



Analysis of factors driving stream water composition and synthesis of management tools—A case study on small/medium Greek catchments

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Abstract

Twenty-nine small- and mid-sized permanent rivers (thirty-six sites) scattered throughout Greece and equally distributed within three geo-chemical-climatic zones, have been investigated in a seasonal base. Hydrochemical types have been determined and spatio-temporal variations have been interpreted in relation to environmental characteristics and anthropogenic pressures. Multivariate statistical techniques have been used to identify the factors and processes affecting hydrochemical variability and the driving forces that control aquatic composition. It has been shown that spatial variation of aquatic quality is mainly governed by geological and hydrogeological factors. Due to geological and climatic variability, the three zones have different hydrochemical characteristics. Temporal hydrological variations in combination with hydrogeological factors control seasonal hydrochemical trends. Respiration processes due to municipal wastewaters, dominate in summer, and enhance nutrient, chloride and sodium concentrations, while nitrate originates primarily from agriculture. Photosynthetic processes dominate in spring. Carbonate chemistry is controlled by hydrogeological factors and biological activity. A possible enrichment of surface waters with nutrients in “pristine” forested catchments is attributed to soil leaching and mineralisation processes. Two management tools have been developed: a nutrient classification system and a rapid prediction of aquatic composition tool. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The Greek peninsula is formed by small basins, drained by relatively small rivers. This is a result of the geologically recent morphology, characterised by mountainous relief with high slopes and dry climatic

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conditions. There are 765 recorded rivers, 45 of which are registered as permanently flowing (Ministry for Development, 2003). Since the 1970s, major Greek rivers are regularly monitored for their quality at a monthly basis by the Ministry of Agriculture, and recently by the Ministry for the Environment Physical Planning and Public Works and the General States' Chemical Laboratory. In general, these rivers belong to catchments with an area over 700 km² and a mean annual discharge over 0.3 km³. Many of these rivers have been studied for their hydrochemical regime (Skoulikidis, 1993; Skoulikidis et al., 1998). Smaller catchments are not, or are only partly, included in the national monitoring networks. Thus, a significant number of small (catchment area < 100 km²) and medium rivers (catchment area 100–1000 km²) have not been studied at all. The total mean annual runoff of the Greek peninsula is estimated to be around 57 km³ (Ministry for Development, 2003). From this total amount, about 3 km³ is groundwater, which drains directly to the sea predominately through karstic springs (Kallergis, 1979). On the other hand, the sum of mean annual runoff of studied rivers is approximately 37 km³. Hence, about 17 km³/a, i.e., 35% of the total Greek runoff enters the sea from river basins with unknown hydrological and hydrochemical regime. This study aims to fill part of this gap.

A river is an open system with strong interactions with its drainage basin. Various abiotic and biotic processes, such as weathering, erosion, sedimentation, evaporation, biological activity, adsorption and desorption, flushing etc., as well as human interference, interact within the watershed, the riparian zone, the river floodplains and the water body itself, determining its aquatic composition. These factors and processes are combined to create a diverse water composition that changes spatially and temporally. Due to the dynamic interrelationships between factors and processes, the identification of the underlying driving forces, that control aquatic composition and its variations is a complex task and requires a special approach (e.g. Garrels and Mackenzie, 1967; Stallard, 1980; Zobrist and Stumm, 1981; Meybeck and Helmer, 1989; Skoulikidis, 1993; Markich and Brown, 1998; Skoulikidis et al., 2002; Interlandi and Crockett, 2003). Moreover, in view of the variable climatic and biogeographical regime and the complex morpho-

logical and geological structure of Greece, this task becomes more ambitious. Among the aims of this article are to present and interpret the composition of small- and mid-sized permanent rivers, in relation to environmental variables and anthropogenic pressures, to distinguish hydrochemical types and to assess particular factors and processes controlling hydrochemical variability.

Through the Water Framework Directive (WFD 2000/60 EC), the EU seeks to impose a methodology to recover degraded water bodies. One of the basic objectives of the Water Framework Directive is the establishment of reference conditions and the ecological classification of water bodies into quality categories. The values of chemical–physicochemical quality elements, complementary to the biological ones should be taken into account for assigning to water bodies high and good quality status (ECOSTAT Report, 2003). In Greece, there is a lack of a national classification system either for biological or for chemical quality elements (Ecomomou and Skoulikidis, 2002). Skoulikidis et al. (2004) developed a macroinvertebrate based biological quality classification system for Greek running waters affected by nutrient impact. In order to fill the gap of chemical classification of small/medium rivers affected by nutrient pollution, the present article proposes a nutrient classification system (NCS). NCS is based on the former biological quality classification system.

The first step for the development of an integrated national ecological quality assessment and classification system includes the design of a representative monitoring network. This will be based on a site pre-classification procedure. Greek surface waters are, in general, of a satisfactory quality concerning toxic substances. Elevated heavy metal and organic micropollutants concentrations are found in a restricted number of water bodies (Skoulikidis et al., 1998; Lekkas et al., 2004). Thus, point and diffuse nutrient sources, together with hydro-morphological alterations, are the major causes of freshwater degradation. In order to facilitate the implementation of the WFD, the present article proposes tools for the rapid prediction of aquatic chemistry and quality in small/medium rivers: a total dissolved ions (TDI) concentration prediction tool (TDI-PT) and a nutrient concentration prediction tool (N-PT).

2. Study area

The study area includes sampling sites that are distributed over the entire Greek territory (Fig. 1). The river sites belong to three geographical zones,

so called geo-chemical-climatic zones, with distinct climatic, geological and hydrochemical characteristics (Skoulikidis, 1993; Skoulikidis et al., 2004): the north-eastern zone (zone 1), the north-central zone (zone 2) and the western zone (zone 3) (Fig. 1).

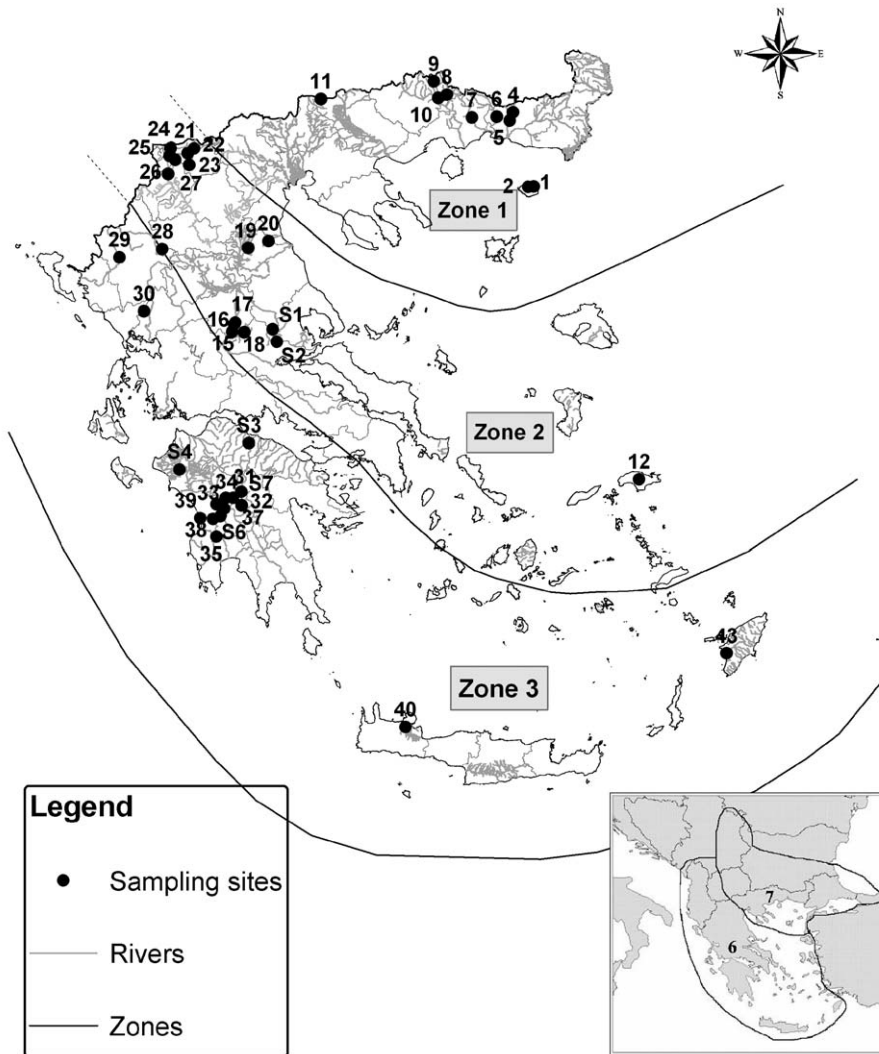


Fig. 1. Greek core geo-chemical-climatic zones (Skoulikidis, 1993; Skoulikidis et al., 2004) and sampling points. The small map shows the Greek ecoregions, according to Illies (1967). Rivers (site names): 1: Foniais (Perasmata), 2: Tsvidogianni (Gria Vathra), 4: Vospos (Symvola), 5: Vospos (Mesochori), 6: Kompasatos (Byzantine bridge), 7: Xanthia (Gorgona), 8: Arkoudoremma (Dipotama), 9: Prasinada, 10: Diavoloremma (Thermia), 11: Poroia, 12: Kokoremma (Manolates), 15: Onochonos (Smokovo), 16: Onochonos (Thrapsimi), 18: Onochonos (Kaitsa), 19: Mavroremma (Olosson), 20: Skamnias (Kalipevki), 21: Florinis-tributary (Drosopigi), 22: Florinis (Florina), 23: Lygos (Tripotamo), 24: Aliakmon (Pisoderi), 25: Aliakmon (Adartiko), 26: Aliakmon (Gavros), 27: Melas, 28: Aaos (Milea), 29: Thyamis or Kalamas (Paliouris), 30: Louros (Roman Aquaduct), 31: Steno (Methydrio), 32: Alpeios (Karytena), 33: Tsouraki, 34: Lousios (Gortys), 35: Pamisos (Vrachopanagitsa), 37: Neda (Eira), 38: Neda (Marina), 39 Neda (Elea), 40: Kiliaris (Aptera), 43: Sianitis (Apolakia), S1–S7 (STAR sites) (see Section 3.9).

Considering major Greek rivers, zone 1 includes rivers with medium hard waters, zone 2 is characterised by hard water rivers, with high magnesium content, while rivers in zone 3 are characterised as diluted (Skoulikidis, 2000a).

These zones are simultaneously characterised by different geological (Fig. 2) and climatic features. Zone 1 is of an acid silicate type, zone 2 belongs to a mafic silicate type, whereas zone 3 is characterised as a carbonate type zone (Skoulikidis, 2000a).

Regarding climate conditions, zone 3 is marked by maximum rainfall, while zone 2 by minimum one, whereas zone 1 has minimum air temperature (Mavromatis, 1980). In addition, a southward, and a less significant eastward, increase in evapotranspiration is evident (Dalezios et al., 2002). Finally, as a result of the climatic conditions, zone 3 is characterised by poor, leached soils (Nakos, 1984).

The catchments, which were analysed for the present study, were selected to be representative of the average geologic and climatic conditions of their respective zones.

3. Materials and methods

3.1. Sampling and data collection

A total number of 29 rivers were examined and 36 sampling sites were selected within the framework of AQEM project (EVK1-CT-1999-00027). The sites were almost equally distributed within the aforementioned geographical zones (Fig. 1). Since anthropogenic activities affect major ion composition (e.g. Berner and Berner, 1987), in order to compare water quality between the zones with confidence that the

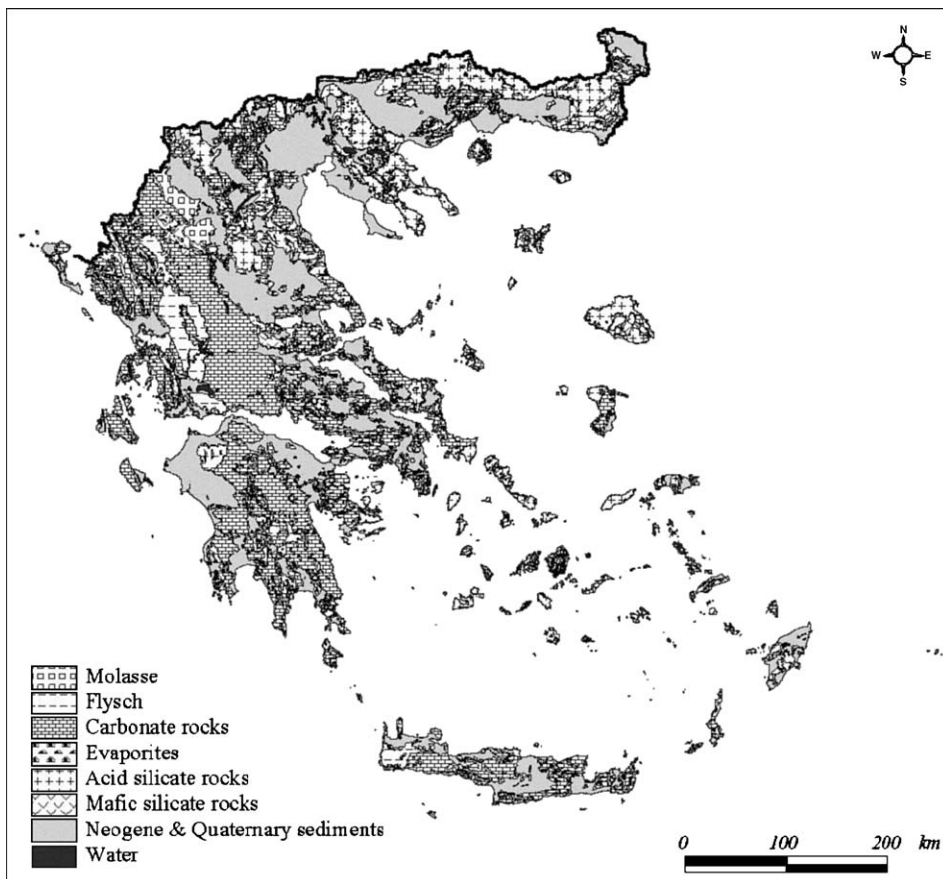


Fig. 2. Basic geological formations in Greek Peninsula (GIS department of Hellenic Centre for Marine Research).

resulting differences are not caused by pollution variability, care was taken so that the sites of each zone would present similar pollution gradient. For that purpose, the sites were pre-classified into five quality categories, ranging from high to bad following a pre-classification procedure (Hering et al., 2003). The site pre-classification was carried out according to anthropogenic pressures, that were assessed in situ and with the help of existing information (national reports, publications, personal communication with local authorities). In each zone, at least three of the selected sites were pre-classified as reference, three as good, three as moderate, one as poor and one as bad (Skoulikidis et al., 2004). Samples were collected three times seasonally (spring, summer, and winter) during the period 2000–2001. At each sampling site, physicochemical parameters (current flow, water temperature, dissolved oxygen, pH, and conductivity) were measured in situ. Samples were kept cool and transferred as quickly as possible to the laboratory where, after filtration through 0.45 μm membrane filters, hydrochemical variables (total hardness, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} , SiO_2) and conventional pollution parameters (nitrate, ammonia, nitrite, orthophosphate and total phosphorous) were analysed. Calcium, magnesium, sodium, sulphate, chloride and potassium were analysed with a Capillary Ion Analyser (US Patent 5,104,506/European patent 0442315 A1). Hydrogen carbonate, carbonate and total hardness were determined by automatic titration (TIM 900—Radiometer). Nutrients were analysed photochemically with a Nova 400 analyser by Merck. The detection limits were: for *N*-nitrate, 60 $\mu\text{g/l}$; for *N*-nitrite, 2 $\mu\text{g/l}$; for *N*-ammonia, 4 $\mu\text{g/l}$; and for phosphorus, 10 $\mu\text{g/l}$. For quality control and quality assurance purposes, a number of samples were tested with more than one of the available analytical methodologies and the results were cross-checked. Information about the site and its catchment, e.g., distance from source, stream order, altitude, slope, catchment area, stream density, geology, land use was gathered by applying GIS methods. Additional data, such as stream morphology, hydrological aspects, floodplain characteristics, river bed substrate composition, river cross sections, riparian vegetation, human impacts and pollution sources, was collected in situ, on the sampling site as well as at the reach scale. The resulting data matrix consists of 6156 observations (36 stations \times 3 seasons \times 57 variables).

3.2. Substrate composition

Substrate composition in the flooded river channel was estimated in situ using the AQEM-protocol (AQEM Consortium, 2002). According to this protocol, the coverage of all substrate types with more than 5% cover is estimated. The appearance of other substrates with <5% cover is just indicated by a spot. The surveyed stretch, for which the substrate composition is estimated, is representative for the stream part and covers an area of 25–50 m.

3.3. Quality control of hydrochemical analyses

Hydrochemical data quality was controlled by simple techniques, such as ion balance and comparison of measured electrical conductivity with the calculated one (Appelo and Postma, 1999). Conductivity was calculated from the sum of ion equivalent conductivities. For that purpose the Fauth's coefficients (Mattes, 1973) were used. Furthermore, an extreme values analysis was carried out, in order to determine the outliers and extremes (Statistica Release 6.0). The extreme values analysis is the analysis of the distribution of values that deviate from central tendencies for their respective groups. The median was used to define the central tendency. In order to calculate the outliers, we multiplied the range of the 25–75% percentiles with 1.5 (outlier coefficient) and the result was added to the 75% percentile and abstracted from the 25% percentile, respectively. These were the limits of the non-outlier range. The same procedure was followed in order to calculate the extreme values, multiplying this time with 3 (extreme value coefficient).

3.4. Hydrochemical classification

To delineate spatial variability in rivers' water quality in terms of major ions, trilinear diagrams were constructed using the method of Piper (1944) (Fig. 5). Using Piper diagrams, it was possible to classify rivers and river zones in different hydrochemical facies, according to Back (1961). Hydrochemical types were defined according to major cation and anion sequences. For water hardness, the classification after Hem (1985) was followed. Finally, a classification of water mineralisation has been proposed.

3.5. The carbonate system

For the calculation of the CO₂ partial pressure (pCO₂) and the calcite and dolomite saturation indices in the water samples (Table 4), a computer programme (Kempe, 1975) has been applied. The programme considers the ion activities deriving from an upper estimation of the ionic strength, calculates the ion pair concentrations and obtains in this way a better estimation of the free ions, to be used for a new approximation of ionic strength (Wigley, 1971).

3.6. Seasonal trends in aquatic composition

Analysis and interpretation of seasonal variability of aquatic composition (major ions, pCO₂, nutrients) is provided with this article. Obviously, just the three seasonal samples alone are not adequate to yield reliable results. Nevertheless, considering the authors experience in interpreting seasonal variations using seasonal data collected at different time intervals (Skoulikidis and Kondylakis 1997; Skoulikidis et al., 1998; Skoulikidis, 2004), the detection of rough seasonal trends has been attempted.

