

Variation of the Chemical and Physical Parameters of the Groundwater in Central Thessaly (Trikala; Greece) as a Function of Geographical Areas and Season Periods in the Last Four Years

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ABSTRACT— *In the present study the groundwater quality was assessed on the basis of physical and chemical analysis [(electric conductivity, pH, nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺)] for the period 2009–2012. The study included two samplings at two different regions (flat and semi-mountainous) during summer and autumn for each year. In addition, a detailed quantitative study between each year, the different season period and geographical region was performed by comparing the nitrate concentrations, the electric conductivity and the pH values. From this detailed analysis of the results, a general outcome is that there are significant differences on the quality of water among the sample areas studied.*

Keywords— water, Greece, Thessaly, nitrate, nitrite

1. INTRODUCTION

Since that ground water comprises the source of drinking water for many people worldwide, particularly in rural regions, the ground water pollution arises as a global concern throughout the scientific community and environmental organizations.[1] Drinking contaminated groundwater can have serious health effects. Diseases such as hepatitis and dysentery may be caused by contamination from septic tank waste.[2] Poisoning may be caused by toxins that have leached into well water supplies. Wildlife can also be harmed by contaminated groundwater.[3] Other long term effects such as certain types of cancer may also result from exposure to polluted water.[4]

From the various sources of contaminations (landfills and hazardous waste facilities, agriculture, mining, above ground and underground storage tanks, septic systems, oil- gas and industrial injection wells), agriculture is considered one of the main non-point sources of ground water pollution by contributing many pollutants to the environment such as phosphates, herbicides, pesticides, nitrates and bacteria.[5] Nitrates and pesticides are common contaminants of groundwater derived from agriculture because the nitrogen from fertilizers, manure, waste and ammonia turns into nitrite and nitrate.[6] High levels of these toxins deplete waters of oxygen. Therefore, the introduction of several legislations or directives on the excessive use of chemicals and fertilizers has been regulated in different countries.[7]

The aim of the current study is the determination of physical (electric conductivity (EC), pH) and chemical (nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺)) parameters of ground water in flat and semi-mountainous areas in the region of north and west Thessaly (a periphery in central Greece). In more details, the research objectives of this work are focusing in the following criteria: (i) to evaluate spatial (semi-mountainous and flat regions) and seasonal trends in the samples that were analyzed and (ii) to compare data with water criteria and identify environmental pressures according to the altitude and during the year. Finally, it should be noted that the intention of this work was never to assess the quality

of ground water in central Greece [8], since for such an assessment many more parameters should have been analyzed and specifically organic compounds and microbiological components [9].

1.2 Study Area and Environmental Data

Thessaly is in the central section of mainland Greece. It consists of four prefectures: Karditsa, Larisa, Magnisia and Trikala, and is comprised of mountainous, semi-mountainous and flat regions. The total area of Thessaly is about 14,036 km² and represents the 11% of the total area of Greek territory. The north and west central Greece comprises of 5,952 km². The mountainous region reaches 2800m high from sea level and is about one third of whole east and west central Greece. The semi-mountainous region reaches 800m high and comprises another one third, while flat region reaches 50 – 100m from the sea level (Figure 1). As far as the climate is concerned, the winters are cold and the summers are hot with a significant temperature difference between the two seasons. At the north and west central Greece the climate is similar Mediterranean. In winters, significant amounts of snow are received by the mountainous areas, while summers are very hot and very dry, with temperatures that reach 40°C. Mean annual precipitation varies between 500mm up to 1850mm at the western mountainous peaks. Generally, rainfall is rare from June to August.



Figure 1: Map of Thessaly (Greece), with the sampling area of the preliminary study

At present, the water Authority of Greece use several mineral springs and wells, as the water requirements constantly increase. Moreover, private owners in semi-mountainous and flat regions of Thessaly also operate several groundwater wells in order to use it for irrigation or even as drinking water. Depth of the wells varies between 25m (minimum) and 200m (maximum), with an average of 80m. However, Thessaly plain comprises the most intensively cultivated and productive agricultural regions of Greece. The main crops cultivated in plain are cotton, wheat and maize while at the foothills (semi mountainous regions) other type of products such as apple, cherry, chestnut and olive trees and grapes are also cultivated.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and Instrumentation

The ground water samples were taken from different regions of east and west central Thessaly in Greece. The samples were received directly from the springs or the drilling during the years 2009, 2010, 2011 and 2012. The sampling occurred two times in each year and the antiseptic glass containers which were used for the collection of the water samples were delivered to the laboratory within 2h. The examined samples are represented in Tables 1 and 2.

The parameters of water quality that investigated were according to the methods given in Standard Methods (APHA, AWWA, WPCF, 21st edition, 2005). Nitrate (NO₃⁻), nitrite (NO₂⁻) and ammonium (NH₄⁺) concentrations were measured by a UV-VIS spectrophotometer (DR 5000, Hach Lange, s.n. 1191850), while the pH and electric conductivity

measurements were carried out by a portable pH meter (HQ11d Hach Lange, s.n. 0629722560002) and a conductivity meter (WTW InolabCond 720, s.n. 08070467), respectively.

The drilling was performed for about 15 minutes before a 1L volume of water was collected in antiseptic glass bottle. After being filled with water, the bottles were sealed with screw caps lined with aluminum foil. The bottles were stored in an ice-cooler at 4°C, reaching the laboratory on the same day. Analyses were carried out as soon as the samples reached the laboratory unless otherwise stated.

