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Nutrient mitigation in a temporary river basin

Ourania Tzoraki · Nikolaos P. Nikolaidis · David Cooper · Elissavet Kassotaki

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Abstract We estimate the nutrient budget in a temporary Mediterranean river basin. We use field monitoring and modelling tools to estimate nutrient sources and transfer in both high and low flow conditions. Inverse modelling by the help of PHREEQC model validated the hypothesis of a losing stream during the dry period. Soil and Water Assessment Tool model captured the water quality of the basin. The 'total daily maximum load' approach is used to estimate the nutrient flux status by flow class, indicating that almost 60 % of the river network fails to meet nitrogen criteria and 50 % phosphate criteria. We recommend that existing well-documented remediation measures such as reforestation of the riparian area or composting of food process biosolids should be implemented to achieve load reduction in close conjunction with social needs.

Keywords River basin · Evrotas · Nutrients · Water quality · SWAT model · TMDL · PHREEQC · Intermittent flow

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O. Tzoraki (✉)
University of Aegean,
Mytilene, Greece
e-mail: rania.tzoraki@aegean.gr

N. P. Nikolaidis · E. Kassotaki
Technical University of Crete (TUC),
Chania, Crete, Greece

D. Cooper
Centre for Ecology and Hydrology (CEH),
Bangor, United Kingdom

Introduction

Rivers with intermittent flow (temporary rivers) are dominant in arid and semi-arid areas of the world, including some 26 % of the southern Mediterranean land surface (Tsakiris et al. 2007). The alternation between low or zero flows and high floods regulates the behaviour and characteristics of these streams to the extent that they are the most hydrologically variable aquatic ecosystems and among the most threatened by any hydrologic alteration (Acuña and Tockner 2010; Dieter et al. 2011; von Schiller et al. 2011). Seasonal drying of the river bed can be amplified either by natural climate variability (natural drought) or by direct human intervention (water diversion, overexploitation) or due to climate change or a combination of these effects (Skoulikidis et al. 2011; Steward et al. 2012).

Hydrological changes have direct consequences on microbial metabolism and nutrient processes (Zoppini et al. 2010). Floods enhance sediment mineralization processes, increase nitrification and denitrification and induce leaching processes (Tzoraki et al. 2007). During the dry season, mineral nitrogen accumulates in the soil, and at the onset of rain, high nutrient loads and concentrations are measured during the rising limb of the hydrograph (Skoulikidis and Amaxidis 2009). Significant nutrient fluxes are transported rapidly into coastal areas as a result of soil and sediment washout. In addition to seasonal flow fluctuations, anthropogenic activities affect the nutrient composition of freshwater in small temporary streams (Karaouzas et al. 2011). In a temporary river, intensively cultivated areas, burned forests, industrial

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effluents such as olive oil mill wastewater, municipal sewage effluents and runoff from waste disposal sites can generate a flush of pollutants (Perrin and Tournoud 2009). These sources of contamination can reduce water quality, cause eutrophication and damage river ecology (Camargo and Alonso 2006; Smil 2001).

In general, freshwater eutrophication is attributed to the combined effect of industrial waste (25 %), agricultural practices (25 %) and to urban sewage (50 %) (Karydis and Kitsiou 2012). Fertilizer use has increased in much of Europe since the 1960s with an increase in agricultural intensification. Both surface waters and groundwaters have shown deterioration in quality due to increased nutrient concentrations. Domestic wastewater is a source of poor freshwater ecological quality, especially in areas where no wastewater treatment works. For the Evrotas, an agricultural basin in Greece, agricultural sources contributed to the generation of the 65 % of the N load and 85 % of the P load (Tzoraki et al. 2008). For this basin and similar agricultural basins, it is likely that agricultural practice is responsible for most nutrient losses to surface water and groundwater.

The European Union, recognizing the intense environmental pressures on water bodies and the resulting deterioration in their quality, established the Water Framework Directive 2000/60 for the protection and management of rivers, aquifers and the coastal zone. Environmental measures implemented to reduce nutrient concentrations and raise ecological status include such activities as planting buffer strips, growing catch crops, changing irrigation methods and wastewater reuse. Buffer strips along watercourses can reduce soil erosion and prevent nutrients and pesticides entering streams. Catch crops help to reduce the mobilization of agricultural pollutants by increasing nutrient uptake and reducing surface and soil erosion. More focussed irrigation methods help in the reduction of water consumption and in the minimization of losses, reducing groundwater overexploitation.

There is growing awareness that nutrient management must be handled at the river basin scale (Demetropoulou et al. 2010). The key to nutrient management at this scale is understanding and quantifying the fate and transport of nutrients in the aquatic environment. Especially for temporary rivers, a crucial role in nutrient fate is played by variability in water flow. Natural surface water–groundwater interaction in temporary rivers is often influenced by lowering of the groundwater table through overexploitation (Larned et al. 2010). The climate-forced or human-induced seasonal variation of the river water balance as a losing or gaining stream has consequences for river ecology and groundwater quality. In river basin management, appropriate measures should be implemented that take into consideration this seasonal variation.

The main objective of this study is to determine the main nutrient processes in a rural temporary river basin, the Evrotas in Greece, and to estimate the effect of particular measures to establish nutrient mitigation. The main steps in that procedure are the following:

(a) Determination of the hydrological regime of the basin, allocation of surface and groundwater, and estimation of the main point and diffuse pollutants sources and chemical loads, and their magnitudes.

The climatic and hydrological status of the basin is determined using long-term existing meteorological and hydrological data, and the main causes of river desiccation investigated. Geochemical modelling (PHREEQC) (Parkhurst and Appelo 1999) is used to understand the vulnerability of groundwater to potential surface water contamination during the transition from extreme drought to wet conditions and to verify the transmission losses.

(b) Assessment of nutrient mitigation pathways of a temporary river environment

The water quality of the surface water, groundwater and spring water network is used to understand nutrient mitigation in the Evrotas basin. The nutrient content of surface and groundwater in the basin delineates and identifies the key ‘contaminated zones’ where the implementation of selected remediation technologies is necessary.

(c) Nutrient modelling using the Soil and Water Assessment Tool (SWAT) Water quality model (Arnold et al. 1998) and total daily maximum load (TMDL) estimation for the dry and wet season.

