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COMPARATIVE GEOCHEMISTRY OF THREE URBAN STREAMS IN ATHENS: KIFISSOS- PODONIFTIS-PIKRODAFNI

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Abstract

The geochemistry of three urban streams in Athens was analysed and compared on the basis of major elements and heavy metals content in water and active sediment. The studied streams of Kifissos, Podoniftis and Pikrodafni run through the Athens basin of a total area of 540 km^2 but differ with respect to the origin of their headwaters i.e., Parnitha, Penteli and Hymettus mountains. The main aim of the study was to determine the geochemical signature of water and sediment within the Athens hydrological basin and evaluate the effect of natural and anthropogenic environment on these water courses. A total of 56 stream water samples were obtained and analysed for major anions, cations and heavy metals (Mn, Cr, Cu, Zn, Pb) as well as nitrate and phosphate concentrations. Active stream sediments were collected at 22 locations along the streams and were analysed for heavy metals (Pb, Zn, Cu, Mn, Cr, Ni, Cd). Results indicated that rock weathering, rather than atmospheric or pollution influx is the dominant process affecting the major ion geochemistry of stream flow in the urban setting. However, Kifissos and Podoniftis waters had higher nitrate and phosphate concentrations indicating greater influence by anthropogenic activities. In general the quality characteristics of water and sediment in the study area were found to be in a good state regarding the studied parameters.
Key words: *hydrogeochemistry, surface water, heavy metals, urban pollution.*

Περίληψη

Παρουσιάζονται τα υδρογεωχημικά χαρακτηριστικά τριών αστικών ρεμάτων της Αθήνας και γίνεται σύγκριση ως προς το περιεχόμενο κυρίων στοιχείων και ιχνοστοιχείων στο νερό και το ενεργό ίζημα. Τα ρέματα που μελετήθηκαν, Κηφισός, Ποδονίφτης και Πικροδάφνη, διατρέχουν το Λεκανοπέδιο Αθηνών αλλά πηγάζουν από γεωλογικά διαφοροποιημένες περιοχές δηλαδή την Πάρνηθα, την Πεντέλη και τον Υμηττό. Ο κύριος στόχος της έρευνας ήταν να προσδιοριστεί ο γεωχημικός χαρακτήρας του νερού και του ιζήματος των ρεμάτων ως προς τους φυσικούς και ανθρωπογενείς παράγοντες που των διαμορφώνουν. Αναλύθηκαν συνολικά 56 δείγματα ύδατος και προσδιορίστηκαν οι συγκεντρώσεις των κύριων στοιχείων και των βαρέων μετάλλων Mn, Cr, Cu, Zn, Pb. Επίσης ενεργό ίζημα από 22 θέσεις κατά μήκος των ρεμάτων αναλύθηκε για τα μέταλλα Pb, Zn, Cu, Mn, Cr, Ni, Cd. Διαπιστώθηκε ότι ο κύριος παράγοντας ελέγχου του χημισμού του νερού είναι η αποσάθρωση των πετρωμάτων. Ωστόσο το

νερό του Κηφισού και της Πικροδάφνης έδειξε μεγαλύτερη επιβάρυνση σε νιτρικά και φωσφορικά ιόντα. Γενικά η ποιοτική κατάσταση του νερού και του ιζήματος των τριών ρεμάτων κρίνεται ικανοποιητική ως προς τις παραμέτρους που μελετήθηκαν.
Λέξεις κλειδιά: *Υδρογεωχημεία, επιφανειακό νερό, βαρέα μέταλλα, αστική ρύπανση.*

1. Introduction

The city of Athens is the most populated area of Greece with a population of 3,074,160 million (in 2011) and is also the 4th most populous European Union capital (2004). The ever increasing urbanization has lead to uncontrollable development around Athens 3 main streams of Kifissos, Pikrodafni and Podoniftis. All three streams have been the recipients of local runoff as well as uncontrollable industrial and residential discharge. The river banks have been altered in many different ways, including, development of houses within the rivers' protection zones. This has resulted in extensive anthropogenic pollution which has disrupted the natural ecosystem.

Microbial contamination due to wastewater is a very common threat in urban environments while contamination by metals and industrial compounds is a long-term concern in industrialized cities (Wong et al. 2012). In this study the geochemistry of water samples and stream sediment samples, from all three streams, has been analysed and compared over a period of one year. The main objective was to determine whether the streams are capable of retaining their natural geochemical characteristics despite the effect of other influxes. In addition, the level of anthropogenic effect on the water course was determined, in order to evaluate the current geochemical state of the streams.

