Hydrogeochemical assessment of groundwater quality in a river delta using multivariate statistical techniques

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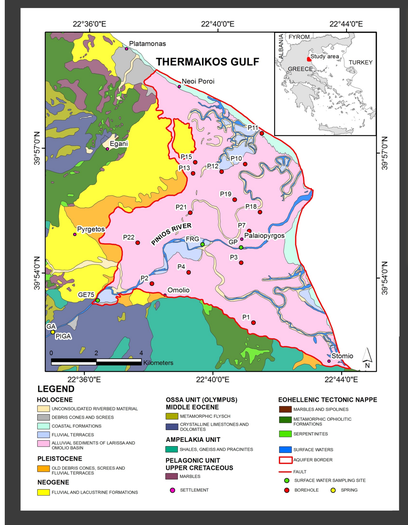
Abstract

The knowledge of the factors controlling the regional groundwater quality regime is important for planning and management of the groundwater resources. This work applies conventional hydrogeochemical and multivariate statistical techniques to identify the main factors and mechanisms controlling the hydrogeochemistry of groundwater in the deltaic environment of River Pinios (Thessaly) as well as possible interactions between groundwater and surface water bodies. Hierarchical Cluster Analysis (HCA) and Principal Components Analysis (PCA) are performed using a data set of physical-chemical parameters from surface water and groundwater sites. The objective of HCA is to group together surface water and groundwater monitoring sites based on similarities in hydrochemistry in order to indicate groundwater-surface water interaction processes. On the other hand, PCA aims at indicating factors responsible for the hydrogeochemical characteristics of the water bodies in the river delta (e.g., water-rock interaction, seawater intrusion, anthropogenic activities).

Introduction



The deltaic plain of Pinios River is located in Central Greece (Thessaly). In this part of the basin, the river flows in a WSW-ENE direction discharging into Thermaikos Gulf. The deltaic plain is mostly occupied by Quaternary alluvial sediments (e.g., sands, clays) which host a shallow groundwater system. The water needs for agricultural purposes are mainly covered by groundwater and river water abstraction.

Objectives

The objective of the present study is to investigate the hydrogeochemical processes and anthropogenic activities that define the quality of the water systems in the study area by applying conventional and multivariate statistical techniques.

The same techniques also helped in the identification of interactions between surface water and groundwater in order to define the conceptual model in the deltaic environment of Pinios River.

Materials and methods

Sampling campaigns were performed between October 2012 and July 2014.
Samples were collected from boreholes (seasonally), surface water sampling sites and springs in and around the deltaic plain of River Pinios.
All samples were filtered by using a Nalgene filtration apparatus and Millipore membrane filters and stored at 4ºC until they were analyzed.
Major ion concentrations were determined in the laboratory of Environmental Chemistry (Faculty of Chemistry, University of Athens, Greece) by using flame emission atomic spectrometry (FAAS, Varian SpectrAA 200), titration (APHA 2012), ion chromatography (Metrohm 820 IC Separator Center, 819 IC Detector) and spectrophotometry (Varian Cary 1E UV-visible spectrophotometer).
Trace element concentrations were measured by means of atomic absorption spectrometry (FAAS Varian SpectrAA 200, Graphite Furnace AAS Varian GTA 100-Zeeman 640Z with autosampler) and Graphite Furnace AAS (Varian GTA 100-Zeeman 640Z).

Results & Discussion

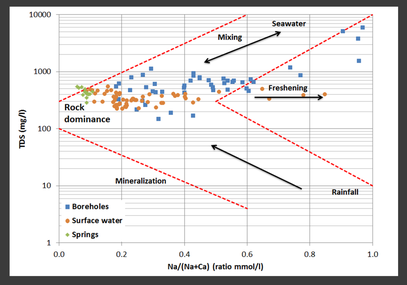
Hydrogeochemical processes

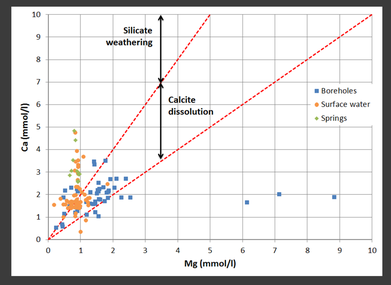
TDS concentrations as a function of the ratio between Na and Na+Ca indicates that the background geology mainly controls groundwater and surface water hydrogeochemistry.

