ASSESSING NUTRIENT DYNAMICS IN A SMALL EASTERN MEDITERRANEAN WATERSHED

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EXTENDED ABSTRACT

The Mediterranean climate is characterized by extended dry and wet periods with a regime of irregular precipitation. Watersheds in the area, especially in the island area of the Aegean Sea, are typically small and drained by temporary rivers and streams. Temporary waters are unique and sensitive ecosystems as well as important components of the local hydrologic systems. In many Mediterranean coastal areas, they are responsible for the total amount of inflow water to the sea and directly associated with most coastal water nutrient balance and quality problems. As a consequence of the climatic changes and the increasing anthropogenic pressures, temporary rivers are expected to encounter longer dry periods and a higher variability that may have a significant effect on those sensitive systems. With regard to the requirements of the European Water Framework Directive, there is a need to better define the quality characteristics of temporary waters and to evaluate the essential features of those river systems in terms of their seasonal variability in nutrient transport. This will contribute to a better understanding, prediction and management of the complex processes of interaction between temporary flowing waters and receiving water bodies in the future.

The present research uses both field measurements and laboratory analyses for the assessment of water quality regarding the nutrient transport in a small eastern Mediterranean watershed. The field work supplied the rate of flow, in situ parameter measurements and water sampling from nine sampling locations representative of the hydrographic network. Physical parameters such as pH, temperature, conductivity, and dissolved oxygen were measured directly in the field during sampling. Chemical analysis of the collected samples was performed using spectrophotometry methods to estimate the nutrient load. The temporal distribution of NO₂⁻-N, NO₃⁻-N, NH₃-N and PO₄³⁻-P concentration was found to be closely related to the seasonal flow variations. Low values of nutrient concentrations were observed during dry periods, while they reached their maximum annual values during rainy periods. NO₃⁻ was found to be the dominant form of DIN (Dissolved Inorganic Nitrogen) in the study area, with few occasional exceptions. The contribution of individual sub-watersheds in water and nutrient loads to the main river was found to be in coherence with the size of the drainage area, the slope and the existence of water springs. Nutrient load in individual sub-watersheds also varied along their route according to a diversity of factors, mainly of anthropogenic origin. The olive cropping methods, light urban wastes, farm wastes and the few olive mills in the area were found to have a significant effect in nutrient spatial and temporal distribution within the watershed. The study results may be indicative of the expected nutrient dynamics and outflow from a small agricultural Mediterranean watershed.

KEYWORDS: Watershed; Water quality; Nutrients; Mediterranean; Runoff.
1. INTRODUCTION
The Mediterranean region is undergoing rapid local and global social and environmental changes (Iglesias et al., 2007). Coastal areas constitute the transition media between terrestrial areas and big water bodies, holding a filtering role with respect to materials coming from their watershed area, which makes these ecosystems particularly sensitive to upstream dysfunctions (Plus et al., 2006). Rivers, as the main transmission pathway from land to the sea, become recipients of agricultural, industrial and urban wastes worldwide. In the Mediterranean region, main contamination factors are agriculture due to the intentional use of fertilizers and also the direct discharge of unrefined urban and farming wastes into the environment (Nicolau et al., 2006, Quilbe et al., 2006). Agriculture is the main non-point polluter in irrigated areas as fertilizers and other agrochemicals drifted from precipitation become the main contaminants in the water that drains out of the root zone and reaches large water bodies (lakes or the sea) and the aquifers (Braud et al., 1999, Chowdary, 2005). The basic unit of all research, development and policy-making related to water is the watershed (Behera and Panda, 2006). A watershed constitutes a geographically dynamic unit unique in its physical characteristics and its behavior varies both spatially and temporally (Behera and Panda, 2006, Dorner and Swayne, 2007).

The present study aims in assessing nutrient dynamics in a small eastern Mediterranean watershed through an evaluation of the spatial and temporal distribution of water flow and chemical watershed characteristics supplied by field measurements and laboratory analyses. The determination of nutrient dynamics in a watershed scale may be a difficult task, mainly because of the observed spatial and temporal variability and complexity of the related factors (Behera and Panda, 2006). In the local scale, the contribution of small rivers and streams in water pollution cannot be ignored, since in many Mediterranean coastal areas, they are responsible for the total amount of inflow water to the sea (Nicolau et al., 2006). However, most Mediterranean countries lack systematic monitoring of surface water quality (Dassenakis et al., 1998) with regard to small rivers and streams. The knowledge of contaminant behavior in large rivers cannot be extended to small rivers (Pionke et al., 1999, Nicolau et al., 2006) due to seasonal variations of hydrological flow and chemical attribute.

2. MATERIALS AND METHODS

2.1 Study area
The study area is located on the island of Lesvos, in the north-eastern Aegean sea in the eastern Mediterranean (Figure 1). The Tsiknias river is located in the north-central part of Lesvos and drains an area of about 90 Km² with a mainly north to south direction. The Tsiknias is the major river discharging into the closed gulf of Kalloni in terms of water amount and nutrient loads contribution. The river estuary is registered as a Natura 2000 network site.