2. Description of Study Area

The examined streams of Kifissos, Pikrodafni and Podoniftis are all situated in, and run through, the Athens Basin. The basin covers a total of 540 km^2 and is bounded by the mountains of Egaleo, Parnitha, Penteli and Hymettus. The streams derive from geologically different areas (Figure 1), influencing their water and sediment geochemical characteristics. Kifissos springs mainly from Mount Parnitha, Pikrodafni from Mount Hymettus whereas Podoniftis from Mount Penteli.

The geology of Attica is quite complex and is consisted of four main alpine geotectonic units (Papanikolaou et al 2004a): a) The lowest-basement unit (relatively autochthon) comprises the metamorphosed formations of Athens and can be found in Mount Penteli and Mount Hymettus. Formations include marble, dolomite, and mica-schist amongst others. b) The Alepovouni unit found in the western side of Mount Hymettus, also characterized by metamorphic formations. c) The Sub-Pelagonian unit, which can be found in Mount Egaleo and Mount Parnitha and consists of carbonate formations such as limestone and dolomitic limestone. d) The Upper Unit of Athens which is basically found in all the internal part of the basin and is divided into two napes. The lower nape is considered to be a "mélange" and was often referred to, as the 'Athens Schist', whereas the upper nape is comprised of limestone.

Kifissos is the longest river of the basin at approximately 33.7 km long and is also considered to be the main pluvial water recipient. As it was previously mentioned it derives from Mount Parnitha and discharges into the Saronic Gulf. Since it springs from Mount Parnitha, it goes through carbonate formations and is therefore expected to have high Ca^{2+} and HCO_3^- concentrations. For the most part it is inaccessible and specifically, for its last 15 km, starting at the area of Nea Halkidona, it is channeled under a highway (Kifissos Avenue) until it discharges into the Saronic Gulf. In terms of its geomorphology, the river is presently in a state of constant erosion.

Until the Upper Miocene the river's basic level was around 100-140 m higher than what it is today (Papanikolaou et al., 2004b). Kifissos is considered to be the most polluted river of the basin. Up