2.2 Methods

2.2.1 Measurement of pH

Measurement of pH is one of the most important and frequently used tests in analytical chemistry. The pH meter that has been used is accurate and reproducible to 0.01 pH unit with a range of 0 to 14 and equipped with a temperature – compensation adjustment. The method that is used is given in Standard Methods for the Examination of Water and Wastewater, 21st Edition by APHA – AWWA – WEF 2005 as 4500 – H⁺. [10]

2.2.2. Measurement of NO₃⁻

The measurement of nitrates is given in Standard Methods for the Examination of Water and Wastewater, 21st Edition by APHA – AWWA – WEF 2005 as 4500 – NO₃⁻ B. [10] A standard curve has been prepared by the measurement of the absorption of NO₃⁻ of different concentrations varying from 0.05 mg/L to 7 mg/L. Before the measurement of each sample, the validation of the curve has been performed by measuring the absorption of a standard solution (7 mg/L), whereas the checking of the curvature of the curve is performed by measuring the absorption of a standard solution (4 mg/L). The conduct of the sample includes the following procedure: 1 mL of HCl is being diluted in 50mL of the water sample at room temperature and the solution is being shaken up for 1 min.

2.2.3 Measurement of NO₂⁻

Nitrite values can be obtained by the automated method given in Standard Methods for the Examination of Water and Wastewater, 21st Edition by APHA – AWWA – WEF 2005 as 4500 – NO₂⁻ B. [10] where the colorimetric method that is used is suitable for concentrations of 5 to 1000 µg/L N – NO₂.

A standard curve is prepared by plotting absorbance of standards against nitrite – nitrogen (NO₂⁻ - N) concentration before the samples are measured. If the sample contains suspended solids, is being filtered through a 0.45 µm pore – diameter membrane filter. The pH of the sample is being adjusted between 5 to 9 with 1N hydrochloric acid (HCl) or ammonium hydroxide (NH₄OH). To 50.0 mL of the sample, or to portion diluted to 50.0 mL, 2 mL of color reagent is added and the solution is being shaken up. The color reagent that is used is prepared as followed: 8.5% H₃PO₄, 1% soulfanylamide and 1% N-(1-naphthyl)-ethylenediamine dihydrochloride. Between 10 min and 2 h after the addition of the color reagent to samples and standards, the absorbance is measured at 543 nm.

2.2.4 Measurement of NH₄⁺

The measurement of ammonium is given in Standard Methods for the Examination of Water and Wastewater, 18st Edition by APHA – AWWA – WEF 1992 as 4500 – NH₃ C. [11]

The direct nesslerization is a method that is indicated for purified drinking waters, natural water and highly purified wastewater effluents, all of which should be low in color and have ammonia – nitrogen (NH₃ – N) concentrations exceeding 20 µg/L. The samples from the drillings that were examined are colorless and have very low concentrations in NH₃ – N.

50.0 mL sample or a portion diluted to 50.0 mL with water was used for the measurement. Since the non-distilled portion contains sufficient concentrations of calcium, magnesium, or other ions that produce turbidity or precipitate with nessler reagent, 1 mL EDTA reagent or 1 to 2 drops Rochelle salt solution is added and mixed well. 2 mL nessler reagent is added and the samples are mixed thoroughly, left for at least 10 min so as the reaction to take place and the absorption is measured at 450 nm in 1-cm light path. A calibration curve is prepared at the same temperature and reaction time used for samples. The absorbance of the sample is measured against a blank reagent and parallel checks are run frequently against standards in the nitrogen range of the samples.

2.2.5 Electric Conductivity

Electric conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility and valence; on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all. In the International System of Units (SI),

conductivity is reported as millisiemens (mS) per centimeter (cm), since the electrode surface area (A) is 1 cm² and the distance between the electrodes is 1cm. The method that is used is given in Standard Methods for the Examination of Water and Wastewater, 21st Edition by APHA – AWWA – WEF 2005 as 2510 B .[10]

Absolute conductance values of standard potassium chloride solution (KCl 0.0100M) have been measured before the sample, in order to calibrate the instrument. The standard reference solution has a conductivity of 1412 mS/cm at 25°C. The cell is thoroughly rinsed with one or more portions of sample, the temperature of the final portion is adjusted to about 25°C and the sample conductivity is measured.

3. RESULTS AND DISCUSSION

Tables 1 and 2 present the measured data of all the examined chemical and physical parameters in flat regions and in semi-mountainous regions, respectively during the study period.

Table 1: Chemical and physical parameters determined in flat regions

Table 2: Chemical and physical parameters determined in semi-mountainous regions

Statistical processing of the nitrate concentrations, electric conductivity and pH in the flat regions in the years 2009, 2010, 2011 and 2012 are depicted on Figures 2-4.