3.7. Statistical treatment of the data set

The data set was treated by means of a set of basic and multivariate statistical techniques. Basic statistics were performed on the data of each river zone separately (Table 1a–c). The coefficient of variation (CV) was used as a measure of the relative dispersion of the different variables.

In order to obtain relationships between the different variables, a Correlation Matrix was performed, on standardized data of the yearly average of the total number of sites, using the Statistica Release 6.0 (Table 6). The correlation coefficient (r) was used to determine the degree of the linear correlation between two variables. Only correlations with $r > 0.4$, which at the same time are significant at $p < 0.05$, have been considered (Swan and Sandilands, 1995). The significance of the correlation coefficient was estimated using a t statistic.

To reveal probable factors and processes controlling aquatic composition, an R-mode Principal Component Analysis (PCA) (Statistica Release 6.0) was

carried out on standardized hydrochemical (yearly average), anthropogenic and environmental data (Table 7). The data set has been reduced by subtracting one out of two depended variables that, according to the correlation matrix, were highly correlated with each other. For example, the variable TDI was erased and conductivity, which is an independent measure, was kept. Similarly, total hardness was discarded and Ca²⁺ and Mg²⁺ concentrations were used.

To assess whether the three river zones present any statistically significant hydrochemical differences and whether seasonal hydrochemical differences within each zone can be statistically accepted, a two-way ANOVA test (Moore and Cobby, 1998) was performed (Table 3 and Fig. 8). By applying this technique it was possible to detect if the differing means per zone or per season were due to real differences or due to random variation. Differences with a p -value=0.05 were statistically accepted. The ANOVA test was carried out on water temperature, pH, electrical conductivity, major ions and dissolved silica.

3.8. A nutrient quality classification system

Fig. 3 illustrates the methodology followed for the establishment of nutrient reference conditions and the development of a Nutrient-quality Classification System (NCS) for non-hydro-morphologically altered small/medium permanent rivers. The NCS was principally based on the average values found in five quality classes of a biological classification system, which has been developed using benthic macroinvertebrates (Skoulikidis et al., 2004). For the definition of reference conditions, the 75th percentile of nutrient concentrations found in reference sites and the 25th percentile of nutrient concentrations found in all sites (EPA, 2000) (Table 8) were additionally considered. The upper limits of nutrient concentrations in good quality class were defined as the median of the average nutrient concentrations of biologically good stations and biologically moderate stations. Similarly, the upper limits of nutrient concentrations in the moderate class were estimated as the median of the average nutrient concentrations found in the moderate and poor classes. The same procedure was followed for the

upper limits of the poor quality class. Finally, the NCS (Table 9) has been slightly modified considering nutrient classification systems from other countries (Tables 10 and 11).

3.9. Prediction of aquatic composition

In order to predict aquatic composition, the multiple linear regression (MLR) technique has been applied, using the Minitab Release 13.1 (Table 13). MLR fits an equation that predicts the dependent variable (Y) from two or more independent variables (X). For the purposes of this work, dependent variables, such as TDI, nitrate, nitrite, ammonium, phosphate and total phosphorous have been calculated from land use, geographical and morphological data. For the selection of the independent variables, the correlation coefficients between dependent and independent variables from the correlation matrix (Table 6) have been used. Several combinations of independent variables have been tested and the most significant ones have been selected. The validation of the equations has been tested by physically based values of the independent variables. Additional tests have been made using data from STAR project (ENVK1-CT-2001-00089), which also considered small/medium rivers.

Fig. 4 is a flow chart illustrating the different steps of the methodology followed in this article.

4. Results

4.1. Presentation of the data set

Table 1a–c illustrate the most important morphological, geological, land use and mean annual hydrological and aquatic quality characteristics of the examined rivers in each one of the examined zones.

4.2. Environmental features

All catchments are small ($<100 \text{ km}^2$) to mid-sized ($100\text{--}1000 \text{ km}^2$) and the three zones revealed similar catchment size–CV values. All rivers presented minimum discharge in summer, and in the majority of them, peak discharge occurred in spring. Only two rivers showed maximum discharge in winter. Con-

cerning river bed composition, cobble material predominated in all zones, followed by boulders. Sand and mud formed only a small portion, while bedrock outcrops and silty/clayey material were minimally represented.

In zone 1, mid-altitude catchments prevail (200–800 m). Compared to the other zones, rivers in zone 1 presented, in average, medium annual water temperature, while differences between spring and winter temperatures were minor. Zone 1 includes catchments with maximum slopes, which are predominately covered with forests and grass or heath. Cultivated areas are very limited. The valley forms are usually U-shaped with wide floodplain. Compared to the other zones, stream width and depth are minimal. River catchments are almost entirely covered with acid silicate rocks and show maximum stream density and maximum flow compared to the other zones. In this zone, pyrite ores appear in Poroia stream (11) (IGME, 1965). The average discharge was medium. The median ratio between spring and summer discharge was very high (65), between spring and winter was high (22) and between winter and summer was low (2.5).

Zone 2 catchments range between medium and high altitudes ($>800 \text{ m}$). Compared to the other zones, the average annual water temperature was minimal. On average, rivers in this zone showed higher water temperature in winter ($8 \text{ }^\circ\text{C}$) than in spring ($7.1 \text{ }^\circ\text{C}$). Catchment slope and stream density are medium. The V-shaped valleys are more dominant, while floodplains are rather narrow. Compared to the other zones, stream width and depth were medium and the average discharge was minimal. The median ratio between spring and summer discharge was medium (16), while the median ratios between winter/summer and spring/winter discharge were low (4.5 and 3.7 respectively). The main part of the catchments is covered by acid silicate rocks, while mafic rocks (ophiolites) are present in four catchments. Carbonate rocks are the second important rock formation, while recent sediments show maximum percentage of participation in the catchments compared with the other zones. In this zone, hydrothermal activity occurs at one catchment [Onochonos (15, 18)]. Regarding land uses, zone 2 catchments present a lower forests and grassland/heathland coverage compared with zone 1 catchments and a higher percentage of agricultural land. Finally, the percentage of urban areas reaches its maximum in this zone.

Table 1

(a) Hydrological (annual average), morphological, geological, land use and hydrochemical (annual average) characteristics of zone 1 catchments

River sites		1	2	4	5	6	7	8	9	10	11	AV	ME	CV
Catchment area	km ²	9.1	2.1	56.7	124.7	555	209.8	113.8	44	20.7	2.9	113.9	50.4	148.2
Site altitude	m	26.6	70.9	108.1	27.9	36.1	148.8	422.9	319.9	689.9	864.8	271.6	128.5	110.4
Catchment altitude	m	825.1	699.0	248.7	248.7	527.6	475.5	1000.6	1000.6	1024.0	481.2	653.1	613.3	46.1
Catchment slope	%	43.7	49.1	38.7	25.2	34.6	33.7	31.5	37.4	37.7	39.9	37.2	37.6	17.7
Stream order		4	2	4	5	7	7	6	6	5	2	4.8	5	37.8
Stream density	m/km ²	4.1	2.2	2.1	1.8	4.3	4.5	3.8	4.4	4.5	1.8	3.3	3.9	36.6
Distance to source	km	7.8	3.9	18.9	29.9	65.6	29.4	21.6	13.5	7.6	3.0	20.1	16.2	93.3
Stream width	m	3.2	2.3	2.2	9.8	14.5	6.9	6.5	6.6	6.1	0.7	5.9	6.3	69.9
Stream depth	cm	28.8	29.3	31.5	15.4	27.9	28.4	15.4	25.5	29.3	11.3	24.3	28.2	30.0
Discharge	m ³ /sec	1.9	1.9	1.4	1.5	7.0	4.6	1.7	4.2	7.1	0.3	3.16	1.91	76.4
Flow	m/sec	2.1	2.2	1.5	1.5	1.4	2.4	1.1	1.5	1.9	3.3	1.9	1.7	33.6
Width of floodplain	m	380.0	6.0	7.0	13.0	26.0	17.0	6.0	7.0	14.0	1.0	47.7	10	245.2
Bedrock	%	0.0	0.0	16.7	0.0	0.0	0.0	0.0	1.7	0.0	0.0	1.7	0.0	310.0
Boulders	%	41.7	40.0	51.7	8.3	3.3	33.3	21.7	31.7	21.7	28.3	26.9	25	56.2
Cobbles	%	30.0	38.3	23.3	55.0	81.7	51.7	51.7	29.0	70.0	46.7	51	51.7	34.7
Pebbles	%	18.3	16.7	6.7	23.3	11.7	11.7	23.3	7.7	8.3	21.7	15.7	16.1	38.5
Sand/mud	%	10.0	5.0	1.7	13.3	3.3	3.3	3.3	3.3	0.0	3.3	4.7	3.3	84.9
Silt/clay	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–
Acid silicate rocks	%	73.4	0.0	100.0	66.0	94.6	93.7	99.4	84.8	100.0	100.0	81.2	94.1	38.1
Mafic silicate rocks	%	22.1	97.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	12.0	0.0	258.1
Carbonate rocks	%	0.0	0.0	0.0	0.0	0.3	4.2	0.0	15.2	0.0	0.0	2.0	0.0	245.0
Flysch and molasse	%	0.0	0.0	0.0	1.1	0.4	0.0	0.6	0.0	0.0	0.0	0.2	0.0	177.7
Lacustrine/marine deposits	%	0.0	0.0	0.0	3.9	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	–
Alluvial deposits	%	4.6	2.2	0.0	28.8	4.7	2.1	0.0	0.0	0.0	0.0	4.2	1.0	208.5
Native deposits	%	90	94.2	79.7	39.64	39	45.05	77.3	71.13	87.63	2.09	62.6	74.2	47.7
Grassland/ heathland	%	10	5.7	20.29	31.76	57.07	52.32	22.7	27.6	12.37	97.91	33.8	25.2	83.5
Heterogenic agricultural areas	%	0.0	0.0	0.01	11.13	2.26	2.53	0.0	1.27	0.0	0.0	1.7	0.0	200.9
Arable land	%	0.0	0.0	0.0	4.48	0.35	0.0	0.0	0.0	0.0	0.0	0.5	0.0	291.7
Permanent crops	%	0.0	0.0	0.0	10.57	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0	316.2
Unvegetated or some vegetated open areas	%	0.0	0.0	0.0	0.79	1.22	0.0	0.0	0.0	0.0	0.0	0.2	0.0	216.8
Inland waters	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–
Inland wet zones	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–
Urban fabric	%	0.0	0.1	0.0	0.82	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.0	226.1
Industrial or commercial units	%	0.0	0.0	0.0	0.65	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	316.2
Mining, landfills and construction sites	%	0.0	0.0	0.0	0.16	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	316.2
Water temperature	°C	12.3	12.5	14.0	15.6	16.2	14.4	10.5	10.7	11.9	10.1	12.8	12.4	16.8
pH		7.7	7.9	8.1	7.9	8.9	8.9	7.8	8.7	8.8	8.4	8.3	8.3	5.7
Conductivity	µS/cm	66.3	91.7	106.0	466.0	259.0	182.7	74.3	340.0	301.3	352.7	224.0	220.8	62.5
Total dissolved ions	mg/l	39.9	60.5	57.1	277.0	167.6	129.8	43.3	204.8	175.5	248.2	140.4	148.7	62.5
Total hardness	mg/l	19.33	35.67	34.33	155.33	105.33	93.67	26.67	168.67	120.00	157.00	91.60	99.50	64.20
Dissolved oxygen	mg/l	9.9	8.54	12.033	10.167	10.14	11.817	11.2	11.467	12.7	9.2	10.7	10.7	12.4
Oxygen saturation	%	95	83	115	102	102	112	99	103	116	84	101	102	11.3
Calcium	meq/l	0.30	0.53	0.44	2.07	1.49	1.46	0.41	3.02	1.98	1.92	1.36	1.47	67.36
Magnesium	meq/l	0.09	0.20	0.25	1.04	0.62	0.41	0.12	0.36	0.42	1.22	0.47	0.39	80.90
Sodium	meq/l	0.26	0.27	0.31	1.76	0.76	0.39	0.21	0.25	0.97	0.19	0.54	0.29	93.71
Potassium	meq/l	0.03	0.04	0.04	0.19	0.07	0.06	0.05	0.07	0.07	0.26	0.09	0.06	87.67

Alkalinity	meq/l	0.38	0.73	0.79	2.55	1.79	1.69	0.58	2.92	2.69	2.10	1.62	1.74	58.5
Sulphate	meq/l	0.13	0.22	0.17	0.90	0.72	0.44	0.18	0.52	0.57	1.74	0.56	0.48	87.26
Chloride	meq/l	0.21	0.21	0.21	1.04	0.31	0.18	0.06	0.11	0.14	0.04	0.25	0.20	114.93
Silicate (SiO ₂)	mg/l	9.23	9.57	9.33	13.56	9.81	12.97	14.76	11.99	13.25	10.85	11.53	11.42	17.6
N-nitrate	mg/l	0.73	0.59	0.26	1.44	0.60	0.35	0.14	0.42	0.18	0.18	0.49	0.38	79.83
N-nitrite	mg/l	0.003	0.002	0.003	0.098	0.004	0.005	0.003	0.003	0.003	0.008	0.013	0.003	226.161
N-ammonium	mg/l	0.123	0.013	0.118	0.186	0.010	0.080	0.007	0.007	0.010	0.036	0.059	0.025	108.323
P-phosphate	mg/l	0.115	0.078	0.062	0.510	0.105	0.156	0.059	0.074	0.079	0.124	0.136	0.092	98.885
Total phosphorous	mg/l	0.179	0.132	0.114	0.590	0.248	0.296	0.079	0.121	0.109	0.176	0.204	0.154	74.088
N/P (Spring)		9.1	10.2	2.8	16.1	0.7	2.0	1.9	2.8	1.4	0.9	4.8	2.4	108.0

(b) Hydrological (annual average), morphological, geological, land use and hydrochemical (annual average) characteristics of zone 2 catchments

River sites		12	15	16	18	19	20	21	22	23	24	25	26	27	AV	ME	CV
Catchment area	km ²	2.2	6.8	463.6	167.8	219.1	48.6	20.1	49.1	428.1	5.1	39.9	378.0	20.8	142.2	48.6	124.6
Site altitude	m	239.9	419.2	180.4	395.1	345.6	705.5	994.3	669.0	600.2	1352	983.3	724.3	1024	664.1	669.0	52.4
Catchment altitude	m	538.2	765.1	334.6	334.6	611.7	1069	1241	985.5	986.0	1735	1481	1240	1241	966.2	985.5	45.8
Catchment slope	%	42.9	31.0	25.0	12.7	26.0	20.5	37.7	34.2	18.1	42.6	36.1	29.1	31.9	29.8	31.0	32.1
Stream order		2.0	5.0	7.0	4.0	6.0	5.0	4.0	5.0	6.0	3.0	5.0	6.0	4.0	4.8	5.0	29.4
Stream density	m/km ²	2.0	6.0	3.3	1.9	3.6	3.5	2.0	3.3	2.3	2.2	2.7	2.9	2.0	2.9	2.7	39.6
Distance to source	km	2.6	4.3	32.5	6.7	29.0	13.2	6.6	17.1	29.2	3.6	10.8	33.6	6.5	15.1	10.8	80.3
Stream width	m	19.3	1.3	7.4	1.5	1.4	1.7	1.1	2.7	31.8	0.8	3.6	10.4	0.7	6.5	1.7	148.0
Stream depth	cm	8.6	9.0	33.2	12.6	13.2	26.0	15.1	12.3	28.0	10.7	17.8	21.3	8.6	16.7	13.2	48.6
Discharge	m ³ /sec	0.0	0.2	7.2	0.3	0.5	0.7	0.2	1.8	14.5	0.1	1.0	4.9	0.2	2.4	0.5	178.3
Flow	m/sec	1.5	1.2	0.9	1.2	1.2	0.9	1.7	2.1	1.8	1.4	1.8	1.8	1.7	1.5	1.5	25.2
Width of Floodplain	m	105.0	2.0	28.0	5.0	5.0	2.0	3.0	8.0	42.0	1.0	4.0	18.0	2.0	17.3	5.0	173.3
Bedrock	%	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	23.3	0.0	0.0	0.0	0.0	2.2	0.0	310.1
Boulders	%	41.7	25.0	0.0	16.7	10.0	6.7	28.3	0.0	16.7	25.0	23.3	13.3	28.3	18.1	16.7	67.8
Cobbles	%	36.7	41.7	78.3	50.0	48.3	50.0	51.7	51.7	45.0	63.3	51.7	71.7	50.0	53.1	50.0	22.7
Pebbles	%	8.3	21.7	3.3	25.0	35.0	21.7	15.0	31.7	3.3	10.0	18.3	11.7	16.7	17.1	16.7	60.7
Sand/mud	%	8.3	11.7	18.3	8.3	6.7	16.7	5.0	13.3	3.3	1.7	5.0	3.3	5.0	8.2	6.7	66.2
Silt/clay	%	0.0	0.0	0.0	0.0	0.0	5.0	0.0	3.3	8.3	0.0	1.7	0.0	0.0	1.4	0.0	191.6
Acid silicate rocks	%	81.4	0.0	0.0	0.0	62.0	37.4	100.0	94.6	51.8	100.0	89.9	41.8	72.2	56.2	62.0	70.2
Mafic silicate rocks	%	0.0	0.0	29.4	56.8	0.0	3.7	0.0	0.0	0.0	0.0	0.0	0.0	17.6	8.3	0.0	213.7
Carbonate rocks	%	18.6	100.0	55.9	12.9	16.0	22.4	0.0	0.0	9.9	0.0	0.0	35.4	0.0	20.9	12.9	141.8
Flysch and molasse	%	0.0	0.0	5.4	4.6	7.0	3.2	0.0	0.0	0.0	0.0	0.0	3.6	0.0	1.8	0.0	142.8
Lacustrine/marine deposits	%	0.0	0.0	0.0	0.0	4.0	19.1	0.0	5.3	22.9	0.0	2.1	16.1	10.2	6.1	2.1	138.7
Alluvial deposits	%	0.0	0.0	9.3	25.7	11.0	14.2	0.0	0.1	15.4	0.0	8.0	3.1	0.0	6.7	3.1	123.9
Native forests	%	95.0	10.8	30.8	2.6	8.8	8.2	89.3	55.8	34.6	72.3	91.2	41.7	44.3	45.0	41.7	77.6
Grassland/ heathland	%	4.5	89.2	41.8	38.6	72.9	75.2	3.2	29.5	28.7	27.7	8.5	45.8	55.2	40.1	38.6	70.5
Heterogenic agricultural areas	%	0.0	0.0	7.2	4.3	0.6	7.0	0.0	11.8	13.4	0.0	0.3	4.6	0.5	3.8	0.6	126.6
Arable land	%	0.0	0.0	19.6	52.7	16.4	9.5	0.0	0.0	20.3	0.0	0.0	2.5	0.0	9.3	0.0	168.9
Permanent crops	%	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.0	0.0	0.1	0.0	264.3
Unvegetated or some vegetated open areas	%	0.0	0.0	0.5	1.1	1.1	0.0	7.5	0.0	0.4	0.0	0.0	5.3	0.0	1.2	0.0	200.5
Inland waters	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-
Inland wet zones	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Urban fabric	%	0.0	0.0	0.2	0.5	0.2	0.1	0.0	2.8	1.8	0.0	0.0	0.1	0.0	0.4	0.1	199.3