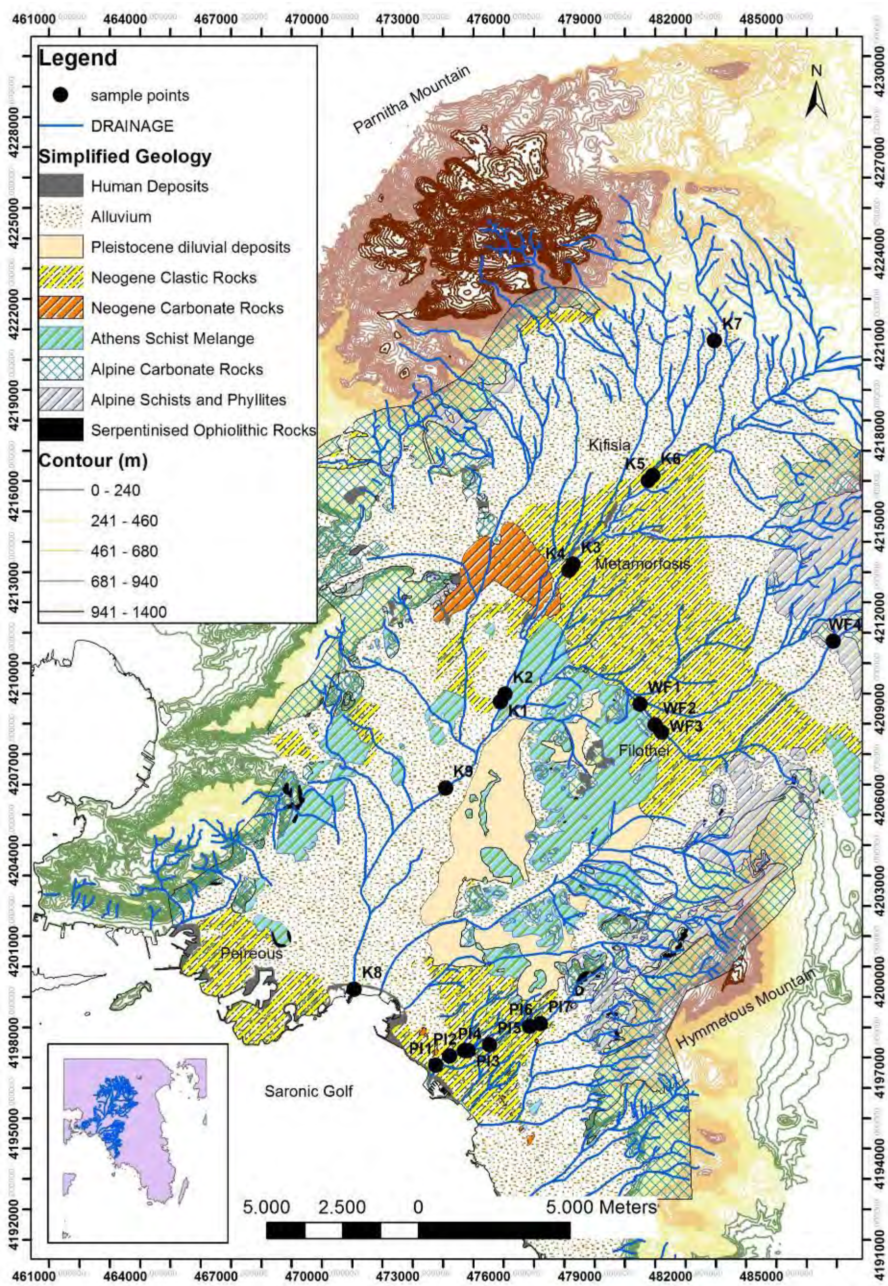

Figure 1 – Location of sampling sites plotted on the simplified geological map of Athens Basin, modified from Papanikolaou et al. 2004a.

until today it has been the recipient of industrial and residential waste, despite numerous legislative protection acts. Many houses and local industries are situated within the 1st class protection zone (A) which is a 50 meter wide zone, along both sides of the river bank.

The Pikrodafni stream is approximately 9.3 km long and is located in the south-western part of the city of Athens. Its drainage basin is around 22.4km^2 and it springs from the western side of Mount Hymettus discharging in the Saronic Gulf (Alimos area). It is considered to be in a better state than the Kifissos River and is one of the few streams of Athens which have been characterized as being of special environmental interest. Around 6.6 km of its length is in its natural state whereas the remaining part is channeled. Pikrodafni has not reached a balanced geomorphological state and is in a continuous state of erosion, as is Kifissos (Papanikolaou et al, 2004b). It also has a continuous, yearlong flow. Despite the fact that there have been attempts for its rehabilitation it is considered to be a degraded natural environment. It is the recipient of local runoff and residential discharge. One of the biggest problems though is the fact that along the river banks there has been uncontrolled and illegal building. Even though the natural habitat has been disrupted various local species of fauna and flora have been reported. The Greek Ornithological association has reported 32 species of birds near the river mouth (2011), which are more than have been reported at the Kifissos River. Out of the reported species, 2 belong in the Greek Red Data Book of threatened species.

The stream of Podoniftis is considered to be a tributary of Kifissos. It is the smallest of the 3 studied streams, since a large part of it runs underground. It springs from the Mountain of Penteli and is then channeled underground until it reaches the area of Filothei in which it runs above ground naturally. Its drainage basin is around 14.3 km^2 and is mainly comprised of carbonate formations which therefore affect the waters chemistry. Podoniftis is considered to be in the best state in comparison to the other 2 streams. The stream has a wide variety of flora and fauna, but there have not been extensive analyses of the species. Characteristic examples of fauna are the frog Rana Ridibunda as well as the nightingale Luscina Magarhynchos. The most characteristic flora species are the Platanus orientalalis, Nerium Oleander and Hedera Helix .

3. Materials and Methods

3.1. Sampling and Analysis of Water

A total of 56 stream water samples were collected from 20 sampling stations covering the 3 streams (Figure 1), 27 of which from Kifissos, 21 from Pikrodafni and 8 from Podoniftis. The samples of Kifissos and Pikrodafni were obtained 3 times during a year long period whereas the samples of Podoniftis twice. All sampling occurred between the period of June 2011 and November 2012. The samples were collected under a wide range of flow conditions, including base and peak flow periods. Water samples were collected in 1L polyethylene sampling bottles which were rinsed 3 times with stream water before collecting the final sample. In situ measurements included parameters such as Total dissolved solids (TDS), Electrical Conductivity, temperature (T), pH and Eh. Samples which were collected for heavy metal analyses were filtered on the site through a plastic syringe fitted with a 0.45μm filter and were acidified using 1ml of nitric acid (HNO_3). They were then refrigerated until analyses were conducted.

Heavy metal (Pb, Mn, Co, Cd, Cr, Cu, Ni, Zn) concentrations were measured by Atomic Absorption Spectrometry (both FAAS and GAAS). Major anion (SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-) concentrations were determined with the use of a HACH DR/4000 spectrophotometer. Total and Ca hardness, from which concentrations of Ca^{2+} and Mg^{2+} were derived, and the bicarbonate anion (HCO_3^-) were measured using the HACH digital titrator, whereas concentrations of K^+ and Na^+ were measured on a flame photometer. All samples which were obtained for the determination of major anion and cation concentrations were unacidified. They were filtered through a 0.45μm filter membrane in the lab and analysed within 24 hours of their collection. All analyses were performed in the Laboratory of Economic Geology and Geochemistry, University of Athens.