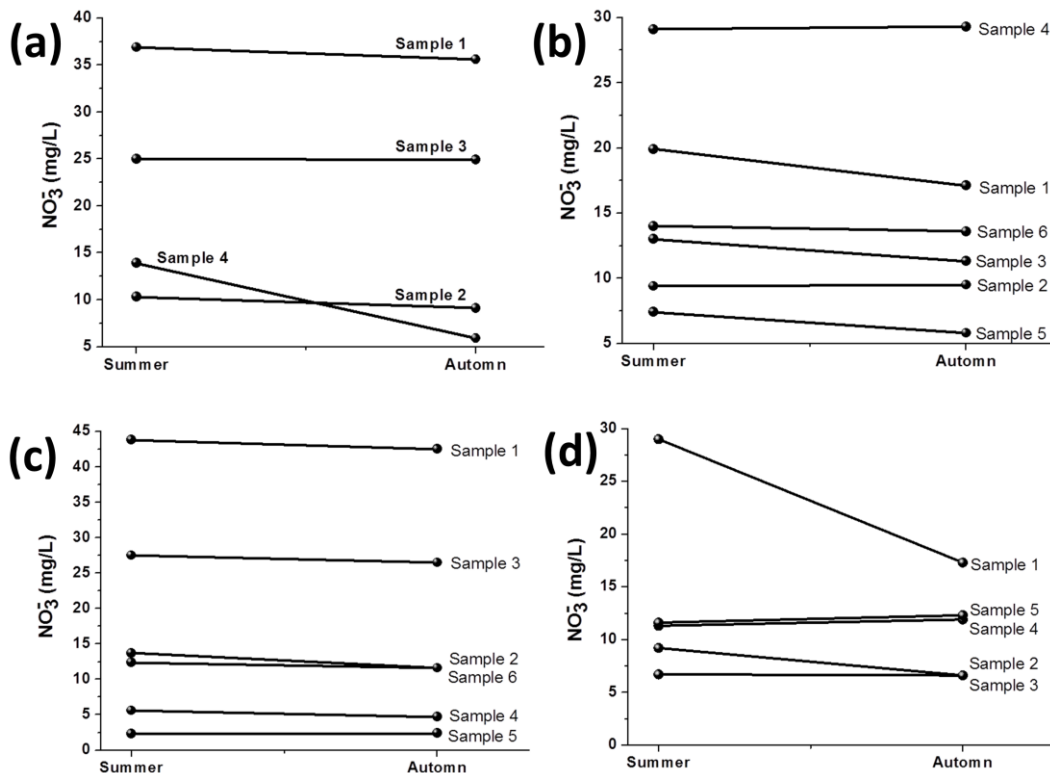


Figure 2: Nitrate concentrations deviations at the summer and autumn of (a) 2009, (b) 2010, (c) 2011 and (d) 2012 in the flat regions

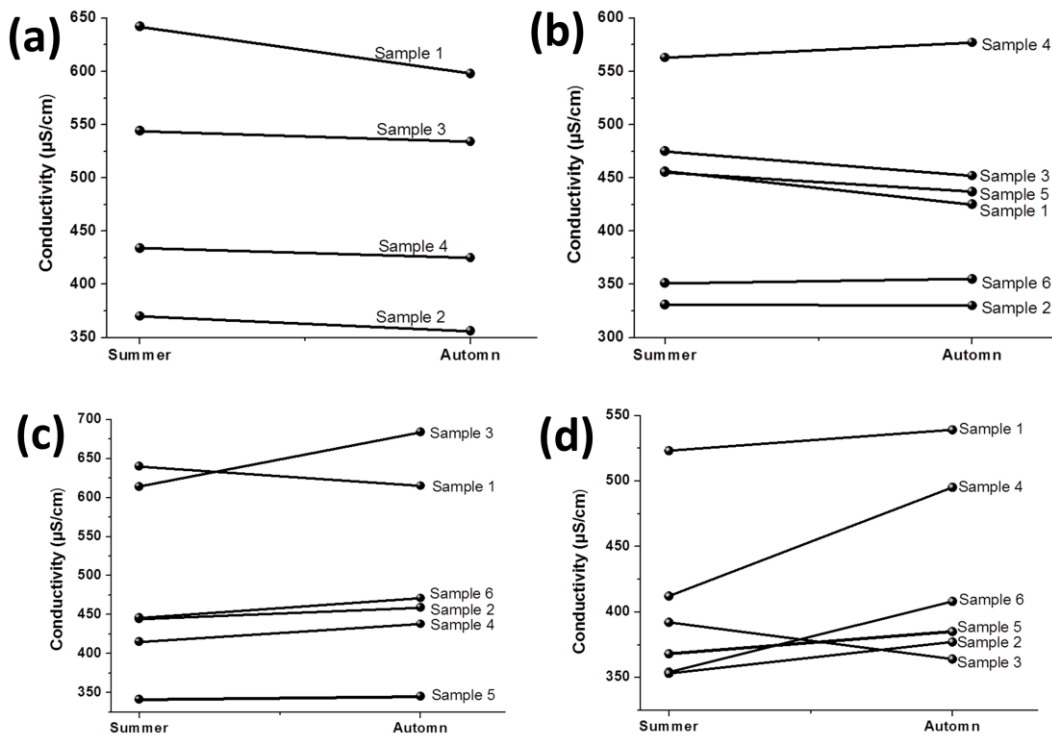


Figure 3: Electric conductivity deviations at the summer and autumn of (a) 2009, (b) 2010, (c) 2011 and (d) 2012 in the flat regions

