Spatiotemporal river water physicochemical profile and pollution hazard mapping in the wider area of Spercheios River catchment (Central Greece)

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Abstract

Human induced activities impose significant pollution threats in river catchments worldwide. The Spercheios river outflows in the Maliakos Gulf and is located at Central Greece and protected under the Natura 2000 European network. The catchment land uses comprise mainly intensive agricultural areas with significant pollution pressures from fertilizers, small factories and domestic wastewater. This study aims to identify and evaluate the impacts of land uses and human activities on the water quality of the river by spatially monitoring the fluctuations of physicochemical properties along the river. Physicochemical data from 10/2014 up to 07/2016 - acquired from three automatic-telemetric monitoring stations in Alamana (natural riverbed), Anthili (artificial riverbed) and Ipati (main river branch) - and chemical data from sampling stations adjacent to the telemetric, were used. Physicochemical data were statistically analysed in hourly, seasonal and annual basis, chemical data were used to evaluate the water physicochemical status of the stations and subsequently all of them were related to the pollution hazard/pressure map of the Spercheios catchment. The results revealed the significant effects of human pressures in the river water quality, especially downstream, and the outputs have been used to propose best practices for the integrated management of the Spercheios river catchment.

Keywords: Spercheios river, physico-chemical properties, catchment, hazard map

1. Introduction

Water resource management is a major challenge today, for socio-financial development, due to its association with downstream ecological impacts and water sources (Thanapakpawin *et al*., 2006).

During recent decades, concerns about the effects of land use changes associated with desertification and agricultural conversion have provoked social and political tensions from local to national scales. Major interests focus on results of landuse change for water supply and demand, at a local and regional level (Thanapakpawin *et al*., 2006). Human activities such as urbanization, industrial and agricultural practices, chemical accidents, dam construction, and natural processes like erosion, could each influence surface water quality. However, the degree that each factor contributes to water quality is ambiguous (Zhang *et al*., 2009a). Thus, determining the prevailing pollution sources can help environmental managers to make reasonable decisions as to the best actions for improving water quality (Zhang *et al*., 2009b). Agricultural land-use is among the most important factors affecting the quality of surface water and groundwater (Fohrer *et al*., 2001). Traditional methodologies to evaluating water quality are based on the comparison of determined parameter values with the existing guidelines but in many cases, this does not readily give information on the status of the source (Debels *et al*., 2005). One of the difficult tasks facing environmental managers is to convert complex data to information for better identifying the sources and type of the pollution (Boyacioglu and Boyacioglu, 2008). This study focuses on the identification of the river basin's pollution sources through the pollution hazard map of the wider area and the main objectives include: (1) the detection of significant pollution pressures and dominant biogeochemical mechanisms responsible for the spatial variations in river water quality and (2) the identification of impacts from the pollution sources (natural and anthropogenic) on the water quality parameters and the chemical composition of the Spercheios River.

2. Methodology

2.1. Study area

The Spercheios river is located in Phthiotis prefecture in central Greece, is 85 Km long and the total area of its drainage basin is 1,907.2 Km^2 (Fig. 1). It is an area of ecological significance included in the Natura 2000 network. A number of temporary streams discharge along the north coast (Akoumianaki *et al*., 2013). The climate in the area of the Spercheios drainage basin belongs to the sub-tropical Mediterranean zone, with warm and dry summer and mild and wet winter. The riparian forest in the upper part of the delta occupies extended areas with width a ranging from few up to several hundred meters. The

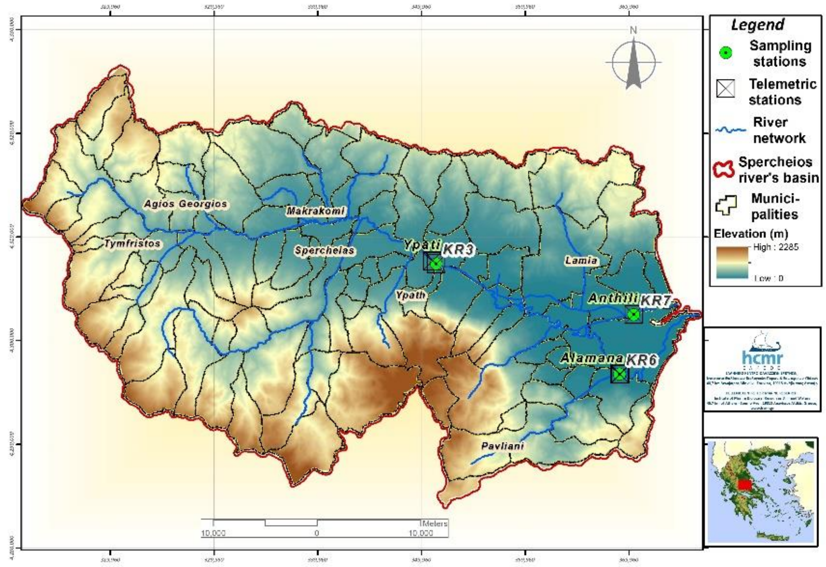

Figure 1. Spercheios River's catchment, sampling and telemetric stations.