The climate of the area is typically Mediterranean, characterized by hot and dry summers and mild rainy winters with high relative humidity. The wind direction shows variations throughout the year. Northern winds dominate in summer (June-September), whereas southern winds dominate in winter (November-March) (Millet and Lamy, 2002). The elevation of the study site ranges from zero to 968 m and the watershed area is characterized as lowland, middle-mountainous. The main part of the watershed is covered by cultivation areas (mainly olive groves), grasslands (some abandoned), and brushwood, and only at the highland areas by pine and oak woods. The soil in the largest part of the area originates from acidic igneous rocks and only in the lowland areas near the estuary do alluvial soils prevail. Soil permeability is characterized as low in most of the area, low-medium in the highland areas, and medium in the north part of the area near the estuary.
Consistent with the majority of Mediterranean streams, the Tsiknias is characterized by seasonal flow for a period of 5-6 months (from November to April), during the highest precipitation levels observed. In addition to seasonality, the water flow characteristics in streams are strongly affected by the local scale precipitation features (intensity, duration, frequency of appearance) as well as the physiographic features of the area (extent, slope, ground cover, soil permeability, underground layers capacity).

Figure 1. Tsiknias watershed, Lesvos Island, Greece and sampling stations.

A previous study conducted on the nearby sea area showed that the amount of nutrients near the river mouths was up to three orders of magnitude higher than the nutrient amount measured in open water mass (Panayotidis et al, 1998). Similarly, Gavriil and Angelidis (2005) highlighted the effectiveness of fresh water inputs by the major streams during winter on the quality of sea water near estuaries. It was also quoted by Arhonditsis et al (2002) in a watershed nearby (the Gera watershed) with similar characteristics, that the nutrient loading due to surface losses from the terrestrial ecosystem during winter was found between 50% and 80% of the respective total annual. As a typical Mediterranean environment, the Tsiknias watershed combines intermittent stream discharge, lengthy dry periods and relatively light anthropogenic activities (Gavriil and Angelidis, 2005). The study area is under moderate pollution pressures. Small towns and villages, semi-intensive cultivation agricultural land, fodder units and natural ecosystems dominate in the area. Thus, agricultural and farm wastes, untreated urban wastes and wastes from olive oil mills and cheese dairies constitute the main pollution factors in the area.

2.2 Sampling and analysis
Measurements in the study area were carried out on a seasonal basis for two hydrological years (July 2007 – June 2009). Nine locations, representative of the watershed hydrographic network, were selected for the field work (Fig. 1). One is located very close to the estuary of the Tsiknias (T) and the other eight are sited upstream (U1, U2, U3, U4) and downstream (D1, D2, D3, D4) in each of the four sub-watersheds. Parameters such as water pH, temperature and dissolved oxygen for the nine sampling locations were measured directly in the field. The stream flow was measured at the sampling location near the estuary (T) as also at the four points located just before the four sub-watersheds discharge in the main stream (D1, D2, D3, D4). Collection of water samples was also carried out at the nine points for laboratory analysis. Each water
sample was used for the estimation of nutrient (NO$_2^-$-N, NO$_3^-$-N, NH$_3$-N and PO$_4^{–}$-P) concentrations. Table 1 includes information about the methodologies used for laboratory analysis.

Table 1. Methodologies used for water analysis

<table>
<thead>
<tr>
<th>Methodology</th>
<th>Source</th>
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<tbody>
<tr>
<td>Nitrate-Nitrogen NO$_3^-$-N</td>
<td>Cadmium Reduction Method-Colorimetric method</td>
</tr>
<tr>
<td>Nitrite-Nitrogen NO$_2^-$-N</td>
<td>Colorimetric Method</td>
</tr>
<tr>
<td>Ammonium-Nitrogen NH$_3$-N</td>
<td>Voltammetric method (Selective Electrode Method)</td>
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<tr>
<td>Phosphate-Phosphorus PO$_4^{–}$-P</td>
<td>Ascorbic Acid Method</td>
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3. RESULTS AND DISCUSSION

Stream waters were found to be well oxygenated. The concentrations of dissolved O$_2$ measured in the field ranged within acceptable values due to the small depth and the roughness of the sub-water floor. The pH values ranged between 7 and 9.15. Fig. 2 shows precipitation heights received from a local weather station located at the central part of the watershed and the flow measured for individual sampling stations.

The water flow measured at the estuary (point T) found to be smaller than the sum of the flow measured in each of the four sub-watersheds contributing to the central flow (Fig. 3a). The small slope of the area between the discharging points of the four sub-watersheds to the main river and the estuary renders a slow laminar flow and consequently favours infiltration. The presence of alluvial soils near the estuary also facilitates infiltration. However, seasonal flow is the main factor increasing this difference. The first precipitation events of a hydrological year replenish the lack of water in the soil caused by a long (>6 months) absence of precipitation. As a result, these flow differences were larger at the beginning of the two hydrological years (Fig. 3a).

