IN STREAM GEOCHEMICAL PROCESSES OF TEMPORARY RIVERS – KRATHIS RIVER CASE STUDY

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ABSTRACT

Temporary waters courses dominate the semi-arid climate of the Mediterranean area. The hydrologic and biogeochemical processes that occur during the wetting and drying periods are not well understood. A preliminary evaluation of the significant hydrologic, sediment transport and geochemical in-stream interactions of Krathis River based on field and laboratory data that were obtained during the first year of an on-going study is presented here. The predominant in-stream processes (major biogeochemical cycles of nitrogen and phosphorous) were assessed.

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ΠΕΡΙΛΗΨΗ

Τα εφήμερα ρέματα καλύπτουν μεγάλο ποσοστό των επιφανειακών νερών στη Μεσόγειο. Οι υδρολογικές και βιογεωχημικές διεργασίες που συμβαίνουν κατά τη διάρκεια των ξηρών και υγρών περιόδων δεν είναι πλήρως κατανοητές. Ο σκοπός αυτής της έρευνας είναι να γίνει μια πρώτη εκτίμηση των σημαντικών υδρολογικών, μεταφοράς στερεών και γεωχημικών διεργασιών στον Κράθι ποταμό βασιζόμενοι σε δεδομένα πεδίου και εργαστηρίου που ελήφθησαν από τη λεκάνη του ποταμού κατά τον πρώτο χρόνο της μελέτης. Προσδιορίστηκαν οι διεργασίες που κυρίως επικρατούν στο ποτάμι (κύριοι βιογεωχημικοί κύκλοι αζώτου και φωσφόρου).

1. INTRODUCTION

The Mediterranean region is characterized by a variety of microclimates ranging from humid, to semi-arid [1]. In the Mediterranean region, the dominant types of streams are the temporary ones. Temporary rivers are natural bodies of water that experience a recurrent dry phase of varying duration. In contrast ephemeral rivers run for short periods after rain has fallen in their catchment [2]. During dry periods, there is lack of water due to droughts, extensive evapotranspiration, water abstraction, high irrigation demand, and overexploitation of groundwater. Drying affects the aquatic habitats and the extent of subsurface-surface water interaction. In the fall, high rainfall intensities occur over crusted or poor soils [3]. This first flood results in significant remobilisation of accumulated debris (first flush effect), intense erosion rates and significant dissolved and suspended solids transport. This causes intense erosion resulting in progressive loss of upper soil and leading to the desertification of the riparian zone. During the wetting and drying periods there is a dynamic interchange between groundwater and surface water occuring in the hyporheic zone. In most types of landscapes the rivers are hydraulically connected to groundwater [4]. Climate and the physiography of the streambed (pool and riffle and meandering stream) control surface water - groundwater interaction [5].

Figure 1 presents a conceptual cross – sectional conceptualisation of the relationship between the river, the hyporheic zone and ground water. The hyporheic zone is comprised of upwelling and downwelling ecotones. How much flow seeps from the river into the hyporheic zone is a function of the hydraulic properties of the bed, its configuration and hydraulic relationship with the groundwater. As water passes through the hyporheic zone, its water quality changes due to different chemical and physical properties, microbial processes, and metazoan community dynamics [6]. The hyporheic zone is characterized as a biogeochemical “Hot Spot” [7]. Hot spot by definition is an area with high reaction rates relative to its surroundings. In addition, “Hot Moments” are short periods of time that significant biogeochemical events are occuring [7].

Temporary rivers dominate the Greek environment. The watersheds of temporary rivers that drain into the sea cover approximately 42.5 % of the total area of Greece [8]. Most of the tributaries of large rivers in Greece can also be characterised as temporary rivers, due to the fact that during the summer they become completely dry. In addition, due to the karcstic environment, infiltration in Greece does not have Hortonian behaviour and thus the tributary rivers have flow only during large storms and they do not sustain base flow. There is a general gap in knowledge of in-stream hydrological (flushing, evapotranspiration, surface water – ground water interaction) and biogeochemical processes (bacterial production and decomposition, nitrification, denitrification etc.) of termporary waters. The tempQsim project (www.tempqsim.net) aimed at filling this gap in knowledge. The project studies temporary rivers in Mediterranean and the particular hydrologic conditions and processes that occur during the wetting and drying periods. The study site in Greece is Krathis River in northern Peloponnese.