The SWAT river basin water quality model is used to estimate the nutrient mass balance in relation to time in different locations within the river basin and can be used for scenario creation to estimate the effect of various measures and climate changes on river water quality. The estimation of maximum allowable loads using the approach of ‘total daily maximum load’ is used to assess the potential effect of existing practices in relation to river flow conditions. TMDLs are estimated based on environmental quality standards (EPA 2007). National and European pollutant thresholds may be used, or ecological thresholds derived from previous studies in similar areas that consider the effect of nutrients on ecological quality. Implemented measures are examined for their capacity to minimize pollution and satisfy the TMDL criteria. Potential measures are suggested for inclusion in the existing management plan of the studied basin to achieve load reduction goals in pursuit of system sustainability.

Site characterization

Site description

The Evrotas basin, on the south-east peninsula of the Peloponnese in Greece, has a river network including temporary and permanently flowing tributaries and reaches (Fig. 1). The river basin is largely agricultural and suffers water pollution problems. The basin covers 1,350 km^2 (up to Vrontamas), with the main river running from north to south between the Taygetos and Parnonas mountains (height 2,400 m). The main tributaries are the Inountas (temporary flow), Mariorema (episodic flow), Xerias, Magoulitsa, Gerakaris, Kakaris and Rasina (permanent flow). Around 40 % of the basin has an elevation greater than 600 m, some 45 % between 150 and 600 m, and the remainder below 150 m. The basin can therefore be characterized as mountainous. Geologically, the basin is a mixture of karstic limestones and less permeable underlying formations, mainly schists and quartzites. This configuration promotes the development of numerous karstic springs at the foot of the Parnonas and Taygetos mountains. There is also a shallow aquifer of mixed permeability in the valley bottom of Sparta. Several karstic springs discharge into the Evrotas and other springs are used to satisfy domestic and irrigation needs. The Sparta aquifer is recharged to the north by surface water and to the west by lateral infiltration of karstic water (Antonakos and Lambrakis 2000).

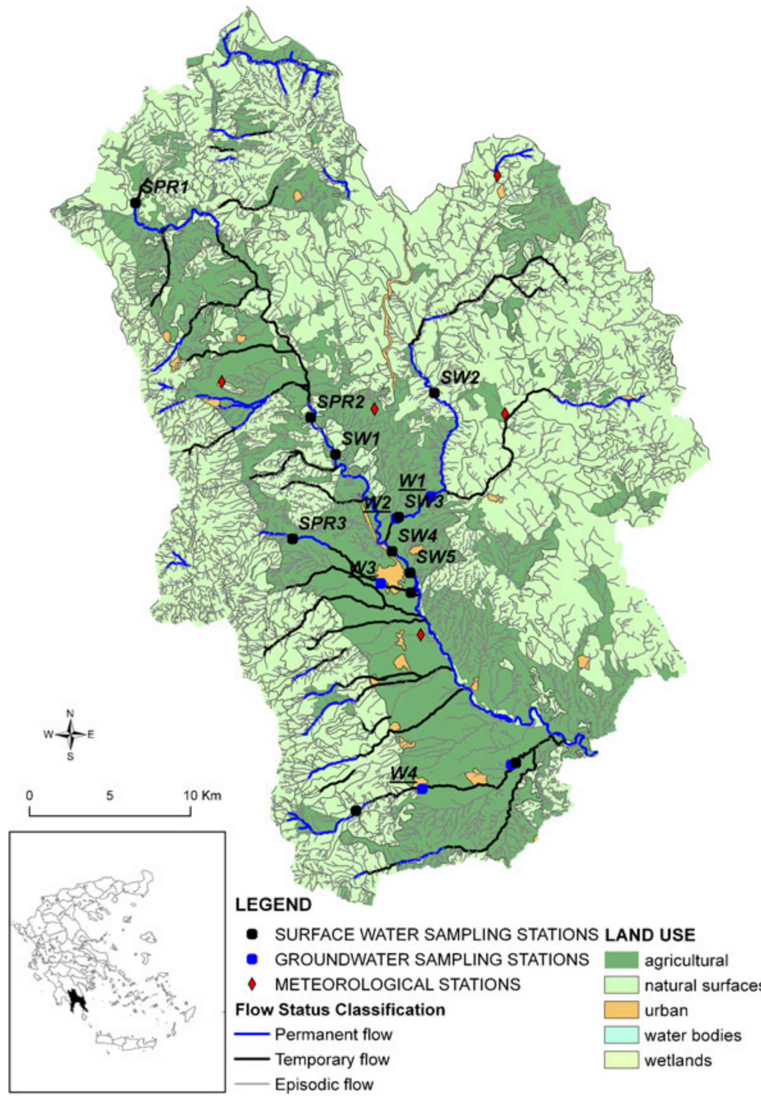
In terms of land use, around 20.4 % is forested and 49.1 % is grassland, with most of the remainder being agricultural (30.2 %). The main agricultural and related activities are livestock farming and small food industries. Of the roughly 408 km^2 of agricultural land, some 26.8 km^2 are the orange trees, 208.9 km^2 the olive trees and 172.3 km^2 cereals. There are also small areas of vineyards and vegetables. Most of the animals (130,540) are free grazing animals (sheep, goats), with in addition 58,070 poultry, 1,729 cows and 100 pigs. Only around 1 % of the basin is either urban or surface water. The population is around 65,000, the biggest town being Sparta with 18,000 inhabitants.

Hydrological monitoring

Precipitation has been measured since the 1970s by the Land Reclamation Service at six stations: Elos (4 m), Riviotissa (163.5 m), Vrontamas (280 m, since 1953), Perivolia (490 m), Sellasia (590 m) and Vasaras (646 m). Three weather stations in the river basin provide daily records of precipitation, temperature, and evaporation (Elos, Riviotissa and Sellasia) (Fig. 1). The mean annual precipitation value ranges from 539 mm (Ellos station) to 1,324 mm (Vrontamas station) and the mean annual precipitation over the catchment is estimated as 802 mm (2000–2007, Thiessen method for average rainfall) and potential evapotranspiration 1,754 mm. The Lang–Gracamin Index is used widely in Greece for the characterization of local climate expressing the ratio of the mean monthly precipitation (in millimeter) to mean monthly temperature (in degree Celsius). Using this index, the Evrotas basin is characterized as humid from November to February and arid from May to October. The period of March to April is a transition phase between humid to arid and the transition phase from arid to humid does not occur in the basin.

