Identification of hydrologic and geochemical pathways using high frequency sampling, REE aqueous sampling and soil characterization at Koiliaris Critical Zone Observatory

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Abstract

Koiliaris River watershed is a Critical Zone Observatory that represents severely degraded soils due to intensive agricultural activities and biophysical factors. It has typical Mediterranean soils under the imminent threat of desertification which is expected to intensify due to projected climate change. High frequency hydro-chemical monitoring with targeted sampling for Rare Earth Elements (REE) analysis of different water bodies and geochemical characterization of soils were used for the identification of hydrologic and geochemical pathways. The high frequency monitoring of water chemical data highlighted the chemical alterations of water in Koiliaris River during the flash flood events. Soil physical and chemical characterization surveys were used to identify erodibility patterns within the watershed and the influence of soils to surface and ground water chemistry. The methodology presented can be used to identify the impacts of degraded soils to surface and ground water quality as well as in the design of to minimize the impacts of land use practices.

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1. Introduction

Koiliaris River Basin (KRB) is a typical Mediterranean watershed situated in Crete. The total watershed area is 130 km^2 and the main land uses include cropland and pasture (35%), olive and orange groves (32.1%), shrub land and brush land (32.3%) and mixed forest (0.6%). The geology consists of 71.8% Plattenkalk, Tripolis and Trypali units, which are comprised mainly by dolomites, marbles, limestone and re-crystallized limestone with cherts; 9.5% calcaric marls in Neogene formations; 6.1% marls in Neogene formations; 6.1% schists and 6.4% quaternary alluvial deposits (Fytrolakis, 1980, Fassoulas 1999). Soils have been formed from limestone, calcareous marls, metamorphic (phyllites-quartzites) rocks and alluvial sediments. The extended karst of the watershed is comprised of Plattenkalk (dolomite-limestones) and limestones of the Trypali unit, which are thick bedded limestones with extensive karstification (Figure 1). Kourgialas et al. (2010) and Moraetis et al. (2010) have described the watershed hydrology and biogeochemical processes related to oxygen and nitrogen variations in surface waters. The main hydrological feature in KRB is the karstic water supply influenced by snow melt processes that account for 80% of total runoff. Extreme flood events account for the remaining 20% of flow (Kourgialas et al. 2010).

The Koiliaris River watershed is a Critical Zone Observatory that represents severely degraded soils due to intensive agricultural activities and biophysical factors. It represents typical Mediterranean soils under the imminent threat of desertification which is expected to intensify due to projected climate change. Soil degradation in the basin is attributed to water erosion, which is due to conventional tilling methods adopted by farmers and to overgrazing of natural vegetation. De-vegetation and adoption of inappropriate cultivation practices induce soil organic matter losses, making soils more susceptible to erosion and desertification with consequences to biodiversity, biogeochemical processes regulating nutrient cycling, water quality, and agricultural economy. Scientific questions that are being investigated at Koiliaris CZO include:

- How do hydrologic and biogeochemical processes affect water quality?
- What are the impacts of land use practices on soil functions and services?

- Which processes contribute to the resilience of Mediterranean watersheds to environmental factors and anthropogenic activities?

The main objective of this study is the identification of hydrologic and geochemical pathways in a geomorphologically complex watershed in the Mediterranean region by combining high frequency hydro-chemical data with targeted sampling for Rare Earth Elements (REE) analysis of different water bodies and geochemical characterization of soils.

2. Methodology

High frequency data from gauging station R1 (multi-parameter Troll9500 by In Situ Inc.) measuring stage, pH, NO_3-N, water temperature and dissolved oxygen (DO) were used for the hydrologic analysis of KRB (Moraetis et al. 2010). Meteorological data from meteorological stations M1, M2 were also used (Figure 1). Water quality monitoring was performed at monthly intervals and included both surface (springs S1-S4 and river R1-R2) and ground (G1-G4 stations) water sampling (Figure 1). Samples were analyzed for pH, DO, electrical conductivity (EC) and redox potential (E_h) in the field. In addition, NO_3-N, NO_2-N, NH_4^+-N, total Kjeldahl nitrogen (TKN), phosphate, chloride, Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) were measured in the laboratory. The chemical parameters were measured colorimetrically with a DR2010 (HACH) spectrophotometer, with the exception of TOC, which was assessed with a Total Carbon Analyzer TOC-5050A. REE analysis was carried out with ICP-MS (ICP-MS-Agilent 7500-CX) according to Jarvis and Jarvis (1985). Thirty two soil samples were analyzed for soil physical (pH, conductivity and particle size distribution) and chemical properties. Organic carbon (TOC) was measured using the Walkley-Black acid dichromate digestion technique (Walkley, 1946) and TKN using Kjeldahl digestion. Macro-aggregate content and mean weight diameter of grains (MWD) were also measured (Elliott 1986).