3.2. Sampling and Analysis of Active Stream Sediment

Stream sediment samples were collected once from each stream, 8 of which were from Kifissos, 10 from Podoniftis and 4 from Pikrodafni, accounting to a total of 22 samples. The sediment sampling also occurred during the year 2011-2012. Field samples were collected with a shovel and treated appropriately by drying in an air oven at 60 ^oC followed by sieving in order to prepare the laboratory samples of 150 μm. Heavy metals were extracted using a mixture of hot nitric (HNO_3)

and hydrochloric (HCl) acids. The concentrations of Pb, Mn, Co, Cd, Cr, Cu, Ni, Zn and Fe were determined by Flame Atomic Absorption Spectrometry (FAAS). Scanning Electron Microscopy (SEM) analysis was performed on most of the water filters, whereas X-Ray Diffraction (XRD) was used for mineralogical analyses of selected sediment samples.

4. Results and Discussion

4.1. Major Parameters of Water Chemistry

Ranges of values for the major measured parameters in water samples from the three streams are presented in Table 1. Also in Table 1 are given the respective median values from Greece Mainland Rivers (Skoulikidis et al. 2006) for comparison. The latter values are representative of water quality in more 'pristine' environments, away from urban centres, however they belong in the same geological and climatic zone with respect to national spatial scale.

Table 1 - Summary of concentration ranges for major water parameters in the studied streams. Median values of river water from mainland Greece (Skoulikidis et al. 2006) are also given for comparison.

Water Parameter	Pikrodafni	Kifissos	Podoniftis	Median values of Greek mainland rivers
T (^oC)	17-27	8-28	12- 23	12.6
pH	7.7-8.4	7.2-9.0	7.3-8.0	8.2
EC (μS/cm)	790-1260	1.1-1476	770- 1228	294
Ca^{2+} (mg/ L)	90-96	97- 182	68-148	30.4
Mg^{2+} (mg/ L)	23-29	0-16	6-35	6.9
Na^+ (mg/ L)	39-110	27-210	43-111	8.5
K^+ (mg/ L)	5.5-8.2	1.4-23	1.7-7	1.9
HCO_3^- (mg/ L)	248-500	290-453	274-386	128
SO_4^{2-} (mg/ L)	76-121	32-700	60-100	15.8
Cl^- (mg/ L)	46-174	7.4-118	11-191	6.4
NO_3^- (mg/ L)	2-24	1-26	2-48	2.3
PO_4^{3-} (mg/ L)	0.45-8.9	0.31-14.4	0.04-4.50	0.5

These zones have been developed as a part of an integrated national ecological quality assessment and classification system. As expected most of the major parameters in the urban streams water, even when comparing their minimum values, exceed the median values of mainland stream water. Profound differences exist for EC, Na^+, SO_4^{2-} and Cl^-, indicative of urban impact on water quality (Wong et al. 2012). Atmospheric deposition and storm-water runoff in urban environments contains a variety of leached constituents including H_2SO_4, HNO_3, organic matter, trace metals and industrial compounds. Furthermore, the leakage, direct discharge or irrigation of wastewater (even when treated) can degrade water quality by increased concentrations of dissolved ions (e.g. Ca^{2+}, Cl^-, Na^+, SO_4^{2-}), nutrients (e.g. N, P) and pathogenic organisms. With respect to measured nutrient concentrations of NO_3^- and PO_4^{3-}, collected data show a high degree of variability related to seasonal fluctuations as well as presence of point sources along the flow path of the studied streams (Figure 2). When compared to the Nutrient Classification System developed by Skoulikidis et al. (2006), most samples fall within the 'moderate' to 'bad' quality categories.