(continued on next page)

Table 1 (continued)

(b) Hydrological (annual average), morphological, geological, land use and hydrochemical (annual average) characteristics of zone 2 catchments																	
River sites		12	15	16	18	19	20	21	22	23	24	25	26	27	AV	ME	CV
Industrial or commercial units	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–
Mining, landfills and construction sites	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–
Water temperature	°C	13.8	16.8	12.6	15.3	16.2	12.2	6.6	13.1	13.1	6.2	10.3	10.7	10.0	12.1	12.6	27.9
pH		8.9	9.3	8.9	8.6	8.8	8.2	8.1	8.6	8.0	7.8	7.9	8.1	7.5	8.4	8.2	5.6
Conductivity	µS/cm	502.7	365.3	536.7	608.3	378.0	293.7	57.3	200.7	395.0	40.0	89.3	190.7	65.3	286.4	293.7	66.9
Total dissolved ions	mg/l	223.4	335.4	351.3	191.8	188.3	30.5	118.4	191.8	26.5	51.5	110.7	38.6	309.4	166.7	188.3	67.5
Total hardness	mg/l	269.33	170.33	299.33	384.50	150.33	132.33	20.67	77.00	141.00	15.00	30.00	97.00	25.00	139.37	132.33	83.73
Dissolved oxygen	mg/l	8.9	6.7	8.6	9.0	8.4	8.6	10.1	8.3	7.7	9.7	12.0	11.6	9.0	9.1	8.9	16.6
Oxygen saturation	%	88	72	84	93	87	81	86	79	59	83	109	107	82	85.3	83.7	16.1
Calcium	meq/l	3.06	2.56	2.24	0.78	2.04	2.07	0.27	1.19	1.91	0.21	0.41	1.52	0.32	1.43	1.52	66.24
Magnesium	meq/l	2.33	0.85	3.75	6.92	0.97	0.57	0.14	0.35	0.91	0.10	0.19	0.42	0.17	1.36	0.57	148.85
Sodium	meq/l	0.37	0.87	0.41	0.15	0.62	0.44	0.14	0.48	0.54	0.12	0.22	0.15	0.17	0.36	0.37	64.51
Potassium	meq/l	0.04	0.05	0.04	0.04	0.09	0.07	0.05	0.14	0.20	0.04	0.08	0.06	0.04	0.07	0.05	69.78
Alkalinity	meq/l	4.80	3.08	4.60	7.17	3.61	2.02	0.49	1.31	2.71	0.33	0.63	2.08	0.55	2.6	2.1	80.1
Sulphate	meq/l	0.63	0.55	0.96	0.18	0.36	0.60	0.10	0.33	0.52	0.12	0.17	0.16	0.16	0.37	0.33	71.51
Chloride	meq/l	0.43	0.27	0.14	0.10	0.34	0.49	0.03	0.31	0.31	0.05	0.18	0.07	0.04	0.21	0.18	72.42
Silicate (SiO ₂)	mg/l	6.22	35.87	20.43	44.77	12.42	16.12	12.54	17.88	18.36	11.48	14.55	11.37	14.43	18.2	14.6	60.7
N-nitrate	mg/l	0.06	0.79	1.35	0.46	1.16	1.56	0.10	0.73	1.67	0.20	0.17	0.52	0.14	0.69	0.52	84.79
N-nitrite	mg/l	0.002	0.053	0.009	0.003	0.008	0.005	0.003	0.016	0.039	0.004	0.006	0.014	0.003	0.013	0.006	126.034
N-ammonium	mg/l	0.010	0.264	0.101	0.182	0.032	0.032	0.013	0.193	1.571	0.018	0.019	0.034	0.011	0.191	0.032	229.697
P-phosphate	mg/l	0.075	0.179	0.123	0.160	0.208	0.134	0.095	0.385	0.535	0.138	0.102	0.181	0.150	0.189	0.150	70.880
Total phosphorous	mg/l	0.185	0.186	0.195	0.196	0.321	0.146	0.124	0.457	0.625	0.151	0.124	0.217	0.194	0.240	0.194	63.547
N/P (Spring)		7.0	4.9	36.9	3.9	3.0	11.1	1.3	3.2	9.4	1.2	0.9	3.7	0.9	6.7	3.7	147.0

(c) Hydrological (annual average), morphological, geological, land use and hydrochemical (annual average) characteristics of zone 3 catchments																	
River sites		28	29	30	31	32	33	34	35	37	38	39	40	43	AV	ME	CV
Catchment area	km ²	16.9	25.0	323.9	17.7	868.6	2.4	112.1	121.4	27.9	38.2	277.6	128.0	7.7	151.3	38.2	158.0
Site altitude	m	1379.6	184.2	90.6	1025.3	307.4	617.9	370.9	105.6	600.5	482.2	5.1	2.2	129.6	407.8	307.4	101.9
Catchment altitude	m	1221.7	657.9	421.8	982.2	679.7	701.2	1074.4	396.2	635.0	635.0	635.0	598.9	266.3	685.0	635.0	39.4
Catchment slope	%	28.2	15.0	29.4	23.6	19.5	46.0	26.4	21.9	31.8	34.6	32.9	27.2	20.1	27.4	27.2	29.2
Stream order		5.0	4.0	6.0	4.0	7.0	3.0	5.0	5.0	4.0	4.0	6.0	6.0	4.0	4.8	5.0	23.6
Stream density	m/km ²	3.1	2.3	2.3	1.7	2.3	2.6	2.3	1.6	2.2	2.0	1.9	3.0	3.3	2.4	2.3	21.8
Distance to source	km	7.4	9.6	42.8	10.1	61.8	3.1	23.0	20.0	7.6	10.4	36.8	21.6	6.1	20.0	10.4	87.1
Stream width	m	6.7	6.5	20.2	1.9	6.7	35.7	13.7	8.5	7.4	6.4	8.1	7.1	1.1	10.0	7.1	90.9
Stream depth	cm	25.4	31.0	34.5	19.9	27.9	13.0	40.2	25.2	17.6	21.3	21.1	66.0	17.4	27.7	25.2	49.5
Discharge	m ³ /sec	1.9	5.5	12.8	0.1	9.2	0.1	14.4	1.3	1.0	1.3	1.4	36.2	0.1	6.6	1.4	155.5
Flow	m/sec	1.2	2.4	2.3	0.4	3.3	1.1	2.7	0.8	1.3	0.9	0.7	3.1	0.9	1.6	1.2	61.1
Width of floodplain	m	13.0	18.0	26.0	3.0	18.0	2.0	18.0	11.0	13.0	10.0	18.0	7.0	2.0	12.2	13.0	60.3

Bedrock	%	16.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.3	0.0	360.6
Boulders	%	20.0	53.3	3.3	6.7	6.7	36.7	31.7	15.0	53.3	43.3	11.7	0.0	16.7	22.9	16.7	81.6
Cobbles	%	53.3	41.7	86.7	70.0	70.0	51.7	53.3	55.0	36.7	50.0	81.7	52.5	45.0	57.5	53.3	26.3
Pebbles	%	5.0	3.3	6.7	16.7	16.7	10.0	10.0	23.3	10.0	6.7	1.7	10.0	31.7	11.7	10.0	72.6
Sand/mud	%	3.3	1.7	3.3	6.7	6.7	1.7	5.0	6.7	0.0	0.0	5.0	0.0	6.7	3.6	3.3	75.5
Silt/clay	%	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	37.5	0.0	3.0	0.0	344.3
Acid silicate rocks	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–
Mafic silicate rocks	%	27.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1	0.0	360.6
Carbonate rocks	%	73.0	83.8	89.1	57.3	49.5	63.8	56.3	48.8	79.7	100.0	65.2	52.6	0.5	63.0	63.8	39.2
Flysch and molasse	%	0.0	1.9	6.2	42.7	29.1	36.3	40.7	26.9	20.3	0.0	26.7	25.2	60.7	24.3	26.7	76.3
Lacustrine/marine deposits	%	0.0	0.0	0.0	0.0	16.0	0.0	3.0	0.0	0.0	0.0	5.8	22.3	35.8	6.4	0.0	178.3
Alluvial deposits	%	0.0	14.3	4.7	0.0	5.4	0.0	0.0	24.3	0.0	0.0	2.3	0.0	3.0	4.2	0.0	175.2
Native forests	%	17.2	0.0	3.0	77.5	21.9	6.3	26.9	1.9	10.1	8.3	7.6	0.0	20.0	15.4	8.3	133.4
Grassland/ heathland	%	82.8	48.8	61.4	12.8	45.5	84.8	52.0	43.9	77.9	78.1	56.2	48.1	55.0	57.5	55.0	34.7
Heterogenic agricultural areas	%	0.0	30.1	20.0	9.7	23.7	8.1	13.3	25.1	8.9	11.2	28.9	26.8	4.9	16.2	13.3	61.7
Arable land	%	0.0	7.1	0.9	0.0	0.4	0.0	2.6	0.5	0.0	0.0	0.0	0.0	10.0	1.6	0.0	194.8
Permanent crops	%	0.0	4.8	0.4	0.0	5.1	0.0	0.7	28.2	0.0	0.0	5.4	22.5	10.0	5.9	0.7	155.7
Unvegetated or some vegetated open areas	%	0.0	8.6	14.3	0.0	1.7	0.8	4.4	0.0	3.0	2.4	1.7	2.5	0.0	3.0	1.7	136.5
Inland waters	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	360.6
Inland wet zones	%	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	360.6
Urban fabric	%	0.0	0.6	0.0	0.0	0.3	0.0	0.1	0.5	0.0	0.0	0.2	0.1	0.1	0.1	0.1	135.2
Industrial or commercial units	%	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	360.6
Mining, landfills and construction sites	%	0.0	0.1	0.0	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	323.0
Water temperature	°C	10.6	14.4	15.6	10.8	16.4	13.9	12.8	16.4	13.0	13.8	14.4	13.9	18.9	14.2	13.9	15.9
pH		8.6	8.3	7.8	8.2	8.2	8.4	8.4	7.5	8.5	8.4	7.7	8.3	8.7	8.2	8.3	4.4
Conductivity	µS/cm	204.7	527.0	548.0	251.7	655.3	319.0	340.7	521.3	334.5	299.3	398.3	240.3	740.0	413.9	340.7	40.7
Total dissolved ions	mg/l	121.7	346.1	398.4	154.6	544.0	183.3	223.9	277.8	169.3	152.3	206.0	153.3	438.9	259.2	206.0	51.2
Total hardness	mg/l	112.33	268.33	275.33	142.67	349.33	159.00	179.00	231.67	151.00	130.33	173.00	123.67	357.33	204.08	173.00	41.26
Dissolved oxygen	mg/l	11.60	9.71	10.46	9.98	9.69	10.11	10.27	7.10	9.69	9.74	6.50	11.19	8.77	9.6	9.7	14.9
Oxygen saturation	%	102	97	106	92	101	101	102	75	94	96	69	111	96	95.3	96.7	12.3
Calcium	meq/l	1.02	4.99	4.57	2.69	5.79	2.98	2.16	4.19	2.72	2.32	3.05	1.99	2.62	3.16	2.72	42.56
Magnesium	meq/l	1.23	0.37	0.94	0.16	1.20	0.20	1.42	0.45	0.29	0.29	0.41	0.47	4.53	0.92	0.45	126.50
Sodium	meq/l	0.22	0.76	0.39	0.12	0.59	0.19	0.19	0.57	0.19	0.20	0.29	0.40	1.36	0.42	0.29	81.64
Potassium	meq/l	0.03	0.05	0.03	0.03	0.13	0.03	0.04	0.03	0.03	0.03	0.07	0.03	0.07	0.05	0.03	62.97
Alkalinity	meq/l	2.35	3.98	3.36	3.22	3.53	3.10	3.34	4.67	3.30	2.65	3.42	2.25	5.74	3.5	3.3	27.1
Sulphate	meq/l	0.08	0.73	2.23	0.12	3.56	0.33	0.95	0.35	0.21	0.27	0.33	0.14	0.61	0.76	0.33	133.39
Chloride	meq/l	0.21	0.65	0.28	0.06	0.30	0.09	0.06	0.45	0.10	0.12	0.26	0.43	1.42	0.34	0.26	108.23
Silicate (SiO ₂)	mg/l	12.72	7.76	6.31	5.07	6.19	5.97	3.55	9.54	5.83	6.04	8.00	2.05	40.17	9.2	6.2	105.6
N-nitrate	mg/l	0.08	2.98	1.03	0.16	2.55	0.14	0.37	1.33	0.31	0.18	0.58	0.62	0.13	0.80	0.37	118.05
N-nitrite	mg/l	0.003	0.131	0.004	0.002	0.081	0.002	0.002	0.013	0.003	0.003	0.006	0.003	0.002	0.020	0.003	201.925
N-ammonium	mg/l	0.015	0.334	0.056	0.010	0.559	0.047	0.023	0.031	0.004	0.007	0.008	0.089	0.011	0.092	0.023	180.277
P-phosphate	mg/l	0.024	0.355	0.042	0.035	0.028	0.036	0.047	0.091	0.028	0.022	0.018	0.064	0.093	0.068	0.036	132.137
Total phosphorous	mg/l	0.034	0.483	0.066	0.040	0.038	0.043	0.055	0.250	0.036	0.027	0.033	0.075	0.250	0.110	0.043	124.064
N/P (Spring)		14.2	4.4	38.9	2.4	151.3	5.1	34.1	20.0	20.2	14.6	56.3	53.4	1.6	32.0	20.0	125.9

For river site names see Fig. 1, AV: average, ME: median, CV: coefficient of variation.

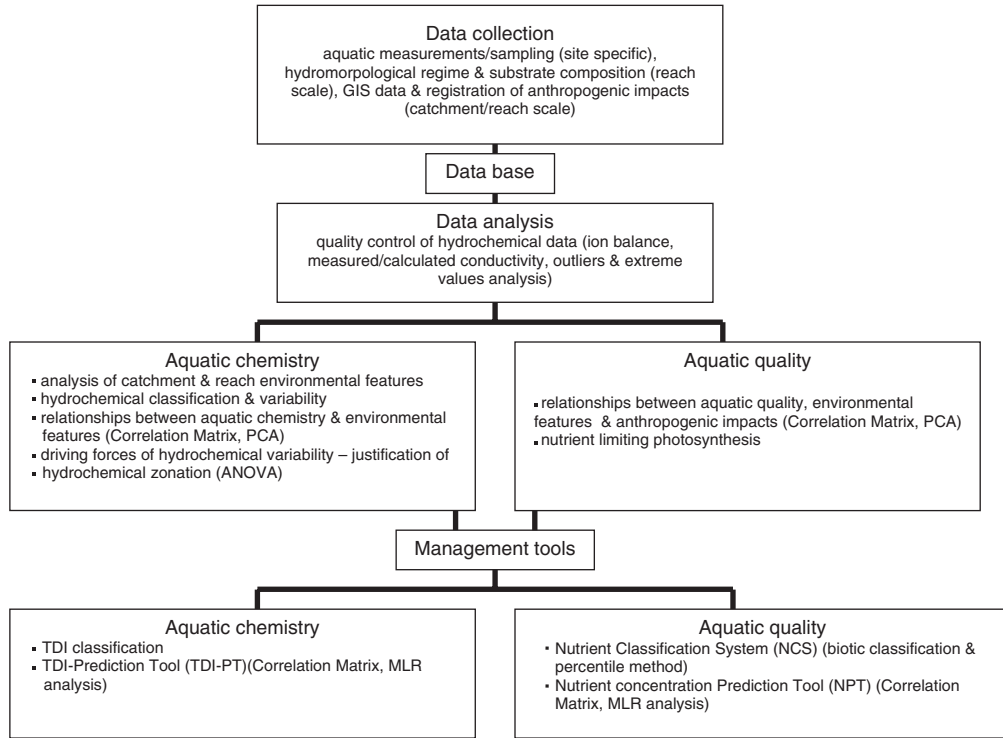


Fig. 3. Flow chart of the applied methodology.

Catchments with medium altitude, minimum slopes and minimum stream density predominate in zone 3. Compared to the other zones, the average water temperature and the average river discharge were maximal. On average, rivers in zone 3 illustrated

higher water temperature in spring (12.3 °C) than in winter (11 °C). The median ratios between spring/summer, spring/winter and winter/summer discharge were low (5, 4.5 and 3.6 respectively). River valleys are characterised by V-shaped forms. Compared to the

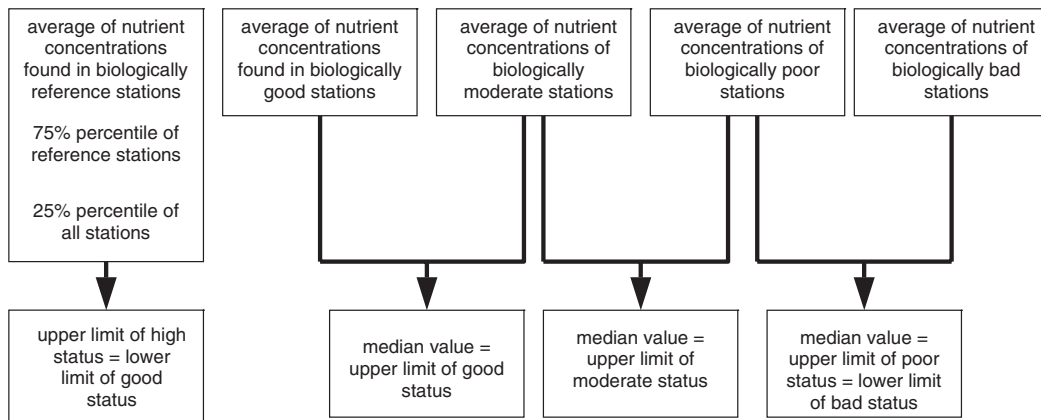


Fig. 4. Methodology applied on the establishment of nutrient reference conditions and the development of the Nutrient Classification System (NCS).

other zones, riverbeds show maximum width and depth. Silicate bedrock is almost absent (except from 28 (Aoos), where mafic rocks are present) and the main rock formations are carbonates and flysch/molassic deposits. In addition, in Alpheios (32) and Louros (30) catchments, Triassic evaporites are present. Forested areas reveal a minimum coverage, while agricultural areas are presented with a maximum percentage.