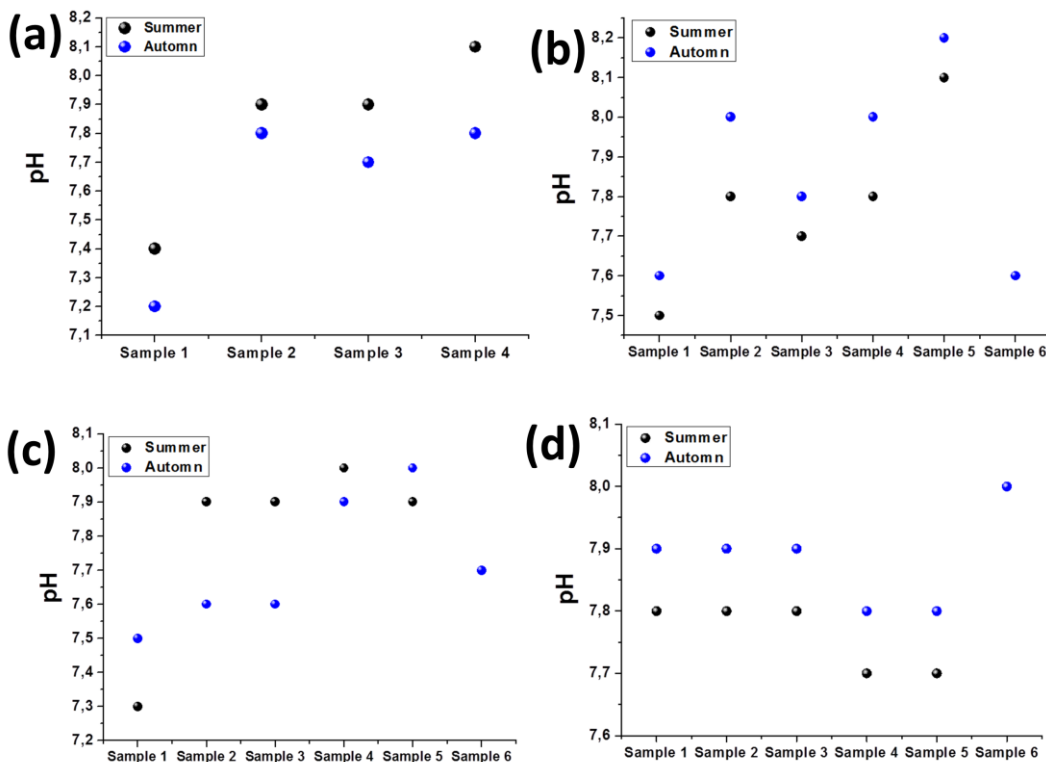


Figure 4: pH deviations at the summer and autumn of (a) 2009, (b) 2010, (c) 2011 and (d) 2012 in the flat regions

As shown on Figure 2, the nitrate concentration is mainly decreased by passing from summer to autumn in all years. However, the electric conductivity shows another trend. While the electric conductivity in all samples decreases from the summer of 2009 to the autumn of 2009, 50% of the samples in the autumn of 2010 exhibit increased electric conductivity

as compared to those of summer 2010 and finally the majority of the samples in the autumn of 2011 and 2012 reveal increased electric conductivity than those of summer 2011 and 2012 (Figure 3). Furthermore, pH demonstrates different behavior than that of nitrate concentration and electric conductivity. The pH for the summer of 2009 is in all samples higher than that of autumn. In contrast, the pH for the majority of the samples in the summer of 2010 and 2012 is lower as compared to those in the autumn, whereas 50% of the samples in the summer of 2011 display higher pH than that in the autumn (Figure 4).

Similar statistical processing of the nitrate concentrations, electric conductivity and pH in the semi-mountainous regions in the years 2009, 2010, 2011 and 2012 has been also performed and presented on Figures 5-7.

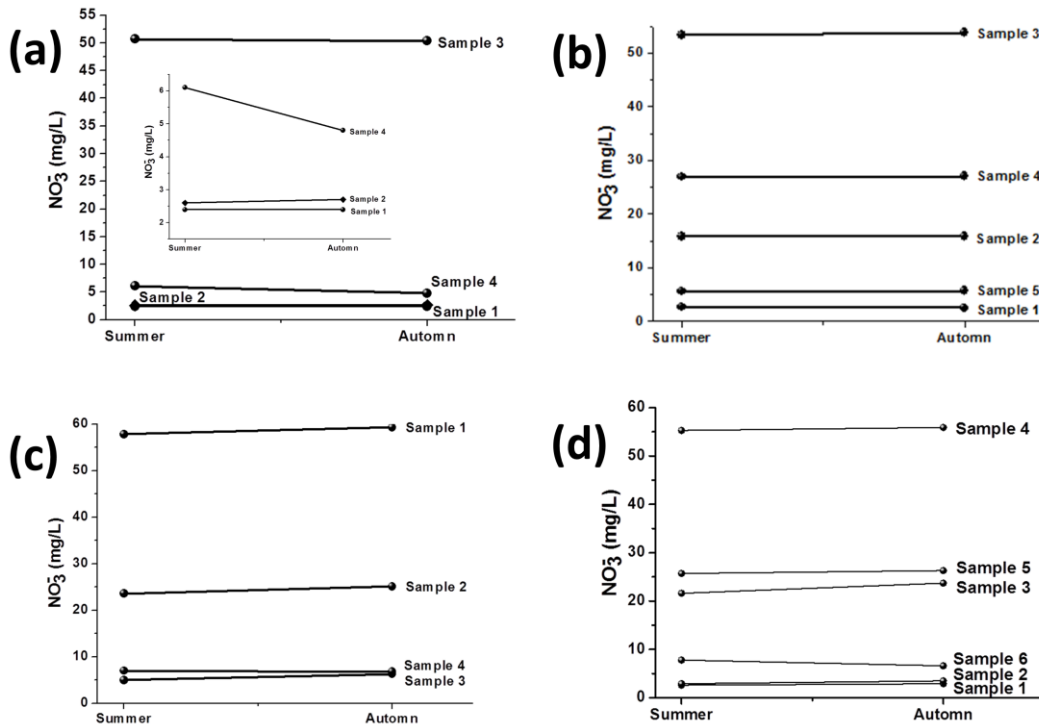


Figure 5: Nitrate concentrations deviations at the summer and autumn of (a) 2009, (b) 2010, (c) 2011 and (d) 2012 in the semi-mountainous regions