Spercheios river Delta occupies an area of 196 Km^2, at 23^o 30΄ longitude and 38^o 50΄ latitude. It extents about 4 Km east of Anthili village and south-east of Lamia city and it is the sixth in size Delta, in the shores of the Greek area (Efthimiou *et al*., 2014).

2.2 Water sampling, telemetric data and chemical determinations

Field sampling measurements of chemical parameters (nutrients) were conducted monthly or bimonthly in a network of three (3) stations along Spercheios River (Fig. 1) from April 2014 to September 2015. Moreover, physicochemical data (water temperature, conductivity, salinity, pH, water level and dissolved oxygen concentration) from 10/2014 up to 07/2016 were acquired from three automatic-telemetric monitoring stations in Alamana (natural riverbed), Anthili (artificial riverbed) and Ipati (main river branch; Fig. 1), located precisely close to the sampling ones. Those data were statistically analysed in hourly, seasonal and annual basis and subsequently examined for interrelationships. Concentrations of nutrients ($NO3^-$, $NO2^-$, $NH4^+$ and $PO4\ 3^-$) were determined in the soluble fraction using an ion analyser Metrohm, the automatic analyzer Radiometer and the photometer Merck Nova 400. To classify the physicochemical status of the river's sites, the River Nutrient Classification System (Skoulikidis et al., 2006) was applied for nutrients and the Norwegian system for dissolved oxygen (Cardoso et al., 2001).

2.3 Hazard mapping

For the identification and assessment of the pollution pressures in the Spercheios catchment, the CORINE 2006 map has been used according to the methodology applied at the COST Action 620 project, (Zwahlen, 2004), focusing on the potential point and nonpoint pollution sources of the catchment tributaries that discharge into Maliakos Gulf. For each recorded land use in the study area, a weighted pollution factor (hazard index), describing the intensity and possibility of each potential land use type to be a pollution source (Andreo *et al*., 2006), was calculated and classified into five hazard categories (from very low to very high) according to Zwahlen (2004; see Table 1).

Table 1: Hazard index values and the corresponding hazard levels according to Zwahlen (2004).

hazard index	hazard index class	hazard level
0-15	1	very low
15-30	2	low
30-45	3	moderate
45-60	4	high
>60	5	very high

3. Results

3.1 Statistical analysis of physicochemical telemetric data

Correlation matrices among all available physicochemical parameters of all the three telemetric stations indicated various negative and positive correlations. The strongest relationships were detected among electrical conductivity and salinity (R^2 = 0.89), dissolved oxygen and salinity and dissolved oxygen and temperature, as it is expected. The correlation between pH and water level indicated low positive correlations (R^2 = 0.165 for Anthili, R^2 = 0.143 for Ipati). Water dissolved mineral substances, aerosols and dust from the air, received human wastes, and support of photosynthetic organisms are processes affecting pH. The carbon dioxide content of water in rivers and streams is less likely to change; mainly activities in the watershed may affect pH. Alamana station implied a negative moderate relationship (-0.38) between water level and pH, which partially can be attributed to photosynthesis by aquatic plants removing carbon dioxide from the water, a fact that can significantly increase pH. Water level was also positively correlated to dissolved oxygen concentration, since the decrease of the water level and the