4.3. Aquatic composition

4.3.1. Evaluation of hydrochemical data

The sum of cations and the sum of anions were highly positively correlated with each other ($r=0.98$). In 75 out of 108 analyses the ion balance percentage ranged between 0% and 5%, and in 28 samples the ion balance percentage ranged between 5% and 10%, which are acceptable errors for the purposes of this study (Hem, 1985; Güler et al., 2002). Finally, in only 5 samples the error ranged between 10% and 15%. These samples were excluded from further analysis. The correlation coefficient between measured and calculated conductivity was high ($r=0.96$). By applying an extreme values analysis on 19 hydrochemical parameters, 149 out of 2052 values (i.e. 7%) were termed as outliers. However, only three values were excluded from further analysis, since the majority of the outlier values could be attributed to geochemical and pollution variability.

4.3.2. Hydrochemical types and characteristics

A Piper diagram of the annual average concentrations of major ions is presented in Fig. 5. According to the classification after Back (1961), the average composition of rivers in zones 1 and 2 belonged to the hydrochemical facies: Ca+Mg, Na+K and HCO_3^- , $\text{Cl}^- + \text{SO}_4^{2-}$, while the average composition of zone 3 belonged to the hydrochemical facies: Ca+Mg and HCO_3^- , $\text{Cl}^- + \text{SO}_4^{2-}$. Considering individual rivers, only three [18 (Onochonos at Kaitsa), 31 (Steno) and 37 (Neda at Eira)] fitted in a diverse hydrochemical facies (Ca+Mg and HCO_3^-).

Table 2 presents the hydrochemical types of the rivers, regarding major ions and total hardness. Concerning the major ion sequences (in milliequivalent per liter), the average composition of the three zones belonged to the same hydrochemical type, i.e.,

$\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. Regarding individual rivers, two hydrochemical types predominated: (i) $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ (16 river sites) and (ii) $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ (10 river sites). Five river sites belonged to the type: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$, while seven river sites belonged to five diverse types. Three of these types revealed magnesium as the dominant cation. In one hydrochemical type, sulphate anions predominated among the anions. Finally, two of the river sites were additionally termed as geothermal type rivers.

In rivers from zone 1, the hydrochemical type (ii) predominated. Rivers from zone 2 demonstrated only one type of anion sequence ($\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$) and the two dominant cation sequences were equally represented. In river 16, 18 (Onochonos at Thrapsimi and Kaitsa), magnesium was the dominant cation. In zone 3, the dominant hydrochemical type was (i). In two of the rivers, 28 (Aoos) and 43 (Sianitis), magnesium was the dominant cation and in 32 (Alpheios) sulphate was the prevailing anion.

Spatial water mineralisation varied considerably, especially in zone 1. Table 2 presents a classification of the rivers according to their TDI concentration. Rivers with a TDI lower than 100 mg/l are classified as slightly mineralised, those with a TDI up to 250 mg/l present low mineralisation. TDI concentrations between 251 and 350 mg/l characterise rivers with medium mineralisation, while rivers with a TDI over 350 mg/l belong to highly mineralised waters. River 24 (Aliakmon at Pisoderi), with a TDI concentration of 37.5 mg/l, was characterised by the lower boundary, followed by 21 (Florinis-tributary) and 1 (Fonias) with 48 and 51 mg/l respectively. Maximum mineralisation was shown by 43 (Sianitis) with a TDI of 571 mg/l, followed by 18 (Onochonos at Kaitsa) with 554 mg/l and 32 (Alpheios) with 547 mg/l. Despite the high spatial variability of riverine solute concentration, an increasing TDI trend from zone 1 to zone 3 was evident. Moreover, there was a lack of highly mineralised rivers in zone 1, while slightly mineralised rivers were not present in zone 3 (Table 2).

On average, total hardness (TH) (expressed as milligram per liter CaCO_3) contributed 57% to TDI. Similarly to TDI, water hardness showed high spatial variability, especially in zone 2. Nevertheless, the dis-

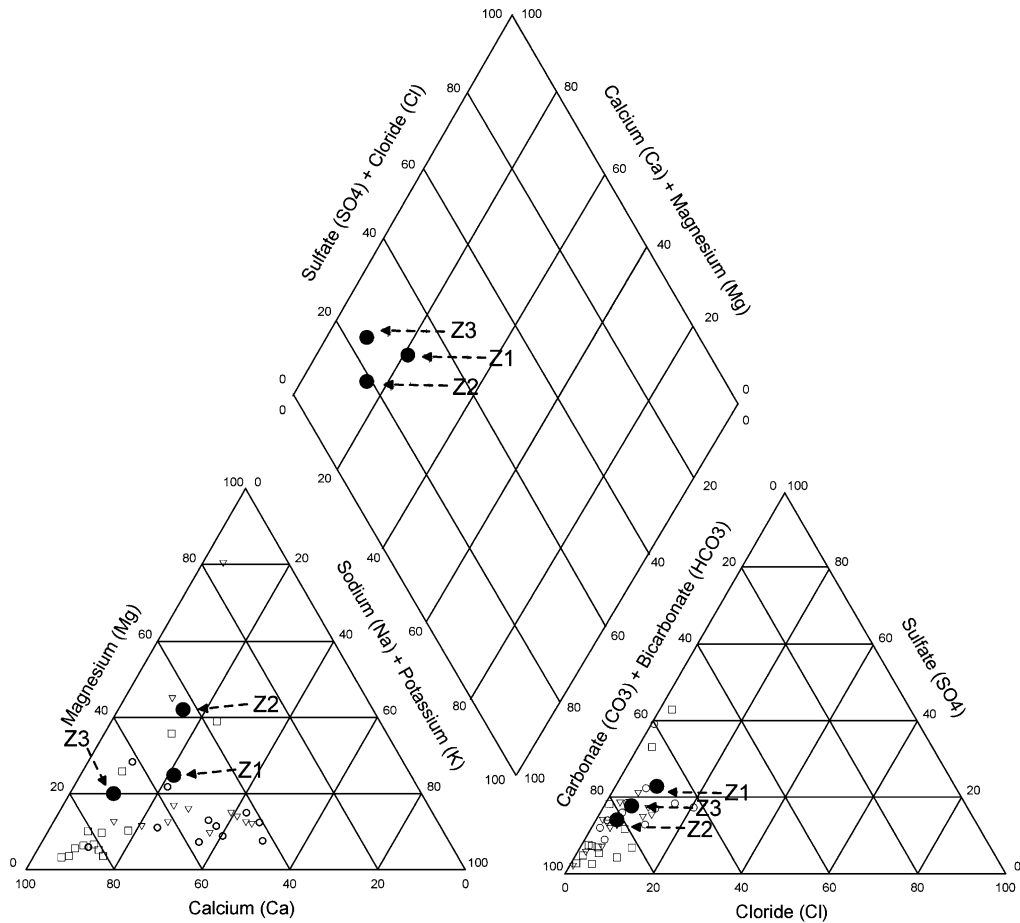


Fig. 5. Piper diagramme on major ions' annual average concentrations (cycles: zone 1 rivers; triangles: zone 2 rivers; rectangles : zone 3 rivers; Z1: average zone 1; Z2: average zone 2; Z3: average zone 3).

tribution of water hardness seems to be also geographically dependent. On average, according to Hem's classification (1970), rivers in zone 1 could be termed as medium hard (TH: 92 mg/l), rivers in zone 2 as hard (TH: 139 mg/l) and those in zone 3 as very hard (TH: 204 mg/l). In addition, none of zone 1 rivers could be classified as very hard and none of zone 3 rivers could be classified as soft (Table 2). Rivers 18 (Onochonos at Kaitsa), 43 (Sianitis) and 32 (Alpheios) presented extreme hardness (>350 mg/l). In contrast, rivers 1 (Fonias), 8 (Arkoudoremma), 24, 25 (Aliakmon, sites Pisoderi and Adartiko), 21 (Florinis-tributary) and 27 (Melas) revealed very soft waters (TH < 30 mg/l).

Considering all rivers, calcium and bicarbonate ions contributed 76% to the TDI, expressed in mg/l. Likewise TDI and TH, calcium and alkalinity concen-

trations showed an increasing trend towards zone 3. In addition, moving from zone 1 to zone 3 rivers, the contribution of calcium and bicarbonate ions to TDI was also increasing (68% in zone 1, 75% in zone 2 and 82% in zone 3, expressed in milligram per liter). As for TDI and TH, minimum alkalinity and calcium levels were detected in 24 (Aliakmon at Pisoderi) with 0.33 and 0.21 meq/l respectively. Maximum alkalinity occurred in 18 (Onochonos at Kaitsa) (7.17 meq/l), followed by 43 (Sianitis), 12 (Kokoremma) and 35 (Pamisos) ranging between 5.74 and 4.67 meq/l. Concerning calcium, highest concentrations ranging between 5.79 and 4.57 meq/l were found in 32 (Alpheios), 29 (Kalamas) and 30 (Louros).

Magnesium concentration showed high variability among the different rivers and especially in zone 2

Table 2
Hydrochemical types of rivers and river zones

Hydrochemical facies	Zone 1	Zone 2	Zone 3
	$\text{Ca}^{2+} + \text{Mg}^{2+} - \text{Na}^+ + \text{K}^+$ and $\text{HCO}_3^- + \text{SO}_4^{2-}$	$\text{Ca}^{2+} \text{Mg}^{2+}$ and $\text{HCO}_3^- + \text{SO}_4^{2-}$	$\text{Ca}^{2+} + \text{Mg}^{2+}$ and $\text{HCO}_3^- + \text{SO}_4^{2-}$
<i>Hydrochemical types</i>	Rivers (sites)		
Calcium types	$\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$	Xanthia, Prasinada, Poroia, Kokkoremma Tsivdogianni, Kompsatos, Arkoudoremma, Diavoloremma	Mavroremma, Skamnias, Lygos, Aliakmon (Gavros), Melas Onochonos (Smokovo), Florinis, Florinis-tributary, Aliakmon (Pisoderi, Adartiko)
	$\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ \text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$	Fonias, Vospos (Symvola, Mesochori)	Louros, Steno, Tsouraki, Lousios, Neda (3 sites) Kalamas Pamisos, Kiliaris
Magnesium types	$\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ \text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ $\text{Mg}^{2+} > \text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$		Onochonos (Thrapsimi) Aaos Onochonos (Kaitsa)
Sulphate type	$\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ \text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^-$		Sianitis
Geothermal type	High temperature, high silicate content		Alpheios
<i>Water hardness (mg/l)—classification after Hem (1985)</i>			
<60 (soft)	Fonias, Tsivdogianni, Arkoudorema, Vospos (Symvola)	Aliakmon (Pisoderi, Adartiko), Florinis-tributary, Melas	
61–120 (medium hard)	Xanthia, Kompsatos, Diavoloremma	Florinis, Aliakmon (Gavros)	Aaos (Milea)
121–180 (hard)	Poroia, Prasinada, Vospos (Mesochori)	Skamnias, Mavroremma, Onochonos (Smokovo), Lygos Onochonos (Thrapsimi, Kaitsa), Kokkoremma	Neda (Eira, Marina, Elea), Lousios, Steno, Tsouraki, Kiliaris Kalamas, Louros, Alpheios, Pamisos, Sianitis
>180 (very hard)			
<i>Total dissolved solids (mg/l)</i>			
<100 (slight mineralisation)	Fonias, Tsivdogianni, Arkoudorema, Vospos (Symvola)	Aliakmon (Pisoderi, Adartiko), Florinis-tributary, Melas	
150–250 (low mineralisation)	Xanthia, Kompsatos	Florinis, Aliakmon (Gavros), Skamnias	Aaos, Kiliaris, Neda (Marina)
251–350 (medium mineralization)	Diavoloremma, Poroia, Prasinada, Vospos (Mesochori)	Lygos, Onochonos (Smokovo), Mavroremma	Tsouraki, Neda (Eira, Elea), Lousios
>350 (high mineralisation)		Onochonos (Thrapsimi, Kaitsa), Kokoremma	Kalamas, Louros, Sianitis Alpheios, Pamisos

ones. On average, zone 2 showed maximum magnesium concentration, followed by zone 3. Magnesium reached its maximum in 18 (Onochonos at Kaitsa) with 6.92 meq/l and its minimum in 1 (Fonias) (0.09 meq/l). Rivers 43 (Sianitis) and 16 (Onochonos at Thrapsimi) showed elevated magnesium levels (4.53 and 3.75 meq/l). Finally, in twenty-three rivers magnesium levels were below 0.82 meq/l.

Zone 1 and zone 2 rivers had respectively maximum and minimum average sodium concentration. Concerning chloride, maximum average concentration was found in zone 3 and minimum again in zone 2. Twenty-four rivers showed sodium and chloride concentrations which were below 10 mg/l. Only a restricted number of rivers presented high concentrations. These rivers were 43 (Sianitis) (1.36 meq/l Na⁺ and 1.42 meq/l Cl⁻), 5 (Vospos at Mesochori) (1.76 meq/l Na⁺ and 1.04 meq/l Cl⁻) and 29 (Kalamas) (0.76 meq/l Na⁺ and 0.65 meq/l Cl⁻). Finally, 10 (Diavoloremma) and 15 (Onochonos at Smokovo) were loaded with sodium (0.97 and 0.87 meq/l respectively). Mean annual sodium and chloride concentrations decreased with altitude (Fig. 6). Moreover, the equivalent Na/Cl ratio in island-rivers approached the respective sea water ratio (0.85).

Rivers in zone 3 revealed maximum average sulphate concentrations, followed by rivers in zone 1. Specifically, 32 (Alpheios), 30 (Louros) and 11 (Poroia) showed very high sulphate levels (1.74–3.56 meq/l), while 28 (Aos), 21 (Florinis-tributary), 31 (Steno) and 24 (Aliakmon at Pisoderi) revealed very low sulphate concentrations (0.08–0.12 meq/l).

Potassium levels were generally low. Average potassium concentration decreased from zone 1 to

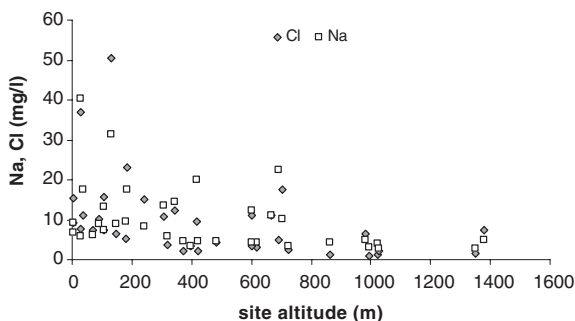


Fig. 6. Mean annual chloride and sodium concentration in relation to site altitude.

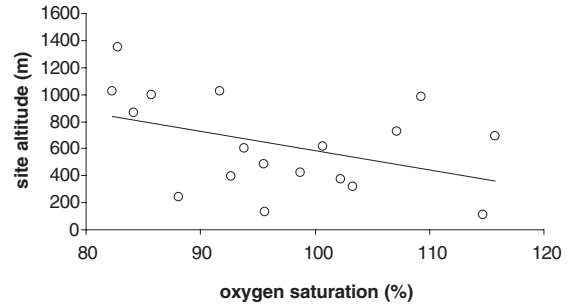


Fig. 7. Correlation between site altitude and mean annual dissolved oxygen saturation in unpolluted rivers.

zone 3. Twenty rivers had potassium concentrations lower than 0.05 meq/l. Only a small number of rivers showed relatively high concentrations. These rivers were: 11 (Poroia) (0.26 meq/l), 23 (Lygos) (0.20 meq/l), 5 (Vospos at Mesochori) (0.19 meq/l), 22 (Florinis) (0.14 meq/l) and 32 (Alpheios) (0.13 meq/l).

Concerning silicate, maximum average concentrations were found in zone 2 and minimum ones in zone 3 (Table 1). The three sites of 15, 16, 18 (Onochonos) as well as 43 (Sianitis) were enriched with silicate (20–45 mg/l). The lowest silicate concentrations occurred in zone 3.

Finally, a decreasing mean annual dissolved oxygen saturation trend in unpolluted rivers (high and good quality class) with increasing altitude was evident (Fig. 7).

The seasonal hydrochemical trends among the rivers varied. The majority of the rivers showed TDI enrichment in summer and winter in relation to spring (median enrichment factors 1.19 and 1.15). When comparing however the summer to winter TDI, only half of the rivers revealed enrichment in summer compared to winter (median enrichment factor 1.02). The median summer/spring and winter/spring TDI-ratios decreased from zone 1 to zone 3. In particular, zone 1 showed a 1.73 summer/spring TDI-ratio, zone 2 a 1.22 and zone 3 a 1.04. The median winter/spring TDI-ratios for zones 1, 2 and 3 were 1.38, 1.16 and 0.92 respectively. The majority of the rivers revealed maximum major ion and silicate concentrations mainly in summer and minimum ones predominately in spring. In winter, a number of rivers showed minimum and others maximum concentrations.

Zonal aquatic quality differences and within-zone seasonal variations were compared by the ANOVA analysis (Table 3 and Fig. 8). Water temperature

Table 3
Results of a two-way ANOVA on aquatic variables

Variable	Source of variation	p-value	Explanation
Water temperature	Zone	0.006	Reject the equality
	Season	0.000	Reject the equality
pH	Zone	0.436	Accept the equality
	Season	0.000	Reject the equality
Conductivity	Zone	0.007	Reject the equality
	Season	0.242	Accept the equality
Ca ²⁺	Zone	0.000	Reject the equality
	Season	0.235	Accept the equality
Mg ²⁺	Zone	0.590	Accept the equality
	Season	0.526	Accept the equality
Na ⁺	Zone	0.264	Accept the equality
	Season	0.050	Reject the equality
K ⁺	Zone	0.061	Accept the equality
	Season	0.273	Accept the equality
Alkalinity	Zone	0.000	Reject the equality
	Season	0.016	Reject the equality
SO ₄ ²⁺	Zone	0.018	Reject the equality
	Season	0.593	Accept the equality
Cl ⁻	Zone	0.760	Accept the equality
	Season	0.163	Accept the equality
SiO ₂	Zone	0.000	Reject the equality
	Season	0.047	Reject the equality

exhibited both seasonal and spatial statistically accepted variations. Water temperature differences between the three zones were stronger expressed in summer. Seasonal differences were stronger expressed in zones 1 and 2 than in zone 3. For pH, only seasonal statistically accepted variations were apparent. In winter, zones 1 and 2 showed significantly lower pH values than in summer and spring. Conductivity exhibited a statistically accepted zonation. The conductivity differences between the three zones were primarily expressed in the summer. In winter and spring, zone 3 revealed significantly higher conductivity levels compared to zones 1 and 2, which showed similar levels. In contrast, within-zone seasonal conductivity variations were not statistically accepted. Similarly, calcium and sulphate exhibited statistically accepted spatial differences, while seasonal variations did not show statistically accepted differentiations. In all three seasons, zone 3 showed significantly higher calcium concentrations than zones 1 and 2, which presented similar levels. Sulphate levels were different between the three zones, predominately in summer. Concerning alkalinity and silicate, both spatial and seasonal differences were

apparent. In all seasons, zone 3 illustrated significantly higher alkalinity levels than zones 1 and 2. Silicate concentration showed a clear zonation in all seasons, with more strong differences in summer. Seasonal silicate differences were statistically accepted and occurred predominately in zone 2. Moving from summer to spring, zone 2 had a clear silicate concentration decrease. For sodium, only seasonal differences were statistically accepted, while for magnesium, chloride and potassium, no spatial or seasonal statistically accepted variations were apparent.