There is a network of six automatic level loggers (Onset Computers, HOBO pressure transducer U20-001-04) recording water level continuously (locations as shown in Fig. 1) and monthly measurements of flow are taken to construct the rating curves. Two of the loggers, at Vrontamas and Vivari, are on the main river; two are on the Oinountas and two on the Rasina. In addition, monthly measurements of flow were made at Vivari and Vrontamas for 1974 to 2011. In the north-west part of the basin, springs at Skortsinos (0.12 m^3 s^{-1} average flow 2007–2008), Vivari (1.05 m^3 s^{-1} average flow 1974–2010) and Zoros (discharging from extensive karstic aquifers estimated to be 2.34 m^3 s^{-1} for 1974–2008) were noted. Downstream at the Sparta gauging station, discharge decreases to 0.65 m^3 s^{-1} (2007–2008 discharge data). The river flow then increases to 3.64 m^3 s^{-1} (1974–2010) downstream of Sparta, close to Vrontamas. To the south-west of Vrontamas, a karst outcrop intersects the river and the Evrotas infiltrates completely, reappearing again in the Skala region (average flow for 2009–2010, 4.2 m^3 s^{-1}) as a cumulative outflow of a complex system of springs.

Fig. 1 Evrotas River basin land use, surface water sampling network and groundwater sampling network



Surface and groundwater abstraction for irrigation contributes to the gradual flow reduction in parts of the main stream. The river basin has numerous water supply and irrigation wells for public use (more than 100) in addition to 3,000 private wells. Most of the wells are located in the Sparta valley. In Evrotas basin farmers, charges are estimated according to the irrigated land and not proportionally to the volume of irrigation water used. For this reason, there are no available records of water consumption per unit area per year. The amount of irrigation can be estimated indirectly using data from the electric power company for agricultural electricity use (Tzoraki et al. 2011). It was estimated that the annual groundwater pumping volume equals to 72 Mm^3/year up to Vrontamas station, for an irrigated land area of 8, 476.1 ha. Direct river abstraction was estimated to be 5 Mm^3/year. These figures suggest an irrigation rate of 0.9 m/m^2 compared to the recommended value of 0.5 m/m^2 annually (Allen et al. 1998; Wriedt et al. 2009). The high irrigation rate is responsible for the desiccation of the main river, especially in extremely dry years. At Vrontamas for instance, the monthly flow was measured to be zero with a frequency of 4 % during the last 40 years (1973–2011). Figure 1-SI shows the average, the minimum and the maximum monthly flow in Vrontamas station showing the absence of river flow in summer months. The groundwater level follows seasonal variation in precipitation, increasing in winter (Fig. 2-SI) due to lateral and vertical recharge, and decreasing in summer. In general, a groundwater level fluctuation of a minimum of 5 m is measured between the wet and dry period.

During the wet period, the groundwater table is high and groundwater recharges the river (Fig. 2a). In contrast during the dry period, the decreased aquifer recharge rate in combination with groundwater overexploitation results transmission losses from the river to the groundwater (Fig. 2b).

Stream classification

Figure 1 shows the aquatic state of the Evrotas river network according to the classification suggested by the MIRAGE project by Gallart et al. (2011). Permanent (P) applies to perennial flow streams; temporary (T) refers to streams where flow ceases after the wet season and only pools remain. Finally in episodic-ephemeral streams water flow and pools are short-lived and occasional. Flow in the Evrotas and many of its tributaries is

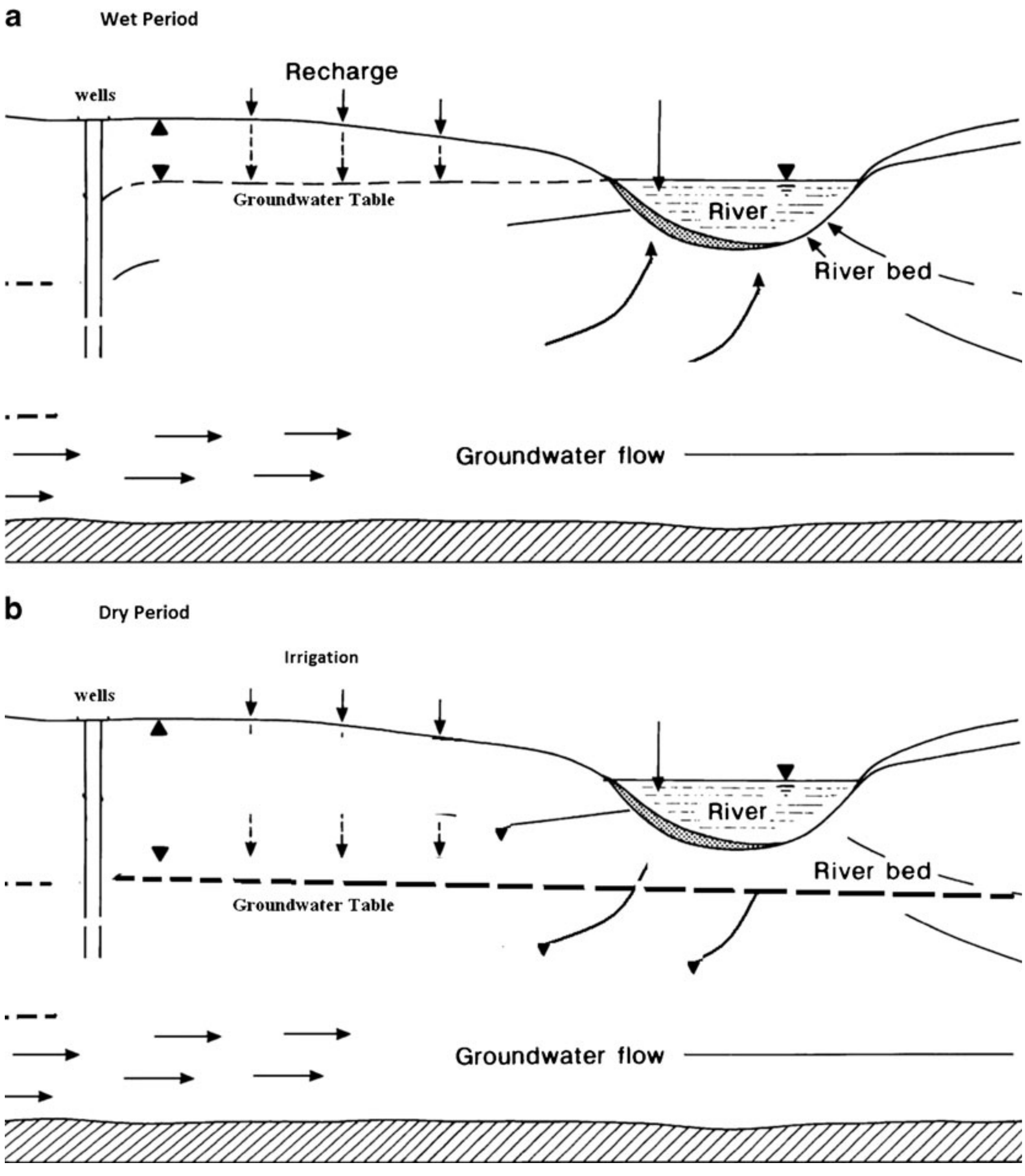


Fig. 2 River hydrologic pattern as **a** gaining stream during the wet period and **b** losing stream during the dry period