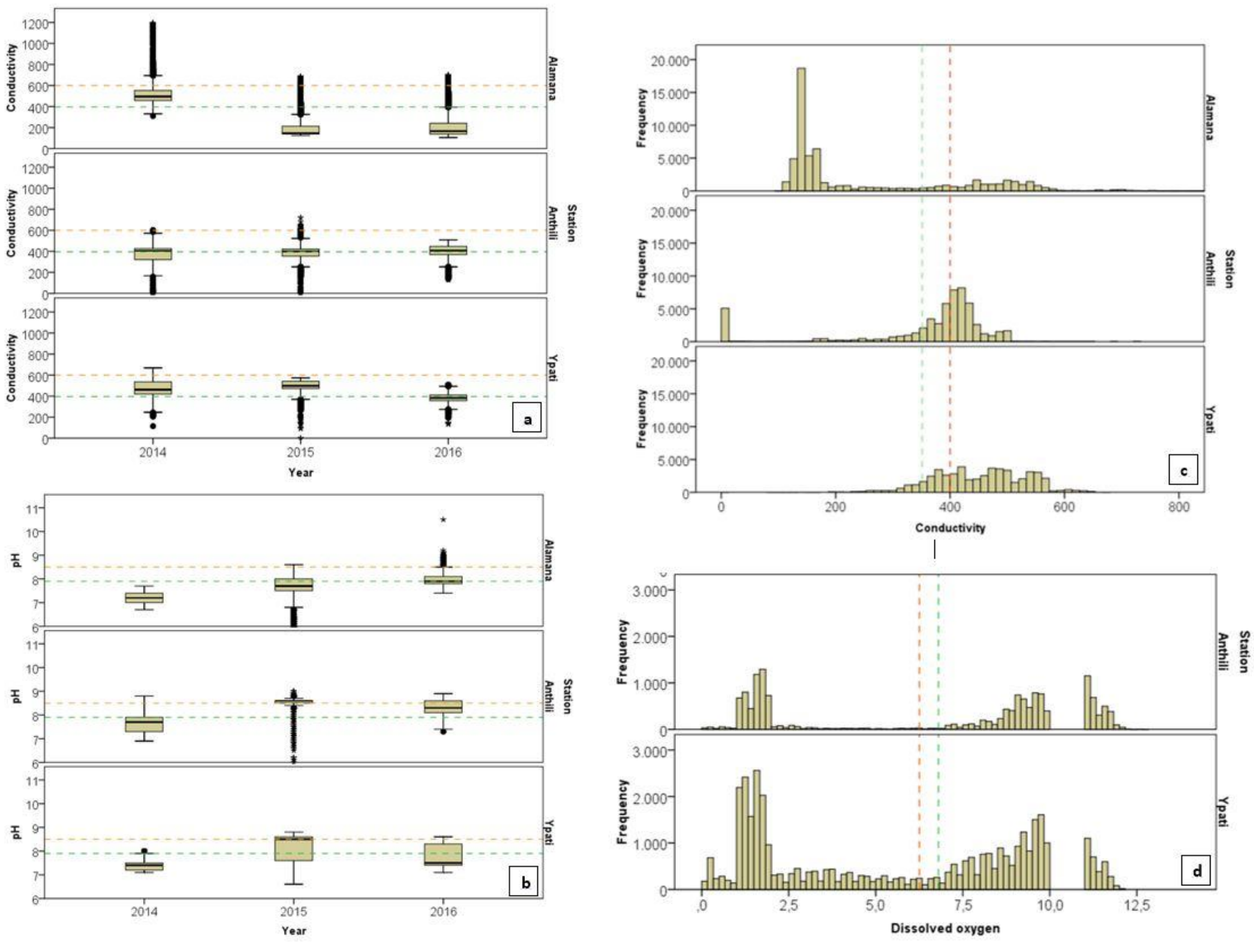

Figure 2. Box plots presenting the annual distribution of (a) electrical conductivity values (b) pH values and frequency charts presenting aggregated data of (c) electrical conductivity values and (d) dissolved oxygen concentrations of all telemetric stations (green line: mean value, red line: median value).

river's flow rate, decreases the mixture of water with air, resulting in further DO decrease. Concerning the annual fluctuation of electrical conductivity values (Fig. 2a), 75% of the Alamana station's measurements on 2014 were close to 550 μS/cm, while on 2015 and 2016 the values ranged around 200 μS/cm. In Anthili station in years 2014 and 2015, values between the 50th and the 75th percentile were pretty close to the median value (400 μS/cm), and in 2016 the 50% of the values were slightly higher than the median one. Ypati station on 2014, presented 75% of conductivity values higher than the median, in 2015 75% of values were close to the mean value (600 μS/cm), and in 2016 50% of them reached the median one of 400 μS/cm. pH values (Fig. 2b) in Alamana station present an increasing tendency from 2014 to 2016 while the 75% of the values reached 7.5, 8.1 and 8.3 in 2014, 2015 and 2016 respectively. The same increasing tendency is detected also at both Anthili and Ypati stations, but 2015 is the year with the highest pH levels (Fig. 2b). According to frequency charts, conductivity values showed no normal distribution. Alamana station presented low conductivity values, Anthili station presented higher conductivity levels while Ypati station presented the highest one reaching almost 600 μS/cm (Fig. 2c). Taking into consideration D.O. variations, Anthili station presented highly fluctuated values, Ypati station's most values were lower than the mean and median ones, while Alamana station's DO values could not be processed due to technical problems of the sensor (Fig. 2d).