4.3.3. Carbonate chemistry

Table 4 illustrates the annual and seasonal variation of pCO₂ and the saturation indices of calcite and dolomite in zones 1, 2 and 3. The majority of the rivers (85%) showed a pCO₂ higher than the atmospheric, i.e., 360 ppmv (ppmv: parts per million partial pressure) according to Hélie et al. (2002), and most of them showed carbonate oversaturation. On average, the three zones showed an excess of pCO₂ compared to the atmospheric, while as moving from zone 1 to zone 3 the pCO₂ increased. Concerning calcite, all rivers in zone 3, the majority of zone 2 rivers and almost the half of zone 1 rivers were oversaturated. Regarding dolomite, the majority of zone 3 rivers were oversaturated, while the majority of zone 2 and zone 3 rivers were undersaturated. As far as gypsum is concerned, all rivers were undersaturated. On average, the three zones presented maximal pCO₂ in winter and minimum in spring. About three-quarters of the rivers showed maximum pCO₂ in winter and the rest in summer. In spring, the majority of the rivers (82%) revealed a pCO₂ lower than the atmospheric. Only three rivers showed minimum pCO₂ in summer. Carbonate oversaturation occurred primarily in summer and secondarily in spring. In winter, most of the rivers were undersaturated regarding dolomite and half of the rivers were undersaturated with respect to calcite. The majority of the polluted rivers, i.e. 5 (Vospos at Mesochori), 23 (Lygos), 29 (Kalamas), 32 (Alpheios) and 35 (Pamisos) (Table 5) revealed high annual pCO₂ levels (937–1166 ppmv) with maximum values in summer (1543–3699 ppmv). Florinis river (22) was an exception presenting very low annual pCO₂ concentration (148 ppmv). During summer the river revealed the lowest pCO₂ value (5 ppmv) observed, causing the highest carbonate saturation among the rivers exam-

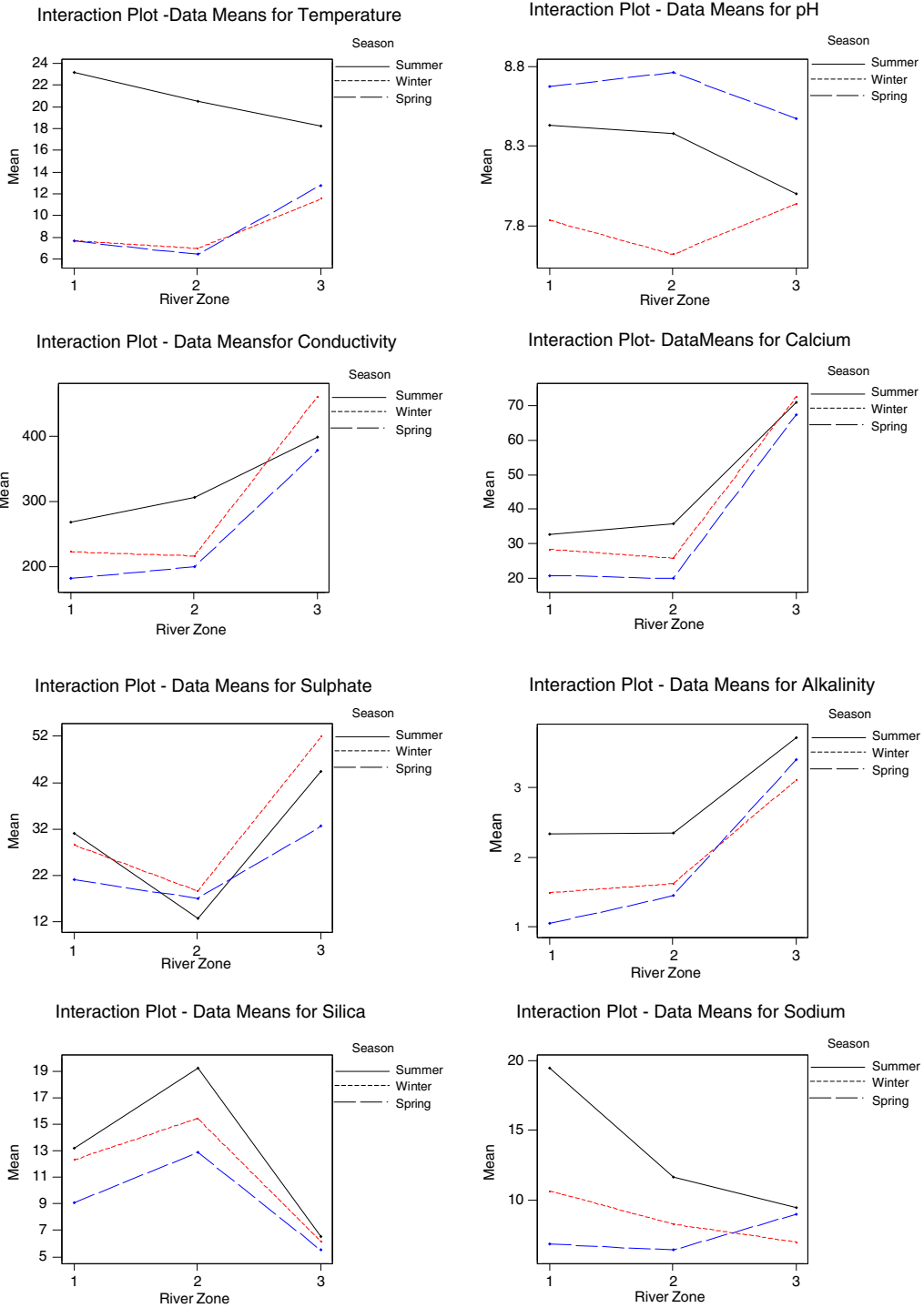


Fig. 8. Graphical presentation of the results of two-way ANOVA on aquatic variables.

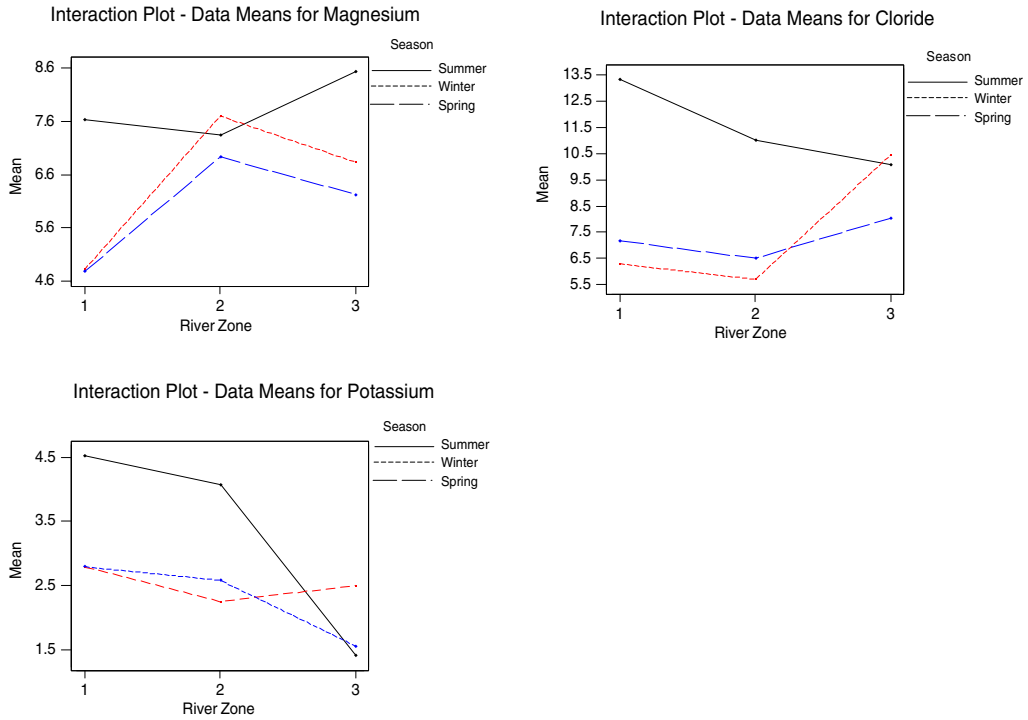


Fig. 8 (continued).

ined (calcite saturation index: 1.61, dolomite saturation index: 1.36). Fig. 9 presents the positive correlation between the excess of pCO₂ (measured pCO₂ minus

atmospheric pCO₂) and the oxygen deficit (oxygen equilibrium concentration minus measured oxygen concentration) for seasonal data.

Table 4
Seasonal and annual variation of pCO₂ (ppmv) and saturation indices of calcite and dolomite in zone 1, 2 and 3 rivers

	Zone 1			Zone 2			Zone 3			
	pCO ₂	Calcite saturation index	Dolomite saturation index	pCO ₂	Calcite saturation index	Dolomite saturation index	pCO ₂	Calcite saturation index	Dolomite saturation index	
Summer	Average	761	0.24	0.07	680	0.31	0.18	1887	0.65	0.37
	Median	437	0.46	0.40	561	0.77	0.59	1409	0.67	0.21
	Range	68/3699	-1.80/1.29	-2.03/1.12	5/2222	-1.35/1.65	-1.47/1.51	201/5113	0.19/1.23	-0.02/1.44
Winter	Average	917	-0.75	-1.04	1550	-0.72	-0.91	2120	0.31	-0.05
	Median	994	-0.84	-1.03	1410	-0.91	-1.17	989	0.32	-0.13
	Range	271/1976	-1.97/0.66	-2.11/0.27	163/3796	-3.17/1.14	-3.34/1.00	387/7187	-0.24/0.99	-0.77/1.00
Spring	Average	100	-0.33	-0.58	107	0.03	-0.15	1013	0.88	0.52
	Median	85	-0.16	-0.25	61	0.03	-0.21	312	1.00	0.56
	Range	34/202	-1.75/1.23	-2.02/0.76	14/495	-2.08/1.78	-2.21/1.72	78/8264	-0.01/1.53	-0.37/1.66
Annual average	593	-0.28	-0.52	779	-0.13	-0.30	1255	0.61	0.28	
Annual median	296	0.14	-0.15	522	0.03	-0.21	690	0.67	0.35	

Table 5
Biological quality classification of the examined rivers (Skoulikidis et al., 2004)

Rivers	Biological classification
Fonias, Tsivdogianni, Arkoudoremma, Prasinada, Diavoloremma, Poroia, Kokkoremma, Florinis-tributary, Aliakmon (Pisoderi), Melas, Steno, Tsouraki, Lousios, Aaos	High
Vospos (Symvola), Onochonos (Kaitsa), Aliakmon (Adartiko, Gavros), Neda (Eira, Marina), Sianitis	Good
Xanthia, Onochonos (Smokovo, Thrapsimi), Mavroremma, Skamnias, Pamisos, Neda (Elea), Kiliaris moderate	Moderate
Kompsatos, Florinis, Alpheiospoor	Poor
Vospos (Mesochori), Lygos, Kalamas	Bad

4.3.4. Anthropogenic impact and biological activity

Table 5 presents the biological classification of the rivers under study. In an annual base, the maximum nitrate concentration (2.98 mg/l N-NO₃⁻) was found in 29 (Kalamas). River 32 (Alpheios) was ranked second (2.55 mg/l), followed by 23 (Lygos) (1.67 mg/l). Twenty-seven rivers showed lower N-NO₃⁻ concentrations than the upper boundary of non-polluted European rivers, which is considered to be 1 mg/l N-NO₃⁻ (EEA, 1999). Concerning nitrite, only six rivers exceeded the 0.015 mg/l of N-NO₂, which corresponds to almost pristine concentration (see Table 8). The maximum concentration (0.13 mg/l) was observed in 29 (Kalamas), followed by 5 (Vospos at Mesochori) with 0.098 mg/l and 32 (Alpheios) (0.081 mg/l N-NO₂). Regarding ammonium, the maximum concentration (1.57 mg/l N-NH₄⁺) was found in 23 (Lygos) river, followed by 32 (Alpheios) (0.56 mg/l). Thirteen rivers exhibited concentrations below the 0.015 mg/l of nearly pristine level (Table 8). Concerning phosphate, all rivers showed higher

concentrations compared to the almost pristine one (0.010 mg/l P-PO₄³⁻). Rivers 23 (Lygos), 5 (Vospos at Mesochori), 22 (Florinis) and 29 (Kalamas) were highly loaded with phosphate (0.36–0.54 mg/l P-PO₄³⁻) and total phosphorus (TP) (0.44–0.63 mg/l TP). In twenty-seven rivers the P-PO₄³⁻ concentration ranged between 0.208 and 0.035 mg/l and TP between 0.321 and 0.040 mg/l. Finally, four rivers showed lower P-PO₄³⁻ and TP concentrations, which ranged between 0.028 and 0.018 mg/l and 0.038 and 0.028 mg/l respectively.

The Nin/P-PO₄ ratio has been applied in order to carry out which nutrient is limiting photosynthesis. In this case, the ratios proposed by OECD (1982) have been considered. Furthermore, the spring nutrient concentrations have been used, since photosynthetic processes prevail during that season (see Section 5.2.5.3). In most of the rivers, including the majority of rivers draining forested catchments (forest cover > 70%), the ratio was below 5 (by weight). The majority of zone 3 rivers showed ratio values above 12, while in zones 1 and 2 values below 5 were prevailed.

The seasonal behaviour of nutrient concentrations exhibited high variability. Polluted rivers [23 (Lygos), 22 (Florinis), 29 (Kalamas) and 32 (Alpheios)] showed maximum nitrate levels in summer, while the majority of upland reference rivers exhibited minor seasonal nitrate differences. Concerning nitrite, no clear seasonal trends were apparent. For ammonium and phosphate, the majority of the rivers showed enrichment during summer while for TP in summer and spring. Minimum ammonium concentrations occurred predominately in spring and minimum phosphate and TP concentrations primarily in spring and secondarily in winter. The majority of reference catchments (Table 5),

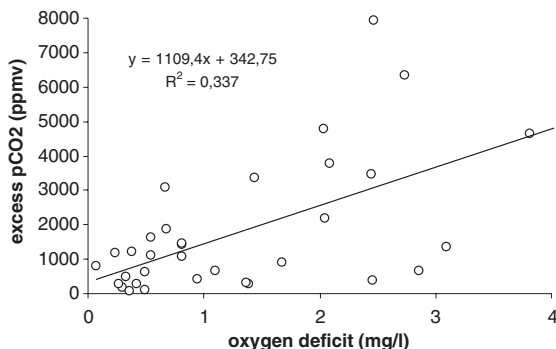


Fig. 9. Correlation between seasonal concentrations of the excess of pCO₂ and the oxygen deficit.

which are almost entirely covered with forests, grass and heath showed maximum TP concentrations in high runoff (spring and winter).

On an annual base, the oxygen concentration ranged between 6.5 and 12.7 mg/l and the oxygen saturation between 68.7% and 115.7%. Twenty-two sites of various biological quality classes were undersaturated as far as dissolved oxygen is concerned. The average dissolved oxygen saturation of these waters was 86%. Minimum and maximum oxygen saturation levels dominated in spring and summer respectively.

Rivers affected by municipal wastes revealed high sodium and chloride concentrations predominately in summer. Specifically, 5 (Vospos at Mesochori) and 29 (Kalamas) showed very high levels, i.e., 1.61 and 1 meq/l Na^+ and 1.14 and 0.49 meq/l Cl^- , respectively.

4.3.5. Relationships between aquatic quality, environmental and anthropogenic characteristics

A Correlation Matrix for water quality, environmental and anthropogenic variables was performed. In Table 6, only essential correlations with a correlation coefficient $r > 0.4$ were illustrated.

According to a PCA carried out on the yearly average values of forty-four variables (Table 7), six components were found to be significant in explaining 73.5% of the variance of the data. The first PCA component accounted for the 1/4 of the total variance and was more heavily weighted on the variables of catchment slope, native forests, acid silicate rocks, water temperature, conductivity, calcium, alkalinity, nitrogen compounds and sum of agricultural areas. Loadings were negative for the first four variables and positive for all the other variables. High negative loadings characterised 32 (Alpheios), 5 (Vospos at Mesochori), 23 (Lygos), 29 (Kalamas), 35 (Pamisos) 43 (Sianitis) and 40 (Kiliaris). Positive loadings were presented by 24 (Aliakmon, at Pisoderi), 21 (Florinis-tributary), 8 (Arkoudoremma), 27 (Melas), 2 (Tsivdogianni) and 25 (Aliakmon at Adartiko).

The second component, which accounted for the 14% of the total variance, was characterised by latitude, acid silicate rocks, silt/clay, urban fabric, potassium, orthophosphate, TP, ammonium (with positive loadings) and carbonate rocks (with negative loading). Rivers 23 (Lygos), 5 (Vospos at Mesochori) and 22

(Florinis) showed high positive loadings. Rivers 34 (Lousios), 40 (Kiliaris), 33 (Tsouraki) and 30 (Louros) were loaded highly negatively.

The third component added a 9.4% to the explanation of variance. The largest contribution to this component came from the following variables: longitude, sodium, chloride, magnesium, silicate, mafic silicate rocks (positive loadings), catchment altitude, ammonium, nitrate and heterogenic agricultural areas (negative loadings). High positive loadings were revealed in 43 (Sianitis), 18 (Onochonos at Kaitsa), 5 (Vospos at Mesochori) and 2 (Tsivdogianni). High negative loadings were found again in 32 (Alpheios), 23 (Lygos) and 29 (Kalamas).

The fourth component, which comprised the 8.2% of the observed variance, integrated acid silicates, sodium, sulphate, dissolved oxygen, industrial units and mining activities (positive loadings) and silt/clay (negative loading). High positive loadings were shown in 5 (Vospos at Mesochori), 32 (Alpheios), 6 (Kompsatos) and 29 (Kalamas). Rivers 23 (Lygos), 18 (Onochonos at Kaitsa) and 28 (Aos) showed negative loadings.

The fifth component (7.2% of the variance) was composed by discharge, sand/mud, lacustrine/marine deposits (positive loadings), gravel, calcium, sulphate, mining areas (negative loadings). Rivers 40 (Kiliaris), 23 (Lygos), 43 (Sianitis), 35 (Pamisos) and 20 (Skamnias) revealed high positive loadings, while 32 (Alpheios) and 29 (Kalamas) showed high negative loadings.