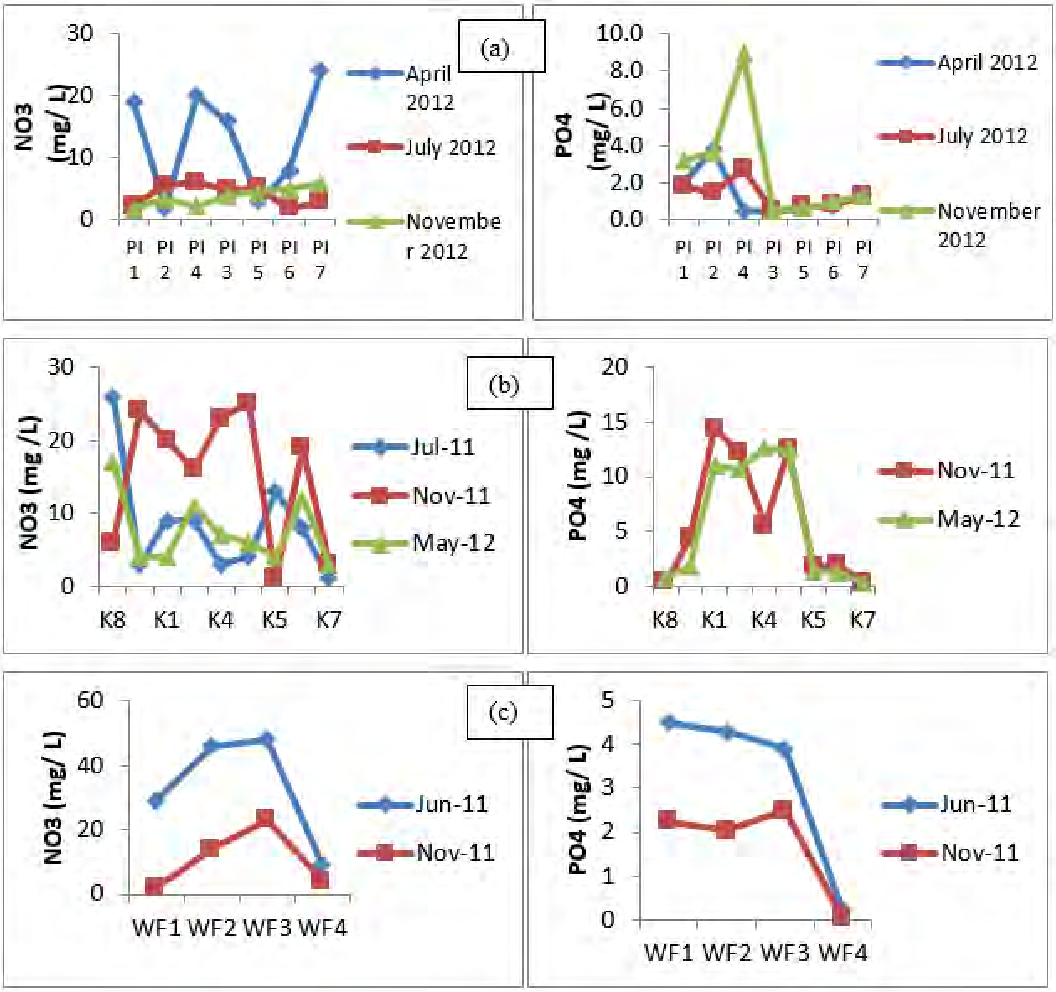

Figure 2 – Variation in NO_3^- and PO_4^{3-} concentrations in water along the studied streams. (a) Pikrodafni, (b) Kifissos, (c) Podoniftis. Data are presented downstream (left) to upstream (right).

Overall concentrations of the measured nutrients in the studied streams showed differences within the same sampling period (March- May 2012) (Figure 3). The highest values of NO_3 were measured in samples from Podoniftis and the lowest in Kifissos, while PO_4 was higher in Kifissos and had minimum values in Pikrodafni. It is noted that this comparison is only indicative considering differences in the spatial extend of sampling along the three streams. Kifisos had the highest concentrations of NO_3^- during the second sampling period (November 2011) in the areas of Kifisia (sampling point K6), Metamorphosis (Sampling points K3,K4) and Nea Halkidona (Sampling point K9). Point sources such as a livestock stable near the sampling area in Kifisia and greenhouse farming near the sampling area in Metamorphosis are the most likely causes of elevated levels of NO_3^-. In the area of Nea Halkidona concentrations were related to the high population density of this region, which had a consequent effect on the urban runoff which feeds into the river. High PO_4^{3-} concentrations were observed in the areas of Metamorphosis and Nea Philadelphia (sampling points K1-K4).This is probably related to the existence of greenhouse farms adjacent to the sampling points which use fertilizers and pesticides, that possibly leak into the river. The abrupt increase in the concentrations of NO_3^- and PO_4^{3-} in sample point WF3 of Podoniftis coincides with the river emerging from its underground channeled bed. The 2 to 4 fold increase in concentrations compared to those observed in the headwaters at Penteli may be explained by unregulated discharges into the river along its underground course. Also worth noting is the significant decrease in concentration of both parameters with distance along the open course of the river through Filothei, probably explained not only by dilution but also by biologically mediated redox reactions taking place in the open air. Anomalous high values in the above mentioned parameters concentrations in Pikrodafni are attributed to point sources along the river course as they are mainly observed at tributaries of minor side inflows.