The objective of this work is to perform an evaluation of the water-riverbed interaction of Krathis River based on field and laboratory data that were obtained during the first year of the study. The analysis will be conducted in the context of “Hot Spots – Hot Moments” concept. An examination of the hydrological and geochemical processes requires the development of a Conceptual Site Model (CSM). The CSM is a planning tool that incorporates site- specific, hydrogeologic and geochemical information to identify contaminants of concern, environmental pathways and processes [9]. It aids the conceptual understanding of the hydraulic connections between the river and its hyporheic zone, the behavior of sediment transfer and the geochemical processes that affect the fluxes of chemicals.

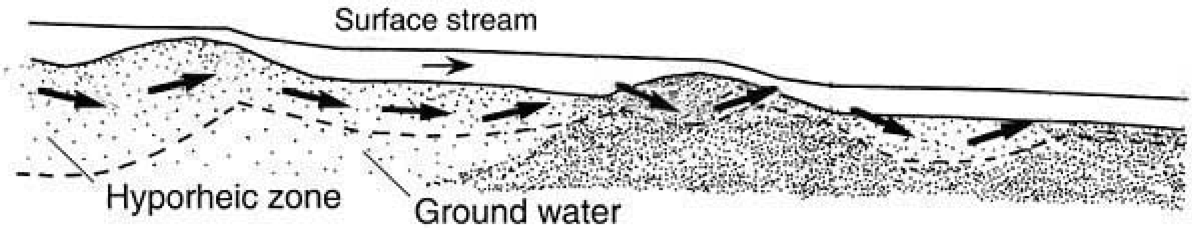

Figure 1: Conceptual schematics of streambed interactions [adapted from 6].

2. SITE DESCRIPTION

The catchment of Krathis River covers an area of 149 km^2 and is located in Achaia Prefecture, in North Peloponnese. The main part of the basin consists of mountainous terrain (mean catchment altitude = 1092 m), resulting in a mean catchment slope of 33%. On its northern part, urban areas and agricultural plains characterize the region. The springs of Krathis River are situated at Chelmos Mountain. After joining Asopos Tributary, which drains the north - eastern part of Chelmos Mountain and Parapotamos Tributary, which drains the western part of the catchment, the Krathis River outflows, following a NNE direction, in the Corinthian Bay (Figure 2). The length of the river is about 30 km [10]. The dominant formations in the catchment are the recent Neogene and Quaternary sediments (60 %) the limestones (22 %) and the Flysch (18 %). Most springs are located in the limestones. Forests cover 75.42 % of the watershed, while the cultivated areas cover 24.36 % [10].

Due to high slope of the riverbed, high erodibility of the bedrock (flysch and recent sediments) and the seasonal climatic variation, the river carries high amounts of sediments towards the sea. Throughout the whole catchment and especially at the southern mountainous region, there are numerous landslides and heavy erosion that result to high sediment loads. Sediment is transferred to the river delta, which forms a well-identified shape. The slope of the river ranges from 15 to 27 % in the southern part to 3-5 % in the northern part of the catchment. The average rate of sedimentation is between 0.80 to 2.5 mm/yr [10]. The travel time is of the order of 6 hours. This indicates that the river is very flushly and has a high capacity for sediment transport.

3. METHODOLOGY

In order to study in-streams processes and groundwater-surface water interaction that occur in the hyporheic zone, it was decided the study a reach of Krathis riverbed (Figure 2). The reach is located in the north part of Krathis River and has a length of 1 km. The field site was divided into three transects and multi-level wells were installed. Nine multi-level well clusters were installed, 3 in each transect. The boreholes were opened using a 12 cm diameter hollow stem auger. Soil samples were taken at regular intervals during the opening of the borehole. Groundwater mini-probes were installed upon the opening of the borehole. The well casing consists of 2.5 cm of flush threaded PVC. The mini-probes were nested vertically in the same well to determine the vertical movement of groundwater and surface /ground water interaction.