The sixth component (5.5% of the variance) was formed by stream order, catchment area, bedrock, pH, magnesium, dissolved oxygen, ammonium, silicate (positive loadings), permanent crops (negative loading). High positive loadings were shown in 23 (Lygos), 32 (Alpheios), 28 (Aos), 4 (Vospos at Symvola) and 18, 16 (Onochonos at Kaitsa and at Thrapsimi). Rivers 5 (Vospos at Mesochori), 35 (Pamisos) and 29 (Kalamas) were negatively loaded.

Finally, the last component, with 4.2% of the total variance was more heavily weighted by site altitude, flysch/molasses, lacustrine/marine deposits, chloride (positive loadings), mafic rocks, alluvial deposits and magnesium. Rivers 43 (Sianitis), 23 (Lygos) and 22 (Florinis) were highly positively loaded, while 18, 16 (Onochonos at Kaitsa and at Thrapsimi) and 2 (Tsivdogianni) showed high negative loadings.

Table 6
Summarised significant correlations between aquatic quality, anthropogenic and environmental parameters

	Tw	pH	EC	DO	DO%	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	TH	SO ₄ ²⁻	Cl ⁻	SiO ₂	N-NO ₃ ⁻	N-NO ₂ ⁻	N-NH ₄ ⁺	P-PO ₄ ³⁻	TP	
Longitude								0.46					0.45							
Latitude	-0.44		-0.57			-0.52				-0.58	-0.54									
Stream density		0.53																		
Distance to source												0.54			0.44					
Site altitude	<u>-0.73</u>		-0.43					-0.42					-0.43							
Catchment altitude	<u>-0.64</u>		-0.53					-0.45		-0.47	-0.50		-0.44							
Catchment area												<u>0.63</u>			<u>0.60</u>		0.42			
Catchment slope	-0.41		<u>-0.61</u>			-0.41	-0.47			-0.59	<u>-0.69</u>				<u>-0.58</u>	-0.45				
Acid silicate rocks	-0.45		-0.54			-0.55				-0.59	-0.58									
Carbonate rocks						<u>0.61</u>														
Flysch/molasse			0.44			<u>0.43</u>				0.46	0.44									
Lacustrine/marine deposits													0.56							
Alluvial deposits			0.46					0.44		0.42			0.43		0.58	0.46		0.55	0.58	
Permanent crops													0.49							
Heterogenic agr. areas	0.42		0.49			<u>0.76</u>					0.44				<u>0.61</u>	0.46				
Arable land			0.45				<u>0.87</u>			<u>0.60</u>	0.51			0.65						
Slope of valley floor	<u>-0.75</u>		-0.45					-0.43					-0.45							
Bedrock																				<u>0.62</u>
Pebbles														0.50						
Sand/mud				-0.45	-0.46									0.44						
Mean depth						0.41						0.42								
Mean flow												0.53								
Water temperature			<u>0.76</u>			0.54		<u>0.62</u>		<u>0.61</u>	<u>0.63</u>		<u>0.62</u>							
pH										<u>0.43</u>										
Conductivity						<u>0.76</u>	<u>0.65</u>	0.49		<u>0.93</u>	<u>0.97</u>	0.56	0.55		0.48					
Dissolved oxygen					0.92															
Ca ²⁺												<u>0.65</u>								
Mg ²⁺														<u>0.71</u>						
K ⁺												0.50								
HCO ₃ ⁻						<u>0.60</u>	<u>0.75</u>				<u>0.93</u>									
Total hardness						<u>0.72</u>	<u>0.74</u>					0.54	0.43		0.42					
Cl ⁻								<u>0.83</u>												0.48
N-NO ₃ ⁻						0.63						0.51						0.48	0.49	
N-NO ₂ ⁻						0.49		0.55				0.44			<u>0.80</u>			<u>0.60</u>	0.56	
N-NH ₄ ⁺									0.49						0.52	0.45		<u>0.63</u>	0.56	
P-PO ₄ ³⁻								0.49	0.64											<u>0.96</u>
TP								0.57	0.56											

Only correlations with $r > 0.4$ ($p < 0.050$) are presented (correlations with $r \geq 0.6$ are underlined), Tw: water temperature, EC: conductivity, DO: dissolved oxygen, DO%: DO saturation, TH: total hardness.

4.4. Management tools

4.4.1. A nutrient classification system

Table 8 shows the nutrient levels in the different biological quality classes according to various classification methods. Table 9 presents the NCS, which was developed according to the method described in Section 3.8. Tables 10 and 11 present the French and Italian classification systems. Finally, Table 12 illustrates a comparison between nutrient background levels in reference forested and non-forested catchments. Most of the nutrients revealed higher concentrations in forested catchments than in non-forested ones. Nevertheless, a *t*-test showed that the differences in concentrations were not statistically significant.

4.4.2. Forecasting aquatic quality

The results of MLR analyses showed that TDI, nitrate, ammonium, phosphate and TP presented significant equations, while nitrite exhibited the less statistically explained variability (Table 13).

Table 14 presents the characteristics of STAR rivers (Section 3.9). The equations were tested only for TDI and nitrate, since a part of the other nutrients fell under the detection limit. Figs. 10 and 11 present the correlations between measured and calculated TDI and nitrate.

5. Discussion

5.1. Environmental features

Since zone 2 is characterised by highland catchments, minimum river water temperature occurs in spring (Table 1b) due to delayed snow melting. Due to milder climate in zone 3, snow melting takes place earlier in this zone and respective rivers present higher water temperature in spring than winter (Table 1c). Zone 3 rivers show maximum runoff (Table 1c) as a result of elevated precipitation within this zone. A number of stream hydro-morphological variables depends on catchment geology. Thus, the width of the floodplain, stream density, water flow and the spring/summer discharge ratio are proportional to the percentage of impermeable rocks in the catchments. As a result, when moving from zone 1 to

zone 3, these variables are decreasing (Table 1). In zone 3 this decrease is additionally enhanced by its karstic geology. Moreover, the width and depth of the riverbed is proportional to the percentage of the easily soluble, carbonate rocks in the catchments. Hence, moving from zone 1 to zone 3, stream width and depth are increasing (Table 1).

5.2. Aquatic composition

5.2.1. Quality control of hydrochemical data

Although, according to McNeil and Cox (1999), conductivity is not a precise surrogate for TDI in waters of wide range salinities, in our case (for conductivities ranging between 40 and 740 $\mu\text{S}/\text{cm}$), it is possible to use ion equivalent conductivities for quality control purposes, since measured and calculated conductivity are highly correlated.

The application of extreme values analysis demonstrates once more that when assessing aquatic quality, simple application of statistical techniques without considering physical interpretation of the results should be avoided. This was clearly illustrated in the case of the outlier values. The majority of the outliers were explained by the variability of the geochemical background and that of anthropogenic impact. For example, the elevated magnesium concentration in 15, 18 (Onochonos) (Table 1b) is triggered by the percolation of hydrothermal groundwaters through mafic bedrock. Similarly, a number of elevated sodium and potassium concentrations are explained by silicate rock weathering (zone 1 rivers) and wastewater impact (Tchobanoglous and Burton, 1991). Moreover, high sulphate levels in 11 (Poroia) are attributed to pyrite weathering, in 30 (Louros) to gypsum dissolution and in 32 (Alpheios) to both coal combustion and gypsum dissolution (Skoulikidis et al., 2000b). Finally, 64 outlier nutrient values, found in bad and poor sites, were attributed to the impact of point and non-point sources of pollution.

5.2.2. Hydrochemical classification

The rivers' and geographical zones' hydrochemical facies, which were derived from the Piper diagrams (Fig. 5), basically mirror their catchment geological characteristics. In fact, in zones 1 and 2, where silicate geology predominates, the alkali ion facies is represented. This facies is lacking in zone 3,

where silicate rocks are almost absent. Moreover, the variability of the geological and mineralogical background of the catchments controls the diversity of

the hydrochemical types found. Meybeck (1981), who calculated the 62% of the total world's runoff, carried out the major chemical types of river waters.

Table 7

Principal Component Analysis on water quality (annual averages), anthropogenic and environmental variables (significant loadings: bold-underlined, high loadings: underlined)

Eigenvalue	10.86	6.16	4.15	3.60	3.16	2.43	1.87
Proportion (%)	25.0	14.0	9.4	8.2	7.2	5.5	4.2
Cumulative (%)	25.0	39.0	48.4	56.6	63.8	69.3	73.5
Eigenvectors							
Variables	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Longitude	0.018	0.009	0.309	<u>0.239</u>	<u>0.217</u>	0.080	0.090
Latitude	0.153	0.274	–0.016	0.146	–0.100	0.061	–0.197
Stream order	–0.109	0.019	–0.163	0.124	0.103	0.253	–0.157
Site altitude	0.162	0.062	–0.136	–0.195	–0.142	0.040	0.209
Mean catchment altitude	0.146	0.060	– 0.244	–0.152	0.014	0.026	<u>0.157</u>
Catchment area	–0.148	0.007	– <u>0.185</u>	0.148	–0.068	0.291	–0.190
Mean catchment slope	0.230	–0.038	0.037	0.119	0.025	–0.106	0.050
Acid silicate rocks	<u>0.177</u>	0.220	0.030	0.204	0.035	0.055	0.055
Mafic silicate rocks	0.036	–0.001	0.140	–0.137	–0.011	0.000	– 0.442
Carbonate rocks	–0.110	– 0.231	–0.158	–0.133	–0.121	–0.067	0.016
Alluvial deposits	– <u>0.185</u>	0.155	0.096	–0.020	–0.052	–0.154	– 0.290
Flysch and molasse	–0.126	– <u>0.220</u>	0.040	–0.060	0.076	–0.017	0.331
Lacustrine/marine deposits	–0.139	0.060	–0.008	–0.068	<u>0.233</u>	0.158	0.321
Bedrock	0.001	0.161	–0.114	–0.105	0.110	0.219	0.058
Gravel	0.065	–0.090	0.067	0.104	– 0.430	–0.113	0.029
Sand/mud	–0.090	0.047	0.101	–0.109	0.324	–0.072	–0.131
Silt/clay	–0.048	0.258	–0.171	– <u>0.213</u>	0.099	0.137	0.115
Discharge	–0.109	–0.055	–0.199	0.057	0.367	0.129	–0.086
Water temperature	– 0.227	–0.060	0.167	0.081	–0.012	0.067	0.024
pH	–0.024	–0.024	0.185	–0.018	–0.084	0.369	0.114
Conductivity	– 0.257	–0.073	0.119	–0.004	–0.144	0.122	0.061
Dissolved oxygen	0.132	–0.047	–0.055	0.286	0.138	<u>0.172</u>	–0.044
Oxygen saturation	0.055	–0.134	0.030	0.345	0.122	<u>0.151</u>	–0.058
Calcium	– 0.216	–0.147	–0.119	0.092	– <u>0.164</u>	–0.026	0.145
Magnesium	–0.125	–0.025	0.289	–0.148	–0.058	0.277	– <u>0.166</u>
Sodium	–0.171	0.133	0.201	0.215	0.014	–0.058	<u>0.189</u>
Potassium	–0.073	0.264	–0.048	0.102	–0.097	0.050	0.171
Alkalinity	– 0.210	–0.122	0.181	–0.135	–0.120	0.135	–0.014
Sulphate	–0.146	–0.051	–0.140	0.236	– <u>0.201</u>	0.180	0.027
Chloride	–0.190	0.073	<u>0.224</u>	0.108	0.113	–0.100	0.255
Silicate	–0.061	0.114	0.300	–0.196	–0.085	<u>0.216</u>	–0.034
Nitrate	– 0.221	0.102	– <u>0.170</u>	0.082	–0.111	–0.073	–0.144
Nitrite	– 0.177	0.138	–0.088	0.165	– 0.183	–0.160	0.013
Ammonium	–0.134	0.231	–0.193	–0.084	– <u>0.002</u>	<u>0.171</u>	0.031
Ortho-phosphate	–0.107	0.351	–0.001	–0.008	–0.015	–0.100	–0.003
TP	–0.121	0.332	0.064	0.024	–0.006	–0.092	0.002
Native forests	0.199	0.100	0.042	<u>0.150</u>	0.086	0.009	–0.026
Heter. agricultural areas	– 0.224	–0.099	–0.215	–0.009	0.059	– <u>0.205</u>	–0.010
Permanent crops	–0.171	–0.065	0.025	0.023	<u>0.253</u>	– 0.272	0.044
Sum of agr. areas	– 0.256	–0.027	–0.013	–0.129	0.087	–0.087	–0.183
Urban fabric	–0.106	0.261	–0.070	–0.114	0.019	–0.029	0.033
Industrial/commercial units	–0.092	0.149	0.100	0.248	–0.004	–0.230	–0.013
Mining	–0.127	–0.031	–0.174	0.226	–0.173	0.125	0.033

Table 7 (continued)

Factor scores							
Rivers	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Fonias	−0.236	1.763	0.962	1.820	0.958	0.893	−1.771
Tsivdogianni	0.256	1.080	2.744	−0.053	0.215	0.748	− 6.114
Vospos at Symvola	0.034	2.932	−0.332	1.644	1.457	3.634	0.707
Vospos at Mesochori	− 11.779	11.419	4.227	12.854	−0.599	− 9.116	−0.254
Kompsatos	−2.288	1.738	0.114	3.515	0.148	2.680	−0.661
Xanthia	−1.293	1.912	0.354	2.664	0.178	1.992	−0.193
Arkoudorema	0.551	1.333	0.364	2.147	0.200	1.728	0.186
Prasinada	−0.670	1.025	0.110	2.177	0.111	2.086	0.417
Diavolorema	−0.331	1.333	0.627	2.808	0.106	2.024	0.934
Poroia	−0.974	2.027	0.408	2.340	− 1.632	2.153	1.202
Kokoremma	−1.271	1.207	1.787	1.652	0.074	2.421	0.708
Onochonos at Smokovo	−3.340	1.629	0.716	1.009	− 1.560	1.271	0.686
Onochonos at Thrapsimi	−4.955	0.767	1.254	0.415	−0.104	3.095	− 4.157
Onochonos at Kaitsa	−5.337	2.040	4.897	− 2.712	−1.160	3.280	− 6.913
Mavrorema	−3.407	2.370	1.031	1.707	−0.497	1.451	−0.034
Skamniias	−4.115	4.366	−0.932	−1.146	1.838	2.409	1.666
Florinis tributary	1.167	1.667	0.257	1.541	0.029	1.259	0.587
Florinis	−3.644	8.409	−1.589	−0.834	1.238	1.485	2.048
Lygos	− 9.311	15.527	− 7.993	− 4.318	4.106	8.765	3.366
Aliakmon at Pisoderi	1.187	1.797	0.220	1.477	−0.349	1.075	0.782
Aliakmon at Adartiko	0.065	2.797	0.090	1.316	0.422	1.687	0.635
Aliakmon at Gavros	−2.081	1.510	−0.659	1.561	0.450	2.418	0.743
Melas	0.345	1.833	0.642	0.664	0.288	1.511	0.215
Aoos	−0.447	2.139	−0.936	− 1.834	0.775	4.229	−0.104
Kalamas	− 9.272	3.518	− 2.602	3.430	− 2.405	− 1.858	−0.245
Louros	−5.051	− 1.410	−1.801	2.671	−0.268	2.206	−0.779
Steno	−1.364	−1.355	−0.204	0.520	0.060	0.809	1.868
Alpheios	− 13.405	0.533	− 8.866	11.553	− 6.381	6.402	1.901
Tsouraki	−1.674	− 1.432	0.073	0.704	−0.624	0.863	1.870
Lousios	−3.278	− 1.602	−0.956	1.102	1.242	2.009	1.066
Pamisos	− 8.319	−0.143	0.611	1.044	2.508	− 3.772	−0.307
Neda at Eira	−1.762	−1.327	−0.200	0.802	−0.706	0.945	1.074
Neda at Marina	−1.585	−1.039	−0.424	0.924	−0.789	0.872	0.312
Neda at Elea	−4.752	−1.248	−0.737	1.006	0.782	0.253	0.769
Kiliaris	− 7.451	− 1.584	−1.761	1.123	8.652	−0.465	1.043
Sianitis	− 7.4643	0.101	5.172	0.455	2.959	2.433	5.537

The predominant hydrochemical type ($\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$) matches the world's most common river type (47% of the world's rivers). This hydrochemical type corresponds to carbonate rock dissolution. In our case, moving from zone 1 to zone 3, this type becomes more frequent (Table 2). The second important river type ($\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$) is, according to Meybeck's findings, an uncommon type (2.5% of the world's rivers). This type occurs primarily in zone 1 and secondarily in zone 2 (Table 2), in catchments with acid silicate rocks with pyrite inclusions

(IGME, 1965). Weathering of plagioclase and pyrite minerals, causes a simultaneous enrichment of river water with sodium and sulphate. The third important river type ($\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$) is a common type, found in 33% of the world's rivers. Magnesium river types (Table 2), belong to catchments with high mafic rock percentage or drain deposits, which are rich in mafic rock debris, as in the case of 43 (Sianitis) river. The extreme sulphate type of 32 (Alpheios) (Table 2) is attributed to the combustion of lignite, to the dissolution of gypsum crystals which are dispersed in the alluvial deposits, and to the dis-

Table 8
Levels of nutrients in the five quality classes according to different methods

Variable	Unit	Quality classes								
		High			Good	Moderate	Poor	Bad		
		Average of reference sites	75% percentile of reference sites	25% percentile of all sites	Almost pristine rivers*	Average of good sites	75% percentile of good sites	Average of moderate sites	Average of poor sites	Average of bad sites
N-NO ₃ ⁻	mg/l	0.24	0.18	0.17	0.1	0.29	0.46	0.93	1.64	2.03
N-NH ₄ ⁺	mg/l	0.022	0.016	0.029	0.015	0.054	0.118	0.072	0.376	0.697
N-NO ₂ ⁻	μg/l	3.00	2.30	3.85	9.1–15.2	4.87	6.39	11.80	48.90	89.40
P-PO ₄ ³⁻	μg/l	77.4	58.1	32.4	10	92.7	159.9	120.0	212.1	467.0
TP	μg/l	115.4	86.5	45.8	–	137.8	217.0	194.4	247.3	566.3

*Meybeck (1982), Meybeck (1986) in Cardoso et al. (2001), Meybeck and Helmer (1989).

solution of underlying Triassic evaporites (Skoulikidis et al., 2000b). The last two river types are not reported in Meybeck's data base. Finally, the Onochonos river at 15 (Smokovo) and 18 (Kaitsa) (Table 2) can be additionally termed as geothermal (Meybeck, 1996), since it contains very high silicate concentration of hydrothermal origin.