temporary (4.3 % of stream network) or episodic (92 %) and only 3.5 % of stream network has permanent flow (total river network length of 5,143 km) (Fig. 1). Therefore in extreme dry years such as 2007 and 2008, almost all tributaries and almost 20 % of main stream ceased to flow during the summer (Skoulikidis et al. 2011; Gamvroudis et al., in review). Flow continues in some parts of the river where inflow from springs is the most significant water source.

Water quality monitoring

The water quality stations were assumed to represent the water quality of springs, groundwater, and streams over the river basin. Water quality has been monitored from 2009 to 2010 periodically at springs (Skortsinos, SPR1; Vivari, SPR2; Magoulitsa Trypi, SPR3), surface water (Steno Vordonias, SW1; Oinountas Kladas, SW3; and Oinountas Vasaras, SW2; Sparta, SW4; downstream WWTP, SW5; Vrontamas, SW6), and groundwater (Kelefina Theologos well (Giannakopoulos well, W1), Kanelakos well (Kladas bridge, W2), Mavridis well (Magoulitsa, W3), Laskaris well (Rasina Xirokampi, W4).

Physico-chemical variables were measured in situ while chemical analysis of water samples, focussing on nutrients, was carried out in the laboratory. Water samples were analysed using a Hack spectrophotometer for nitrogen as nitrate(NO_3-N) (Cadmium Reduction Method, 8039), nitrogen as nitrite (NO_2-N) (Diazotization Method, 8507), ammonia (NH4-N) (Salicylicate Method, 10023), dissolved inorganic phosphorus (PhosVer3 Method, 8048), total organic carbon (TOC) (Direct Method, Low Range, 10129), chemical oxygen demand (COD) (Low Range, 8048) and phenols (Folin–Ciocalteu method). Physicochemical variables pH, Eh, dissolved oxygen and conductivity were measured in situ using the following electrodes: Orion 9107 pH meter, Orion 081010 dissolved oxygen meter and Orion 011050 Conductivity meter.

Process modelling

We have modelled the water quality of the Evrotas stream network using two approaches. First, the PHREEQC model (Parkhurst and Appelo 1999) has been applied, to estimate the contribution of source end-members to river water. This focusses on the geochemical characteristics of the water, rather than nutrients. Secondly, we have used SWAT model (Arnold et al. 1998) to account for the spatial and temporal variability in nutrient concentrations.

PHREEQC geochemical modelling

PHREEQC estimates the end-member proportions and amounts (i.e. milliequivalent) of mineral species and gas mole transfers that are responsible for the differences in solute composition between waters of mixed origin. An uncertainty limit is specified by the user for each component. The model was applied to the Evrotas main stream to understand the contribution of surface water to groundwater and especially the vulnerability of groundwater during the transition from dry to wet conditions. The ultimate goal of the modelling is the assessment of river bed transmission losses to groundwater, especially during the dry period, since they insist actually the main inflow into the groundwater. Possible end-members (initial solutions) considered in the model were the Trypi spring, Skoura groundwater and Psichiko surface water. Trypi spring water reflects the composition of Taygetos karst where limited human pollution is present and therefore configures a “karstic water footprint,” water rich in calcite, magnesium and carbonate minerals. In contrast in Skoura, the groundwater composition is the final product of the long residence time of water through the alluvial Sparta plain that is enriched with nutrients and pesticides. Psichiko surface water represents the mean surface water quality of Evrotas main stream. We modelled both wet and dry periods using water quality data from the Greek Ministry of Agriculture. The dry periods of the years 2002, 2003 and 2004 were selected for the modelling application in Evrotas basin, these years having a good data record. During the dry period of 2003, the groundwater elevation for instance in Koniditsa well reached −25 m in October 2002, but the following dry periods reached −14 m in September 2003 and −19 m in October 2004. According to Standardized Precipitation Index (SPI) methodology, 2003 and 2004 can be characterized as wet years, but 2002 as an extreme dry year (Fig. 2, SI). Modelling was carried out for the wet period of 2003 (SPI >0) and groundwater was replenished to reach −6.5 m. Table 1, SI gives the average composition of spring water, groundwater, and stream water used in modelling for the wet and dry seasons.

SWAT nutrient modelling

The SWAT model was used to simulate the hydrology and water quality of the Evrotas river basin, focussing on the nutrient budget. A detailed description of the calibration and validation procedure of hydrological processes in the Evrotas basin can be found in Gamvroudis et al., in review. For water quality, SWAT was calibrated for the period 2009–2010. Taygetos mountain water quality was calibrated by using nutrient measurements from the Vivari monitoring station, and water quality at Kladas was assumed to be representative of the Parnonas mountains. The main stream water quality was calibrated using data from the stations at Sparta, downstream of WWTP and at Vrontamas. A manual calibration procedure of water quality was followed based on the minimization of the root mean square error (RMSE) between field and predicted data.

The recommended fertilizer application rates of the Ministry of Agriculture were used for the estimation of the nutrient load from agricultural activities. It is estimated that crop production contributed 74 % of the N load (1,446.5 t year^{-1}) and 70 % of the P load (252.2 t year^{-1}) and livestock production contributed 23.4 % of the total N (454.9 t year^{-1}) and 26.6 of the total P load (134.3 t year^{-1}). Nitrogen and phosphorus loads were inserted as monthly values of organic and mineral phosphorus and nitrate, ammonia, nitrite and organic nitrogen and COD into the various sub-basins of SWAT model.

