



Nutrient flows and related impacts between a Mediterranean river and the associated coastal area



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ABSTRACT

Taking into consideration the Water Framework Directive's requirements, water samples were collected monthly and/or bimonthly between 2014 and 2015 from Spercheios River, its estuary and the adjacent Maliakos Gulf in order to assess the quality of these water bodies. A study on dissolved nitrate, nitrite, ammonium, phosphate and chlorophyll-a concentrations was carried out, to investigate the impact between the river and the associated coastal area and assess the nutrient loads based on water flows from Spercheios River into the marine system. Furthermore a seasonal distribution of nutrient concentrations have been studied, dividing the sampling period into dry and wet season according to the river's discharges.

Correlation analysis and hierarchical cluster analysis among the available chemical data were conducted in order to enhance the detection of the two systems' interaction. Nutrients' concentrations increased from upstream to downstream sampling stations, particularly in areas where human-induced activities are detected. Marine samples were characterized by lower nutrient concentrations than the river ones, and the ecological quality of Maliakos Gulf, based on chlorophyll-a values, is characterized as moderate, except for the stations close to the river, which constantly presented poor quality.

Chemical analyses and statistical analysis indicated high nutrient flows and a strong impact between the freshwater and marine systems, accompanied by the profound effect of the adjacent aquafarming areas and the wastewater treatment plant of Lamia city. The highest nutrients' and chlorophyll-a values of the coastal stations were detected close to the river mouth and they were decreasing towards the outer Maliakos Gulf.

1. Introduction

The Water Framework Directive (WFD, 2000/60/EC) was approved in 2000, by the European Union (EU) members, with the purpose of establishing a framework for the protection of inland surface waters, groundwater, transitional and coastal waters. It requires the monitoring and classification of all European surface and ground waters on several biological and physical–chemical criteria, in order to ensure a 'Good Ecological Quality' of all water bodies (Capela et al., 2016). In 2008, the European Commission introduced a second integrative instrument for the protection of the marine areas in the form of the Marine Strategy Framework Directive (MSFD, 2008/56/EC). The aim of the MSFD is to ensure that European marine waters achieve Good Environmental Status (GES) by 2020, meaning that their natural states should not be significantly altered by human activities and that their biodiversity should be maintained. Due to the heterogeneity of the European seas, it is up to the Member States to define what GES means for their national waters (Loizidou et al., 2016).

Globally, large rivers play an important role in the terrestrial–marine linkage. Rapid increases in population and economic activity in the last decades have promoted eutrophication of coastal and estuarine waters through a massive influx of nutrients and other biogenic elements (Anderson et al., 2002; Li et al., 2007). Delta-front estuaries of large rivers are complicated marine systems and important interfaces between continents and the oceans. They experience material fluxes that have a global impact on marine biogeochemistry and preserve a record of natural and anthropogenic environmental changes (Bianchi and Allison, 2009 in Jiang et al. (2014)). Those transitional waters are usually under high environmental pressure and they have a relatively lower amount of studies performed, within this context, compared to the other water resources (Martinez-Haro et al., 2015 in Capela et al. (2016)). Furthermore, the threshold values for nutrients in transitional waters have not been considered in WFD and are established by each member state (Devlin et al., 2011 in Caetano et al. (2016)).

Moreover, river estuaries are excellent ecological study sites

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because biotic and abiotic mechanisms, that vary spatially and temporally, control the dynamics of organisms in the entire system. Also they are characterized by higher productivity (Ryther, 1969) and play a major role in supporting the commercial fisheries of coastal areas by providing habitat and food resources for juvenile commercial fish and shellfish (AFS and Smith, 1966; EPA, 1982; Levinton, 1982).

Freshwater inflows deliver high levels of nutrients (e.g., N, P species), organic carbon and other elements in the river plume, caused by land use transformation and anthropogenic emissions, along the salinity gradient that stimulates the primary production, the modification of aquatic food webs, and the occurrence of algal bloom and severe hypoxic events in coastal environments (Turner and Rabalais, 1994; Sundareshwar et al., 2003; Whitney et al., 2005; Gong et al., 1996; Ning et al., 1998; Lohrenz et al., 1999; Dagg et al., 2004; Harrison et al., 2008; Frame and Lessard, 2009). In addition, the freshwater discharge or salinity variation affects the planktonic community structure in the estuaries and coastal marine areas (Smayda, 1997; Li, 2002; Irwin et al., 2006; Chen, 2009; Jiang et al., 2014). The phytoplankton in these environments is inevitably influenced by physical and chemical factors induced by abundant loading of riverine, highly variable inshore–offshore water exchange, oceanic circulation, and water mass movement (Dagg et al., 2004). Nutrient inputs, caused by anthropogenic activities, enhance phytoplankton growth, disturb the balance of the water ecosystem, results in water quality degradation and provoke water eutrophication (Bricker et al., 2008; Nixon, 1995; Halpern et al., 2008; Conley et al., 2009). Therefore, phytoplankton biomass has been included in the WFD and MSFD (Borja et al., 2011; Ferreira et al., 2011) as one of the quality assessment parameters. The concentration of the photosynthetic pigment chlorophyll-a (chl-a) in the water is widely used as a proxy of phytoplankton biomass (Cullen, 1982; Jeffrey and Vesik, 1997). Chlorophyll is still the most common index of phytoplankton biomass in ecological studies, because it is both easy to measure in situ and from satellite measurements (Boyce et al., 2010).