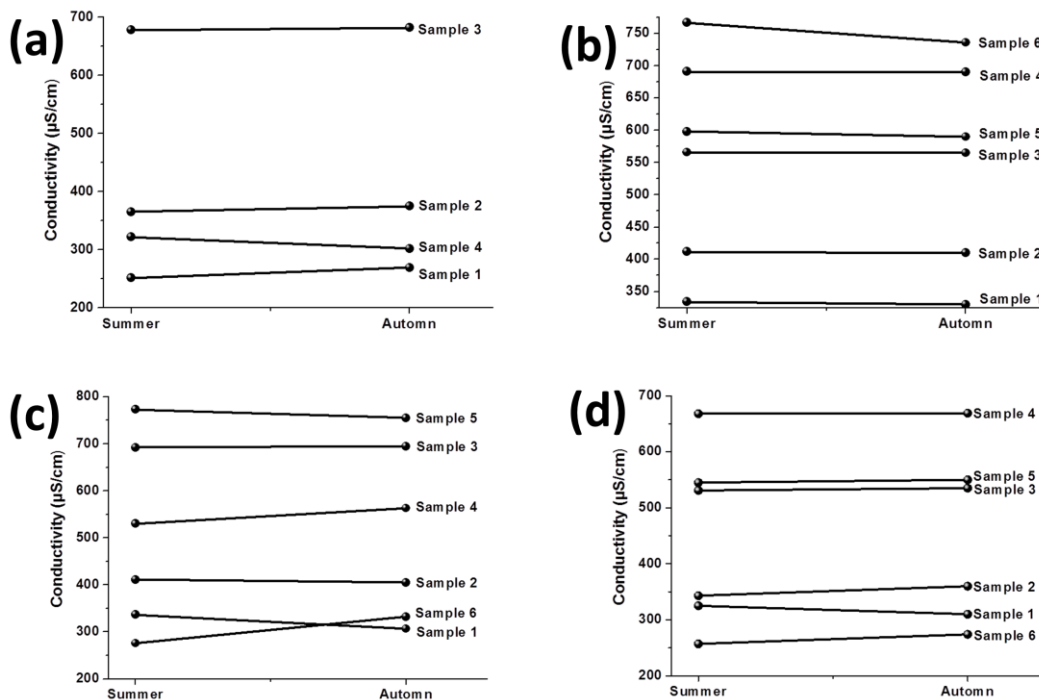


Figure 6: Electric conductivity deviations at the summer and autumn of (a) 2009, (b) 2010, (c) 2011 and (d) 2012 in the semi-mountainous regions

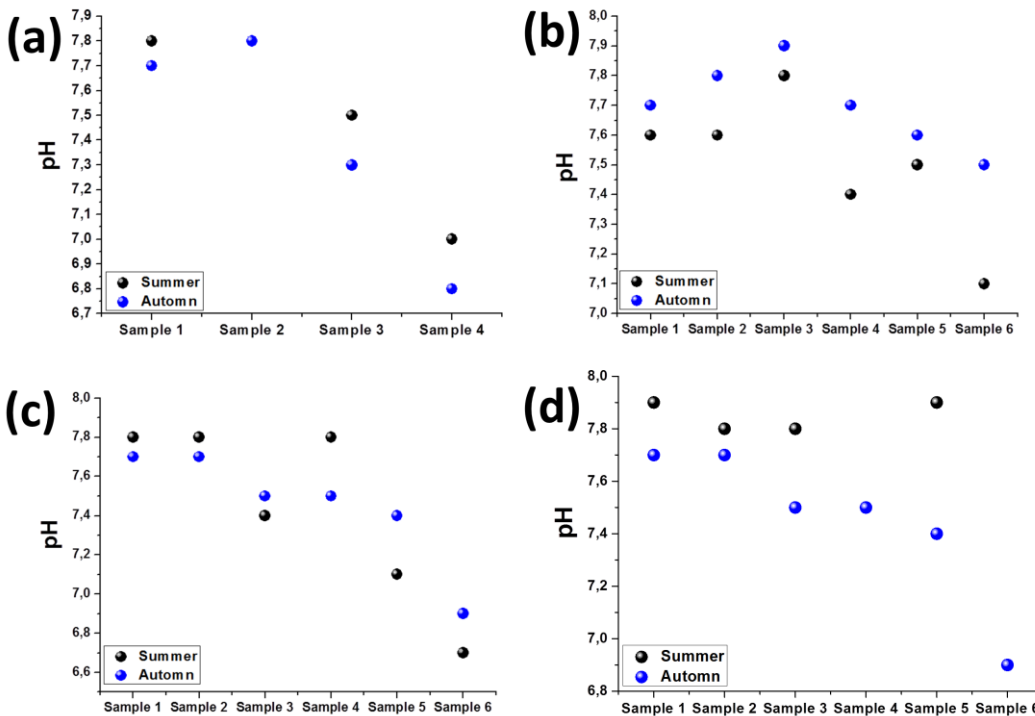


Figure 7: pH deviations at the summer and autumn of (a) 2009, (b) 2010, (c) 2011 and (d) 2012 in the semi-mountainous regions

