted)

Stallard RF (1985) River chemistry, geomorphology and soils in the Amazon and Orinoco basins. In: Drever JI (ed) The chemistry of weathering, NATO ASI Series. Dordrecht: D. Reidel, pp 293–316