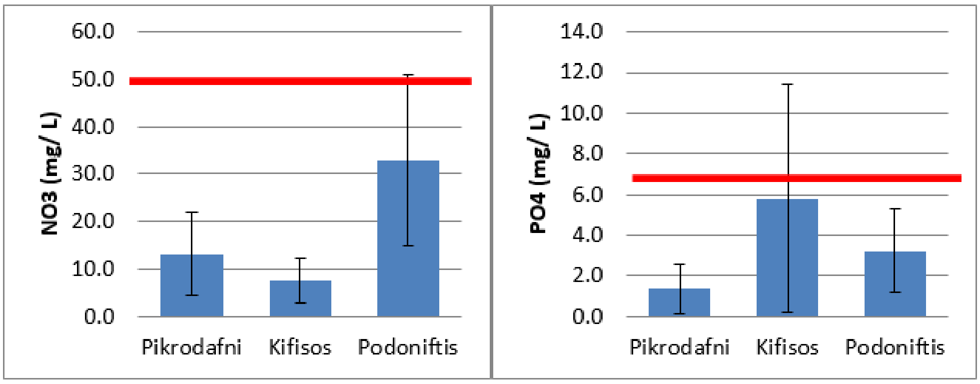

Figure 3 – Comparison of NO_3^- and PO_4^{3-} concentrations in water from the three studied streams during spring 2012. Bars denote one standard deviation. Thick horizontal lines indicate the upper concentration limit in drinking water.

Differences between the studied streams' water quality in terms of major ions were identified by plotting the data on a Piper diagram (Figure 4). Water type derived from this diagram reflects catchment and geological characteristics influencing ion concentrations. Although anthropogenic influence has affected water quality, clustering of water samples in the Piper diagram demonstrates

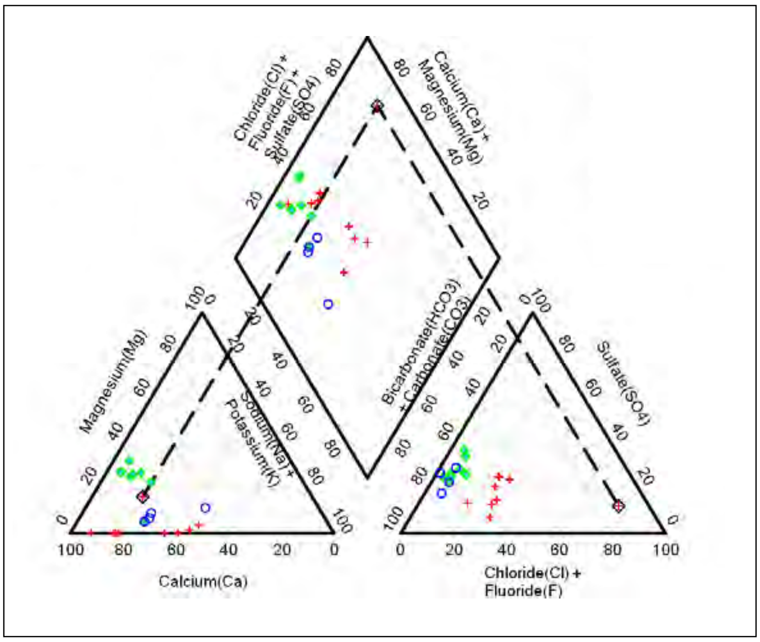

Figure 4 – Piper diagram showing differences in water type between the three studied streams. Crosses denote Kifissos samples, diamonds Pikrodafni samples and open circles Podoniftis samples.

the geological control over some of the major elements, especially Mg which is higher in samples from Pikrodafni mirroring the contribution of Hymettus dolomite marble dissolution in water quality characteristics.

The health of urban waterways is also reflected in their ability to support and maintain a balanced community of organisms of substantial species diversity. Although the study of biological diversity was beyond the scope of this research, some evidence of the streams' ability to support natural habitats was provided by the abundant numbers of diatoms observed by SEM on used water filters (Figure 5). Diatoms have been used as indicators of environmental change in rivers and lakes as several genera respond to eutrophication (Harding and Kelly, 1999; Stevenson and Pan, 1999). Detailed studies of diatom assemblages in rivers and streams can be statistically analysed to establish their relationship to the environmental factors, thus providing valuable data for bioassessment of river health.