TMDL estimation using flow duration curves

TMDL estimation using the approach of load duration curves is based on the relationship between stream flow and loading capacity (EPA 2007). River flow is separated into flow classes, typically very high flow with exceedance probability between 0 and 10 %, high flow ranging from 10 to 30 %, moderate flow from 30 to 70 % where baseflow is the main hydrologic component and finally low flow (70–100 %), which may include zero flows. In practical applications of the TMDL approach, a variety of different flow classes have been selected. The Evrotas is a typical temporary river with no flow for at least 1 month of the year and supported by baseflow for almost 6 months. As a result, flow is usually very low and flow separation into several classes is unrealistic.

Since areas suffering high pollution are restricted mostly in the main stream, TMDL estimates were calculated at three stations in that area. Flow duration curves at Vivari, downstream of the WWTP and Vrontamas (period 01 January 2009–31 December 2010), have been used to generate load duration curves, on which TMDLs can be based. Vivari is located actually just before the pollution is started, WWTP is located in the centre of polluted area and finally Vrontamas at the very end edge. Monthly water quality data (nitrate, ammonia, phosphate, total nitrogen and total phosphorus) for the same period (period 01 January 2009–31 December 2010) have been used for the estimation of fluxes. The Greek River Nutrient Classification System (GR-NCS) has been used (Lashou 2010) for nutrient threshold selection instead of drinking water thresholds. The nutrient thresholds suggested by Lashou (2010) are lower than drinking water safety thresholds but have been selected through a detailed analysis of nutrients fluxes in classification procedure of the physicochemical status of Greek rivers. Under this classification, the nitrate-N concentration was selected as 0.89 mg L^{-1}, for nitrite-N as 0.016 mg L^{-1}, for ammonia-N 0.036 mg L^{-1}, for phosphate-P 0.028 mg L^{-1}, for total N 2.27 mg L^{-1} and for total P 0.084 mg L^{-1}.

Results

Water quality analysis

The springs at Vivari, Magoulitsa and Skortsinos represent the water quality of the Taygetos karst and the wells (W1–W4) of the alluvial aquifer. W1 reflects the water quality of Parnonas and W2 of Taygetos. W3 is located centrally in the alluvial floodplain reflecting agricultural activities and W4 is located close to the down-gradient limit of the alluvial aquifer. Table 1 shows average values for physico-chemical variables and concentrations of the main pollutants namely COD, NO_3-N, NO_2-N, NH_4-N, PO_4-P and phenols, at the surface water, springs and wells for the monitoring period 2009–2010.

The nutrients levels of the river are low (mean NO_3-N value 1.2±0.4 mg L^{-1}) and pH value (8±0.4) and the anion and cation composition are indicative of karstic origin water (Ca/Mg=2.4), with sea salt aerosol influence for sodium and chloride (Na/Cl=1.1). Figure 3-SI presents the concentrations of pollutants along the main

Table 1 Average (mean) values and standard deviation (SD) of common parameters for water quality in 13 sites of the Evrotas River during the sampling period 2009–2010

Site	Code	Variables	Conductivity	COD	N-NO_2^-	N-$N0_3$	N-NH_3	TN	P-PO_4	Phenols
		Units	μS cm^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
Wells										
Giannakopoulos Well (W1)—(Kelefina Theologos)	W1	Mean	637.1	3.22	0.01	0.87	0.08	3.28	0.15	0.65
		SD	141.0	5.26	0.00	0.55	0.19	1.18	0.27	0.62
Kanelakos Well (W2)—(Kelefina, Kladas Bridge)	W2	Mean	590.6	2.09	0.01	0.87	0.09	3.12	0.14	0.62
		SD	54.2	4.64	0.01	0.57	0.23	0.64	0.37	0.49
Mavridis Well (W3)—(Magoulitsa Sparta)	W3	Mean	635.6	4.62	0.01	3.74	0.03	6.90	0.13	1.19
		SD	82.9	7.91	0.01	3.27	0.02	3.07	0.32	2.46
Laskaris Well (W4)—(Rasina Xirokambi)	W4	Mean	506.7	13.53	0.02	1.79	0.19	4.81	0.10	0.55
		SD	66.0	24.01	0.04	1.73	0.28	2.06	0.18	0.31
Springs										
Skortsinos	SPR1	Mean	590.7	8.39	0.00	1.09	0.03	3.17	0.09	0.28
		SD	112.7	5.03	0.01	0.75	0.04	2.05	0.17	0.36
Vivari Sellasias	SPR2	Mean	545.6	10.67	0.00	1.23	0.04	2.89	0.08	0.40
		SD	169.8	6.48	0.00	0.75	0.03	1.04	0.09	0.27
Magoulitsa	SPR3	Mean	339.0	15.14	0.00	1.00	0.04	2.65	0.03	0.36
		SD	63.2	10.30	0.00	0.82	0.03	1.00	0.01	0.26
Surface water										
Steno Vordonias	SW1	Mean	567.0	12.90	0.00	1.28	0.04	3.32	0.05	0.36
		SD	185.3	10.38	0.00	0.76	0.04	1.17	0.06	0.32
Kelefina Vasaras	SW2	Mean	617.3	9.18	0.00	0.77	0.03	2.50	0.03	0.30
		SD	99.0	8.13	0.00	0.50	0.03	0.86	0.02	0.22
Kelefina Kladas	SW3	Mean	531.2	10.93	0.00	0.72	0.05	2.23	0.11	0.34
		SD	102.2	5.47	0.00	0.50	0.03	0.68	0.19	0.29
Sparta Bridge	SW4	Mean	557.5	24.88	0.01	1.16	0.05	3.59	0.09	0.34
		SD	53.4	45.26	0.01	0.65	0.05	4.15	0.15	0.41
Downstream WWTP	SW5	Mean	574.7	9.58	0.03	1.78	0.15	3.83	0.21	0.47
		SD	92.4	11.91	0.04	1.28	0.39	2.27	0.37	0.21
Vrontamas Bridge	SW6	Mean	564.7	7.74	0.04	1.66	0.05	3.56	0.08	0.39
		SD	61.7	7.37	0.05	1.15	0.02	1.48	0.07	0.26

river corridor at sampling points: Steno Vordonias, Sparta, downstream WWTP and Vrontamas. Nitrate-N (NO_3-N), nitrite-N (NO_2-N) and ammonium-N (NH_4-N) show maximum values at the WWTP site, while downstream the concentrations of the pollutants are lower. Higher values of phosphate-P are observed in the section between Sparti and downstream WWTP and then decline downstream. The COD value was higher at Sparta bridge (mean value 24.9 mg L^{-1} for the sampling period 2009–2010), and then lower at Vrontamas (mean value 7.7± 7.4 mg L^{-1} for the sampling period 2009–2010; Table 1). Seasonally, there is an increase in COD concentration during the dry period and a decrease during the wet period. The significant decrease of COD concentration observed at Vrontamas could be ascribed to dilution by ephemeral stream flow originating in the Parnonas mountains that join the Evrotas, and also potentially to in-stream attenuation processes.

