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Student Research Thesis

# Hydrochemical Characterisation and Time Series Comparison of Ground- and Surface Water in Troia, Turkey

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## Abstract

As a continuation of earlier investigations, this study aims to advance the understanding of the hydrogeological and hydrochemical situation in the Historical National Park of Troia in north-western Turkey. For this purpose, a field campaign was undertaken in August 2006 which involved the collection of water samples and measurement of hydrochemical on-site parameters at designated sampling points. This data was then evaluated and interpreted using statistical and graphical methods. The second part of the study included a temporal comparison of hydrogeological data that has been accumulated in the study area from 2002-2006.

Several different water types occur in the Troad, ranging from Ca-HCO<sub>3</sub> and Mg-HCO<sub>3</sub> types to Mg-Cl and Na-Cl types. Groups distinguished by cluster analysis mostly corresponded with these water types. Investigations into the age of the sampled water using the hydrogen isotope tritium found that, despite of differences in chemical composition, the waters are likely to originate from recharge younger than 20-30 years. The chemical composition of the investigated groundwater can be linked to its origin, with water from the sedimentary sequences of the Troy ridge generally showing a higher degree of mineralisation than that from igneous or metamorphic rocks in the east and southeast of the study area.

A comparison of the depth of the groundwater table and the amount of water discharged at measuring points showed a noticeable increase in both during the time period 2002-2006. This may be connected to the climatic situation at the time (dry summers in the early part, wetter winters in the later part of the time period) but other factors such as water extraction and irrigation practices in the region may also play a part and are difficult to quantify.

The nitrate concentration in sampled waters was also compared over 5 years and found to increase noticeably, a fact attributed to the intense use of fertiliser in the region and probably insufficient sewage disposal.

## Acknowledgements

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# 1 Introduction

Even though the ancient city of Troia and the surrounding Historical National Park are mainly the focus of archaeological studies, the geology and hydrology of the area has also been investigated. The hydrogeological and hydrochemical investigations that have lead to the present study were initiated in 2001 by Prof. Dr. Christian Wolkersdorfer (then of Freiberg University of Mining and Technology) with the aim of characterising the waters and aquifers of the Troad. With this fundamental information it might further be possible to draw conclusions about the water supply of ancient Troia.

Field campaigns involving the collection of water samples and the determination of on-site parameters were carried out during the summers of 2002, 2003, 2004 (only on-site parameters) and 2006. A few samples were also taken in 2001.

The purpose of the current study can be divided into two main parts:

- 1) to give a broad hydrochemical characterisation and analysis of the water samples taken in 2006
- 2) to provide a temporal comparison of hydrogeological data that has accumulated since 2002.

By comparing parameters such as the depth of the groundwater table or concentrations of selected elements over time, changes that have occurred in the hydrological situation of the Troad can be uncovered and possible explanations for these changes may be provided. This in turn gives a better understanding of hydrogeological and hydrochemical processes acting in the study area.

The present study was preceded by four diploma theses and a geological survey carried out at the Department of Geology, TU Bergakademie Freiberg. These studies (Blume 2003, Weber 2003, Bergmann 2003 and Lippmann 2003) are referred to throughout this manuscript.

## 2 Site description

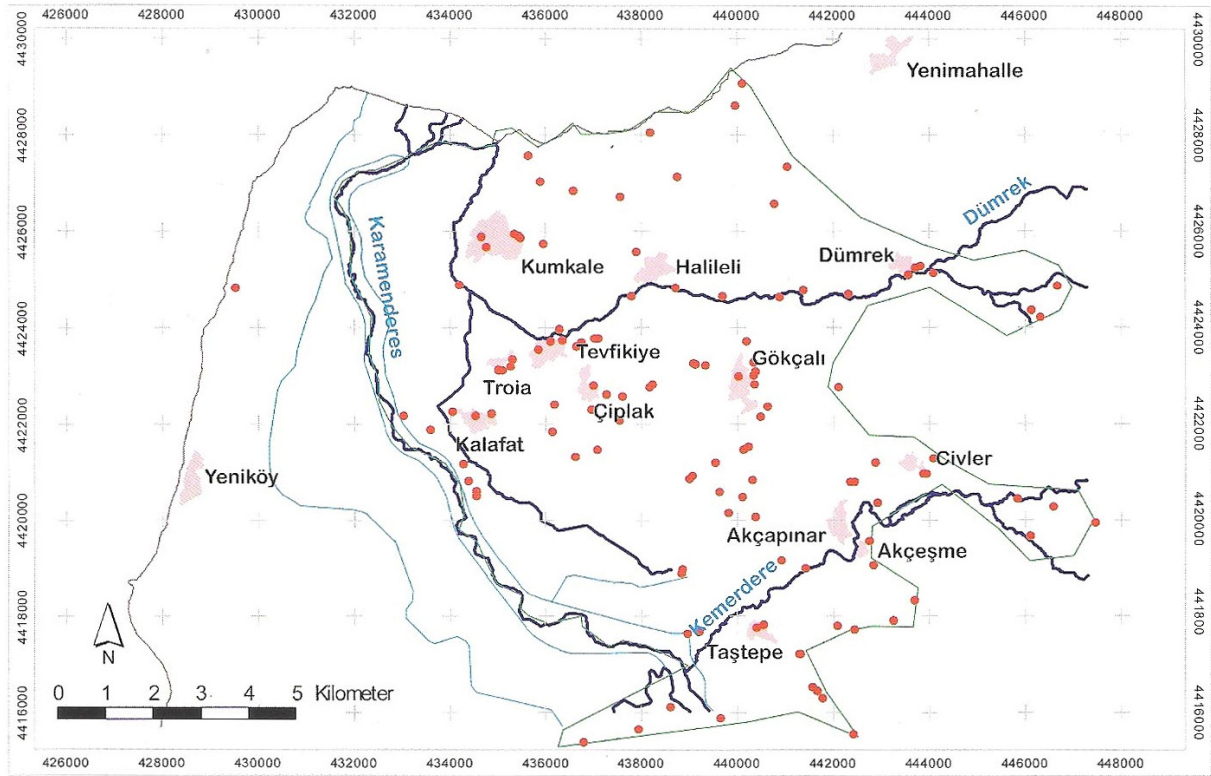
### 2.1 Location

The study area is located in the northwest of the Biga Peninsula in northwestern Turkey and has a size of approx. 100 km<sup>2</sup>. At its centre stand the remains of the historical city of Troia (Fig. 1).



**Fig. 1:** Map showing the location of the study area in NW Turkey (source: <http://geology.com/turkey-map.gif>)

To the north the study area is bound by the Dardanelles, to the west by the Karamenderes River and to the east by the foothills of the Ida Mountains. The closest city is Çanakkale, approx. 30 km to the northeast of Troia. Several villages are located within the study area, such as Kumkale and Halileli in the north, Dümrek, Civler and Akçapınar in the east and Taştepe in the south (Fig. 2). Tefikiye is the village directly bordering the archaeological site of Troia. The Izmir-Çanakkale highway dissects the study area in a north-south direction.



**Fig. 2: Map of the study area. The red dots show the location of sampling points in the year 2002 (Wolkersdorfer & Göbel 2004)**

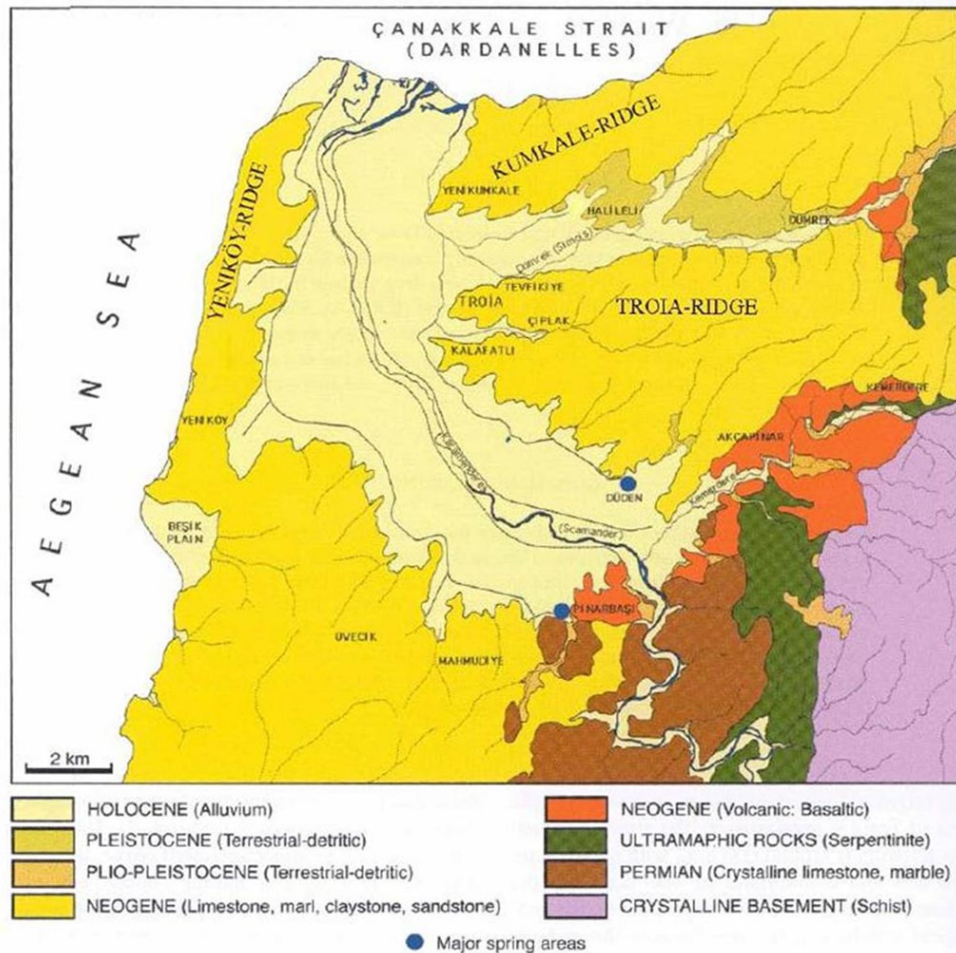
## **2.2 Geomorphology and Geology**

Detailed geological surveying of the study area was carried out in the year 2002 by the students Katrin Bergmann and Pia Lippmann. Readers seeking more details on this subject are asked to refer to their work (Bergmann 2003; Bergmann & Lippmann 2003; Lippmann 2003). The following section will only give a short overview.

Wide, flat river plains and broad, sloping ridges, rising to steeper hill country in the east characterise the morphology of the study area. The Karamenderes is the main river of the area, originating in the Ida Mountains in the east of the Biga Peninsula and ending in a delta in the Dardanelles. It has a total length of 124 km and a catchment area of 1962 km<sup>2</sup> (Höhfeld 2001; Özcan et al. 2007).

The oldest geological units are found in the eastern hills of the study area, where highly metamorphosed palaeozoic and mesozoic rocks such as serpentinite, schist and marble occur. Further to the west and north, these are overlain by neogene sediments, composing the Troy and Kumkale ridges and the alluvial plains of the Karamenderes and Dümrek. Basalts in the

southwest of the study area, by the villages Akçapınar and Akçeşme, formed during a period of intense volcanism 4-10 million years ago (Bergmann & Lippmann 2003). The river Kemerdere has cut into these rocks and formed a narrow, steep-sided gorge below the village of Akçeşme.



**Fig. 3: Geology and geomorphology of the Historical National Park of Troia and surroundings (Weber 2003, originally from Kayan 2000)**

The Troy ridge, running from east to west in the centre of the study area, and the Kumkale ridge in the north are composed of a succession of sand, carbonate and clay sediments that were deposited in shallow marine and lacustrine environments during the upper Miocene and Pliocene. Through neotectonic processes, these sediments were slowly uplifted and tilted (Kayan 2001; Bergmann 2003). During the Quaternary, the Karamenderes and Dümrek rivers eroded the sedimentary sequences to form what today are the Troy, Kumkale and Yeniköy ridges, intercepted by flat alluvial plains (Fig. 3).