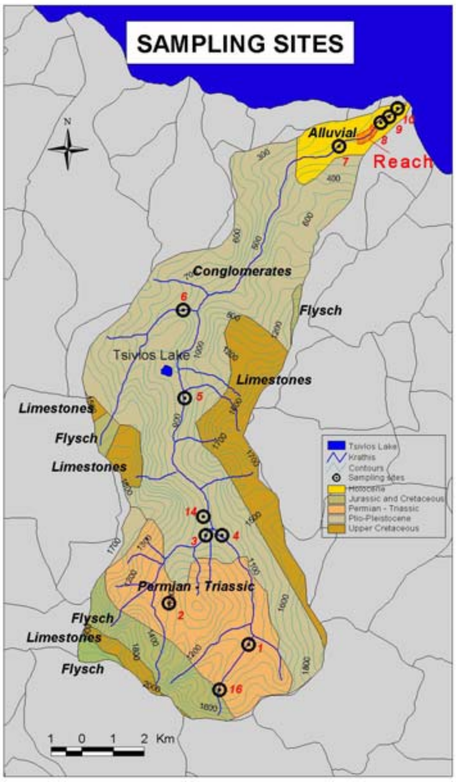

Figure 2: Geologic Map of Krathis river basin, the reach site and the monitoring network.

An automatic telemetric monitoring system was installed directly upstream of the reach. The system consists of a meteorological station, a water level recorder and an automatic station for the measurement of temperature, dissolved oxygen, pH, conductivity and turbidity. The system is measuring the above mentioned parameters every 10 minutes and the data is transferred on line to Hellenic Centre of Marine Research. An autosampler collects water samples on episodic event basis and during low flow. Furthermore, water samples were collected and physicochemical parameters were measured in situ on a monthly basis at several sites along the river course (Fig. 2). The samples were analyzed for all major ions (calcium, magnesium, sodium, potassium, bicarbonate, sulphate, chloride), silicate, nutrients (nitrate, nitrite, ammonia, total nitrogen, phosphate, total phosphorus), Dissolved Organic Carbon (DOC) and suspended matter. Organic carbon, total nitrogen and total phosphorusanalyses were additional performed for suspended matter.

The hydraulic characteristics of the riverbed sediment and groundwater - surface water interaction were studied through a variety of methods. Pumping tests (slug-in) were used to determine the hydraulic conductivity in the field. Injection-withdrawal tracer studies were used to evaluate various hydraulic properties and examine the percent recovery of the tracer. Finally, experiments were conducted to determine the infiltration rate. Regular infiltrometers were used to develop the rate of infiltration of the riverbed under undisturbed conditions. The infiltrometers consisted of a 50 cm cylinder that was inserted into the sediment. The cylinder was filled with water and the time it took for the water to drain into the sediment was measured.

Laboratory measurements were conducted to evaluate the physicochemical properties of the riverbed. 34 soil samples were analyzed in order to estimate the physicochemical properties of the riverbed. The following parameters were analyzed: dry bulk density, porosity, soil moisture, particle size distribution, pH, redox potential, spesific surface area (BET method), mineralogical and chemical composition (XRD, XRF) and organic matter (OM) (as Ash Free Dry Mass), organic –

total carbon (TOC), total nitrogen (TN) (HCN analyser) and organic total phosphorous (TOP). The soil pH was measured using an Orion, 9107 pH meter. When the soil sample was extremely fine, Laser Diffraction Size Analysis was conducted. Specific surface was estimated with the BET method using a NOVA 2200 QUANTA CHROM analyser. The Redox potential of the soil was estimated through batch experiments. 50 g of soil sample were added to a 600 mL beaker. Then Deionized (DI) water was filled to 500 ml. The suspension was stirred with a magnetic stirrer. The beaker was sealed and a steady flow of nitrogen gas was introduced into the system to remove the oxygen. The Eh, DO, Temperature and Conductivity were monitored continuosly until the system was stabilized (Orion, 9107 pH meter and ORP meter, Orion 081010 D.O. meter, and Orion 011050 conductivity meter). Analysis of organic matter, TP, TN and XRD were carried out in the biofilm, the active surface layer and in the bed sediments.

4. RESULTS

4.1 Riverbed hydraulic characterization

The groundwater table at the riverbed was in June 2003 16 m below surface. From the eighteen wells (mini-probes up to 5 m in depth) that were installed in clusters were dry from June through October since groundwater and surface water are not connected hydraulically. In November, the river started rechanging the groundwater and wells had piezometric heads indicating downward vertical gradients. The hydraulic conductivity was 0.8-1.1 mm/s (slug-in tests). The infiltration experiments that took place in Krathis showed that the equilibrium capacity was 0.889 mm/min and the initial infiltration capacity was 0.457 mm/min. Horton's infiltration constant (representing the rate of decrease in infiltration capacity) was 0.058/min.