5.2.3. Carbonate chemistry

In rivers, carbon dioxide is typically supersaturated due to in-stream organic matter decomposition exceeding photosynthetic uptake and the inflow of CO₂-supersaturated groundwaters (Kempe, 1982; Kempe et al., 1991; Jones and Mulholland, 1998; Jones et al., 2003). In the case of small/medium Greek rivers, pCO₂ variations are attributed to respiration and photosynthetic processes and groundwater contribution (see Sections 5.2.5.1 and 5.2.5.3). The positive correlation between the excess of pCO₂ and the oxygen deficit (Fig. 9) indicates the influence of respiration (high pCO₂–low oxygen concentration) and photosynthesis (low pCO₂–high oxygen concentration) on carbon dioxide and oxygen equilibrium.

Table 9
Nutrient Classification System (NCS) for not hydro-morphologically altered small/medium sized rivers based on annual average concentrations found in 36 sites scattered throughout Greece

	Unit	Quality classes				
		High	Good	Moderate	Poor	Bad
N-NO ₃ ⁻	mg/l	<0.22	0.22–0.60	0.61–1.30	1.31–1.80	>1.80
N-NH ₄ ⁺	mg/l	<0.024	0.024–0.060	0.061–0.20	0.21–0.50	>0.50
N-NO ₂ ⁻	μ g/l	<3.0	3.0–8.0	8.1–30.0	30.1–70.0	>70.0
P-PO ₄ ³⁻	μ g/l	<70	70–105	106–165	166–340	>340
TP	μg/l	<125	125–165	166–220	221–405	>405.13

A number of zone 1 rivers show carbonate oversaturation, despite the limited occurrence of carbonate constituents (mainly in the form of plagioclase) in their basins and the respective minimal carbonate constituents in river water. This is due to their low pCO₂ (see Sections 5.2.5.1). The carbonate saturation in most of zone 2 rivers is triggered by the higher contribution of carbonate formations in their catchments. Finally, rivers in zone 3, despite their high pCO₂, are highly oversaturated with respect to carbonates (Table 4). This is due to the prevalence of, mostly karstified, carbonate aquifers and the transport of carbonate minerals in particulate form (Skoulikidis, 1990).

5.2.4. Nutrients and biological activity

According to Skoulikidis (2004) biological quality strongly depends on nutrient concentrations. In absence of major industrial pollution in Greece, this finding emphasizes the importance of studying nutrients in running waters as major pressures on biota.

In general, seasonal nitrate variability is mainly controlled by agricultural soil leaching and dilution processes. Municipal wastewater discharges enhance

Table 10
Nutrient quality classes in French rivers (Brunel et al., 1997)

	Unit	Quality classes				
		High	Good	Moderate	Poor	Bad
N-NO ₃ ⁻	mg/l	<0.45	2.3	5.6–11.3	11.3–18	>18
N-NH ₄ ⁺	mg/l	<0.07	0.07–0.39	0.39–1.55	1.55–6.22	>6.22
P-PO ₄ ³⁻	μg/l	<65	65–163	163–196	196–653	>653
TP	μg/l	<100	100–300	300–600	600–1000	>1000

Table 11
Nutrient quality classes in Italian rivers (Decreto Legislativo, 1999)

		Quality classes				
		High	Good	Moderate	Poor	Bad
N-NO ₃ ⁻	mg/l	<0.07	<0.34	<1.13	<2.26	>2.26
N-NH ₄ ⁺	mg/l	<0.023	<0.077	<0.39	<1.17	>1.17
TP	µg/l	<70	<150	<300	<600	>600

nutrient, sodium and chloride concentrations predominately in summer. Florinis (22), although biologically characterised as a poor river (Table 5) has a nitrate concentration below the upper limit of none polluted rivers. The low nitrate concentration of this river is attributed to intense photosynthesis, which takes place predominately summer. In unpolluted rivers, ammonia and phosphate present relatively high concentrations in summer. This is attributed to mineralization processes of natural organic matter which accumulates in backwaters or standing waters of the river corridor. During spring, rivers draining pristine, forested catchments are enriched with TP indicating forest soil leaching processes.

The TinN/P-PO₄³⁻ ratio, indicates that during spring, when photosynthesis predominates, the limiting nutrient is site-dependent (Table 1). Zone 3 rivers, reveal a phosphorous limited photosynthesis (N/P > 12), while zones 1 and 2 show mainly a nitrogen limited one (N/P < 5). The majority of the rivers draining forested catchments, show also nitrogen limited photosynthesis (N/P < 5). This is a common case for temperate forest ecosystems (Gundersen and Bashkin, 1994).

5.2.5. Driving forces of aquatic quality

According to the PCA (Table 7), the hydrochemical variability of the rivers is controlled by the following factors: Weathering of carbonate rich alluvial deposits, combined with irrigation return flows are components of the first controlling factor. Carbonate weathering stimulates calcium and alkalinity concentrations and causes enhanced conductivity in river water. In addition, agricultural activities enrich rivers with nitrates and possibly with nitrites. This factor is expressed in flat, alluvial, cultivated catchments drained by mineralised and polluted rivers such as 32 (Alpheios), 5 (Vospos at Mesochori), 23 (Lygos), 29 (Kalamas), 35 (Pamisos), and 40

(Kiliaris) or highly mineralised rivers 43 (Sianitis). On the other hand, in steep forested acid silicate catchments, where alluvial deposits are minimally represented and cultivated areas are lacking, respective rivers are not polluted and show low mineralisation [24, 25 (Aliakmon at Pisoderi and Adartiko), 21 (Florinis-tributary), 8 (Arkoudoremma), 27 (Melas), 2 (Tsivdogianni)].

A second important factor is urban wastewater pollution, which chiefly affects northern Greek rivers, with silty/clayely riverbed [23 (Lygos) and 5 (Vospos at Mesochori)]. Municipal wastewaters enrich these rivers with ammonium, phosphate and TP. A simultaneous potassium increase is mainly attributed to acid silicate rock weathering. In contrast, a number of southern Greek carbonate catchments [34 (Lousios), 40 (Kiliaris), 33 (Tsouraki), 30 (Louros)], which are not or are minimally affected by urban wastewaters, show low concentrations in the aforementioned nutrients.

The third factor is comprised by three components: a) marine aerosol which enriches river water with sodium and chloride, b) mafic rock weathering that causes high riverine magnesium and silicate concentrations and c) nitrate and partly ammonium which originate from agrochemicals, applied on heterogeneous agricultural areas. The first two components affect the aquatic composition of eastern lowland catchments [43 (Sianitis), 18 (Onochonos at Kaitas), 5 (Vospos at Mesochori) and 2 (Tsivdogianni)], which are partly covered with mafic rocks [16, 18 (Onochonos), 2 (Tsivdogianni)]. The third component is expressed mainly in western large lowland carbo-

Table 12
Nutrient background levels in forested and not forested catchments (average values)

		“Pristine” forested catchments	“Pristine” not forested catchments
Number of catchments		9	5
Average forest cover	%	84	19
Average catchment altitude	m	1005	944
N-NO ₃ ⁻	mg/l	0.28	0.18
N-NH ₄ ⁺	mg/l	0.023	0.019
N-NO ₂ ⁻	mg/l	0.028	0.036
P-PO ₄ ³⁻	µg/l	79.8	73.2
TP	µg/l	124.2	99.5

Table 13

Results of MLR analysis for dependent variables applied in 36 sites

Dependent variables	<i>p</i> -value (ANOVA)	<i>R</i> ²	Normality of residuals	Regression equation
TDI	<0.05	0.739	Satisfied	TDI=1973 – 33.1 latitude – 0.227 mean altitude of subcatchment – 7.37 mean slope of subcatchment
NO ₃ ⁻	<0.05	0.539	Satisfied	NO ₃ =0.923+0.158 heterogenic agricultural areas +0.165 alluvial deposits
NO ₂ ⁻	<0.05	0.414	Satisfied	NO ₂ =0.173 – 0.00419 mean slope of subcatchment+0.414 industrial or commercial units
NH ₄ ⁺	<0.05	0.651	Satisfied	NH ₄ = – 0.0474+0.000604 subcatchment area+0.244 urban fabric+0.0321 bedrock
PO ₄ ³⁻	<0.05	0.654	Satisfied	PO ₄ =208+17.0 alluvial deposits+434 urban fabric
TP	<0.05	0.628	Satisfied	TP=106+7.62 alluvial deposits+154 urban fabric

nate catchments, drained by polluted rivers [32 (Alpheios), 23 (Lygos) and 29 (Kalamas)].

The fourth factor concerns the enrichment of waters with sodium and sulphate of anthropogenic (wastewater discharges, coal combustion) and geogenic (plagioclase and pyrite weathering, gypsum dissolution) origin. Elevated sodium and sulphate concentrations originate exclusively from anthropogenic activities [32 (Alpheios), 29 (Kalamas)], from both anthropogenic activities and geochemical processes [5 (Vospos at Mesochori), 6 (Kompsatos) and 7 (Xanthia)], or are solely of geogenic origin in unpolluted rivers [10 (Diavoloremma), 11 (Poroia), 9 (Prasinada) and 8 (Arkoudoremma)].

The fifth factor concerns rivers that are exclusively affected by dissolution of Triassic gypsum deposits [32 (Alpheios), 29 (Kalamas)].

The sixth factor includes biological activity. Since part of the latter drain mafic rocks [28 (Aos) and 16, 18 (Onochonos at Thrapsimi and Kaitsa)], magnesium and silicate are also represented in this factor.

Finally, the seventh factor is comprised by two components: a) the portion of chloride and sodium that originates from the dissolution of lacustrine/marine sediments and b) the weathering of ophiolites, which enriches water with magnesium. The first component affects mainly highland catchments with high percentage of lacustrine/marine deposits, such as 43 (Sianitis), 23 (Lygos) and 22 (Florinis). The second component affects catchments with high percentage of mafic rocks [16, 18 (Onochonos at Thrapsimi and Kaitsa) and 2 (Tsvidogianni)].

The influence of individual factors and processes controlling aquatic quality are described below in detail.

5.2.5.1. Geological and hydrogeological factors. The ultimate source of most dissolved ions is the mineral assemblage in rocks near the land surface. In addition, climatic patterns tend to produce characteristic plant communities and soil types, which affect aquatic composition. Moreover, the processes of rock weathering are strongly influenced

Table 14

Characteristics of STAR rivers (for locations see Fig. 1)

River site	Site latitude	Catchment altitude	Catchment slope	Alluvial deposits	Heterogenic agricultural areas	TDI	Nitrate
		m	%	%	%	mg/l	mg/l
Gorgopotamos bridge (S1)	38.49	1449	25.8	0.0	0.0	246.3	0.89
Gorgopotamos village (S2)	38.50	1336	25.1	0.0	0.7	242.0	1.00
Tsivlos (S3)	38.04	900	35.2	0.1	1.2	343.5	0.25
Piros (S4)	38.05	722	20.1	8.0	4.0	278.5	2.71
Kalonero (S5)	37.17	418	16.4	1.5	13.8	358.7	3.27
Artiki (S6)	37.17	345	10.3	19.0	16.5	404.2	6.84
Tsouraki 2 (S7)	37.28	1009	24.6	0.0	0.0	276.7	0.78

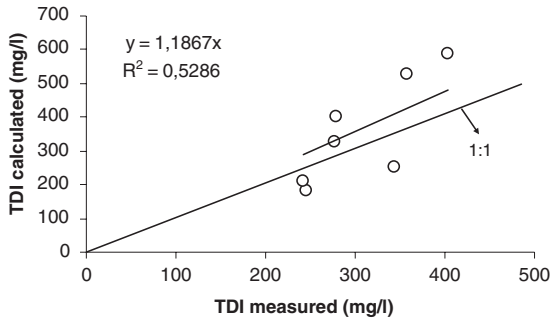


Fig. 10. Correlation between measured and calculated total dissolved ion concentration for STAR river data.

by temperature and by the amount and distribution of precipitation (Hem, 1985). Climatic and geological features are often cited as the most important environmental controls on stream solutes at a global scale (Webb and Walling, 1996). Also, in the case of major Greek rivers it has been shown that geology and climate are major drivers of aquatic composition (Skoulikidis, 1993). However, when comparing the aquatic composition of the three geo-chemical-climatic zones, for both major and small/medium rivers, it is not possible to distinguish, which of these two factors is the most important. This is due to the fact that the three zones are simultaneously characterised by different climatic and geological features. Nevertheless, an analysis of the present data set can provide evidence on the importance of geology in controlling riverine solute concentrations. The following facts support this argument:

Zone 3 catchments are characterised by maximum TDI (Table 1c), despite their maximum precipitation and surface which causes dilution. In this zone, geochemical processes “mask” climatic ones, since carbonate dissolution overrides dilution.

For most of the water quality variables, zonal hydrochemical differences are stronger expressed than seasonal variations within each one of the zones (see Section 4.3.2), i.e. geochemical variability “masks” seasonal climatic variations.

Other signs on the influence of geology on aquatic quality are:

Moving from zone 1 to zone 3, solute concentration shows a statistically significant increase (see Section 4.3.2). The southwards mineralisation increase is also true for major Greek rivers (Skoulikidis, 1993)

and is attributed to the respective increase of more soluble and easily weatherable bedrock, i.e. carbonates, flysch/molasses, lacustrine/marine and alluvial deposits (Meybeck, 1987; Meybeck and Helmer, 1989). Particularly for calcium and alkalinity, the southwards increase, both in concentration and percentage, in relation to TDI, is explained by the respective increase of carbonate minerals in the river basins. In zone 2 additional alkalinity sources are mafic silicate rocks (Drever, 1982). Weathering of mafic rocks enriches river water with magnesium and silicates. Hence, these constituents reach their maximum concentrations in zone 2 and especially in catchments with high ophiolite percentage. The high TDI and TH variability in zone 2 rivers (Table 1b) is caused by respective magnesium and alkalinity fluctuations, which, in turn, are attributed to the high variability of carbonate and mafic rock percentage in the catchments of this zone (Table 1b). The relatively high magnesium concentration in zone 3 rivers (Table 1c) is attributed to dissolution of dolomitic limestone and for 28 (Aaos) and 43 (Sianitis) to weathering of mafic rock minerals. The decrease of potassium concentration from zone 1 to zone 3 (Table 1) is attributed to the respective decrease of acid silicate rocks. Weathering of silicates contributes to the high SiO₂ concentration in zones 1 and 2 (Table 1a, b), while the limited occurrence of magmatic and metamorphic silicate rocks in zone 3 causes low SiO₂ concentrations (Table 1c). Sodium primarily derives from acid silicate rock weathering. An additional source of sodium and chloride are lacustrine/marine sediments. This is evident in the case of 43 (Sianitis) (Table 1c). Due to its extreme sodium value, zone 3, which is characterised by the absence of acid magmatic and meta-

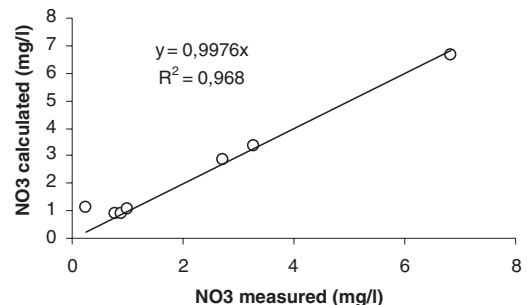


Fig. 11. Correlation between measured and calculated nitrate concentration for STAR river data.

morphic rocks, shows higher average sodium concentration than zone 2 (Table 1b, c). Other rivers, which possibly owe their high sodium and chloride concentrations to lacustrine/marine sediments are: 20 (Skamnias), 23 (Lygos), 32 (Alpheios) and 40 (Kiliaris) (Table 1b, c).

The influence of hydrogeological factors on aquatic quality characteristics is outlined below:

Water temperature is affected by altitude and latitude (see Section 5.2.5.2). In addition, water temperature is controlled by hydrogeological factors. For example, the higher annual temperature in zone 3 rivers (Table 1) is triggered by the contribution of karstic groundwaters in river runoff, which smoothens temporal water temperature variations. Similarly, seasonal temperature variations are stronger expressed in zones 1 and 2 rivers (Fig. 8), which exhibit higher contribution of overland flow in river runoff, than in zone 3 rivers. The strong negative correlation between water temperature and slope (Tables 6 and 7) is also attributed to hydrogeological factors. In fact, rivers with steep slopes are characterised by low groundwater contribution to river runoff. In steep river basins, runoff is almost exclusively represented by overland flow which, more directly than mixed (surface and subsurface) flow, reflects air temperature variations. Furthermore, steep upland catchments include rivers with low solute concentrations (Tables 6 and 7), due to their low base flow fraction. Seasonal hydrochemical variation is also affected by hydrogeological factors. Indeed, zone 3 rivers show weaker seasonal hydrological and hydrochemical changes compared to zone 1 and zone 2 rivers (see Sections 4.2 and 4.3.2 and Fig. 8). This is attributed to the mostly karstic character of zone 3 catchments, which smoothens seasonal hydrological and hence hydrochemical variations. Finally, the general carbonate oversaturation in the summer is not caused by low $p\text{CO}_2$ (Table 4). It is triggered by base flow contribution, which is rich in carbonate constituents. Rivers draining alluvial deposits are enriched with solutes, and especially with bicarbonates, sodium and chloride (Table 6). This is partly due to the contribution of alluvial groundwaters (which are rich in solutes) to river runoff. Carbon dioxide is the main driver of chemical weathering (Garrels and Mackenzie, 1971). Dissolved carbonates, the major constituents of river solutes, originate from the dissolution of carbonate

rocks in the subsoil zone, where dissolved carbon dioxide is far in excess of atmospheric equilibrium. They are then transported in streams and rivers through groundwater (Kempe, 1982). Hence, carbonate chemistry of a river is largely a question of the geologic structure and petrography of its drainage basin (Parizek et al., 1971; Kempe, 1982). The positive correlation between pH and stream density (Table 6) provides evidence of the importance of hydrogeological factors on carbonate chemistry. Watersheds with high stream density are characterised by impermeable rock formations (see Section 5.1) with small groundwater aquifers, whereas basins with low stream density consist of permeable, frequently karstic, formations with large aquifers. It is assumed that, rivers from carbonaceous basins (mainly zone 3 rivers) are enriched with carbon dioxide due to groundwater contribution. In contrast, rivers draining mainly impermeable rocks (zone 1 and zone 2 rivers) are predominately rainfall-fed and present lower $p\text{CO}_2$.