Changes in sea level during the Quaternary resulted in widely differing coastlines. Sea levels were up to 100 m lower during the quaternary ice ages, with the Dümrek and Karamenderes being tributaries to the Dardanelles, which existed as a river. Rising temperatures and precipitation in the Holocene meant that sea levels rose. Around 5000 BC, the sea had transgressed up the Karamenderes valley to lie just before Pinarbaşı in the south of the study area (Kayan 2001).

## **2.3 Climate**

Troia experiences a mediterranean climate, with hot, dry summers and cool, wet winters. Strong winds blowing from the northeast or northwest are a common occurrence in summer. In winter, cold air masses from northern Europe may occasionally bring frost and snow (Höhfeld 2001). Table 1 shows mean monthly temperatures and precipitation for Çanakkale from the years 1999 to 2006. Rainfall distribution is very uneven, with over 90% of precipitation falling from October to May, resulting in very dry summers. Maximum temperatures in the high thirties are often reached during the summer months, meaning that what little rain does fall evaporates rapidly.

**Tab. 1: Mean temperature and precipitation data for Çanakkale, time period 1999-2006 (NOAA/NCDC)**

	J	F	M	A	M	J	J	A	S	O	N	D	Year
<b>mean Temp.</b> [°C]	6.5	6.4	9.1	12.8	18.0	23.1	26.1	26.0	21.4	16.7	11.9	8.1	<b>15.5</b>
<b>mean Precip.</b> [mm]	71.9	94.0	73.9	42.3	27.8	12.8	9.8	1.4	19.8	51.2	94.6	84.7	<b>584.1</b>

## **2.4 Land use**

Agriculture occupies a large percentage of land in the Troad. The once extensive swamps in the Karamenderes and Dümrek plains have been drained and turned into fields, where primarily tomatoes, peppers, melons, sunflower and cotton are grown. Most farms in the area around Troia range in size from 0.2 to 7.9 ha (Özcan et al. 2007). As opposed to more traditional crops such as olives, these crops have a high demand for water and need frequent irrigation. Water for this purpose is supplied from the Düden and Kirkgöz springs and the Karamenderes river, being channelled in irrigation canals. Several deep boreholes also supply

irrigation water. As agriculture continues to be intensified in the area (Schwaderer 2003; Özcan et al. 2007) water resources are strained.

The hill country in the east and southeast of the study area is covered in dry conifer forest. Large parts are under state control and used for forestry purposes, while shepherds use it as a grazing ground for sheep and goats (Höhfeld 2001).

## **2.5 Hydrogeology**

The groundwater table in the study area is found between 0 and 15 m below ground level, with a large majority of wells (90%) displaying water tables between 0 and 6 m below ground level. The intense groundwater production from wells and boreholes in the Karamenderes and Dümrek plains for irrigation and drinking water purposes has led to significant drawdown in these areas. Water tables have in parts been lowered by 9 – 11 m in the Dümrek and 2 – 9 metres in the Karamenderes plain (Wolkersdorfer & Göbel 2004). As a result, the Dümrek riverbed is often completely dry in the summer months. The hydraulic properties of sediments composing the Troy ridge were investigated by Bergmann (2003), who concluded that four sandstone layers with hydraulic conductivities between  $10^{-6}$  and  $10^{-7}$  m/s and thicknesses from 4 – 7 m are most likely to act as aquifers. Layers of clay and siltstone with much lower permeabilities ( $10^{-8}$  –  $10^{-9}$  m/s) are bedded between the sandstone sequences and inhibit the flow of groundwater. Blume (2003) gives a flow direction of west to southwest which complies with the dipping of strata of the Troy ridge. The sediments of the quaternary alluvial plains are a mixture of fine layers (silt, fine sand) intercepted by medium and coarse sands (Göbel et al. 2003). For these grain sizes, hydraulic conductivities of  $10^{-3}$  –  $10^{-6}$  m/s can be assumed (Hölting 2005).

A groundwater recharge of 60 mm per year has been calculated for the study area by Blume (2003) using the water budget equation, though this value might be lower due to high surface run-off associated with high intensity rainfall events (Blume 2003). Groundwater is only recharged during the wet winter months, when more than 90% of the year's precipitation falls. Water discharges from numerous small springs on the flanks of the Troy and Kumkale ridges as well as in the hills of the East and Southeast. The only large and constant groundwater discharges are from the Düden spring in the Southeast with a discharge of 20 l/s and the Kirkgöz springs in the south of the study area, close to Pinarbaşı, discharging 600-1500 l/s (Blume 2003).



### 3 Materials and Methods

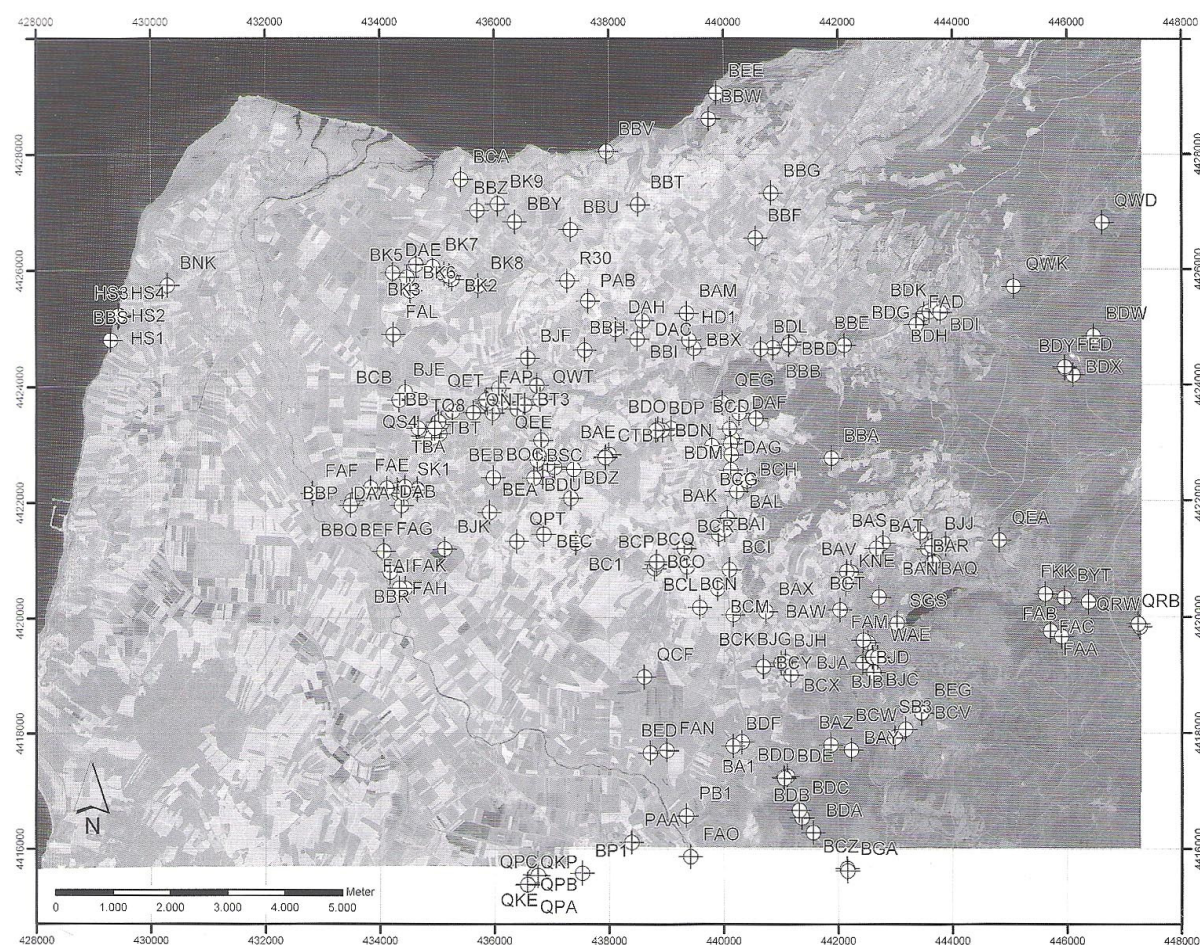
#### 3.1 Field methods

##### 3.1.1 Sampling points

On-site parameters were measured at altogether 144 measuring points. At 37 of these (35 groundwater, 2 surface water), water samples for field and laboratory analysis were taken in addition.

The sampling points can be grouped into a variety of different types, ranging from river water, springs and tap water to dug wells and boreholes. Many sampling sites act as watering points for animals, predominantly sheep and goats. Detailed descriptions and photographs of a range of sampling points (using the same sample site designations) can be found in Weber (2003) and Wolkersdorfer et al. (2004). The geographical location of the sites is shown in Fig. 4.

Each point is distinguishable by a unique 3-letter code.



**Fig. 4: Location of sampling points in the study area. Points that were added after 2003 are not displayed on the map (Wolkersdorfer et al. 2004)**

### 3.1.2 On-site parameters

At each site, the investigated field parameters included water temperature, pH, specific electrical conductivity (EC), total dissolved solids (TDS) and dissolved oxygen content. Oxygen and temperature were measured using a *HACH O<sub>2</sub> LDO HQ20* probe and pH by a *WTW pH 320* sensor. Due to the malfunctioning of the *MYRON P6* multi-parameter probe during large parts of the field campaign, the measurement of redox potential could not be undertaken at most sites.

For ease of measurement, the probes were usually suspended in a plastic jug, through which the water (pumped or free-flowing from pipes or taps) could run. Values were taken when all parameters had reached a stable level, generally after at least 5 minutes of measuring.

Wherever possible, the amount of water discharging from wells and springs was measured using a measuring cylinder and a stopwatch. Usually, 5-6 repeated measurements were taken and the mean value calculated to guarantee greater accuracy.

At dug wells, the water level below ground surface was measured using a dipper.

### 3.1.3 Water sampling and field analysis

The sampling techniques varied according to the type of sampling point. Water from dug wells and boreholes was pumped using a small pump connected to a 12 V battery. Samples were taken after the on-site parameters had stabilised. Where applicable (eg. at animal watering points and wells) water was sampled directly at the outflow from the tap or pipe. The plastic sampling bottles of varying sizes were rinsed three times with sample water before being filled and sealed.

Samples for isotope and main element analysis were filtered using 0.45 µm cellulose-acetate filters by *Sartorius*. Filtered sample water was also used for the on-site photometric analysis of Fe<sup>2+</sup>, total Fe, NO<sub>2</sub>-N and NH<sub>4</sub><sup>+</sup>, using a *HACH Colorimeter DR/890* and *HACH* reagents. The sample designated for the analysis of trace elements was additionally acidified with five drops of HNO<sub>3</sub>. A summary of sample types and their treatment is given in Table 2.

**Tab. 2: Water sample types collected in 2006 and their treatment and storage**

Sample type	Sample size	Treatment	Storage
Tritium ( <sup>3</sup> H)	1000 ml	none	room temp.
stable isotopes ( <sup>2</sup> H/ <sup>18</sup> O)	250 ml	none	room temp.
main elements	250 ml	none	refrigerated
trace elements	50 ml	filtered, acidified	refrigerated



To determine the acid and base capacity ( $K_s$  and  $K_b$ ), samples were titrated in the field using a *HACH* digital titrator.  $K_s$  was determined by drop-wise adding 0.01 mol/l HCl to 25 ml sample water until a pH of 4.3 was reached. Similarly, for the determination of  $K_b$ , 0.05 mol/l NaOH was added until pH 8.2.

### **3.2 Laboratory analysis**

The water samples taken in Turkey ( $n = 37$ ), were taken to Germany for analysis. The major cations and anions were determined by ion chromatography at the Hydrogeology Department of the Freiberg University of Mining and Technology using an *Eppendorf/Biotronik IC 2001*. Tritium measurements were also carried out at Freiberg, at the Institute for Applied Physics using *Quantulus* liquid scintillation counting (LSC). For the analysis of trace metals, samples were taken to the Institute for General Ecology and Environmental Protection at the Tharandt campus of the Dresden University of Technology. There, samples were analysed using ICP-MS.