4.2 Riverbed sediment characterization

The particle size distribution of the sediment samples indicated that the riverbed consists of large particles (42 % > 2 mm diameter) and of a large proportion of fine particles of colloidal size (5 % < 63 μm). In other words, the particle size distribution was very well graded from very large sizes to colloidal sizes indicating the propensity for extremely low hydraulic conductivity. The Uniformity Coefficient ranged from 0.1 to 16 (average 6.6) for borehole A1, from 7 to 12 (average 9.5) for borehole B2 and from 3 to 11 (average 7.5) for C1. The dry bulk density of borehole samples ranged from 1.731to 1.76 g/cm^3 (average 1.74 g/cm^3). The porosity of the samples ranged from 13.13 to 28.44 (average 23.05). The soil moisture content of the borehole samples ranged from 0.22 to 10.12 (average 2.573) and the pH value ranged from 7.57 to 7.80. Finally, the particle size distribution revealed a large proportion of fine particles of colloidal size.

The average dry bulk density of surface samples was 1.45. The porosity of surface samples ranged from 18.22 to 35.83 (average 26.9). The soil moisture content of the surface samples ranged from 0.32 to 35.83 (average 9.08) and the pH ranged from 7.61 to 7.71. During the soil sampling, it was observed that large riverbed areas were covered with sediments of fine particle size distribution (Hot Spots) that overlay the more gravely material described above. The fine material is highly impacted by the wetting and drying cycles and it flushes out in the first rain events in the fall. These spots are characterized as follows: extremely fine particle size distribution (average bulk density = 1,35 g/ml; average uniformity coefficient D_{50} = 38 μm), and high BET (6.5 m^2/gr). The organic matter content ranges between 0.9 and 3.23% (average 1.65%), OC between 0.13 and 0.89% (average 0.4%), TC between 6.7 and 8.4% (average 7.5%), TN between 0.010 and 0.047% (average 0.023%), OP between 0.0006 and 0.0065% (average 0.0032%) and TP between 0.013 and 0.038% (average 0.024%). The redox potential experimental results showed that the sediments did not have any reducing power. The dissolved oxygen level was low during the experiment and the Eh was about 307 mV.

4.3 Water quality characterization

Surface water samples have been collected on a monthly basis as well as on an episodic event basis. Table 1 presents the average water chemistry directly upstream of the reach. The average baseflow (July-September) dissolved nutrients and carbon concentrations, directly upstream of the reach, were 0.97 mg/l for nitrate, 5.8 μg/l for nitrite, 5.4 μg/l for ammonia, 0.61 mg/l for TN, 6.7 μg/l for phosphate and 23 μg/l for TP. The average discharge was 0.29 m^3/s. The suspended matter, concentrations were 6200 ug/g for POC, 47000 ug/g, for PIC, 900 ug/g, for PTN and 10 ug/g for PTP. The apparent partitioning coefficient between dissolved and particulate phase for P and N was estimated to be 435 and 1475 ml/g respectively, indicating a high portion of particulate transport. In the spring (April-May), the river water concentrations exhibited a dilution for most of dissolved and particulate concentrations. The average discharge was 9.7 m^3/s. Only phosphate (average 107 μg/l), PTP (average 26 μg/g) and PIC (average 67000 μg/g) showed increase compared to the dry season. Two flood events were sampled automatically during October 2003. For the first event, 12 samples were collected. During the second event, 11 samples were taken. The results showed that major ions and dissolved nitrogen compounds, except ammonia, presented lower concentrations compared to baseflow conditions. Phosphate and TP revealed a slight increase (average 9.9 and 42 μg/l respectively), while ammonia, revealed a substantial increase (70 μg/l). Finally, concerning the particulate phase, there is a substantial enrichment of POC, PIC and PTN compared to the dry season ranging between a factor of 25 and a factor of 50. The partitioning of N and P in the episodic event are two orders of magnitude higher than the base flow indicating significant suspended matter and nutrient transport flushing out to the coastal zone.