3. Results and Discussion

The basic hydrological features are the karstic water supply (R1) from Stylos spring (S2) and the Keramianos ephemeral tributary R2 (Figure 1). The Keramianos tributary drains a small sub-catchment that generates surface runoff due to the schist geologic formation. The tributary then enters a karstic gorge (aligned with a fault line) where major transmission losses occur. Flash floods pass through the gorge several times a year and contribute about 20% of the total runoff, altering the hydrologic and geochemical features of the R1 gauging station (Moraetis et al. 2010).

Figure 2a presents a flash flood event (24/1/10) where the runoff in R1 increased from 20 m^3/s to 50 m^3/s within 5 hours. This flash flood was consistent with rainfall recordings of stations M1 and M2. The contribution of Keramianos increased both the EC and the concentration of NO3-N (4-fold increase). Figure 2b presents another hydrograph (24/2/10) where the flow increased from 12 to 16 m^3/s. The increase in flow was not associated with a significant rainfall event based on the records in both meteorological stations, while the EC decreased and the concentration of N-NO_3 was maintained constant. The increase in temperature, from 13.2 ^oC to 18.2 ^oC, the previous two days suggests that flow changes were caused by snow melt which is in accordance with the changes in its chemical composition.

The hydrologic pathways suggested by the high frequency sampling can be corroborated by monthly sampling of the surface and ground water bodies within the watershed for basic anion and cation composition and REE. Figure 3 presents typical REE composition from four sampling points that correspond to different soil types and geologic features. The results were normalized to shales composition NASC (Gromet et al. 1984). The REE analysis revealed a Eu positive anomaly suggesting that the water is related with hydrothermal solutions or diagenetic environments (Siby et al. 2008, MacRae et al. 1992) rather than marine sedimentation. On the other hand, the Ce negative anomaly observed mainly in gauging station (R1) and Stylos spring (S2) is related to marine sedimentation environment (limestones) (Sholkovitz 1994). Moreover, earlier work (Kourgialas et al. 2010; Moraetis et al. 2010) identified two karstic reservoirs, one upper with fast discharge (very karstified limestones-Trypalis, Tripolis units) and one lower with slow discharge (bedded limestones-Plattenkalk). The Plattekalk limestones (lower karstic reservoir) have been through intense diagenesis (Seidel et al. 1982) and that explains the Eu positive anomaly. According to Figure 3 the water bodies from different areas of Koiliaris watershed have common origin, which is the lower karstic reservoir.

The average water chemistry and a Piper diagram are shown in Figure 1s and Figure 2s, respectively (supplementary information). The Piper diagram identified two groups of samples, group A (S1, R1, G3, S3) and group B (S2, R2, G2, G3) with different characteristics. Group B exhibited higher variability in most of the chemical parameters (N-NO_3, E.C., SO_4, hardness) compared to group A (Figure 1s-boxplots). Zourbos spring S4 was differentiated from the other sampling stations due to marine influences (high chloride and high conductivity). Nitrogen-nitrate concentration in G2, R2, S2 and G3 (group B) were much higher compared to group A (S1, R1, G1, G4). Analogous observations can be made in Figure 1s, for hardness and chloride concentrations. Group B samples were comprised of shallow wells (well G3 and G2), an ephemeral river (Keramianos ephemeral river, R2) and one spring (Katoxori spring, S2), where most of the soils are agricultural soils and grazing lands (Table 1). These results are consistent with the high frequency data and can be used for the apportionment of the mass fluxes from the different geochemical environments.

Finally, soil physical and chemical characterization surveys were used to identify erodibility patterns within the watershed and the influence of soils to surface and ground water chemistry. Three different geo-environments identified in Koiliaris watershed according to soil parent material, altitude, and soil type (Table 1). Geo-environments 1, 2, and 3 are related to soil types of calcaric lithosol, calcaric regosols and eutric lithosols, respectively. A comparison of soil parameters for uncultivated and cultivated soils from the three geo-environments revealed that soils calcaric lithosols and regosols have significantly higher total organic carbon (TOC), total Kjeldahl nitrogen (TKN), macro-aggregates content, and mean weight diameter of grains (MWD) than eutric lithosols (found in the sub-catchment of Keramianos tributary). Similarly, uncultivated soils had higher values in the above parameters than cultivated ones indicating the impacts of cultivation to soil quality. The erodibility of eutric lithosols was found to be significant and affects the surface and ground water quality as indicated by previous measurements (Figure 1s and 2s).