### **3.3 Methods of data analysis and presentation**

#### **3.3.1 Data quality control**

In order to process and interpret hydrochemical data, it is first necessary to verify its accuracy. To give an indication of the correctness of water analyses, the anion-cation balance is calculated. Because the sample solutions have a neutral electrical charge, the sum of cations in mmol(eq)/l should equal the sum of anions in mmol(eq)/l (Hounslow 1995). This can be expressed in the following equation:

$$\text{Reaction error} = (\Sigma_{\text{cations}} - \Sigma_{\text{anions}}) / (\Sigma_{\text{cations}} + \Sigma_{\text{anions}}) * 100\%$$

For this study, a reaction error of less than 5% was taken as tolerable analysis accuracy. Of the investigated samples ( $n = 36$ ) 75% displayed errors below 5%, signifying an acceptable analysis. Values above the 5% level are all positive, showing a lack of anions. The most likely cause for this is an inaccurate  $\text{HCO}_3^-$  concentration.  $\text{HCO}_3^-$  was not measured directly, but calculated from  $K_s$  and  $K_b$  which were determined by titration in the field, increasing the margin for error.

The cation-anion balance was calculated for all samples with *PHREEQC-2 for Windows* using the *Phreeqc.dat* database.

### 3.3.2 Correlation coefficient

The determination of the *Pearson* product-moment correlation coefficient serves the purpose of determining if a linear relationship between two variables exists (DVWK 1999). The strength of this linear relationship is measured on a scale from -1 to +1 and the larger the absolute value of the correlation, the stronger the linear relationship between the two variables. *Pearson's* correlation coefficient  $r$  is calculated according to the following equation, where  $x$  denotes variable 1 and  $y$  variable 2 (DVWK 1999):

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}}$$

In order to test that the correlation coefficient between two variables differs from 0 and a significant correlation exists, a t-test is applied (DVWK 1999). In this study, the chosen significance level was 1%, therefore p-values smaller than 0.01 denote a significant correlation between variables. Results of the correlation analysis are displayed in a correlation matrix. The parameters that were tested for correlation include specific electrical conductivity (EC) and the main ions ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ).

### 3.3.3 Water Types

The water samples were grouped according to their hydrochemical composition. Only the main ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ) were considered for the determination, as they are contained in the highest concentrations. For each sample, their concentration in mmol(eq)/l was calculated and expressed as a percentage of the total main ion concentration. The dominant ions (>20 mmol(eq)%) were then used to determine the water type, as is shown in the following example.

Example:

Ion equivalents in water sample:     $\text{Mg}^{2+}$ : 64%     $\text{Ca}^{2+}$ : 24%     $\text{Na}^+$ : 10%     $\text{K}^+$ : 2%  
     $\text{HCO}_3^-$ : 55%     $\text{Cl}^-$ : 28%     $\text{SO}_4^{2-}$ : 13%     $\text{NO}_3^-$ : 4%

→    **Mg-Ca-HCO<sub>3</sub>-Cl-type**

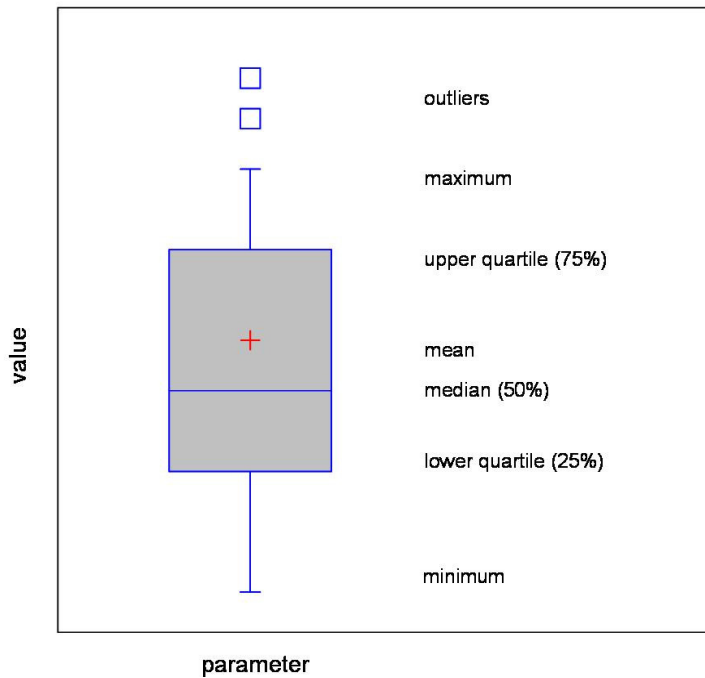
### 3.3.4 Cluster analysis

A hierarchical cluster analysis was performed with *Statgraphics Centurion XV* to designate groups of samples with similar properties. Objects are aggregated stepwise according to the calculated distances between them. Data points that lie closest together (i.e. have similar features) are therefore grouped first (Otto 2007). In this case, the euclidean distance was applied and the clusters aggregated according to the furthest neighbour method (complete linkage). The output is in form of a dendrogram.

Of the 37 water samples, 35 were used as input data for clustering. Two samples, QRW and QWO, were not considered, as their chemical analyses were incomplete. The same parameters that were already used by Weber (2003) in her master thesis were incorporated into the cluster analysis for this study: pH, EC,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , Cl, Ca, Mg, Na, K, Si, Sr, Ba, F, and Li. Weber (2003) selected these parameters based on frequency histograms that were constructed for each parameter. The above listed parameters had histograms with a bimodal appearance, indicating the existence of clusters.

### 3.3.5 Box-and-whisker plots

Box-and-whisker plots (also simply called box plots) are used to display numeric data sets and to highlight distinct statistical features within the data. The plot shows percentiles, means and outliers and is useful in giving a visual comparison between data columns (Fig. 5). The box plots for this study were constructed using *Statgraphics Centurion XV*.

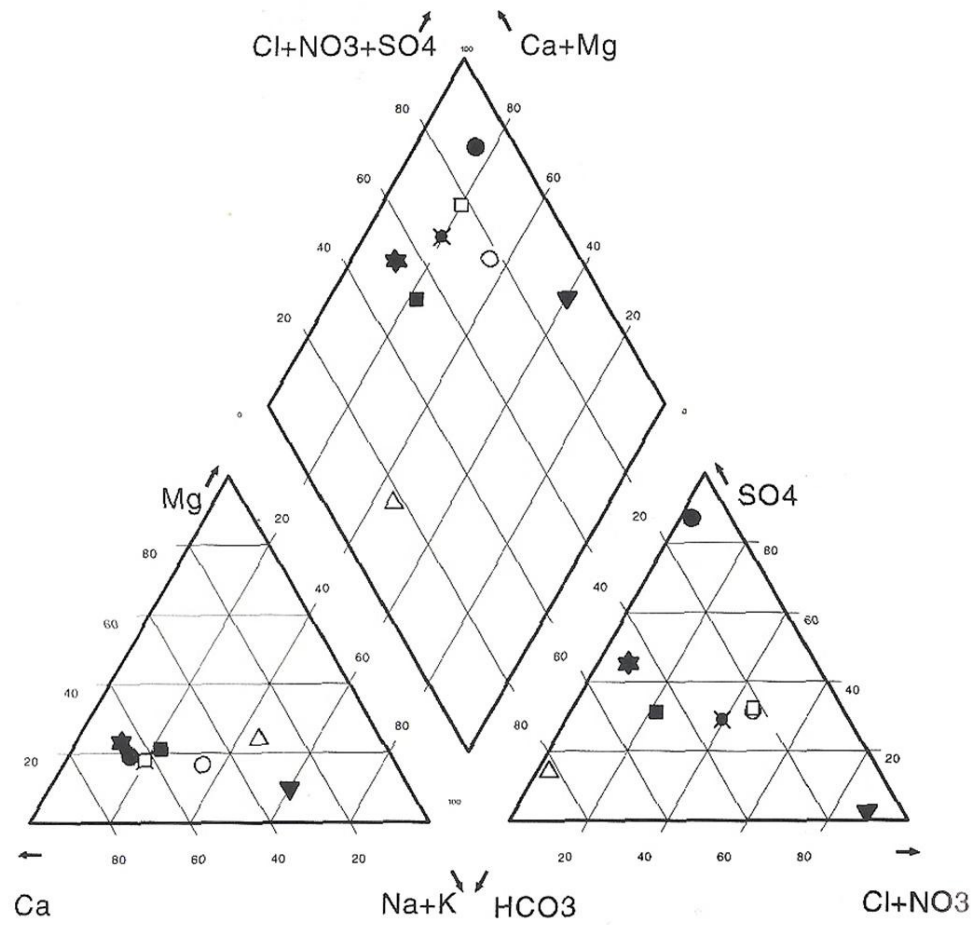


**Fig. 5:** Exemplary box-and-whisker plot showing statistical features

### 3.3.6 Piper diagrams

Piper diagrams are useful for displaying and comparing complete analyses of several water samples on a single diagram. The concentrations of main ions (in mmol(eq)/l) are plotted for each sample on the separate triangular anion and cation diagrams, as well as on the combined rectangular plot (Fig. 6). Samples with similar ion concentrations should lie close together on the diagrams, whereas very different samples should be distanced from each other. This clustering effect can make it possible to distinguish different water types.

The USGS software *GW-Chart* was used to plot the piper diagrams for this study.



**Fig. 6: Exemplary piper diagram (DVWK 125)**

## 4 Results and Discussion

### 4.1 Hydrochemistry and isotope hydrology

#### 4.1.1 On-site parameters

Field parameters in 2006 were taken at altogether 144 of originally 176 measuring points. The remaining sites were either dry, could not be found or simply did not exist anymore.

##### 4.1.1.1 pH and specific electrical conductivity

The pH values lie within a relatively narrow range from 6.60 to 8.56, with a mean of 7.28. As is shown in Fig. 7, a large proportion of the measured waters have a pH between 6.8 and 7.6. Surface water from the region's rivers (Dümrek, Kermerdere, Karamenderes) generally displays values towards the higher end of the scale, averaging 7.77 ( $n = 10$ ). Compared to this, water pumped from dug wells and boreholes showed below-average pH values with a mean of 7.14 and a median of 7.06 ( $n = 48$ ). Other obvious patterns or trends could not be distinguished.