Exploring the results of the year 2009 for the semi-mountainous regions, it is observed that no special trend can be concluded concerning the variation of the nitrate concentration (Figure 5a) however the majority of the samples exhibit increased electrical conductivity in the autumn (Figure 6a) and pH in the summer (Figure 7a). Comparing these results with those from the flat areas in the year 2009, it is evident that although the pH values are higher in the summer for both regions (flat and semi-mountainous), the electric conductivity values in the flat areas are higher in the summer, while in the semi-mountainous regions are higher in the autumn. Moreover, despite the fact that the 50% of the samples in the year 2010 reveal increased nitrate concentrations in the autumn, all the samples demonstrate increased pH and decreased electric conductivity values in the autumn. This behavior is also recorded previously for the electric conductivity and pH values of the samples analyzed in the flat areas for the year 2010. Furthermore, the nitrate concentrations of the samples from the semi-mountainous regions for the year 2011 are higher in the autumn as compared to the summer. On the other hand, the 50% of the samples display pH and electric conductivity values higher in the summer. These results are somehow contradictory with those obtained from the samples received in the flat areas for the year 2011. For example, even though the pH values present similar trends for both regions, the electric conductivity in the flat areas tends to be higher in the autumn, whereas only the 50% of the samples have higher electric conductivity values in the autumn. Likewise, the nitrate concentrations at the flat areas are lower in the autumn and at the semi-mountainous regions are higher in the same season period. For the year 2012, the majority of the pH values are higher at summer than autumn in contrast to the flat regions where the pH values are higher at autumn. The electrical conductivity is slightly higher in autumn than in summer at both flat and semi-mountainous regions and finally the nitrate concentrations are higher at autumn than summer in semi-mountainous regions.

Verification of the aforementioned general conclusions could be extracted by studying the measurements during the years from 2009 until 2012 and by detecting the differences over time and in the two different seasons. These results are shown in the Figures 8-10 for the flat regions and in the Figures 11-13 for the semi-mountainous regions.

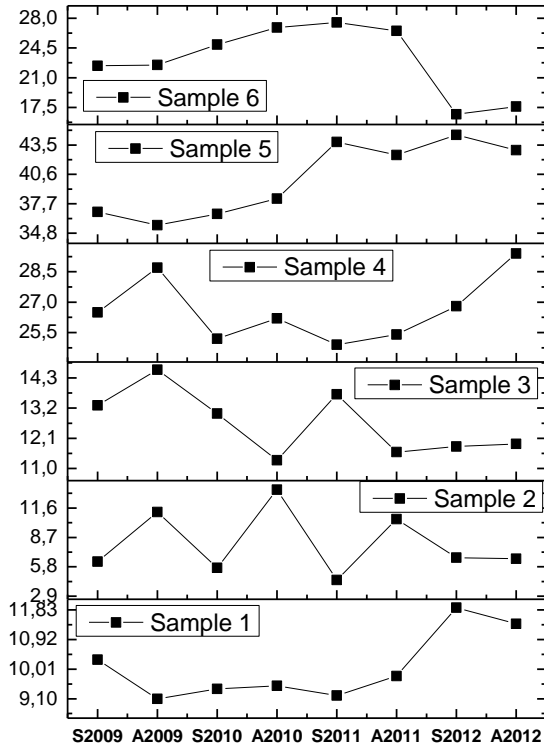


Figure 8: Nitrate concentrations deviations for each sample starting from summer 2009 until autumn 2012 in the flat regions

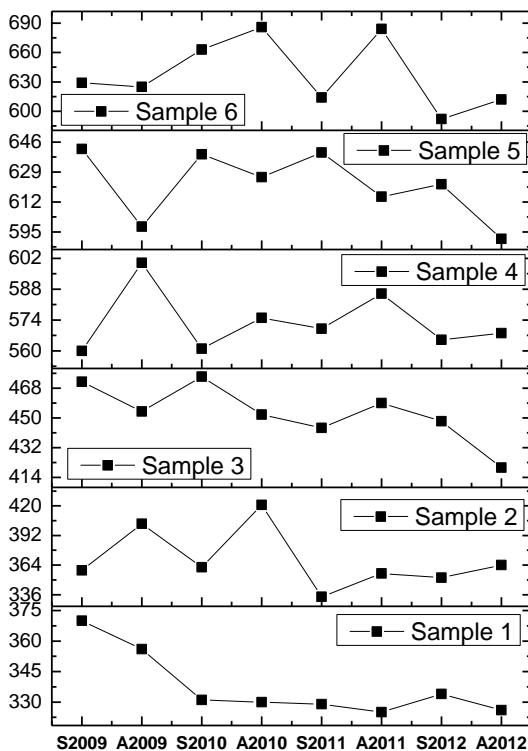


Figure 9: Electric conductivity deviations for each sample starting from summer 2009 until autumn 2012 in the flat regions

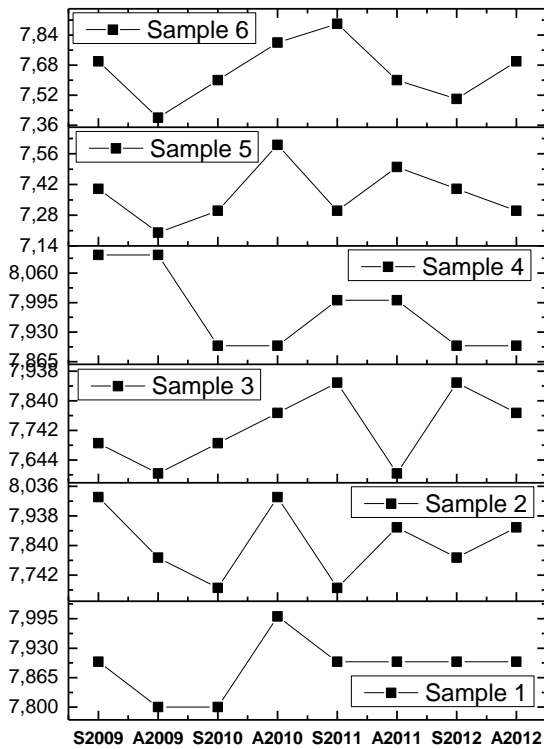


Figure 10: pH deviations for each sample starting from summer 2009 until autumn 2012 in the flat regions