TABLE 1: Average (April-November) Quality of Krathis River (CV: coefficient of variation)

Parameter	Mean	Median	CV (%)	Parameter	Mean	Median	CV(%)
Disch. (m^3/s)	3.6	1.8	130	Cl (mg/l)	6.7	6.1	52
Cond. (μS/cm)	180	172	13	NO_3 (mg/l)	0.73	0.70	29
Temp. (^oC)	16.4	16.2	44	NO_2 (μg/l)	3.9	3.5	35
pH	8.30	8.28	3	NH_4 (μg/l)	5.6	5.6	15
Redox (mV)	336	334	13	PO_4 (μg/l)	63.2	8.9	145
D.O. (mg/l)	9.98	10.20	15	TN (mg/l)	0.311	0.311	138
Ca (mg/l)	45.4	48.5	12	TP (mg/l)	0.146	0.146	119
Mg (mg/l)	16.8	16.9	12	POC (mg/l)	0.752	0.551	97
Na (mg/l)	4.5	3.8	46	PTC (mg/l)	10.6	7.8	121
K (mg/l)	1.7	1.9	28	PTN (μg/l)	90.2	70.9	72
HCO_3 (meq/l)	2.9	3.0	7	PTP (μg/l)	4.2	2.8	71
SO_4 (mg/l)	40.9	38.0	23	TSS (mg/l)	161	130	103

5. DISCUSSION AND CONCLUSIONS

5.1 Hydrologic Conceptual Site Model

The emerging hypothesis of the hydrologic behaviour of the riverbed of Krathis can be summarized as follows. The river in the lower catchment is recharging the groundwater due to low groundwater table. The system does not have a hyporheic zone that runs parallel to the river, but a zone with vertical gradients consistent with the recharging process.

5.2 Sediment Conceptual Site Model

Due to high erodibility of the rocks forming Krathis basin and the high slopes, the catchment is marked by intense erosion. High erosion rates, high riverbed slopes and low travel time of river water cause high amounts of riverine sediments, which are deposited in the lower portion of the river (and in the reach). Due to this process, particulate organic matter and particulate nutrients are deposited in the reach. The sediments in the reach area up to a depth of about 0.5 m (maximum rebar depth), are under oxic conditions. It is assumed that a significant fraction of riverine particulate organic matter and nutrients originate from forest soils (average TSS 296 mg/l). These fine sediment deposits are consistent with the hot spot concept because they have very different characteristics than surrounding material. The mobility of these hot spots has been documented, however the impact to coastal zone remains unclear.

5.3 Water Quality Conceptual Site Model

Phosphorous, and nitrogen are being transported to the river reach through dissolved and particulate transport. The apparent partitioning coefficients estimated for each element revealed that under base flow conditions 10 % and 20 % of the total mass of P (20 Kg/d), and N (652 Kg/d) respectively were transported by the solid phase. In-stream processes that affect the fate and transport of P in the dissolved phase include sorption to suspended matter, uptake, precipitation and mineralization of organic P. Sorption to suspended matter was shown to be a significant factor affecting its fate. Phytoplankton uptake does not affect significant the fate of P in the aqueous phase since this is a fast flowing river and the ecological quality assessment indicated that aquatic biota richness is low. Organic P concentrations were significantly, however, the rate of mineralization should be estimated for appropriately assessing the significance of the process.

The processes that affect the fate and transport of nitrogen in the aquatic phase include nitrification, denitrification, mineralization, and ammonia sorption and volatilization. The levels of oxygen in the stream and the sediments as well as the high concentration of nitrate and the low concentrations of nitrite and ammonia indicated that the nitrification process is active and significant. On the other hand, the oxic environment indicated that denitrification is non-existent. Mineralization (like in the case of P) should be studied since there is a significant portion of total N is in the organic form. The pH levels (pH of 8.2) and the iron oxide content (2.5 %) of the sediment and suspended material indicated that ammonium ion sorption and ammonia volatilization were not significant. Finally, deposition and scouring and benthal releases of N and P are processes that should be studied in the context of hot spots and hot moments.

The geochemical information obtained through base flow and episodic event basis as well as aquatic and sediment sampling lead us to the formation of an initial hypothesis on the important processes that affect the fate and trasport of nutrients in temporary rivers. This analysis aided in the planning of the experiments and studies that are necessary for a comprehensive understanding of the in-stream N and P cycles.

ACKNOWLEDGEMENTS

This project was funded by the European Commission, EESD Specific Programme (Contract N^{o} EVK-CT – 2002 – 00112) "Evaluation and Improvement of Water Quality Models for Application to Temporary Waters in Southern European Catchments – TempQsim''.

The present article is dedicated to the Mykonian self-educated naturalist and archeologist Stavros Polykandriotis, who passed away on the 15th of August, 2002.

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