Predicting the responses of ecosystems to nutrient loading is a challenge, because there are multiple factors that regulate biogeochemical transformations (Seitzinger et al., 1983 and Nowicki, 1994 in Sundareshwar et al., 2003). The differential responses to nutrients found among trophic groups and their subsequent interactions limit our predictive capability. Therefore, the temporal and spatial linkage between the biotic and abiotic continuum is important for understanding the various coastal estuarine systems, and for improving the biological integrity of estuaries. In this context, the validity of the concept of a river continuum within and between the freshwater and seawater zones must be addressed.

The aim of this study was a) to investigate the nutrient load of Spercheios river and its transport to the coastal waters, b) to identify the major factors affecting nutrient dynamics in this system, and c) to estimate the impact of riverine nutrient input on the ecological quality of the adjacent coastal area. This would provide information for the classification of the water bodies of Spercheios river and Maliakos Gulf within the WFD and MSFD contexts. Thus, in this study, data on nutrient concentrations and chlorophyll-a in Spercheios River and the adjacent Maliakos Gulf based on observations made in the period from 04/2014 up to 09/2015, are presented and the spatio-temporal variation in nutrients and chlorophyll-a concentrations in the river–estuary continuum have been investigated and discussed.

2. Materials and methods

2.1. Study areas

Spercheios river is located in Phthiotis prefecture in central Greece, is 85 km long and the total area of its drainage basin is 1907.2 Km² (Koutsogiannis and Tsakalias, 1995; Fig. 1). It springs from Timfristos (2312 m), Vardousia, Orthris, Oiti and Kallidromo and empties in

Maliakos Gulf, where its delta is formed. In the area of embouchure, the main river bed divides into three new beds, the old bed, the newer bed and the diversion bed. It is an area of ecological significance included in the Natura 2000 network. 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 and the greatest part is detected in the upper part of the river (from Makrakomi to Messopotamia).

The Delta and the lowland sedimentary area of Spercheios river, geologically consist of quaternary depositions and specifically clays, sand, pebbles gravels which compose a gentle to flat landscape (slope 0–15%), on which the cultivated agricultural areas extent as well the bounds of the divaricated river bed, deltaic marshes and tidal area. Finally, lowland areas extend east of the Athens-Lamia National Road and have been created from the transport and deposition of suspended particulate matter from the river. The Spercheios river Delta occupies an area of 196 Km², at 23° 30′ longitude and 38° 50′ latitude. It extends 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).

Maliakos Gulf (22° 31′; 38° 45′) is aligned in an east west direction, it is separated by two headlands to inner-west and outer-east Maliakos and it covers ca 200 km². Maximum depth is 25 m in the inner gulf and 50 m in the outer. The inner Maliakos communicates with the Aegean Sea through the outer Maliakos Gulf and it is a 91.5 km² semi enclosed shallow marine protected area (Poulos et al., 1996). The construction in 1958 of a spillway discharging north of the Spercheios river mouth led to the propagation of 0.94 km² of land into the gulf in 2000, while irrigation for agricultural purposes has decelerated the propagation of the previously active ‘birdfoot’ delta. Wind direction (from the west and the northwest) and the tidal movements (tidal range: 1 m) enable an anticlockwise water mass circulation pattern in the gulf that allows the homogenization of the water column throughout the year and the fast turnover of the water masses (Kormas et al., 2003).

Mussel farming has been expanded in Maliakos gulf in late 1990s after several earlier pilot commercial cultivation trials. The mussel farm (*Mytilus galloprovincialis*) is located in the inner part of Maliakos Gulf (Fig. 1). Other anthropogenic activities in the area include intensive agriculture, fishing and aquaculture farms in the inner and outer part (Dimitriou et al., 2015).

2.2. Water sampling

Field sampling measurements of physicochemical, hydromorphological and biological parameters were conducted monthly or bi-monthly in a network of thirteen (13) stations (Fig. 1) from April 2014 to September 2015. Eight (8) of them were sampled along Spercheios river (KR1 to KR8) and five (5) in the adjacent Maliakos Gulf (KR9 to KR13).

Portable instruments (Aquameter™-Aquaread AP-2000 and SBE 19plus V2 SeaCAT profiler CTD) were used to measure water temperature, conductivity, salinity, pH, turbidity and dissolved oxygen concentration in river and sea, respectively. River water discharge was measured by using the OTT C20 current meter (OTT, Hydromet).

In order to standardise calibration techniques, Aquaread® provide plastic calibration bottles into which the AP-2000 can be directly inserted. AP-2000 is easily calibrated in the field using just one calibration solution (RapidCal). RapidCal calibrates EC at 2570 µS/cm, the pH 7.00 point and the optional Optical Electrode Zero point simultaneously. As a general rule, pH and EC are calibrated as close to 25 °C as possible. Optical electrodes are calibrated as close to their deployment temperature as possible. DO 100% saturation point is calibrated in damp air using a fresh water -moist clean cloth or piece of tissue paper wrapped around the open end of the probe, covering all

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