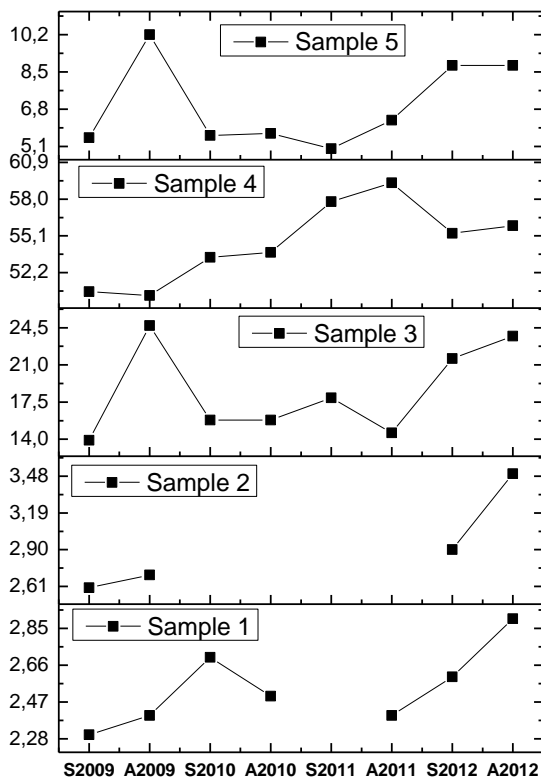


Figure 11: Nitrate concentrations deviations for each sample starting from summer 2009 until autumn 2012 in the semi-mountainous regions

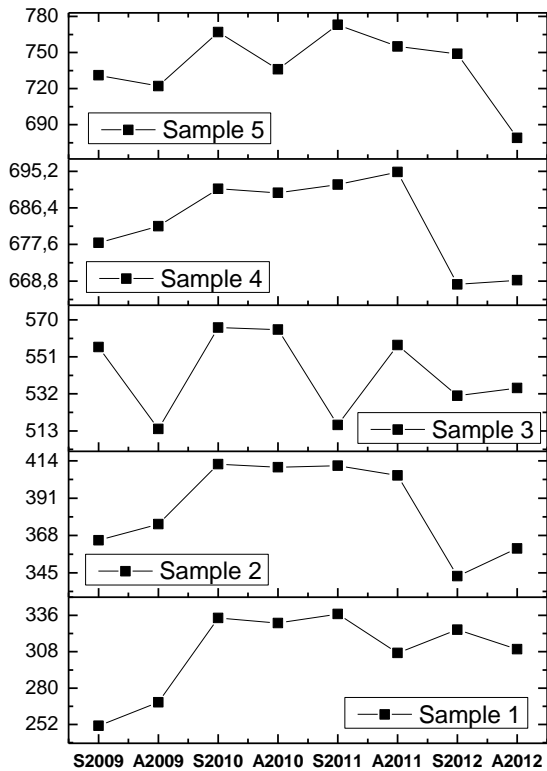


Figure 12: Electric conductivity deviations for each sample starting from summer 2009 until autumn 2012 in the semi-mountainous regions

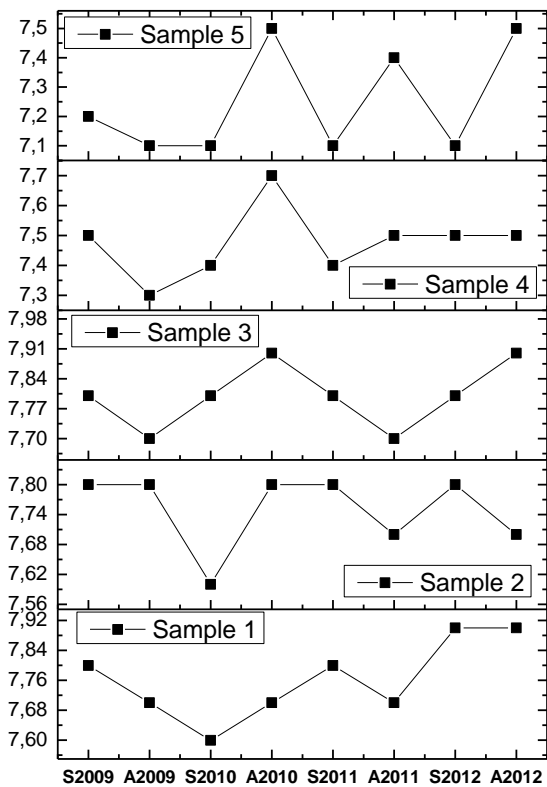


Figure 13: pH deviations for each sample starting from summer 2009 until autumn 2012 in the semi-mountainous regions

Analyzing the Figures above, it is obvious that the differentiations over the years, at first glance at least, are small but not significant neither for the nitrate concentrations, nor for the pH and the electrical conductivity values, depicting that the extensive use of fertilizers in the region does not highly affect the composition of groundwater. Although, a more thorough examination of these Figures both for the flat and semi-mountainous regions shows a downward tendency of the electric conductivity over these four years. On the other hand, the pH values tend to increase for all regions.

It would be very interesting to observe the variation of these parameters over time in two seasons envisaged for both the flat regions and for the semi-mountainous regions. For this reason, for all samples measured in the laboratory from summer 2009 to winter 2012, we constructed the following bar charts for three of the parameters that are studied in this paper, in particular for pH, electric conductivity and nitrates.