3.2 River water physicochemical status monitoring

According to the physicochemical telemetric data and the nutrient analysis, the physicochemical status of the Spercheios River indicates a degradation from the upstream parts (KR3, good quality status) to the deltaic sites (KR6 and KR7– moderate status). This is the result of the pollution pressures aggregation along the river and the intensive point pollution sources that are detected in the lowland areas. The presence of bad quality in KR7 for both N-$NH4^{+}$ and P-PO_4^{3-} is possibly due to the Lamia city waste water treatment plant that discharges near this station. Moreover, the moderate and poor quality, provoked by the concentrations of N-$NH4^{+}$ and N-NO_2^{-} usually encountered in the deltaic site KR6, indicate potential impacts mainly from domestic sewage and secondly fertilizer runoffs, which are also accompanied by the relatively low dissolved oxygen levels (Table 2). According to Markogianni *et al*., 2017, the same sampling period was divided into wet and dry season based on the Spercheios River discharges. The physicochemical water status during the wet season, is good for KR3 station whereas the downstream stations KR6 and KR7 have moderate status, especially due to ammonium concentrations. Dry period implies an even downgraded physicochemical status of stations KR6 and KR7, whose qualities are characterized as moderate and poor (due to high ammonium and phosphate values).

Table 2. Physiochemical classification of Spercheios river's water samples.

	DO (mg/l)	N- NO_3^-	N- NO_2^-	N- NH_4^+	P- PO_4^{3-}	Physicoche-mical status
KR3	10.88	0.77	0.01	0.02	0.01	Good
KR6	5.32	0.43	0.04	0.17	0.13	Moderate
KR7	9.02	0.54	0.03	1.23	0.67	Moderatee

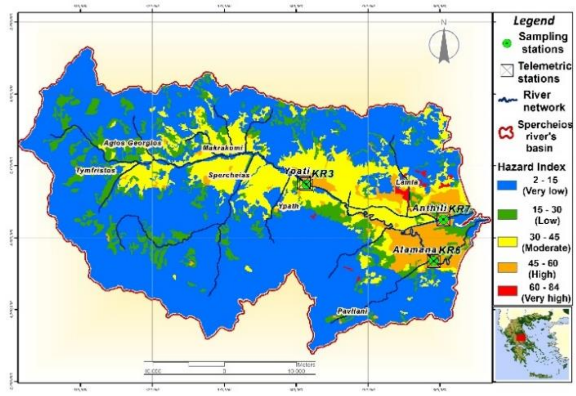

Figure 3. Hazard map of Spercheios river's basin.

3.3 Hazard mapping

The developed hazard map indicates that the highest pollution pressures in the Spercheios River's catchment are close to the deltaic sites, in the eastern part (Fig. 3) where the intensification of the pollutant pressures (agriculture, wastewater treatment plant output) is detected. The spatial trend of the hazard index in the particular basin denotes a surcharge from the upstream parts (forests, heath land) to the lowland areas (agriculture, paper and olive mill industries and urban areas). Those lowland areas are characterized as of moderate and high hazard level while the natural vegetation areas (forests, lowland vegetation) cover the largest area of the basin (more than the 60% according to Markogianni and Dimitriou, 2016) and both with the pastures are classified as of very low and low hazard potential (Fig. 3).

4. Conclusions- Discussion

Intensive agricultural activity increases erosion and sediment load, and leaches nutrients and agricultural chemicals into groundwater, streams, and rivers (Foley *et al.*, 2005). Rivers are highly vulnerable to pollution attributing to their role in carrying off the municipal and industrial wastewater and run-off from agriculture in their vast drainage basins (Carpenter *et al*. 1998; Jarvie *et al*. 1998 in Zhang *et al*., 2009a).

This study involved sampling and analysis of a large and complicated environmental parameters at the Spercheios river's basin, which is mainly occupied by agricultural land. The parameters elaborated, are quite difficult to interpret because of the dominant interrelationships among them and the physical characteristics of the monitoring sites. The statistical analysis indicated high conductivity and low DO values in Anthili station mainly due to the presence of the wastewater treatment plant output while Ypati station demonstrated high oxygen values since it is located at a relatively undisturbed part of the river. The water physicochemical status assessment and the produced hazard map of the Spercheios River's basin contributed to further understanding and verification of the effects of land-uses on the river water quality. The physicochemical status of the Spercheios River showed degradation from the upstream parts (KR3, good quality status) to the deltaic sites (KR6 and KR7– moderate status), where domestic sewage, fertilizer runoffs and intensive point pollution sources are detected. Those same areas (lowlands) are coincident with areas characterized as of moderate and high pollution hazard, mostly due to the presence of agricultural areas. The lack of appropriate infrastructure for the water pollution regulation and alleviation (e.g. wastewater treatment facilities) in the wider area of the Spercheios River leads to significant pollutant inflows in various parts of the river.