Examining water quality, the main conclusion is that the station located downstream of WWTP shows heavy contamination. Dissolved oxygen concentrations at the site range from 1.67 to 7.70 mg L^{-1}, these values being attributable to malfunctioning of the WWTP. This monitoring station also showed the highest phosphate, TOC and nitrite content.

The Sparta aquifer is recharged from the mountainous region through the karst. Nitrate-N values from springs (for instance Magoulitsa; mean value 1.0±0.8 mg L^{-1}) are much lower than in the Sparta aquifer (mean value 3.7±3.3 mg L^{-1}) suggesting that pollutant concentrations in the valley increased due to intense agricultural activities. A gradual pollutant decrease from Sparta towards Vrontamas area is observed, even though large quantities of nutrient loads are entering the groundwater in that area. For instance, the average nitrate-N concentration in well W3 was measured to be 3.74 mg L^{-1}, with a decreasing trend in the direction of flow reaching 1.79 mg L^{-1} in Vrontamas well (W4). The highest concentration of phenols was observed in Sparta valley (W3) where many olive mills operate. The olive oil mill wastewater even after pretreatment with calcite contains high COD and phenol concentrations. In the Vrontamas region, there are also higher COD values in groundwater (W4). Serious pollution problems in the Evrotas basin originate not only from point sources but also from agricultural activities. The nitrate-N concentration in wells (W3) is much higher than in river water, suggesting a strong attenuation capacity in the riparian zone. Previous studies (Tzoraki et al. 2008) indicated high denitrification capacity of Evrotas sediments and mineralization potential ranging between 0.13 and 3.29 mg kg^{-1}.

In general, the intensive cultivation, livestock and the presence of septic tanks results in high fluxes of nitrogen, phosphorus and COD into the river water and the groundwater. The evidence in the Evrotas basin is that farmers use inorganic fertilizer (N, P, K) above recommended amounts. Particularly around Sparta and in the coastal area, intensive agricultural activity reduces water quality. Point sources of pollution in the Evrotas basin include urban runoff, olive mills, orange juice press wastewater, livestock farms and units that produce edible olives. The wastewater treatment plant of Sparta was designed to serve a population of 40,000, but today the plant serves 21,300 and operates with a daily organic load of 1,152 kg BOD_5. The treated effluent is discharged directly into the river of Evrotas. In addition, there are 91 olive mills and other small units that produce edible olives and other food products. During the production season, each olive mill produces on average 11.7 m^3/h wastewater, which is either stored in evaporation lagoons or discharged to nearby streams causing surface and groundwater pollution. Olive mill wastewaters have high concentrations of organic load, solids, nitrogen and phosphorus, and can be toxic to some organisms due to the high content of phenols and low pH. The WWTP contributes 14 t/year N and 2 t/year P and the remaining point sources 28 t/year N and 9 t/year P, respectively. Discharge from the WWTP affects mainly the midportion of the Evrotas main stem (from Sparta bridge to the Vrodamas gorge). This stretch of the river is classified as failing to reach good ecological status (ranging from moderate to poor) according to Skoulikidis et al. (2011).

PHREEQC geochemical modelling

PHREEQC modelling indicated that aquifer is recharged during the wet period by water of karstic origin (79–100 %) and surface water (0–21 %). In the dry period, groundwater recharge is attributed mainly to surface water transmission losses (81–100 %) and less to karstic water (0–21 %). During the extreme dry year of 2002, there was no groundwater recharge from surface water. Calcite is dissolved during the wet period but during the dry period precipitates form. Also, dolomite creates precipitates during the wet period and is forced to be dissolute during the dry period.

SWAT nutrient modelling

The SWAT model was able to capture the seasonal and inter-annual variability of the flow. The annual average hydrologic balance of the Evrotas basin downstream to Vrontamas was estimated as follows: precipitation 923 mm, snowfall 65.8 mm, evapotranspiration 425.6 mm, total water yield 116.49 mm, irrigation 295 mm for agricultural areas and groundwater recharge of deep aquifer 304.1 mm. The water mass balance is positive and the demands of irrigation and drinking water are covered. However, in the Sparta floodplain, which is located in the centre of the river basin, water needs are higher than the available water resources and due to overexploitation the groundwater quality has been degraded.

Nutrient concentrations for the period 2009–2010 (Table 1) were used for the calibration of a number of parameters of the model. First, the simulated nitrate concentration was adjusted using the parameters NPERCO (nitrate percolation factor) (0.8), SHALLSTN (nitrate in shallow aquifer) (300 mg N/L), CDN (denitrification rate) (0.04) and LATORGN (organic nitrogen in baseflow) (100 mg L^{-1}) parameters. Simulated phosphate concentration was adjusted by PPERCO (phosphate percolation factor) (15), and GWSOLP (dissolved phosphorus in groundwater) (0.01 mg L^{-1}) to minimize RMSE between predicted and measured concentrations at all monitoring stations. Following RMSE (in mg L^{-1}) estimates are 1.376 for nitrate-N and 0.096 for phosphate-P at Vivari, with corresponding values of 0.714 and 0.363 at the WWTP monitoring station and 1.934 and 0.091 at Vrontamas. In Table 2-SI are the goodness of fit of nitrate-N, nitrite-N, ammonia-N and phosphorous-P and organic-N, regarding RMSE and the mean measured concentration of the variables in six location in the river.

Figure 3 shows the temporal variability of nitrate-predicted concentrations and their comparison to field values at the monitoring station downstream of the WWTP for the period 2008–2009. The model captures well the temporal variability of nutrient concentrations. Figure 4a, b shows the spatial distribution of nitrogen and phosphorus annual loads (average 2009–2010) as estimated by the SWAT model. It is clear that increased loads are entering the Evrotas especially to the north-east and the most polluted part is the main stream close to Sparta.