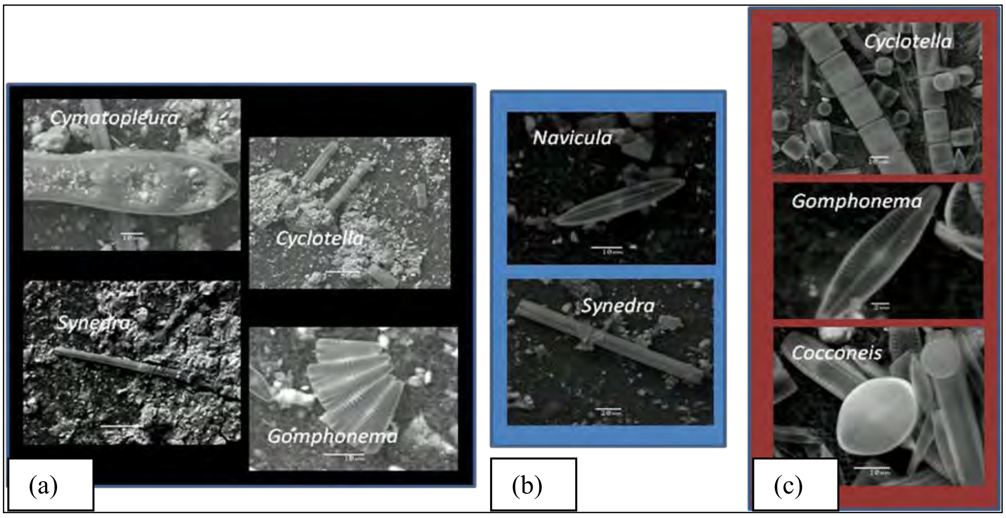

Figure 5 – SEM microphotographs of water filters in backscattered electron mode, showing abundant numbers of diatoms of various genera in the studied streams. (a) Kifissos, (b) Podoniftis, (c) Pikrodafni.

4.2. Heavy Metals in Water and Stream Sediment

Urban runoff can have elevated turbidity and high concentrations of metals such as Cu, Fe, Pb and Zn as a result of erosion from roads, parking lots and buildings. However the most significant source of heavy metals in urban environments is industry (Paul and Meyer, 2001). Measured concentrations of heavy metals in water samples from this study were not significant. Most of the determined parameters were below detection limits for all samples and all sampling periods. The three metals that showed measurable concentrations were Mn, Ni and Cu (Figure 6). From this only Mn in Kifissos samples reached the concentration of 50 μg /L but was near 10 μg /L in the samples from the other two streams. Ranges in concentrations of heavy metals in the stream sediment samples are presented in side by side boxplots in Figure 7.

Concentrations of all metals were within the expected background values and comparable to concentrations measured in urban soils of Athens (Massas et al. 2010). The highest concentrations of all metals were measured in samples from Pikrodafni and maximum concentrations were determined for Mn among all heavy metals. High concentrations of this particular element are probably linked to biogeochemical processes within the streamwater-sediment interface. Data of heavy metal concentrations are also comparable to values reported by Panagiotopoulos et al. (2010) for surficial and sub-surficial sediments obtained from the lower course of the Kifissos

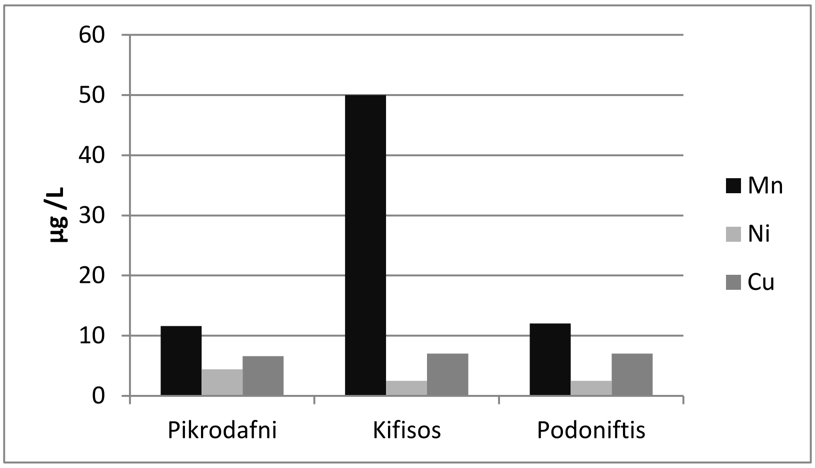

Figure 6 – Comparison of heavy metal concentrations in water samples from the three streams during the spring 2012 sampling campaign.