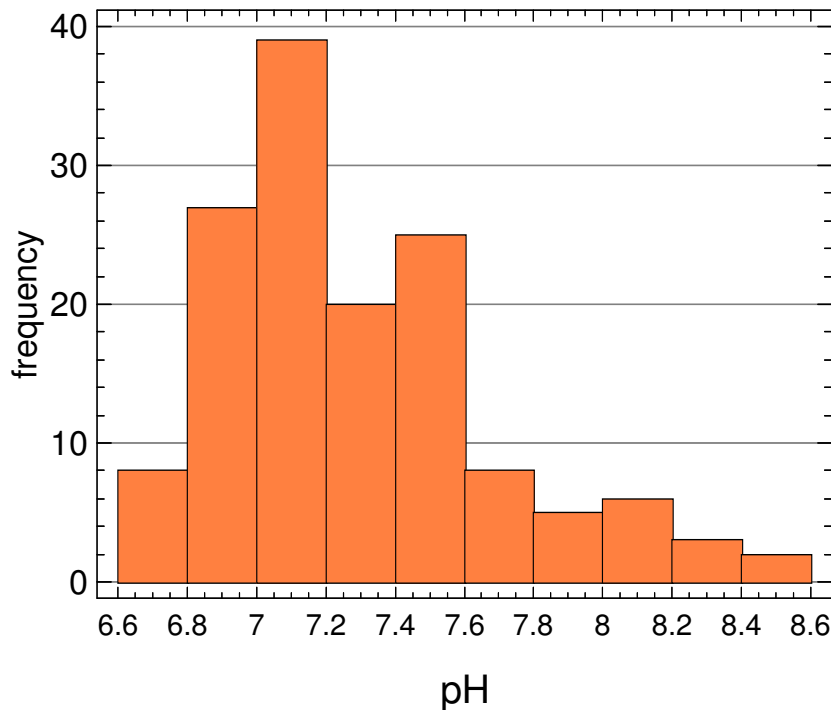
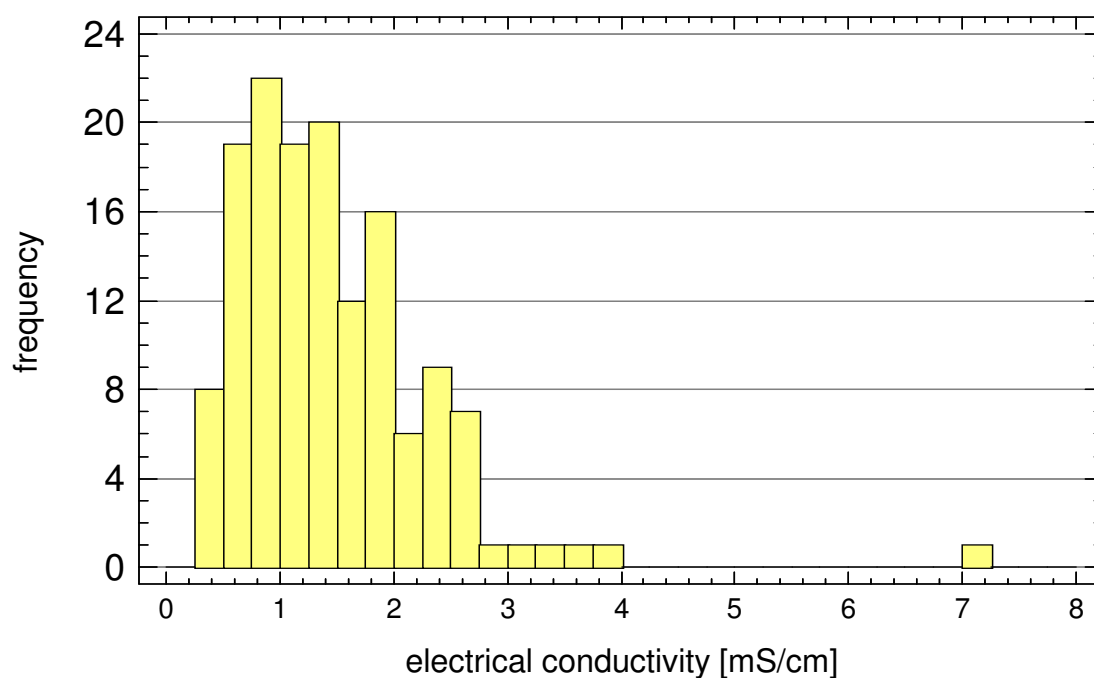


Fig. 7: Frequency histogram showing the spread of pH-values measured in 2006 ( $n = 144$ )

The specific electrical conductivity (EC) gives an indication of the degree of mineralisation of the water. In the study area, EC displayed large variations and ranged from a low of 444  $\mu\text{S}/\text{cm}$  to a high of 7135  $\mu\text{S}/\text{cm}$ . Most waters were found in the range from 500 – 2000  $\mu\text{S}/\text{cm}$  (Fig. 8). The highest value belongs to the sample point BBP, an unused dug well west of Kalafatlı.

River water shows the lowest conductivities of all sample types, with a mean of 602  $\mu\text{S}/\text{cm}$ . This can be explained by the direct input of precipitation, which generally has very low electrical conductivities. Due to water-rock interactions, groundwater in Troia has much higher electrical conductivities than surface water. The mean EC measured in dug wells and boreholes is 1867  $\mu\text{S}/\text{cm}$ . EC is not only influenced by the rock or sediment type from which the water originates, but also by anthropogenic activity such as the use of fertilizer or insufficient sewage treatment.



**Fig. 8:** Frequency histogram displaying the spread of specific electrical conductivities measured in 2006 (n = 144)

#### 4.1.1.2 Temperature and Oxygen

The water temperature ranges from 15.8 °C to 30.2 °C. As expected, cooler temperatures occur in waters originating from springs and dug wells, whereas surface water (rivers) and tap water mostly have temperatures in the mid- to high 20's due to their direct exposure to sunlight and warm summer air temperatures.

Even though redox potential could mostly not be measured (see section 3.1.2), the dissolved oxygen content (given in mg/l and % saturation) gives an indication of the redox conditions in the water. As water percolates through the unsaturated zone, it is depleted of oxygen by the respiration processes of micro-organisms. Therefore groundwater, lacking contact to the atmosphere, generally has lower oxygen concentrations than surface water. Organic material present in groundwater acts as a reducing agent and can further lead to oxygen depletion (DVWK 1996).

As a result, the oxygen saturation in water pumped from deeper horizons is relatively low with a median value of 12.7%, whereas all other types of measuring points (tap water, spring water, river water etc.) have much higher degrees of oxygen saturation.

#### 4.1.2 Major ions

The following section will give a brief overview of the major ion contents found in the waters of Troia. The spread of concentrations ( $n = 35$ ) are presented as box-and-whisker plots in Fig. 9. Potassium ( $K^+$ ) was omitted from the diagram because of its generally low concentrations (median = 2.07 mg), with 92% of values lying between 0 and 7 mg/l and only three samples showing significantly higher values (35.2, 52.7, 225 mg/l). Also not shown are the analysis results of sample BBP, whose extremely high values for  $Cl^-$  (1865 mg/l) and  $Na^+$  (1316 mg/l) distorted the diagram and point to a potential contamination source.

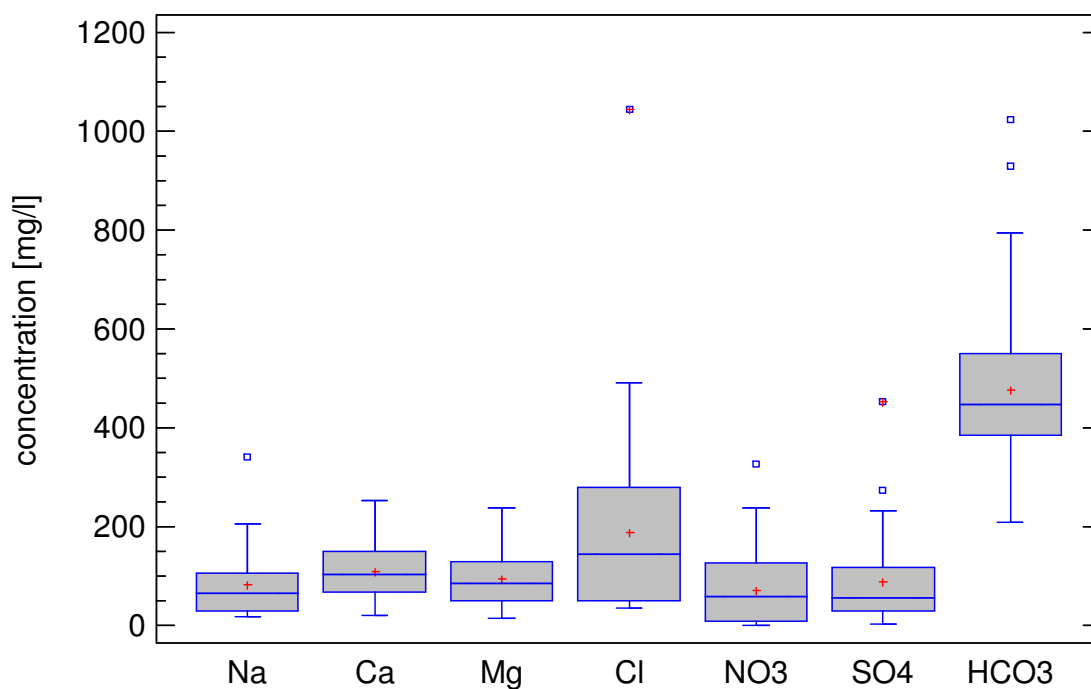


Fig. 9: Major ion concentrations of Troian water samples ( $n = 35$ )



Unfortunately, in most cases the exact rock or sediment types from which the sampled groundwater originates are not known, though a few broad generalisations of the connection between rock type and main groundwater constituents can be made. As was already mentioned by Weber (2003) and is still relevant for the 2006 samples, concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  are higher in waters from the Kumkale and Troy ridges, where neogene sediments (carbonates, claystones, sandstones) predominate. Lower concentrations are found on the quaternary alluvial plains of the Karamenderes and Dümrek Rivers.

The distribution of chloride in the samples is difficult to characterize. The lowest concentrations (between 35 and 40 mg/l) were found in the Karamenderes and at sampling points in the hills of the east and south of the study area, away from settlements and intensive agriculture and where volcanic and metamorphic rocks occur. Higher concentrations tend to be located closer to villages and fields, though there are exceptions to this observation. In addition to geological conditions, anthropogenic activities (sewage, fertiliser, insufficient garbage collection) may play a part. Two samples, BBV and BBW, taken in close vicinity of the sea, show elevated chloride and sodium concentrations ( $\text{Cl}^-$ : 356, 258 mg/l;  $\text{Na}^+$ : 157, 129 mg/l) that may be explained by sea-spray or the intrusion of saltwater.

Chloride and sodium are two ions that correlate strongly ( $r = 0.914$ ). Both also have a significant effect on the specific electrical conductivities, as is shown by their correlation coefficients with EC. Further *Pearson* correlation coefficients of the main groundwater constituents are shown in Table 3.

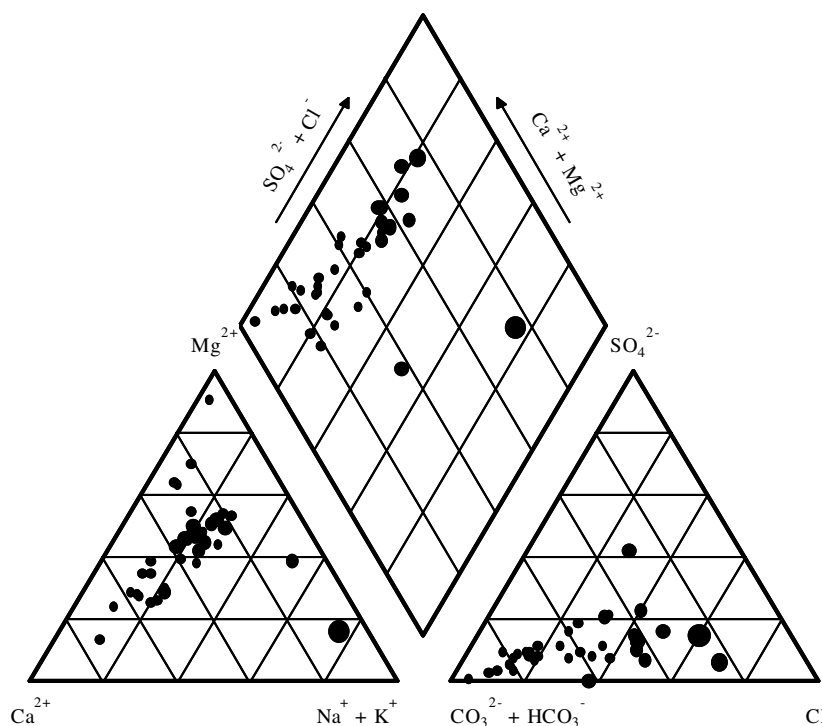
**Tab. 3: *Pearson* correlation coefficients for 2006 water samples (n = 36). Bold values indicate a significant correlation ( $p < 0.01$ )**

	EC	Na	Ca	Mg	Cl	$\text{NO}_3$	$\text{SO}_4$	$\text{HCO}_3$
EC	*							
Na	<b>0.911</b>	*						
Ca	<b>0.443</b>	0.164	*					
Mg	<b>0.661</b>	<b>0.378</b>	0.281	*				
Cl	<b>0.980</b>	<b>0.914</b>	<b>0.452</b>	<b>0.566</b>	*			
$\text{NO}_3$	0.154	-0.069	<b>0.482</b>	0.221	0.055	*		
$\text{SO}_4$	<b>0.768</b>	<b>0.731</b>	0.363	<b>0.441</b>	<b>0.720</b>	0.255	*	
$\text{HCO}_3$	<b>0.615</b>	<b>0.597</b>	-0.062	<b>0.684</b>	<b>0.530</b>	-0.184	0.270	*

For all major ions, the mean values lie higher than the median values, suggesting that the means are influenced by outliers (Fig. 9). This is especially the case for  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ . Samples that display very high values for a given component (in brackets) are, for example, the already above mentioned dug well BBP ( $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ), the dug well BAF ( $\text{Na}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ) and the wells BAH ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ), QNT ( $\text{NO}_3^-$ ), QEE ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ) and BEA ( $\text{SO}_4^{2-}$ ). BBP and BAF are both unused wells with probably stagnating water (low oxygen concentrations, smell of  $\text{H}_2\text{S}$ )

The occurrence of elevated nitrate levels is connected to the use of fertiliser and insufficient sewage treatment. The problem of high nitrate concentrations in some samples was already mentioned by Wolkersdorfer & Göbel (2004) and Weber (2003) and will be further discussed in section 4.2.4.