TMDL estimation using flow duration curves

Although most flow periods are characterized by increased nutrient inputs into the river, to delineate the areas where remedial action is needed we should use the simulation results of SWAT model. By estimating the nutrient loads in each stream that satisfy the GR-NCS by multiplying the GR-NCS nutrients values by the mean simulated annual discharge of 2009–2010 and comparing with the real average annual nutrients loads of the same time-period, we can estimate the streams that fail to satisfy the GR-NCS criteria. As it is shown in Fig. 4c, d, almost 58.5 % of river network fail to satisfy nitrogen criteria and 49.5 % phosphate criteria. Streams that experience increased loads are located mostly in Sparta valley due to agricultural activities or in upstream areas, possibly due to intensive livestock rearing.

The required load reduction estimated by TMDL approach is very high in almost all streams during all flow periods. Nitrate loads exceed the water quality standards for almost all flow classes with the exception of the low flow period (Table 2). Loads increase downstream indicating nitrate amendment by numerous streams that drain the agricultural areas and are connecting to the main stream. During low flow periods, reclaimed wastewater discharged to the river (and thus sustaining its flow) may enhance river organic and inorganic nitrogen content. Dissolved inorganic phosphate load is higher at low flows than at high flows. The small dilution ratio and increased temperatures during

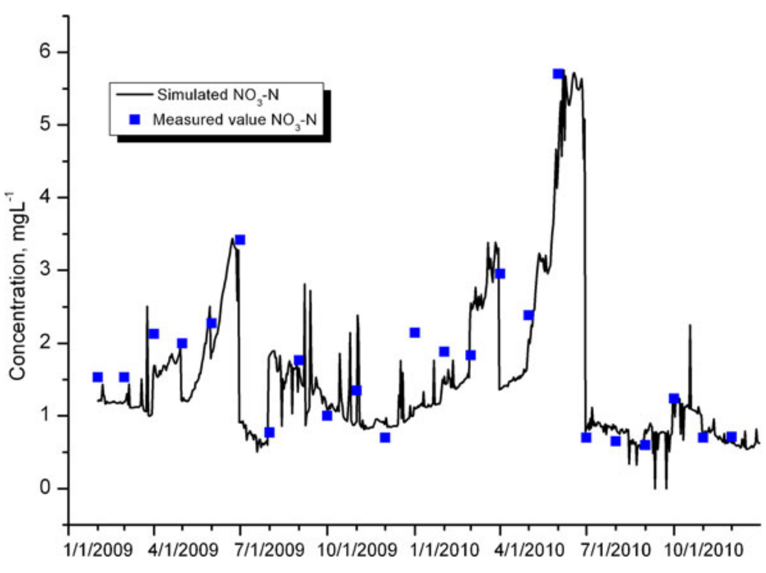


Fig. 3 Nitrate-N in WWTP monitoring station for the calibration period 2009–2010 (*black line* predicted values, *blue spots* field values)

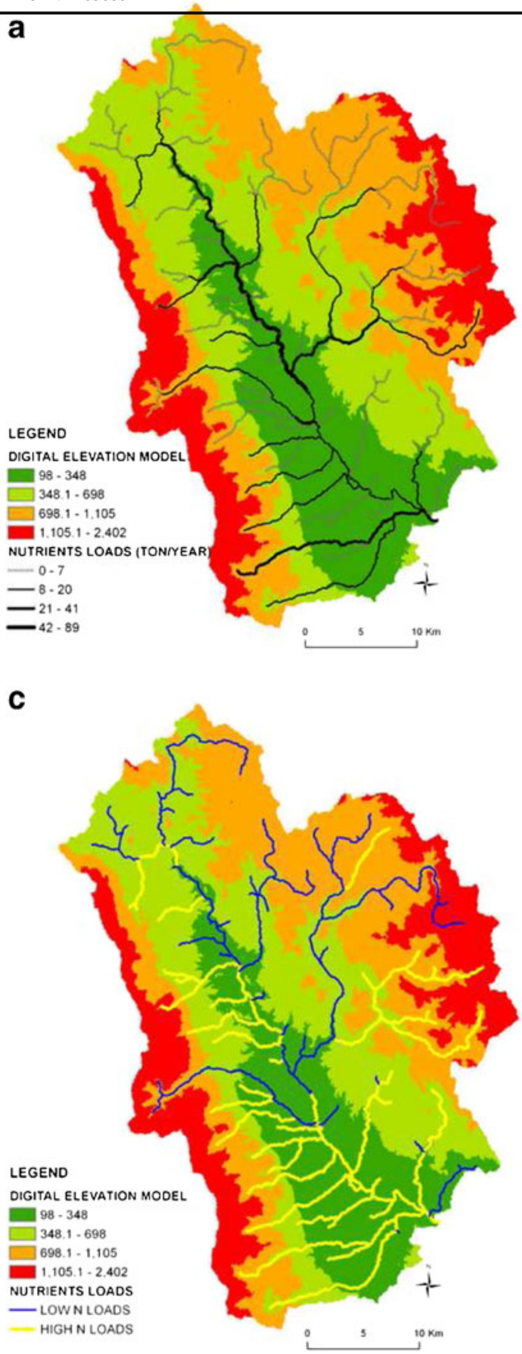


Fig. 4 **a** Nitrate annual loads; **b** phosphorus annual loads in Evrotas basin; **c** Evrotas streams that satisfy (*blue line*) or fail (*yellow line*) the target flux for meeting the water quality standard GR-NCS for nitrogen (left) and **d** Evrotas streams that satisfy (*blue line*) or fail (*yellow line*) the target flux for meeting the water quality standard GR-NCS for phosphorus (*right*) loads

the low flows enhance the hypothesis that river sediments act as phosphate source.