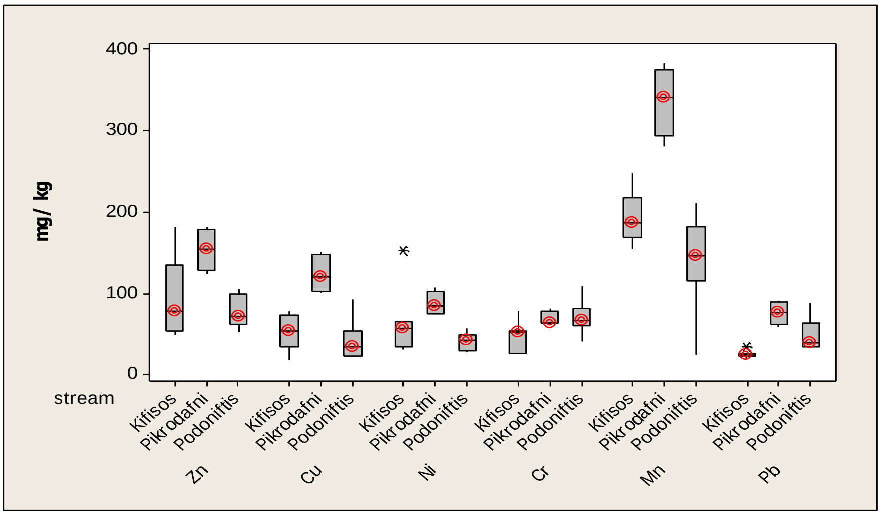

Figure 7– Box plots of heavy metal concentrations in stream sediments showing values within the normal background expected in urban environments.

River. In their study, the calculated enrichment factors for the identified heavy metals, with the baseline taken from a pristine area in the adjacent Saronikos Gulf, were very low. In contrast, the enrichment factors for the measured hydrocarbons were particularly high. This data underscore that the study of pollution in such environments is multicomponent, thus we must reserve judgement about the general quality of the urban stream systems.

5. Conclusions

The geochemistry of three urban streams in Athens was analysed and compared on the basis of major elements and heavy metals content in water and active sediment. Results indicated that rock weathering, rather than atmospheric or pollution influx is the dominant process affecting the major ion geochemistry of stream flow in the urban setting. Water samples from different streams are of a different Ca-Na-HCO_3 type indicating the effect of different lithological types on water chemistry. However, Kifissos and Podoniftis samples had higher nitrate and phosphate concentrations indicating greater influence by anthropogenic activities. Heavy metals in water did not have significant concentrations. Also, heavy metal concentrations in sediment samples were generally low; samples from Pikrodafni showed relatively higher concentrations than the other two streams.

In general the quality characteristics of water and sediment in the study area were found to be in a relatively good state regarding the studied parameters, capable of supporting abundant diatom populations. With appropriate management, the abiotic substrate of the studied streams could provide an opportunity for the evolution of a healthy ecosystem and development of so needed ‘green belts’ within the urban environment of Athens.

6. References

Harding J.P.C. and Kelly M.G. 1999. Recent developments in algal based monitoring in the UK, in: Prygiel et al. (eds) Use of algae for monitoring rivers III, *Agence de l’eau Artois Picardie*, France. Pp 26-34.

Massas I., Ehaliotis, C., Kalivas D. and Panagopoulou, G. 2010. Concentrations and availability indicators of soil heavy metals; the case of children's playgrounds in the city of Athens (Greece), *Water, Air, and Soil Pollution*, 212(1–4), 51–63.

Panagiotopoulos I., Kapsimalis V., Hatzianestis I., Kanellopoulos T.D. and Kyriakidou C. 2010. Environmental status of the metropolitan river (Kifissos) of Athens, Greece, *Environmental Earth Science*, 61, 983-993.

Papanikolaou D.I., Lozio S.G., Soukis K. and Skourtsos E., 2004a. The geological structure of the allochthonous ‘Athens Schists’, *Bulletin of the Geological Society of Greece vol. XXXVI, Proceedings of the 10th International Congress,* Thessaloniki, April 2004, 1550-1559 (in Greek with English abstract).

Papanikolaou D., Bassi E. K., Kranis H. and Danamos G., 2004b. Paleogeographic evolution of the Athens Basin from Upper Miocene to present, *Bulletin of the Geological Society of Greece vol. XXXVI, Proceedings of the 10th International Congress*, Thessaloniki, April 2004, 816-825 (in Greek with English abstract).

Paul M.J. and Meyer J.L. 2001. Streams in the urban landscape. *Annu. Rev. Ecol. Syst.,* 32, 333-365.

Skoulikidis N. Th., Amaxidis Y., Bertahas I., Laschou S. and Gritzalis K.. 2006. Analysis of factors driving stream water composition and synthesis of management tools—A case study on small/medium Greek catchments. *Science of the Total Environment*, 362, 205-241.

Stevenson R.J. and Pan Y. 1999. Assessing environmental conditions in rivers and streams with diatoms, in: Stoermer E.F. and Smol J.P (eds) The Diatoms: Applications for the Environmental and Earth Sciences. *Cambridge University Press*, UK. Pp.334-351.

Wong C. I., Sharp J.M., Hauwert N., Landrum,J. and White K. M. 2012. Impact of urban development on physical and chemical hydrogeology, *Elements*, 8, 429-434.