Further indication of the connections between major ions and EC is given by the Piper diagram depicted in Fig. 10. The size of the plotted points is proportional to the specific electrical conductivity of the given sample. It shows that the higher the EC, the more the anions are dominated by chloride as opposed to  $\text{HCO}_3^-$ , as was already shown by the significant correlation between EC and  $\text{Cl}^-$ . The shift in cation composition is not so easily discernible, a slight increase in sodium and corresponding decrease in calcium equivalents can be noticed with rising EC.



**Fig. 10: Piper diagram of water samples taken in 2006 (n = 36). The size of the points indicates increasing specific electrical conductivity.**

### 4.1.3 Statistical analysis of main hydrochemical composition

#### 4.1.3.1 Water types

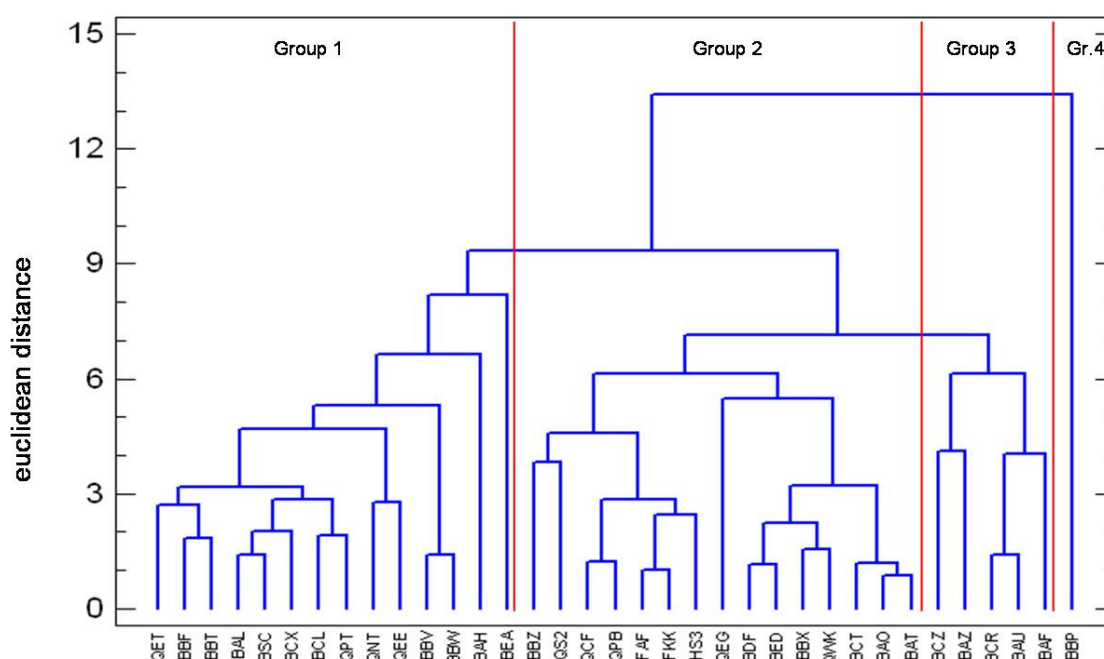
Table 4 lists the water types and corresponding samples. The colour coding of sampling points is connected to the results of the cluster analysis which will be discussed in the next section (4.1.6.2). Several broad spatial trends can be observed. In the east and southeast of the study area, Ca-Mg-HCO<sub>3</sub> type waters predominate, evolving to Mg-Ca-HCO<sub>3</sub> and Mg-Na-HCO<sub>3</sub> types in a westward direction on the Troy ridge. Further to the west, in the lower regions of the Troy ridge, the chloride component becomes stronger and Mg-Ca-Cl waters occur in addition. Samples on the Kumkale ridge in the northern part of the study area mainly display Mg-Na-Cl or Mg-Na-HCO<sub>3</sub> type waters.

**Tab. 4: Water samples and their designated water types. The colour coding refers to groups distinguished by cluster analysis (Group 1, Group 2, Group 3, Group 4)**

Water Type	Sample
Mg-HCO <sub>3</sub>	BAZ
Mg-Ca-HCO <sub>3</sub>	BCZ, BBX, QWK
Mg-Ca-HCO <sub>3</sub> -Cl	QEG, QPT, QS2
Mg-Ca-Cl-HCO <sub>3</sub>	QET
Mg-Ca-Na-HCO <sub>3</sub> -Cl	BBF, BCL
Mg-Ca-Na-Cl-HCO <sub>3</sub>	BAH, BAL, BSC, QEE
Mg-Ca-Cl-HCO <sub>3</sub> -NO <sub>3</sub>	QNT
Mg-Ca-SO <sub>4</sub> -Cl-HCO <sub>3</sub>	BEA
Mg-Ca-Na-HCO <sub>3</sub> -Cl-SO <sub>4</sub>	BBZ
Mg-Na-Ca-HCO <sub>3</sub>	BCR
Mg-Na-Ca-HCO <sub>3</sub> -Cl	BBT
Mg-Na-Ca-Cl-HCO <sub>3</sub> -SO <sub>4</sub>	BBV
Mg-Na-Ca-HCO <sub>3</sub> -Cl-SO <sub>4</sub>	BBW
Mg-Na-HCO <sub>3</sub> -Cl	BAU
Ca-HCO <sub>3</sub>	QRW
Ca-Mg-HCO <sub>3</sub>	BDF, QPB, BCT, BED
Ca-Mg-HCO <sub>3</sub> -Cl	BAO, BAT, HS3
Ca-Mg-Na-HCO <sub>3</sub> -Cl	QCF, FAF, FKK
Ca-Mg-Na-Cl-HCO <sub>3</sub>	BCX
Na-Mg-HCO <sub>3</sub> -Cl	BAF
Na-Cl-HCO <sub>3</sub>	BBP

#### 4.1.3.2 Cluster analysis

The results of the cluster analysis (the input parameters were already mentioned in section 3.3.4) show the existence of four main clusters or groups (Fig. 11). A number of subgroups may also be identified, but for ease of evaluation the author will focus on the four main groups.



**Fig. 11: Results of the cluster analysis depicted in a dendrogram showing the division into four main groups**

For easier visualisation, the groups have been plotted on a Piper diagram (Fig. 12). As is seen on the anion triangle, Group 1 is characterised by elevated chloride concentrations and resulting high electrical conductivities. The ratio of cations in the samples composing Group 1 is similar, as is illustrated by the tight cluster in the centre of the cation triangle. Group 2 is distinguished by clearly lower chloride concentrations and electrical conductivities than Group 1. A pattern in the distribution of cations in Group 2 is not so easy to observe, the concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  vary, while  $\text{Na}^+$  and  $\text{K}^+$  are generally low.

Except for sample BAF, the members of Group 3 display conductivities in the lower part of the spectrum. What distinguishes this group from Group 2 is that their magnesium content is much higher than calcium. No other direct similarity can be found, except that the origin of these samples is the east and southeast of the study area (except BAF), where metamorphic and volcanic rocks predominate. The last “group” (Group 4) is composed of only one sample, the dug well BBP. With its high electrical conductivity and element concentrations, it is separated from all other samples.

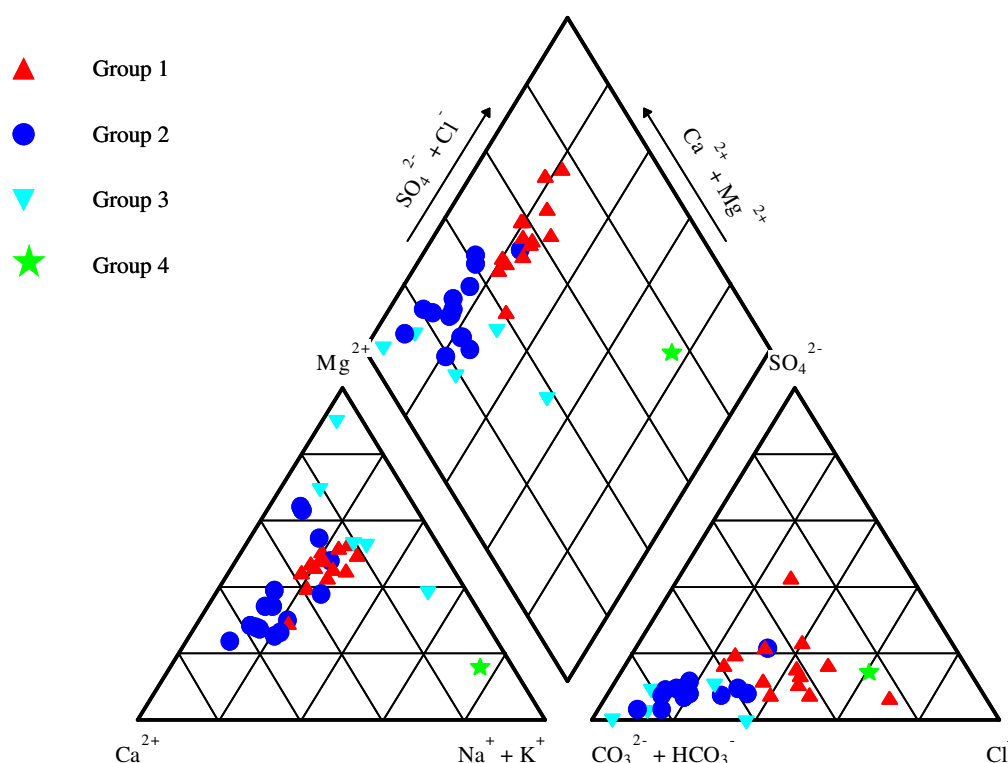


Fig. 12: Piper diagram displaying the groups distinguished by cluster analysis (n = 35).

#### 4.1.3.3 Discussion

The groups separated by cluster analysis correspond well to the determined water types. Most Group 1 members belong to Mg-Ca-Cl-HCO<sub>3</sub> or Mg-Ca-HCO<sub>3</sub>-Cl water types, where Mg<sup>2+</sup> is the dominant cation and mostly Cl<sup>-</sup> the dominant anion. Group 2 are mainly Ca-Mg-HCO<sub>3</sub> types, with some Mg-Ca-HCO<sub>3</sub>. Here Cl<sup>-</sup> is subordinate to HCO<sub>3</sub>, which is also reflected in the lower electrical conductivities. Group 3 is mainly distinguished by Mg-HCO<sub>3</sub> types (Tab. 5).

Tab. 5: Summary of the main characteristics of groups designated by cluster analysis

	~ EC range [ $\mu\text{S}/\text{cm}$ ]	Main water types
<b>Group 1</b>	1400 - 3900	Mg-Cl, Mg-HCO <sub>3</sub>
<b>Group 2</b>	500 - 1400	Ca-HCO <sub>3</sub>
<b>Group 3</b>	1000 – 1350 (2500)	Mg-HCO <sub>3</sub>
<b>Group 4</b>	7135	Na-Cl

A subdivision of water samples from Troy into groups using cluster analysis has already been carried out by Weber (2003). In some aspects, her work differs from the results obtained in this study, even though the same methods (euclidean distance, complete linkage) and input parameters were used. The composition of input samples is not totally identical, with some sampling points not sampled anymore in 2006, while others, e.g. QET, QPB, FAF and QWK do not occur in the 2002 analysis.