The contribution of individual sub-watersheds to the main flow (Fig. 3b) is related mainly to the size of each area, but the slope and the existence of water springs in the area participate as well. The contribution of point D2 to the central channel flow was found to be the most significant, due to the springs enclosed in the area, the large elevation difference and the fact that it is the largest sub-watershed of the four. This effect of existing springs on the flow is also suggested by the lowest surface water temperature value measured in point D2 for the majority of the water samples. It is worth noting that at
the sampling campaign carried out on December of 2008, D2 was the only stream found to have water flow. In the hydrological years 2007-2008 the precipitation height in December 2007 was approximately double than the height in December 2008 (95.5 mm and 53 mm in December 2007 and 2008 respectively). As a result, in the 2008-2009 hydrological year, water flow was delayed in all streams, even in the main river Tsiknias, except for D2 point, due to the springs discharging to the stream. Contrarily, the sub-watershed 1 was found to make the least significant contribution to the main flow, due to the small extent of its drainage area and the small elevation difference along the main channel.

\[\text{Figure 3.} \quad (a) \text{ Flow at the estuary (T) and sum of the four sub-watersheds flow} \quad (\text{measured values}) \quad \text{and (b) contribution of individual sub-watersheds to the central channel flow (\%)}\]

DIN values (Fig. 4a) seem to follow precipitation trends in the first hydrological year (2007-2008), while in the second hydrological year they follow a downward trend, probably because of a washout caused by the first high precipitation events. PO\textsubscript{4} measured values (Fig. 4b) seem to follow precipitation trends.

\[\text{Figure 4.} \quad \text{Precipitation height with (a) DIN measurements and (b) PO}\textsubscript{4} \text{ measurements.}\]

According to the laboratory analysis results, NO\textsubscript{3} concentrations dominated other forms of DIN (NO\textsubscript{2}, NH\textsubscript{3}) as it was expected in well oxygenated, lightly polluted waters. DIN and its forms measured in each sampling station are presented in Fig. 5. A substantial increase of NH\textsubscript{3} and NO\textsubscript{2} percentages against NO\textsubscript{3} is notable in diagrams 5a and 5b respective of D1 and D2 sampling points. This irregularity has an apparent effect in DIN
forms contributing to central discharge (Fig. 5e) and can be easily linked with the release of “fresh” agricultural and urban wastes in the environment. This can be prospective, especially in these two points (D1, D2) located in an area (eastern side of the watershed) dominated by fodder units and cultivation land.

**Figure 5.** Contribution of NO$_3^-$; NH$_3$; NO$_2$ to DIN loadings at (a) D1; (b) D2; (c) D3; (d) (D4) and (e) T sampling points (percentage values).

Fig. 6 imprints the average nutrient values along their route for each individually sub-watershed. Diversification of nutrient values along their route occurs mainly due to the multiple pollution sources along the streams. However, some noteworthy deflections occur by these estimations. The average value of NO$_3^-$ in sampling station U4 was found to be extremely high compared to the other three upstream stations (Fig. 6a), revealing the existence of a cheese dairy nearby the sampling point. High values of NO$_2^-$ and NH$_3$ were found in U2 (Fig. 6b and 6c), due to the location of the sampling station next to a village. Urban wastes significantly affect water quality because of the absence of waste treatment in the study area. NO$_2^-$ and NH$_3$ values also found high D1 and U1 stations
respectively. This can be prospective by the existence of many fodder units along the
route U1-D1. Most of the PO4- values measured along the stream flow showed an
increase from U to D stations (Fig. 6e), due to the intense flow (steep slope), followed by
a decrease in flow rate and laminar flow. The exception of D3 low value indicates
possible consumption, possibly explained by many abandoned olive groves in this area.

Fig. 6d establishes the fact that even though D2 (watershed 2) contributes the most with
regard to the water flow, it is the least significant contributor with regard to nutrient
concentrations.

**Figure 6.** Average values of NO3, NO2, NH3, DIN and PO4 along their route in
each individually sub-watershed (U: Upstream, D: Downstream, T: Tsiknias).

4. SUMMARY AND CONCLUSIONS

The present research used both field measurements and laboratory analyses for the
assessment of water quality regarding the nutrient transport in the small eastern
Mediterranean watershed of the Tsiknia river, Lesvos island. The contribution of
individual sub-watersheds in the amount of water discharging into the main river was
found to be consistent with the size of the drainage area, the slope and the existence of water springs. The observed temporal and spatial variations of nutrient concentrations in individual sub-watersheds can be attributed mainly to anthropogenic activity as well as to climate and watershed characteristics (i.e. rainfall height and intensity, slope gradient). The olive cropping methods, light urban wastes, farm wastes and a few olive mills existing in the area, were found to strongly affect the nutrient spatial and temporal distribution within the studied watershed.

REFERENCES