4. Conclusions

Diverse hydrologic and geochemical data such as high frequency hydro-chemical data with targeted sampling for Rare Earth Elements (REE) analysis of different water bodies and geochemical characterization of soils were used for the identification of hydrologic and geochemical pathways. The methodology presented in this study is an important tool for the identification of interrelationships of hydrological pathways and soil were processes with highly variable time scales operate concurrently. REE analysis can be used for the identification of the origin of water bodies within the watershed. The high frequency monitoring of water chemical data highlighted the chemical alterations of water in Koiliaris River during the flash flood events. Targeted water quality sampling together with soil characterization can be used to identify the impacts of degraded soils to surface and ground water quality. This type of information can be used in the design of a program of measures that would improve the quality of water and minimize the impacts of land use practices within the watershed (Figure 1s and Figure 2s).

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Table 1. Description of geo-environments in Koiliaris-CZO including geology, soil cover land use and soil data.

	Geo-environment #1		Geo-environment #2		Geo-environment #3	
Soil parent material	Limestones (Plattenkalk and Trypalis units)		Alluvial formations and Neogene formations (Marls and Calcaric Marls)		Schists	
Geomorphology and soil Type	mountainous/ semi-mountainous Calcaric Lithosols		semi-mountainous/ Lowland Calcaric Regosols		semi-mountainous Eutric Lithosols	
Mineralogy of parent material	calcite and dolomites and intercalations of quartz, minor muscovite		calcite, quartz, illite, kaolinite		quartz, chlorite, muscovite, illite	
Main crops	olive trees		Olive, citrus and vegetables		olive trees	
Animals, No	6510		68330		15374	
Water sampling sites	Karstic aquifer (S1, G1, G4)		Sedimentary aquifer (S3, S4, G2)		Negligible water potential (G3, S2)	
Main surface water bodies	Koiliaris River (R1)		Koiliaris River (R1)		Keramianos tributary (R2)	
	Uncultivated soils	**Cultivated soils**	**Uncultivated soils**	**Cultivated soils**	**Uncultivated soils**	**Cultivated soils**
Dry Bulk Density (g/cm^3)	0.99	1.08	1.14	1.13	1.14	1.17
pH	7.49	7.46	7.65	7.58	6.01	6.27
TOC (%)	4.33	2.07	2.68	2.08	1.37	1.42
TKN (%)	0.40	0.25	0.28	0.23	0.08	0.11
C/N	10.8	9.1	9.6	9.1	16.6	13.9
Macroaggregates (g/100 g soil)	76.4	59.7	62.6	51.7	24.9	26.7
MWD	2.85	2.68	2.33	1.79	1.68	1.65

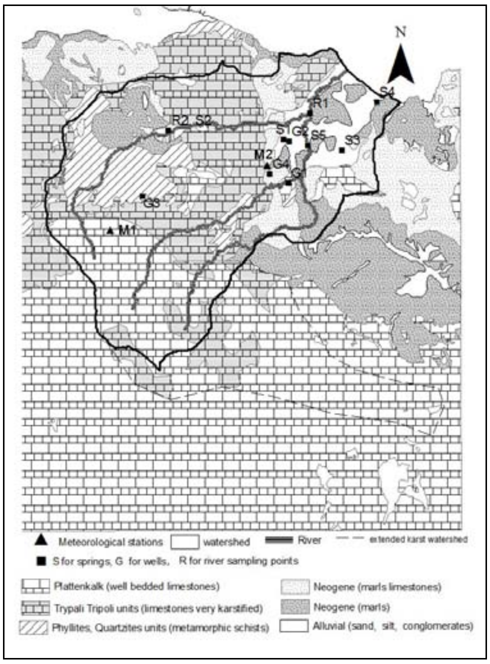

Figure 1 Geological setting of Koiliaris River basin. Sampling points S1, S2, S3, S4, G1, G2, G3, G4, R1, and R2 (where S denotes spring, G ground water well and R river sampling points) and meteorological stations (M1, M2). S1 spring supplies Koiliaris main stream R1 (gauging station). R2 is an ephemeral river supplying water during flood events.