Weber distinguishes 3 groups mainly on their EC values, with Type 1 having an EC < 1900  $\mu\text{S/cm}$ , Type 2 1900-3600  $\mu\text{S/cm}$  and Type 3 > 3600  $\mu\text{S/cm}$ . These groups roughly correspond to Group 2, Group 1 and Group 4 subdivided in this study. Group 3, with EC between 986-1362  $\mu\text{S/cm}$  and  $\text{Mg}^{2+}$  concentrations clearly higher than  $\text{Ca}^{2+}$  was not distinguished by Weber (2003).

#### **4.1.4 Iron, nitrite, ammonium**

These three ions were measured in the field using a photometer. Especially the results for total Fe and Fe(II) are seen as inaccurate and in some cases not realistic. This is due to the fact that in 73% of all samples, the determined concentration of Fe(II) is higher than the total Fe concentration. The total iron content should include both Fe(II) and Fe(III), therefore it is logical that Fe(II) should be lower than total Fe. Because it cannot be established which of the two methods of analysis is inaccurate (if not both), results for neither total Fe nor Fe(II) will be further discussed in this study.

Nitrite ( $\text{NO}_2^-$ ) and ammonium ( $\text{NH}_4^+$ ) occur in low concentrations in most samples. Nitrite ranges from 0.002 to 0.354 mg/l (median 0.009 mg/l), with only sample BEA (0.354 mg/l) exceeding the WHO guideline of 0.2 mg/l for long-term exposure to nitrite (WHO 2005). In the presence of oxygen,  $\text{NH}_4^+$  is quickly oxidised to  $\text{NO}_2^-$  and further to  $\text{NO}_3^-$ , therefore  $\text{NO}_2^-$  and  $\text{NH}_4^+$  can only persist in water depleted of oxygen, which is not the case for most samples. Most measured ammonium levels hover between 0.01 and 0.04 mg/l, with the highest value of 4.67 mg/l found in the unused dug well BAF in a reducing environment.

#### **4.1.5 Trace elements**

A large number of trace elements were analysed in the water samples collected during the 2006 field campaign. Most elements are contained in very low concentrations or below the detection limit. An exception to this rule is arsenic, which in some samples shows

concentrations exceeding the 10 µg/l guideline set by the WHO for drinking water (WHO 2005). By far the highest arsenic concentration (87 µg/l) is found in the dug well BBP, which also displays the highest concentrations for several other trace elements, such as Mn, Ni, Mo, U, Co and Sb.

Elevated arsenic concentrations in the Troian spring cave (26.4 µg/l, sample QS2) are seen by Wolkersdorfer & Göbel (2004) to be the result of a natural geogenic anomaly.

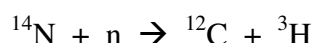
Readers interested in a more detailed evaluation and discussion of trace element concentrations in the waters of Troia should refer to Weber (2003) and Wolkersdorfer et al. (2003).



## 4.1.6 Tritium

### 4.1.6.1 Introduction

The radioactive hydrogen isotope tritium ( $^3\text{H}$ ) is incorporated into meteoric water molecules by oxidation and becomes part of the hydrologic cycle, reaching groundwater at some stage. Tritium is naturally produced by cosmic-ray bombardment of nitrogen and deuterium in the upper atmosphere:



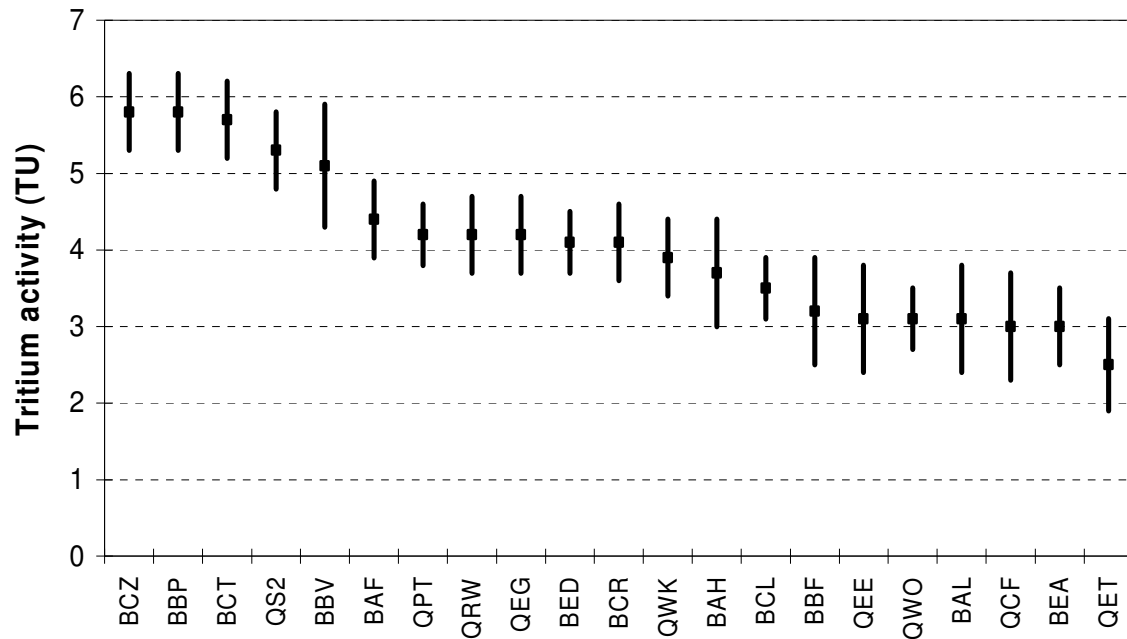
A significant source of tritium has been the atmospheric testing of thermonuclear bombs, which occurred from 1952 to 1980 and raised  $^3\text{H}$  levels in the stratosphere by several orders of magnitude. Tritium in global precipitation peaked in 1963 and has since then been declining, now being close to natural levels (Clark & Fritz 1997).

These natural, cosmogenic tritium concentrations in precipitation are given by Kazemi-Fard et al. (2006) as 3-6 TU in Europe, though these values have to be considered with some caution as very few measurements of pre-bomb tritium levels exist (Clark & Fritz 1997). One tritium unit (TU) represents one THO molecule in  $10^{18}$   $\text{H}_2\text{O}$  molecules (Kazemi-Fard et al. 2006).

Tritium has a short half-life of 12.43 years, which enables it to be used for the dating of young groundwater (Clark & Fritz 1997), though its continuing decay will make it hard to discern the bomb-peak in the future .

### 4.1.6.2 Results and Discussion

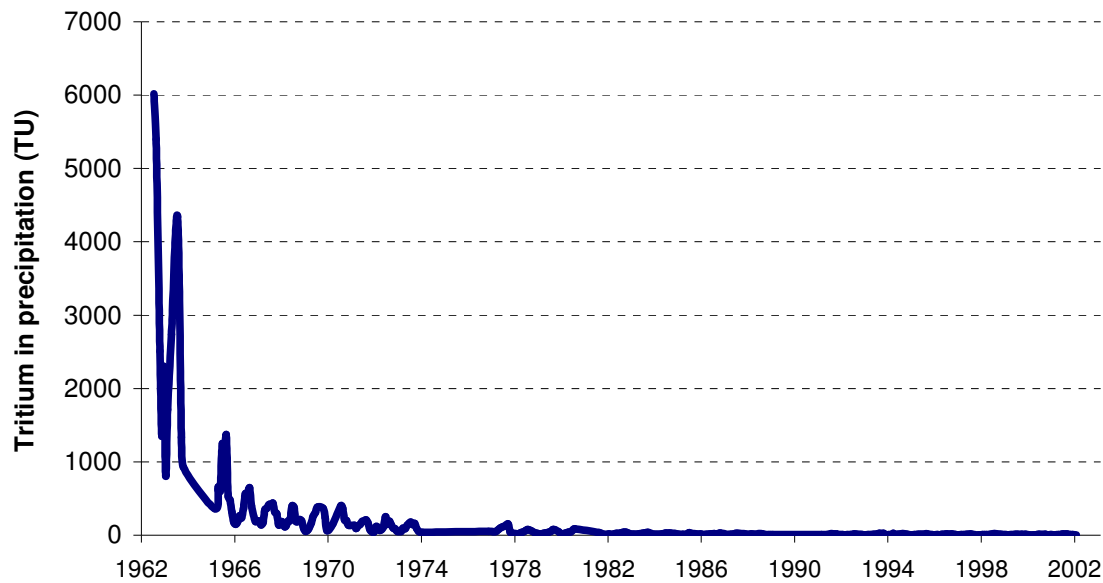
Altogether, 21 samples were taken for the analysis of tritium. The tritium activities of all samples lie within a very close range from 2.5 to 5.8 TU (Fig. 13). There are no noticeable patterns linking location or sample type with tritium activity.



**Fig. 13: Tritium activities in Troian water samples taken in 2006**

An exact age for the sampled groundwater cannot be given with certainty, as the initial tritium value of the recharge water is not known. No tritium data is available for the Troia region, the nearest location with a reasonably complete data set (1963 – 2002) being the GNIP (Global Network of Isotopes in Precipitation) station in Ankara, 600 km inland to the east. The tritium input curve for Ankara shows tritium values peaking at 6020 TU in 1963 and then sharply declining (Fig. 14). Values for the late 1990s to 2002 generally range from 5 to 16 TU.

Tritium concentrations generally show a pronounced continental effect, with levels at the coast being lower than further inland (Clark & Fritz 1997). Therefore it can be assumed that  $^3\text{H}$  concentrations in precipitation in the Troad are also lower than in Ankara. Verification for this assumption is given by data available for Antalya, a coastal city in southern Turkey, where tritium levels of the late 1990s lie between 3 and 8 TU (IAEA/WMO 2004).



**Fig. 14: Concentration of tritium in atmospheric precipitation at Ankara, Turkey (IAEA/WMO 2004)**

Assuming that tritium concentrations in the precipitation of Troia are similar to those of Antalya, the water samples show equal to slightly lower tritium values than are found in current precipitation. The water may therefore be derived from very recent recharge, where tritium has as yet undergone little decay, or represent a mixture of submodern and bomb-peak recharge. Several factors point to the first scenario being most likely. Groundwater was sampled from shallow aquifers, with the water table in the sampled dug wells for example lying between 2 and 3 m below ground level (an exception is the borehole BED, where water originates from depths of around 100 m). Even though the sedimentary sequence of the Troy ridge includes layers of low permeability ( $k_f$ :  $10^{-8} - 10^{-9}$  m/s) between the sandstone aquifers, these are thin and Blume (2003) suspects local inhomogenities (preferential flow pathways) that greatly increase the calculated permeabilities, thereby reducing the retention time of replenishing water. Further evidence supporting swift recharge of groundwater and high turnover time is given by the elevated nitrate concentrations found in many of the samples (up to 237 mg/l). These high values are mainly caused by large-scale fertilisation of crops, which has only been carried out in the study area since the start of intensive agriculture about 20 to 30 years ago (Özcan et al. 2007). The water samples are therefore likely to be constituted from recharge younger than about 20 – 30 years, if not having been mixed with very old groundwaters.

The chemical signature of Troian groundwater (predominance of Mg-HCO<sub>3</sub> and Ca-HCO<sub>3</sub> types) also gives an indication of age. Water-rock interactions over long periods of time often result in a shift from Ca or Mg to Na as the major cations due to ion-exchange processes. Mg-HCO<sub>3</sub> and Ca-HCO<sub>3</sub> types are therefore more typical of young groundwater (Hölting 2005).