5.2.5.2. Climate and hydrology. When comparing the three zones, river water temperature varies significantly (see Table 3 and Fig. 8). The diminishing of water temperature with increasing catchment latitude and altitude (Table 6) is the result of climatic influence (see Section 2). Furthermore, rivers draining semiarid areas, such as the islands, are affected by salinisation, since water gradually evaporates as it moves from more humid uplands to the lowlands (Meybeck, 1996) and consequently show enrichment in major ions. Intra-annual variations in climatic and discharge rates are major drivers of the respective hydrochemical fluctuations in rivers. The seasonal regime of solute concentrations in river water is controlled by three main processes (Fig. 12), that are governed by hydrological factors: (i) dilution, during spring and selectively during winter, (ii) concentration, due to evaporation and base flow contribution, during the dry season (in summer, river water is practically represented by groundwater) and (iii) enrichment due to flushing of soil-salts (e.g. Edwards, 1973; Walling and Foster, 1975; Semkin et al., 1994), following flood events, occurring in autumn, winter and rarely in spring (Skoulikidis, 1993). The relative importance of the aforementioned processes controls the intra-annual solute concentration variations in a river (Skoulikidis, 2000a). The strong seasonal hydro-

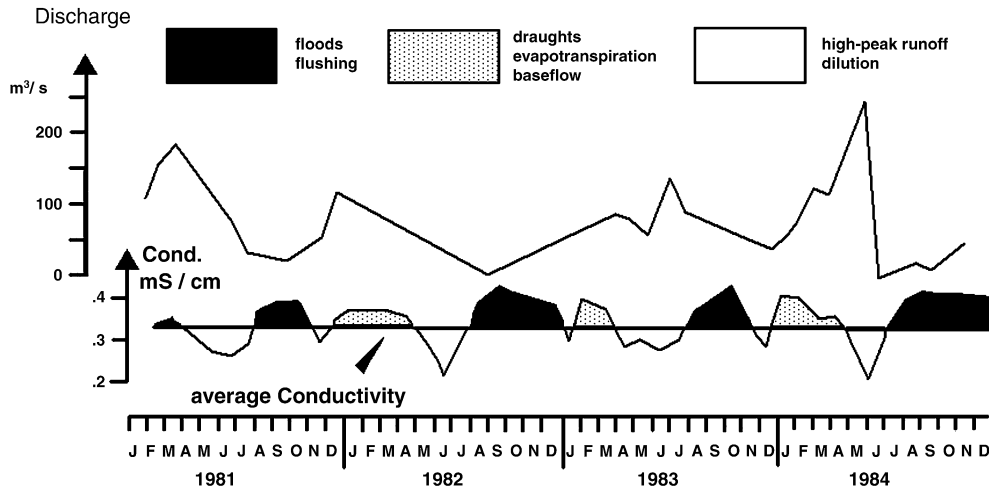


Fig. 12. Typical example of riverine monthly variations of discharge and conductivity and mechanisms controlling solute concentrations.

logical fluctuations in zone 1 rivers cause respective seasonal solute variations. The general solute enrichment in summer in relation to spring in the rivers under study, results from both the evaporation/base-flow effect, which predominately occurs during the dry season, and the dilution effect in the spring. The demonstrated hydrochemical differences between the three zones are more intense in summer (see Section 4.3.2 and Fig. 8), when river flow is almost exclusively represented by base flow. The latter mirrors geochemical features better than overland flow. Solute enrichment in winter compared with spring results from the combined action of winter-flushing and spring dilution. Due to flushing processes, a number of rivers showed maximum annual solute concentrations in winter. For some rivers flushing processes masked dilution, even in spring.

5.2.5.3. Anthropogenic impact and biological activity. As the Correlation Matrix and the results of PCA and MLR analysis (Tables 6, 7 and 13) indicate, anthropogenic factors enrich river waters with nutrients. Untreated urban wastewaters and irrigation return flows cause relatively high nutrient concentrations in a number of rivers, which according to biological aspects, were characterised as poor and bad. Nitrates originate mainly from agricultural activities, while the main source of ammonia, phosphate and total phosphorus are municipal wastewaters (Table 7). Furthermore, part of the sodium and chloride can be attributed

to the impact of municipal wastes (Tchobanoglous and Burton, 1991; Skoulikidis, 1993). Moreover, irrigation, and especially sprinkler irrigation, leaves a residual that is commonly much higher in salt concentration than the original water. According to UNEP/GEMS (1991), the most important factor causing freshwater salinisation is irrigation. In fact, the increase of irrigation activities as well as the increased use of sprinkler irrigation techniques in Greece (Kosmas et al., 1996), contributed to an increase of salt accumulations in the upper soil profile (Yassoglou, 1995). The positive correlations between heterogenic agricultural areas, conductivity, calcium and TH, also between arable land, conductivity, magnesium and TH and finally between permanent crops and chloride (Table 6) could be partly attributed to irrigation activities. Finally, an indirect increase of major ions, and especially of earth alkalies and bicarbonate, could be triggered by organic matter respiration. This is attributed to the increase of the solubility product of respective salts as a result of $p\text{CO}_2$ increase.

As aforementioned, groundwater enriches the examined rivers with carbon dioxide. An additional CO_2 source is the in-river organic matter respiration. Studies of $p\text{CO}_2$ in natural waters provide an important indication on carbon dioxide exchange between air and river water. If $p\text{CO}_2$ surpass 360 ppmv, i.e., the atmospheric pressure, then the water becomes a source of carbon dioxide to the atmosphere. If $p\text{CO}_2$ falls below 360 ppmv, then the water is a sink for atmospheric carbon dioxide. When respiration dominates, $p\text{CO}_2$

overrides the atmospheric pressure. When photosynthesis prevails, carbon dioxide is consumed by aquatic flora and $p\text{CO}_2$ falls below the atmospheric pressure. Hence, $p\text{CO}_2$ has been used in anthropogenically altered aquatic ecosystems as an indication for the dominance of either respiration or photosynthesis (Kempe, 1982; Kempe et al., 1991; Depetris and Kempe, 1993; Maberly, 1996; Neal et al., 1998). The positive correlation between the excess of $p\text{CO}_2$ and the oxygen deficit (Fig. 9) supports the argument of a biological influence on riverine carbon dioxide. High $p\text{CO}_2$ in combination with the low oxygen concentration and saturation is attributed to decomposition of organic wastes. In fact, in summer, when water discharge is low and organic matter concentration is high, the majority of polluted rivers, e.g. 5 (Vospos at Mesochori), 32 (Alpheios), 23 (Lygos), 29 (Kalamas) and 35 (Pamisos), is marked by respiration. An exception is 22 (Florinis), which is characterised by active photosynthesis. Low $p\text{CO}_2$ combined with high oxygen concentration and saturation in spring [e.g. in Vospos at 4 (Symvola) and 5 (Mesochori), 6 (Kompsatos), 7 (Xanthia), 8 (Arkoudoremma), 9 (Prasinada), 10 (Diavoloremma), 12 (Kokoremma), 25 (Aliakmon at Adartiko) and Gavros, 28 (Aoos), 32 (Alpheios) and 40 (Kiliaris)] provide evidence for the predominance of photosynthetic processes. Photosynthetic activities trigger carbonate saturation. In fact, although in-river carbonate concentrations in spring are minimal due to dilution, the majority of the rivers reveal carbonate oversaturation, due to the low $p\text{CO}_2$.

5.2.5.4. Marine influence. A portion of chloride and sodium in rivers that are in the vicinity of the sea is attributed to marine aerosol. The marine influence is demonstrated by the exponential decrease of these ions with altitude (Fig. 6). This finding is confident with the general exponential chloride decrease, as the distance from coast increases (Meybeck, 1996). Furthermore, the eastward increase of sodium and chloride concentrations (Tables 6 and 7) is partly attributed to marine influence. Moreover, the Na/Cl ratio in the island-rivers tends to be close to the respective sea water ratio. It should be noted however that the increase of sodium and chloride in the lowlands is additionally triggered by the fact that lowland rivers are in general more affected by municipal wastes, irrigation and base flow than upland ones.

5.2.5.5. Geomorphological factors. As discussed above, altitude affects river water temperature. In addition, catchment slope influences aquifer characteristics which in turn control the base flow fraction in river flow. The latter drives spatial and temporal variations in solute concentration. Moreover, solute enrichment caused by flushing processes is more dominant in zones 1 and 2, which include rivers with large floodplains. Finally, the general decrease of oxygen saturation in highland rivers of high and good quality (Fig. 7) could be attributed to the influence of altitude on the equilibrium concentration (Knoben et al., 1995).

5.2.5.6. Land use. As aforementioned, agricultural land uses affect the salt balance in the rivers. In addition, “pristine” forested catchments could supply the river water with more nutrients than catchments with low forest cover.

5.3. Management tools

Additionally to a TDI classification (Table 2), a Nutrient Classification System (NCS), a Total Dissolved Ion (TDI) concentration Prediction Tool (TDI-PT) and a Nutrient concentration Prediction Tool (N-PT), which can be applied for water management purposes, have been developed. These tools could be proved useful to the Greek authorities facing the challenge of implementing the WFD. The following chapters discuss and describe the advantages of these management tools.

5.3.1. Nutrient Classification System

The NCS, compared with the French system, shows in general lower levels in all quality classes. The reference values of phosphate and TP, which are slightly higher in the NCS are an exception. Compared to the Italian system, NCS shows relatively higher nitrate levels in the high, good and moderate quality classes and higher TP levels in the high and good quality classes. In addition, reference-NCS TP levels are higher than those established for US (Kansas) by Dodds and Oakes (2004), which was 50 mg/l. It should be mentioned, that the partly higher reference nutrient levels could be caused by the fact that a number of nutrient measurements were around the detection limits (see Section 3.1). This could partly

cause a slightly higher estimation of the reference concentrations. In addition, there are indications that the partly higher nutrient levels in NCS could be caused by the forests, which mainly cover unpolluted river basins. In fact, ammonia, nitrate, phosphate and TP reveal relatively higher (however not statistically of significant difference) reference concentrations in “pristine” forested catchments than in “pristine” not forested ones (Table 12). Catchment altitude seems not to be an underlying factor since forested and non-forested catchments show only slight altitude differences (Table 12). Forest soil leaching enriches the surface runoff with nutrients. For example, Bond (1979) attributed phosphorus enrichment in a mountainous river to vegetation leaching. In addition, forest ecosystems may accumulate considerable amounts of nitrogen in biomass and soil organic matter (Gundersen and Bashkin, 1994), which can be leached as nitrate to surface waters (Dies and Wright, 1995; Borken and Matzner, 2004). In Greece, reference sites of a mountainous forested subcatchment in a north-central river (Aliakmon) revealed higher phosphorous levels compared to those in more lowland sites of worse biological quality (Skoulikidis et al., 2002). Similar results for organic nitrogen, organic phosphorous, nitrate and ammonia showed another medium-sized, mountainous Peloponnesian river (Krathis), which is being currently intensively studied in the framework of the European project tempQsim (EVK1-CT-2002-00112) focusing on nutrient dynamics (Skoulikidis, 2004). The increase of TP concentration along with the discharge in forested catchments of the rivers under study provides evidence of soil leaching processes.

The higher nutrient concentrations in rivers located in forested catchments are not exclusively caused by forest soil leaching. According to in situ observations in a number of mountainous forested catchments, soil organic matter and leaf litter accumulate in backwaters, standing waters and ponds. It is assumed, that in-stream organic matter mineralisation releases nutrients which are partly assimilated and partly enrich the surface waters.

The NCS could be proved useful for water management purposes. In fact, NCS could provide a basis for the classification of small/medium Greek rivers according to their nutrient concentrations. These rivers are in general less polluted and support more

demanding water uses than major Greek rivers. Therefore, different nutrient classification systems should be created. NCS will assist the implementation of the WFD in two ways. Firstly, water bodies not covering the demands of the WFD (good status) could be identified (WFD—Annex II, 1.5). Secondly, NCS could be applied for the establishment of chemical reference conditions (WFD—Annex II, 1.3) and for chemical quality classification purposes, which acts complementary to the biological quality classification (ECOSTAT Report, 2003).

5.3.2. Prediction of aquatic quality

Woli et al. (2004) have successfully predicted nitrate concentration from upstream land uses by applying linear regression analyses. Similarly, Buck et al. (2004) related TN and TP concentrations to land uses. In addition, Kronvang et al. (2003) and Dodds and Oakes (2004) used MLR analysis to relate TP concentrations to upstream land uses and other environmental variables. In the framework of the present article, MLR analysis based tools were developed for rapid prediction of total dissolved ion (TDI-PT) and nutrient concentrations (N-PT) in running waters. The TDI-PT and N-PT predict the solute concentration and nutrient levels of small/medium Greek rivers using environmental variables, which can be easily extracted by GIS applications. The necessary layers are a DEM, the CORINE land cover and a simplified geological map of the country (Fig. 2). In the following, the equations presented in Table 13 are tested against various scenarios.

TDI: by entering the minimum values of latitude, catchment slope and altitude found in the data set, the resulting TDI was 649 mg/l. This value can be accepted as realistic for a hypothetical lowland catchment in Crete island, where evapotranspiration and high subsurface contribution to surface runoff enhance solute concentrations. Similarly, by applying mean values for the aforementioned variables, the resulting TDI was 408 mg/l, which is a realistic value for a hypothetical mid-altitude catchment with median slopes in central Greece. On the other hand, by setting maximum values in the equation, the resulting TDI became 43 mg/l. However, a permanent northern Greek river, with a mean catchment altitude of over 1000 m and a slope of about 50%, is unlikely to exist. Moreover, the comparison between measured

and calculated TDI for STAR river data was satisfactory (Fig. 10). Thus, the equation for the prediction of TDI can be used for rapid TDI estimation.

Nitrate: A hypothetical rather mountainous, pristine catchment could be characterised by the absence of alluvial deposits and heterogenic agricultural areas. In that case, the nitrate concentration of the respective river would be 0.92 mg/l. The estimated nitrate background level is <0.97 mg/l. Moreover, in a hypothetical river, draining a catchment covered entirely with extensively cultivated alluvial sediments, could theoretically reach a nitrate concentration of 33 mg/l. Those high nitrate levels appear only in very rare cases in Greek surface waters (e.g. in river Evros, data Ministry for Agriculture 2001). Moreover, the comparison between measured and calculated nitrate for STAR river data was very satisfactory (Fig. 11). Hence, the nitrate equation is capable for rapid nitrate prediction.

Nitrite: The minimum slope of the examined “pristine” catchments is 24%. A flat, “pristine” catchment would show a nitrite concentration of 0.07 mg/l. This value is only slightly higher than the upper limit of nearly pristine rivers (0.05 mg/l). The maximum slope of catchments with bad quality is 25% and the maximum area covered by industrial/commercial units is 0.65%. For these values the nitrite concentration would reach 0.21 mg/l, which is a realistic concentration for polluted rivers. As a result, the nitrite equation seems to be physically based.

Ammonium: The minimum catchment area of reference rivers is 2.1 km² and the minimum bedrock percentage is 0. For these values the ammonium concentration was –0.046 mg/l. On the other hand, a representative polluted river would have an ammonium concentration of 1.64 mg/l, which is a realistic value. Thus, the ammonium equation can be applied only for predicting concentrations of polluted rivers.

Phosphate: The phosphate concentration in a reference river with a lack of alluvial deposits in its catchment would be 208 µg/l. This is an acceptable value for reference phosphate conditions (<215 µg/l). A river draining an alluvial urbanised catchment would reach a phosphate concentration of 3.14 mg/l, which is a rather possible value. Hence the equation is applicable for predicting phosphate both in “pristine” and polluted rivers.

TP: A river crossing a reference catchment without alluvial deposits would show a TP concentration of 106, which is lower than the estimated background level (<125 mg/l). A river in an alluvial urbanised catchment would reach a TP concentration of 620 mg/l, which corresponds to a realistic TP value of a bad quality river. Thus, the TP equation is capable of predicting TP in rivers with a wide quality range.

N-PT could be proved useful for the implementation of the WFD. For the estimation of spatially based reference conditions (WFD—Annex II, 1.3) and ecological quality classification purposes a site pre-classification procedure is commonly followed (e.g. AQEM Consortium, 2002). Hence, N-PT could be applied for an initial site selection. N-PT could additionally be used for the assessment of impact, i.e. to assess if any surface water bodies will fail to meet the environmental quality objectives of the WFD (WFD—Annex II, 1.5). Finally, N-PT could assist the design of surveillance monitoring programmes (WFD—Article 8, Annex V) in a national level.

6. Conclusions

This article refers to permanent hydro-morphologically not altered small/medium Greek rivers. These rivers present strong spatial variations in hydro-morphological features and aquatic composition. In some cases, the geochemical background (i.e. evaporites, ophiolites, sulphide minerals) and geothermal activity give rise to uncommon and rare hydrochemical types. Based on geologic, climatic and hydrochemical criteria of major rivers, Greece was separated into three initial zones (Skoulikidis, 1993; Skoulikidis et al., 2004). The hydrochemical differentiation of these three zones regarding also small/medium rivers justifies this zonation. In fact, rivers situated within different zones reveal stronger dissimilarities in their aquatic quality than those located in the same zone. The main differences between the three zones concern conductivity (primarily in summer), sulphate and silicate (over the year) concentrations. In addition, calcium and alkalinity concentrations differentiate zone 3 from zones 1 and 2. Geologic factors govern spatial hydrochemical differences (TDI, TH, major ion concentrations) and hydro-morphological variations (stream density, water flow, and width of the flood-

plain). In addition, catchment geology controls hydrogeological features, which in turn affect spatiotemporal hydrological, water temperature and solute concentration variations and influence, together with biological activity, dissolved carbon dioxide levels. The latter regulates carbonate saturation and dissolution. Spatial hydrochemical variation is more pronounced in the summer, when river flow is base flow. Altitudinal differences in sodium and chloride concentrations are due to the influence of marine aerosol as well as climatic and hydrogeological factors. In polluted water bodies, municipal wastewaters and irrigation activities additionally increase sodium and chloride concentrations. Temporal hydrological fluctuations are governed by climatic and hydrogeological factors, which control rainfall and evaporation as well as the relative proportions of overland flow and subsurface flow in river runoff. These factors drive temporal variations in solute concentrations. Nitrate enrichment is primarily caused by agricultural activities, while ammonia, phosphate and total phosphorous mainly originate from municipal wastewaters. In summer, polluted rivers are marked by respiration. In spring, photosynthesis prevails in most of the rivers regardless their water quality. There are indications that “pristine” forest areas possibly enrich surface runoff with nutrients. This fact is attributed to forest soil leaching and in-stream mineralisation of natural organic matter. In these areas, nitrogen limits photosynthetic activity. Two management tools have been developed: a nutrient classification system and a tool for rapid prediction of aquatic composition. A major advantage of NCS is that it is based on a biotic classification system which is sensitive to nutrient impact. If hydrochemical data are not available, TDI-PT and N-PT could be applied for rapid, desk-top assessment of TDI and nutrient concentrations in running waters using GIS-derived environmental data. The management tools are based on a realistic and relatively representative sampling network for Greek conditions. The management tools could be used within WFD related national projects for the following purposes: a) site pre-classification, b) establishment of chemical reference conditions and chemical classification, c) identification of waters that will possibly fail to meet the requirements of good status and d) design of surveillance monitoring programmes.

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