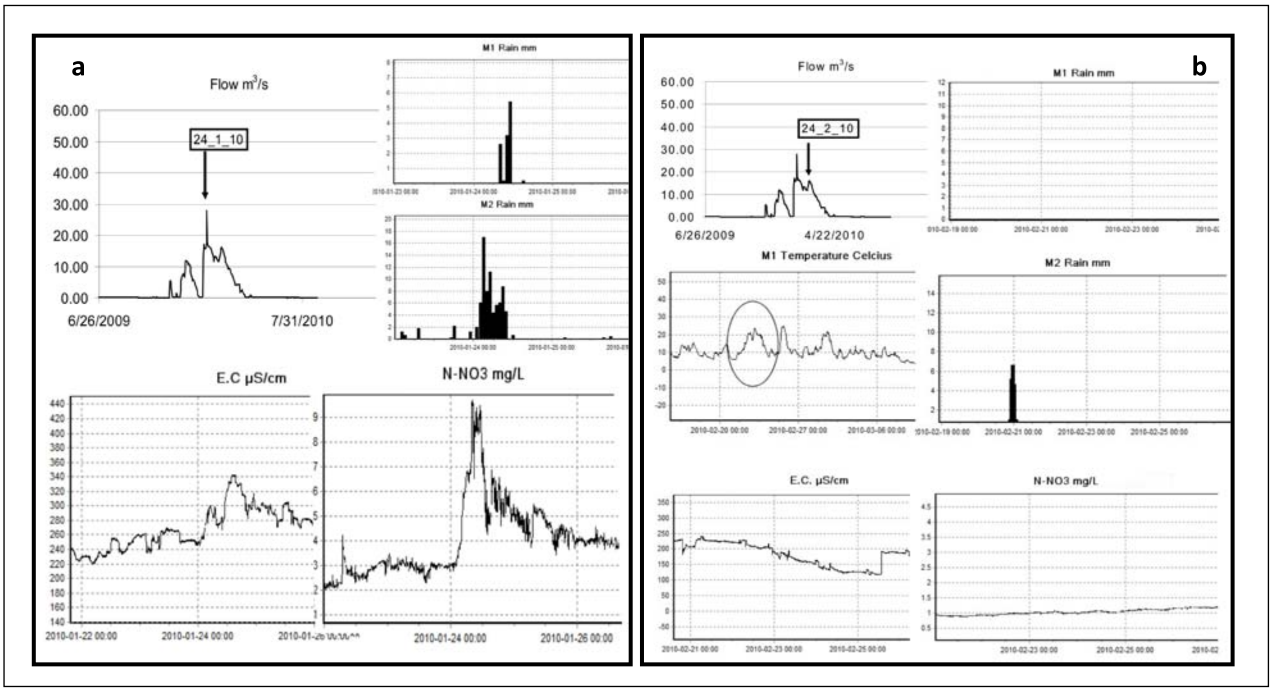

Figure 2. a. Flood event in 24/1/10 recorded from gauging station R1 and meteorological stations M1 and M2 (rain), R1 data include N-NO3 concentration, electrical conductivity (E.C.) and flow. b. Flow peak in 24/2/10 recorded from gauging station R1 and meteorological stations M1 and M2 (rain), N-NO3 concentration, electrical conductivity (E.C.) and temperature from M1 station are shown.

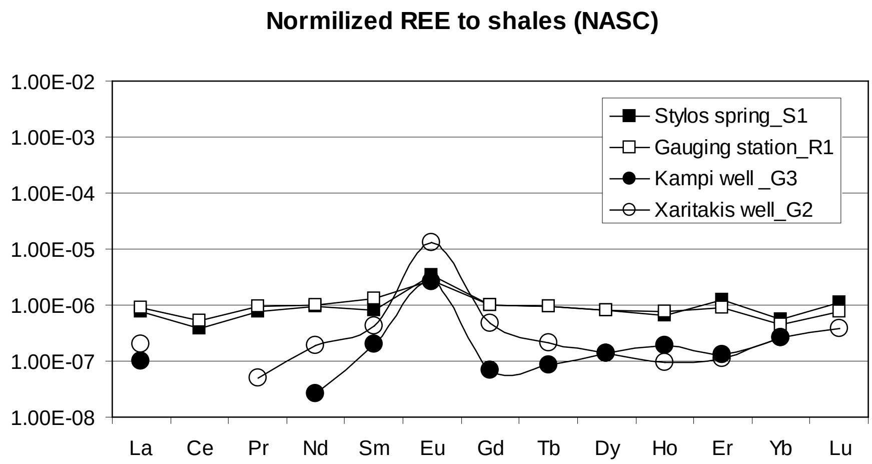

Figure 3. REE analysis in 4 water samples from the November 2010 sampling campaign.