## **4.2 Time Series**

Hydrogeological and hydrochemical investigations have been conducted in the study area from the years 2001 to 2006. The most complete data series are available for 2002, 2003, 2004 and 2006 (no field campaign was undertaken in 2005). The following section will look at comparing several different measured parameters, such as discharge, water table height and main ion concentrations from the different years. In order to have a consistent and reliable comparison, only sampling points with complete data for all four years were included in the analyses.

### **4.2.1 pH and electrical conductivity**

Neither pH value nor EC show any obvious changes over the observed time period. The good buffering properties of the region's carbonate rocks prevent large fluctuations in pH. Specific electrical conductivity has slightly increased at some measuring points but also decreased at others, so that the overall mean and median of all measuring points has remained similar from 2002 to 2006.

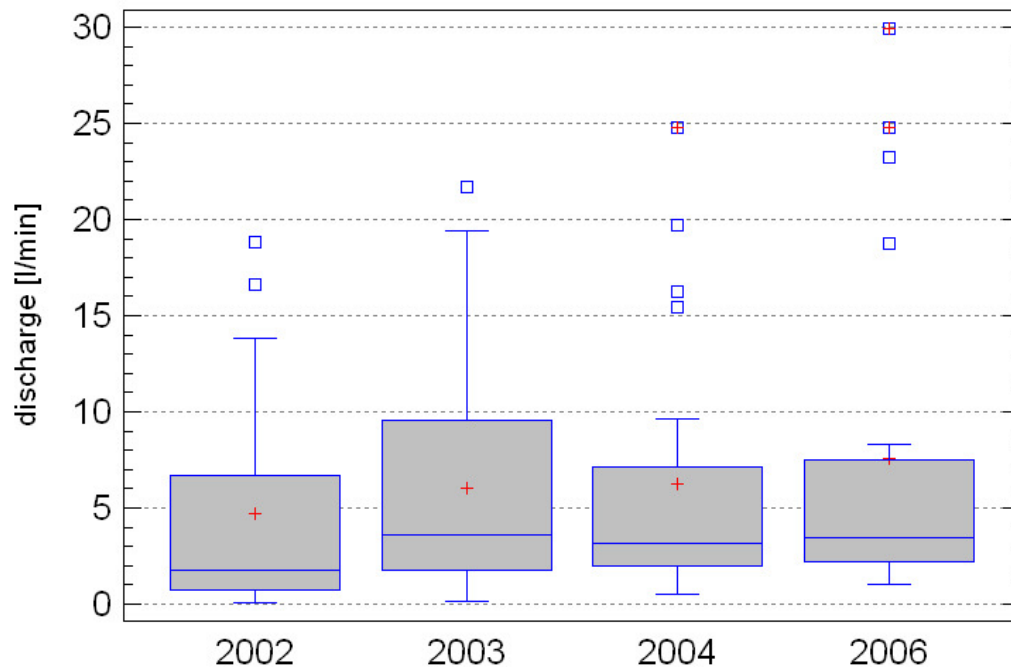
### **4.2.2 Discharge and depth of water table**

The amount of water that is discharged from wells and springs gives an indication of the status of the region's water supply. In dry years, with little precipitation, it is expected that discharge and groundwater tables will be lower than in wetter years, therefore hydrogeological data will be compared with meteorological data.

Fig. 15 shows the discharge measured at wells and springs in litres per minute, while the depth of the water table below the top of the well is presented in Fig. 16.

The discharge measuring points are spread over the whole study area and display greatly varying discharges, ranging, for example, from 0.054 to 18.8 l/min in the year 2002. What has to be kept in mind when contemplating Fig. 15 is that changes in the higher discharge levels have a greater visual impact on the graph than changes of the same order of magnitude in the lower discharge levels. For example, an increase in the discharge of measuring point BBG from 0.42 l/min in 2003 to 1.16 l/min in 2004 has a higher significance (176% increase) than

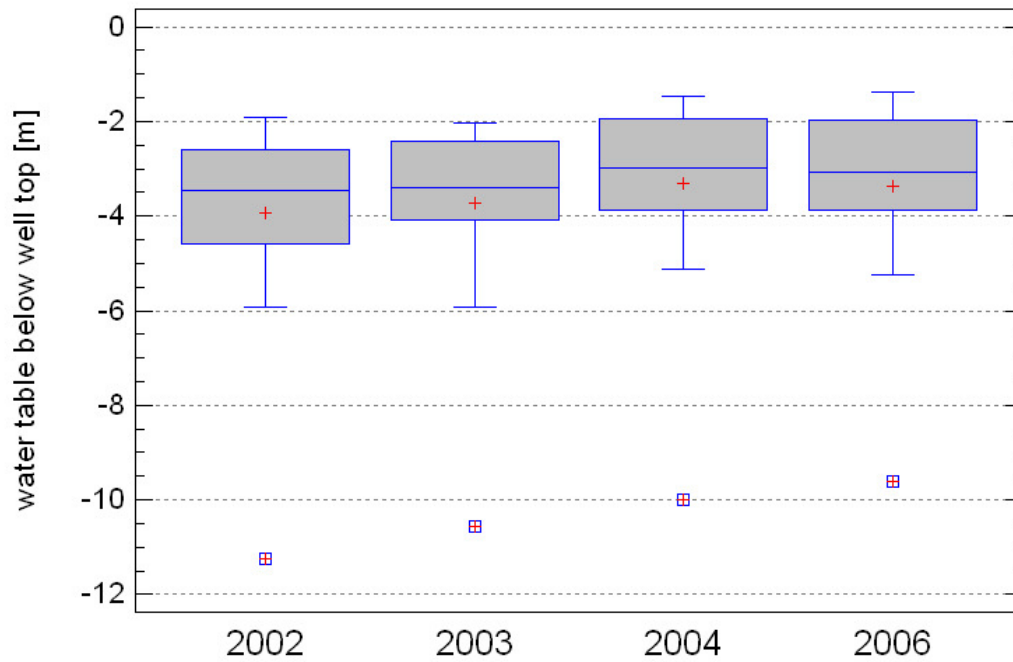
the change from 13.85 l/min (2002) to 19.38 l/min (2003) at BAO with only a 40% increase, even though the latter has greater visible influence on the shape of the box-plot.



**Fig. 15: Comparison of discharge measured at wells and springs in Troia over four years (n = 21)**

Both median and mean discharge values have risen over the time period. That over 50 % of values lie below 4 l/min can be seen from the position of the median. The outlying values show that there are few measuring points with high discharge, though all of them have increased over the given time period. The lowest discharges occur in the year 2002, while the median values of the other three years are similar (Fig. 15).

Like the discharges, groundwater tables measured in wells have also risen in the study area. Once again the year 2002 displays the lowest values. A distinct increase is noticeable from 2003 to 2004, while levels have remained almost the same from 2004 to 2006 (Fig. 16).



**Fig. 16: Level of the groundwater table compared over four years (n = 20)**

#### 4.2.2.1 Discussion

It has been postulated that the above mentioned increase in discharge and rise in water table may be connected to the amount of precipitation that has fallen in the observed period. Of course other factors, such as the withdrawal of water for agricultural and drinking purposes in the region also play a major part and are difficult to quantify.

Meteorological data (temperature and precipitation) for Çanakkale, 30 km to the northeast of the study area, is presented in Table 6. The total annual precipitation of the years 2000 to 2006 varies from 439 - 766 mm. Though 2001 received the most rainfall in total, it was very unevenly distributed, with only 12 mm falling over five months from June to October. It can be assumed that this extremely dry summer of 2001 put considerable strain on the region's water resources (for example increased and prolonged groundwater extraction for irrigation) that may have led to a lowered groundwater table in the shallow aquifers of the Troad.

**Tab. 6: Monthly temperature and precipitation data for Çanakkale from 2000-2006 (NOAA/NCDC)**

		Months												Mean/Total
		J	F	M	A	M	J	J	A	S	O	N	D	
<b>Temperature</b> (°C)	<b>2000</b>	4.1	7	7.9	14.6	17.8	22.4	25.9	25.6	21.2	15.7	13.7	9.5	15.5
	<b>2001</b>	8.7	8.6	13	13.3	18	22.8	27.4	27.2	22.4	17.5	11.1	3.9	16.2
	<b>2002</b>	4.9	9.3	9.8	12.1	18.2	23.3	26.6	25.7	21.2	16.6	13.3	6.8	15.7
	<b>2003</b>	8.5	2.2	5.5	9.8	18.5	24	25.6	26.4	20.2	16.9	11.2	7.5	14.7
	<b>2004</b>	5.4	6.5	9.5	12.7	17.1	22.6	25.3	24.8	-	18	12.7	9	14.9
	<b>2005</b>	6.8	6	8.2	12.8	17.9	21.9	25.5	25.7	21.7	14.9	10.5	9.1	15.1
	<b>2006</b>	3.1	5.6	8.7	13.2	17.7	22.2	24.8	26.4	21.3	16.2	10.4	7.5	14.8
<b>Precipitation</b> (mm)	<b>2000</b>	18	103	87	27	12	8	0	5	trace	131	18	30	439
	<b>2001</b>	60	69	8	120	65	0	0	2	10	0	193	239	766
	<b>2002</b>	58	74	58	34	2	8	24	0	55	71	138	78	600
	<b>2003</b>	55	103	16	83	15	0	0	0	23	88	8	120	511
	<b>2004</b>	218	50	28	51	14	22	1	4	trace	6	46	63	503
	<b>2005</b>	90	144	27	8	73	5	33	0	13	47	219	71	730
	<b>2006</b>	53	85	124	4	17	23	8	1	71	38	34	26	484

The precipitation that fell over the winter of 2001/2002, even though high with 622 mm (Oct–Mar), possibly did not deliver enough recharge to replenish groundwater stocks, giving an explanation for the low water table and discharges measured in July and August 2002. The following years show no obvious abnormalities in their precipitation pattern. The winter of 2005/2006 can be considered as wet, with 599 mm occurring from October to March. This may have influenced the higher discharges measured in August 2006.

### 4.2.3 Major ions

Data of the major ion concentrations in the waters of Troia is available for the years 2002, 2003 and 2006. Even though a field campaign was undertaken in 2004 by Wolkersdorfer, no water samples were collected. To determine if any obvious changes have occurred over the mentioned time period, the data has been plotted on a piper diagram (Fig 17). At first sight, no distinct patterns can be distinguished, especially on the anion triangle. On the cation triangle, a slight shift towards higher sodium and/or magnesium concentrations is noticeable for 2003, though the clustering and overlapping of the plotted points make any precise statement impossible. Even though single samples may have changed in composition, the overall sample population does not indicate any significant changes in the concentrations of major ions.