References

Akoumianaki, I., Papaspyrou, Sokratis, Kormas, Ar. Konstantinos, Nicolaidou, Artemis, (2013), Environmental variation and macrofauna response in a coastal area influenced by land runoff, *Estuarine, Coastal Shelf Sci*., 132, 34-44.

Andreo B, Goldscheider N, Vadillo I, Vias JM, Neukum C, Sinreich M, Jimenez P, Brechenmacher J, Carrasco F, Hotzl H, Perles MJ, Zwahlen F., (2006), Karst groundwater protection: first application of a Pan-European approach to vulnerability, hazard and risk mapping in the Sierra de Lybar (Southern Spain), *Sci Total Environ*, 357, 54-73.

Cardoso A.C., Duchemin J., Magoarou P., Premazzi G., (2001), Criteria for the identification of freshwater subject to eutrophication. Their use for the implementation of the "Nitrates" and Urban Waste Water Directives. EUR 19810 EN, EU - JRC, 87.

Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H., (1998), Non-point pollution of surface waters with phosphorus and nitrogen, *Ecological Applications*, 8(3), 559–568.

Debels P, Figueroa R, Urrutia R, Barra R, Niell X, (2005), Evaluation of water quality in the Chilla´ n River (Central Chile) using physicochemical parameters and a modifiedwater quality index, *Environ Monit Assess*, 110, 301–322.

Efthimiou Georgios, Topaloglou Charalampos, Monachou Styliani, Kaprana Konstantina, (2014), Change detection in Natura 2000 area of Spercheios river in central Greece using remote sensing and GIS. *Journal of International Scientific Publications: Ecology and Safety*, 8, 1314-7234.

Fohrer, N., Haverkamp, S., Eckhardt, K., Frede, H., (2001), Hydrologic response to land-use changes on the catchment scale, *Phys. Chem. Earth*, 26, 577–582.

Foley, J.A., DeFries, R., Asner, G.P., Barford, C., Bonan, G., Carpenter, S.R., Chapin, F.S., Coe, M.T., Daily, G.C., Gibbs, H.K., Helkowski, J.H., Holloway, T., Howard, E.A., Kucharik, ChJ, Monfreda, Ch., Patz, J.A., Prentice, I.C., Ramankutty, N., Snyder, P.K., (2005), Global consequences of land use, *Science*, 309, 570-574.

Jarvie, H. P., Whitton, B. A., & Neal, C., (1998), Nitrogen and phosphorus in east coast British rivers: speciation, sources and biological significance, *Science of the Total Environment*, 210/211, 79-109.

Markogianni Vassiliki and Dimitriou Elias, (2016), Landuse and NDVI change analysis of Sperchios river basin (Greece) with different spatial resolution sensor data by Landsat/MSS/TM and OLI, *Desalination and Water Treatment*, 57(60), 29092-29103.

Markogianni Vassiliki, Varkitzi Ioanna, Pagou Kalliopi, Pavlidou Alexandra, Dimitriou Elias, (2017), Nutrient flows and related impacts between a Mediterranean river and the associated coastal area. *Continental Shelf Research*, 134, 1-14.

Skoulikidis N., Amaxidis Y., Bertahas I., Laschou S., Gritzalis, K., (2006), Analysis of factors driving stream water composition and synthesis of management tools – a case study on small/medium Greek catchments, *Sci. Total Environ.*, 362, 205–241.

Thanapakpawin P., Richey J., Thomas D., Rodda S., Campbell B., Logsdon M. (2006), Effects of landuse change on the hydrologic regime of the Mae Chaem river basin, NW Thailand. *Journal of Hydrology*, 334, 215-230.

Zhang, Y., Guo, F., Meng, W., Wang, X.Q., (2009a), Water quality assessment and source identification of Daliao river basin using multivariate statistical methods, *Environ. Monit. Assess.*, 152, 105-121.

Zhang, Q., Li, Z.W., Zeng, G.M., Li, J.B., Fang, Y., Yuan, Q.S., Wang, Y.M.,Ye, F.Y., (2009b), Assessment of surface water quality using multivariate statistical techniques in red soil hilly region: a case study of Xiangjiang watershed, China, *Environ. Monit. Assess.*, 152, 123-131.

Zwahlen F., (2004), Vulnerability and risk mapping for the protection of carbonate (karst) aquifers. Final report of COST Action 620. European Commission, Directorate-General XII.