Target measures which control the nutrient content of fresh water can reduce any eutrophication threat and enhance ecological quality. In the Evrotas, the flow during the dry period is effectively the outflow of the Sparta wastewater treatment plant. TMDL approach suggests the need for a reduction of TN of almost

Table 2 Required load reduction (in percent) in various flow classes in the Evrotas (period 2009–2010)

Site	Variable	High flows 0–10 %	Moderate flows 10–30 %	Low flows 30–70 %	Dry conditions 70–100 %
Vivari	NO_3-N	52.6	36.7	36.0	NR
	NO_2-N	NR	NR	NR	NR
	NH_4-N	NR	NR	NR	60.9
	TN	49.9	9.2	35.0	NR
	PO_4-P	NR	NR	38.2	70.2
Downstream WWTP	NO_3-N	57.0	51.8	48.9	63.6
	NO_2-N	NR	NR	50.7	58.8
	NH_4-N	55.1	40.0	83.9	46.8
	TN	41.9	25.6	48.3	54.2
	PO_4-P	59.9	39.9	90.1	85.2
Vrontamas	NO_3-N	58.4	63.5	52.1	NR
	NO_2-N	79.6	NR	71.9	NR
	NH_4-N	NR	28.8	27.6	19.7
	TN	30.0	36.8	46.8	NR
	PO_4-P	0.5	13.2	67.2	38.0

54 % and phosphate 85 % downstream of the WWTP. The main action in achieving this would be to modify Sparta WWTP operation to enhance nutrient removal. Even at high dilution ratios during high flows, nutrient fluxes in the river remain very high and the TMDL approach suggests reductions of nitrogen and phosphorus loads that exceed 50 %. A nutrient flush is observed during high flows and specific measures that reduce flood velocity may help reduce loads generated by such flushes, by reducing mobilization and allowing time for in-stream processes to remove contamination. An important pollution threat remains the nutrient contribution from livestock production. Upland streams fail to achieve good ecological status because of contributions by grazing livestock. Measures such as grazing restriction should help in nutrient reduction. Finally, agricultural intensification is associated with high phosphorus and nitrogen emissions in Evrotas main stream. Figure 4c, d shows that 100 % of the main stream (length 23.9 km from Sparta bridge up to Vrontamas) does not satisfy P thresholds and 89.8 % does not satisfy N thresholds.

Management recommendations

The combined use of SWAT and the TMDL concept in the Conceptual Nutrients Mitigation model indicates that the majority of streams in the Evrotas basin fail to satisfy water quality criteria. Substantial load reduction in all flow classes is required. Remediation technologies have been demonstrated in the Evrotas basin in the past during EnviFriendly project, including planting of riparian poplar trees and the reuse of treated olive mill wastewater for fertilization and irrigation. At the same time, important work has been done to raise stakeholder and public awareness in order to achieve the ultimate goal of river ecosystem services sustainability (Demetropoulou et al. 2010). A riparian area downstream of Sparta WWTP was selected for the study of nutrient remediation by the root system of poplar trees. This demonstrated the high accumulation capacity of poplars trees in their above ground biomass through nutrient sorption by their long root system and the associated metabolic reactions. Therefore, poplar tree planting is highly water demanding; thus, the reforestation with native species such as black pine (*Pinus nigra*) and Platanus along the main stream riparian area may be the most effective buffer zone remediation system in the Evrotas basin. Common macrophytes such as reeds (*Phragmites australis* and *Arundo donax*) also cover long river sections, regulating the river nutrient budget. Previous studies in Evrotas drainage canals (Stamati et al. 2010) showed that groundwater phosphorus (100 % TP) and nitrogen (76.5 % NO3-N) are entrained in reed biomass. The harvesting of reed biomass in June has been shown to regulate nitrogen release back into the river. Reed mass management was demonstrated as a low-cost measure to enhance river sustainability.

With regard to point source pollution, it was demonstrated that the use of olive mill wastewater for maize irrigation is effective in improving soil fertility (Moraetis et al. 2011). Compost from olive press factory by-products, after years of application to soils, increases soil fertility and enzyme activity (Roberto et al. 2012). Various studies have shown the fertility value of compost created by the biosolids of the orange treatment process (Gelsomino et al. 2010) or the high trace metals sorption affinity of biochar created by these biosolids (Pellera et al. 2012). Several low-cost technologies exist and are performed all over the world for the management of olive and orange process biosolids without detriment to water resources. Some of them were demonstrated in the Evrotas basin accompanied by additional stakeholder training in the technology of converting food industry by-products to high additive value products.

In the Evrotas, the irrational use of synthetic fertilizers and pesticides to improve land productivity has had serious implication in water resources. The main stream receives nutrient leaching resulting in nitrate fluxes up to 89 t/year and phosphate up to 21 t/year (Fig. 4). Environmental concerns have to be integrated into the efficient food production to reduce nutrients emissions, protect land degradation and water resources deterioration. Measures for sustainable agriculture have to consider economic efficiency and social responsibility, since the adaption of agricultural innovations is becoming even more difficult due to the splitting of the land into numerous small farm units. Sustainability objectives in agriculture need to include caps on fertilizer application rates, buffer strips establishment, crops rotation, improve irrigation efficiency by replacing open conduit systems with closed, irrigation with reclaimed wastewater and irrigation with only the recommended amounts of water and changing the irrigation water pricing policy. Finally, livestock production in Evrotas upland areas results in land degradation, deforestation and nutrients emissions into streams. Even though livestock are extremely important to the livelihood of Evrotas smallholder farmers, the adoption of modern farming practices such as enclosure or rotational grazing should help significantly in the direction of river sustainability.

Conclusions

The flash flood character of the Evrotas basin and the long periods with no rain affect the surface and groundwater quantity and their interactions. River water composition affects groundwater both during the wet period (0–21 %) and the dry period (81–100 %). River transmission losses are an important component of water mass balance during the transition from wet to drought that significantly affect groundwater quality. Geochemical modelling provided quantitative information on the timing and magnitude of the vulnerability of groundwater to potential surface water contamination. It is demonstrated that during the transition from wet to drought conditions, the majority of groundwater in the alluvial floodplain is composed of surface water.

The use of hydrological and water quality models assessed the nutrients fluxes temporally and spatially in each stream and was used for the estimation of the necessary loads reduction in relation to flow variability. The majority of Evrotas streams do not satisfy ecological quality standards. Nutrient reduction is necessary in all flow classes and appropriate measures to achieve this should be adopted. Even though the established technologies have been shown to be highly effective at pilot scale, they have not been extended to basin scale, due to a lack of resources and political commitment. The extension of the above well-documented measures in the Evrotas at larger scales should substantially improve the water quality of the Evrotas streams. Further improvement requires the active and continuous involvement of the stakeholders and public. A key component in that process is the adoption of these measures by the local stakeholders, the local community and public authorities. Different target groups (such as farmers, sheep and goats owners, public authorities) should be involved early and actively and be encouraged to adopt new practices and technological innovations that will improve the ecological status of the Evrotas river basin. Effective public involvement through a continuous process from planning to implementation should ensure effective decision-making.

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