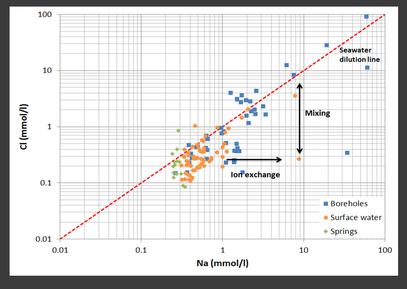
The dissolution of calcite is the main hydrogeochemical process as a result of water-rock interaction. The increased Mg concentration that was recorded in some sampling sites can be attributed to Mg-bearing minerals found in several geological formations (e.g., ophiolites). Silicate weathering is mainly observed in the spring samples.

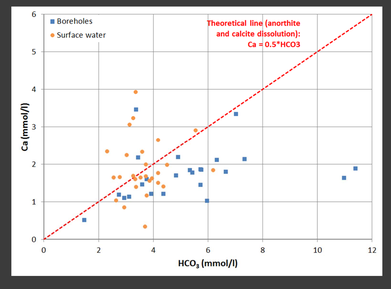
Freshening has affected samples from boreholes and surface water, with some samples reflecting a mixture between seawater and water undergoing some freshening.

Water in several boreholes undergoes some moderate mixing with seawater while in a few cases ion exchange was observed.







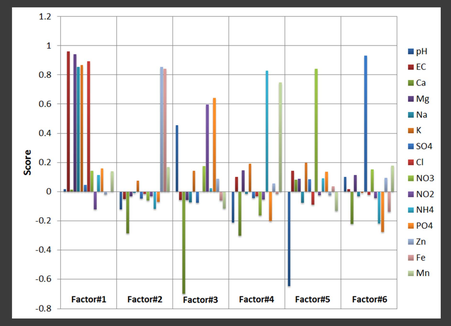


Principal Component Analysis

A data set of fifteen variables (pH, Electrical Conductivity, Ca, Mg, Na, K, Cl, SO_4, NO_3, NO_2, NH_4, PO_4, Zn, Mn, Fe) was used for PCA and aimed at providing insight into the main factors controlling the hydrogeochemical processes in the deltaic plain.

Eigenvalues, percent of variance, cumulative percent of variance for PCA of data set

Factor	Total	% of variance	Cumulative (%)
1	4.321	28.809	28.809
2	1.758	11.722	40.531
3	1.636	10.909	51.439
4	1.310	8.732	60.172
5	1.127	7.513	67.685
6	1.119	7.460	75.144
7	0.856	5.705	80.84
8	0.612	4.082	84.931



Factor #1: Salinity

Factor #2: Rock-water interaction

Factor #3: Agricultural pollution (increased PO_4 and NO_2 concentrations)

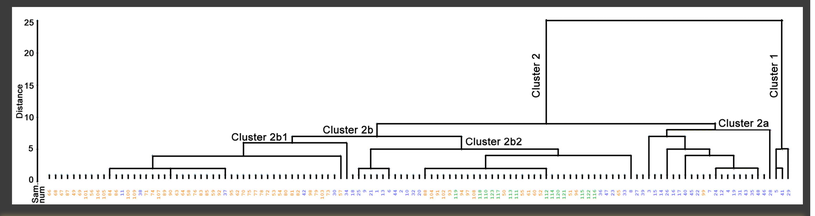
Factor #4: NH_4 contamination

Factor #5: Agricultural pollution (increased NO_3 concentration)

Factor #6: SO_4 contamination

Hierarchical Cluster Analysis

A data set of fifteen variables (pH, Electrical Conductivity, Ca, Mg, Na, K, Cl, SO_4, NO_3, NO_2, NH_4, PO_4, Zn, Mn, Fe) was used for HCA and aimed at classifying the samples into a small number of mutually exclusive groups based on the similarities among the samples. Ward Linkage method and Pearson distance were applied as the measure of similarity and distance between the clusters.



Cluster 1: Groundwater samples from boreholes

Cluster 2b: Mixture of samples from boreholes, surface water, and springs

- **Cluster 2b1: Mainly surface water samples**
- **Cluster 2b2: Mixture of samples from boreholes, surface water, and springs**

Conclusions

The dissolution of carbonate minerals is the main hydrogeochemical process controlling the hydrochemical composition. Silicate weathering is also concluded by the ion ratio processing, while trace elements (e.g., Fe, Mn) are attributed to local dissolution of the trace element bearing minerals inside the alluvial sediments. Multivariate statistical techniques verified the water-rock interaction and revealed that different anthropogenic activities are mainly responsible for N-enrichment in the water samples. Moreover, HCA showed similar chemical characteristics between the water samples from the boreholes, the springs and the surface waters indicating that interaction between the different water bodies is taking place in the plain. The results also revealed that seawater intrusion is of small scale.

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