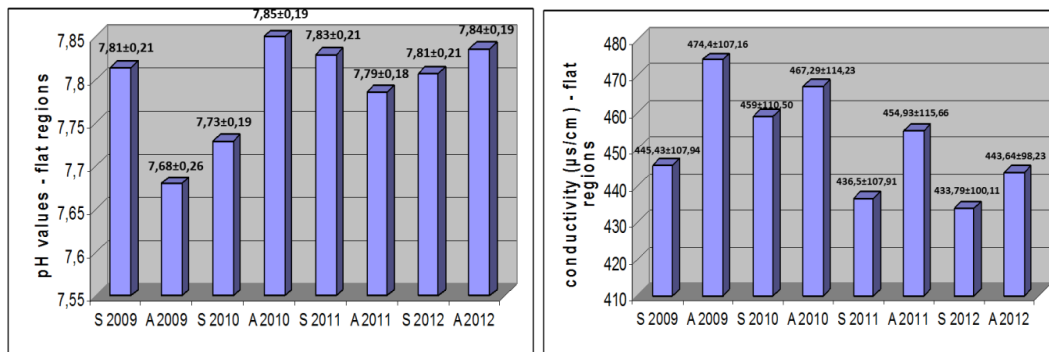


Figure 14: pH and electric conductivity deviations for all samples starting from summer 2009 until autumn 2012 in the flat regions

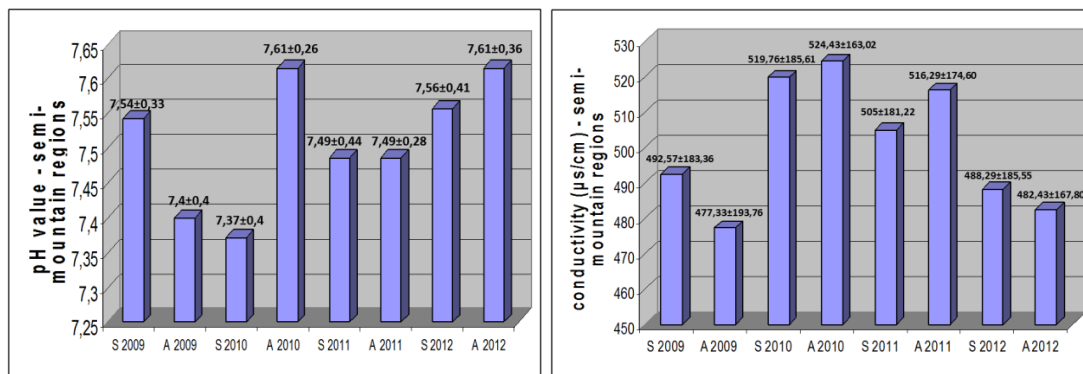


Figure 15: pH and electric conductivity deviations for all samples starting from summer 2009 until autumn 2012 in the semi-mountainous regions

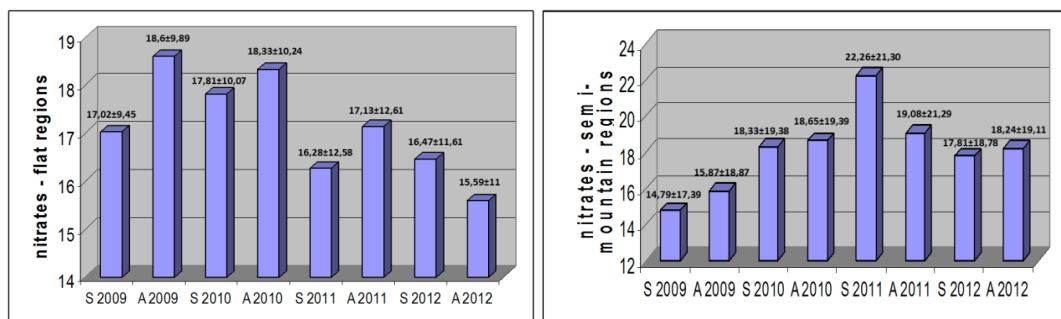


Figure 16: Nitrate deviations for all samples starting from summer 2009 until autumn 2012 in the flat and semi-mountainous regions

If someone observes the average values along with their standard deviations it can be concluded that there is a small but significant reduction of nitrates in the flat regions, which we can attribute to the reduction of nitrogen fertilizer

through denitrification programs, yet an equally small increase in the semi-mountainous regions. On the contrary, both the pH and the conductivity remain almost constant during the last four years, showing a stability in an environment burdened continuously.

4. CONCLUSIONS

From the analysis of the results, it emerges that the variations in the values of the parameters that were examined are probably due to the extensive use of fertilizers during the year since the main land use is agricultural. Moreover, a significant differentiation in the values of nitrates was observed during the year and from one region to another. Initially, in almost all flat regions that the samples were taken there is a noticeable reduction in the corresponding value from summer to autumn. Although the drillings have sufficient depth and they are insulated in order to avoid contact with surface waters or less water depth, they are probably affected in a small percentage. This results in a reduction in the values of the nitrates because of the reduction in the amount of the surface waters or less water depth. This can possibly explain the reduction in the conductivity and the small fluctuations in the values of pH during the year. In contrast, it is obvious that there is no significant differentiation in the values of nitrite and ammonium regardless of the region altitude and the time of the year that the samples were taken. This is due to the fact that there is no difference in microbial load or that the fertilizers do not affect the values of these two parameters.

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