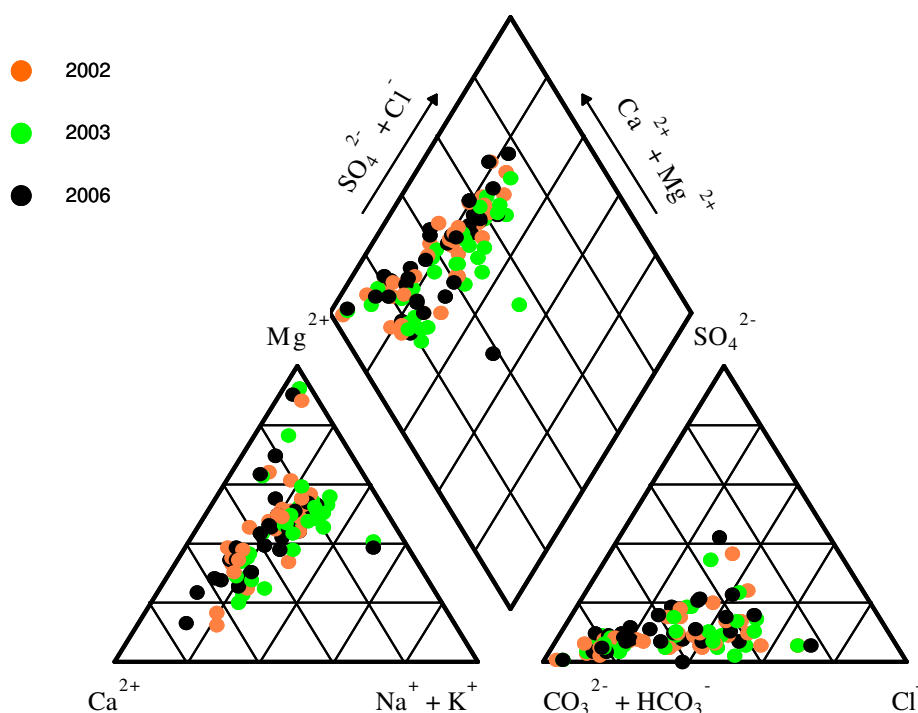
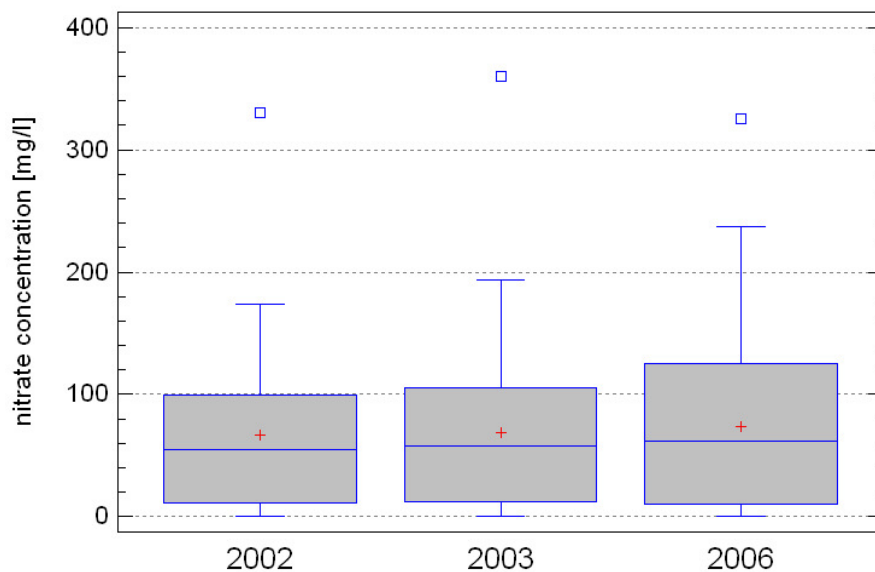


Fig. 17: Piper diagram displaying the spread of water samples from three separate years

#### 4.2.4 Nitrate

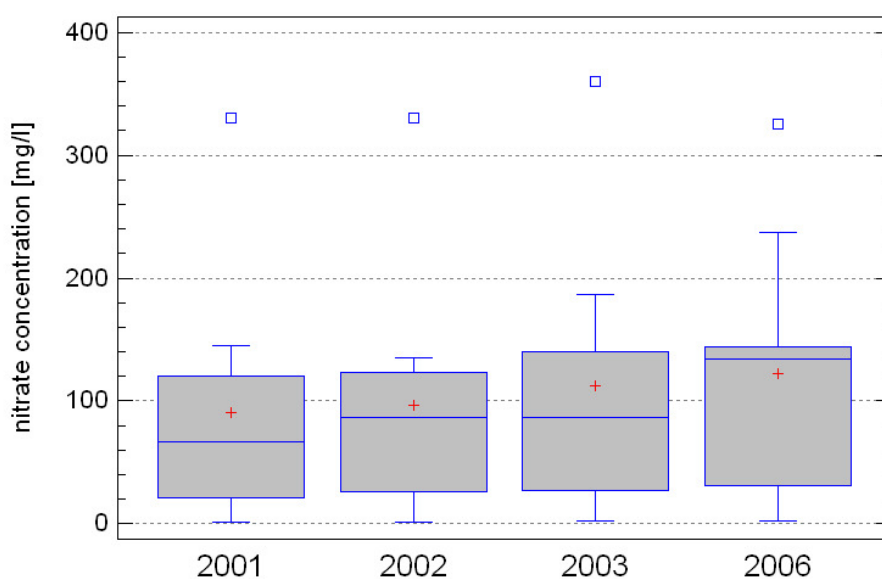
During the evaluation of data for this study, it was noticed that nitrate ( $\text{NO}_3^-$ ) concentrations seemed to have risen over the years. To establish if this assumption can be verified, a separate section is herewith dedicated to the change in nitrate concentrations from 2001 to 2006.

Nitrate is a very mobile species in the saturated and unsaturated zone and shows little interaction (DVWK 1996). Because of its function as an essential plant nutrient, it is a main component of many fertilisers. Excess nitrate that has not been absorbed by plant roots is easily washed out by precipitation and leaches into the groundwater, a common side-effect of over-fertilisation. High nitrate concentrations can lead to algal blooms in surface water (eutrophication) and also have adverse health effects when found in drinking water. Part of the  $\text{NO}_3^-$  taken up by humans is reduced to  $\text{NO}_2^-$ , which in infants oxidises haemoglobin and diminishes its function as an oxygen carrier. This dangerous condition is called methaemoglobinemia, or “blue baby” syndrome (DVWK 1996).



**Fig. 18: Spread of nitrate concentrations compared over three years (n = 34)**

Mean and median nitrate concentrations have steadily risen in the period from 2002 to 2006 (Fig. 18). Of course not all sampling points have experienced increases, at some, nitrate concentrations have fallen or stayed the same. Most samples with elevated concentrations that are above the WHO guideline value for drinking water of 50 mg/l (WHO 2005) originate from the fringes of settlements or from areas of intensive agriculture. For nine sampling points, data is available for the year 2001 as well as for 2002, 2003 and 2006 and once again the rising trend is noticeable (Fig. 19).



**Fig. 19: Nitrate concentrations in Troian water samples in a 4-year comparison (n = 9)**

The sites sampled in the 4-year comparison are mostly located in the central part of the study area, around the villages of Tevfikiye and Çiplak.

Of special concern are the sampling points QET (144 mg/l) and QEE (237 mg/l) in Tevfikiye that are used as drinking water by fieldworkers and their families (Wolkersdorfer et al. 2004). Their nitrate concentrations far exceed the WHO guideline for drinking water of 50 mg/l. As a possible explanation, Wolkersdorfer et al. (2003) give animal excrements passing through permeable sediments from stables and farm yards located not far from the spring.

It is very likely that the increasing nitrate concentrations in the study area are linked to excessive fertilisation of crops and possibly also to the impact of domestic sewage.

## 5 Summary and Conclusion

Hydrogeological and hydrogeochemical investigations have been carried out in the study area since 2001, culminating in the 2006 field campaign which is subject of this thesis. The 2006 results have in part confirmed and reinforced what previous studies (Wolkersdorfer et al. (2003, 2004); Weber (2003) etc.) have found, but also include new findings such as the results of tritium measurements and the time series comparison of hydrogeological parameters.

### **5.1 Hydrochemistry and isotope hydrology**

The common occurrence of carbonate sediments in the study area has resulted in well-buffered waters, with pH values fluctuating around neutral.

Specific electrical conductivity has been one of the most important parameters in distinguishing different water types. The sampled waters show a wide range of conductivities which reflect their origin and chemical composition. Groundwater that emerges from the sedimentary sequences of the Troy and Kumkale ridges has a high degree of mineralisation, caused by water-rock interactions over a prolonged period of time. Compared to this, river water from the Dümrek and Karamenderes, as well as groundwater originating from igneous and metamorphic rocks shows lower mineralisation and conductivities. This spatial pattern not only applies to electrical conductivity but also to concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  which are higher in samples from the Troy and Kumkale ridges. Samples with high EC generally also display elevated chloride and sodium concentrations, a connection that is further accentuated by *Pearson* correlation coefficients between these parameters that are close to 1.

Both grouping methods that were applied to the data (water type designation and cluster analysis) gave similar results and mostly adhere to the spatial and chemical differences already mentioned above. Group 1 distinguished by cluster analysis, with  $\text{EC} > 1400 \text{ mg/l}$  is composed of Mg-Cl and Mg- $\text{HCO}_3$  water types, whereas Group 2 has lower conductivities and mainly Ca- $\text{HCO}_3$  types. Group 3 is largely composed of Mg- $\text{HCO}_3$  types originating from volcanic and metamorphic rocks in the south-east of the study area.

Investigations into the isotopic composition of samples suggest that water retention times in the unsaturated zone are low and the sampled groundwater of young age. Despite the range in water types (which can be an indicator for different ages), all samples show very similar tritium signatures.

## **5.2 Time Series**

The main irrigation pumps (boreholes with motor pumps) are located on the Karamenderes and Dümrek plains in quaternary aquifers and operate day and night in the summer months. Wolkersdorfer & Göbel (2004) found that groundwater tables have been lowered by up to 11 metres in the Dümrek and by up to 9 metres in the Karamenderes valley. Drinking water for the surrounding villages is also sourced from boreholes on the river plains. The current study compared water tables in dug wells for the years 2002 - 2006 and found that there was a noticeable increase. All wells that were included in this comparison are located on the Troy or Kumkale ridges or the hill country in the east or southeast of the study area. The rising water table indicates that these locations are not affected by water extraction from quaternary aquifers of the river floodplains. Rather, the water table is rising again to higher levels after the extremely dry summers of 2001 and 2003. Similarly, an increase in water discharged from springs was also noticed and can be attributed to slightly higher precipitation during the winters of later years.

Farmers on the Troy ridge have boreholes equipped with pumps that are used on demand. Because the extraction quantity and the frequency of pumping over the time period of 2002-2006 are unknown, no conclusions can be drawn as to how this practice has affected discharges and the height of the groundwater table. This kind of information is needed in order to make more reliable statements as to why water levels have changed. Also of interest would be to know whether agricultural practices have changed during this time, as different crops and cropping methods have an impact on soil infiltration and surface runoff.

## **5.3 Anthropogenic impact**

The impact that human activities have on Troian water cannot be overlooked but is also difficult to quantify. Large tracts of the study area have been transformed from swamps to high intensity agricultural land in a matter of decades, a change that brings with it the need for irrigation and fertilisation. No studies into the use of fertiliser and its impact on groundwater of Troia over prolonged periods of time (years) are known to exist. Özcan & Kavdır (2005) investigated groundwater samples from the Karamenderes floodplain with respect to their nitrogen content from December 2002 to September 2003 and found that nitrate concentrations increased markedly during the crop growing season, pointing to fertiliser impact.

Though not the main aim of this study, nitrate concentrations from 2001 to 2006 were compared and found to increase. This increase was especially obvious in samples located in the vicinity of Tefikiye.

Sources for water pollution other than fertilizer can be found in and around the villages, where an official garbage collection often seems to be lacking and domestic waste is frequently strewn over backyards and adjoining fields. The fate of sewage is not known by the author, but it is suspected that treatment and disposal is insufficient by western European standards, thereby posing as another possible water contamination source.

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## 7 Appendix

Tab. 7: Main on-site parameters measured in Troian waters

Measuring point	pH	T [°C]	EC [μS/cm]	O <sub>2</sub> [mg]	O <sub>2</sub> [%]
BA1	7.43	26.3	819	6.71	83.6
BAD	7.40	20.6	1282	7.91	89.5
BAE	7.01	16.7	1932	1.29	13.4
BAF	7.41	17.8	2469	0.06	0.6
BAG	7.44	25.4	963	9.02	111.4
BAH	6.80	23.4	3860	4.24	50.7
BAI	7.17	21.7	1727	5.00	57.7
BAK	6.76	20.1	1846	3.92	43.5
BAL	6.92	17.3	2267	1.20	12.7
BAN	6.91	21.5	2519	6.91	61
BAO	6.90	18.2	1278	3.51	38.1
BAP	6.89	19.8	1493	4.40	49.3
BAQ	7.17	25.9	739	7.21	90.4
BAR	7.18	19.1	1912	0.29	3.1
BAT	6.89	18.6	1264	6.34	68.9
BAU	7.15	23.1	1362	6.75	80.3
BAV	6.96	19.3	2318	0.42	4.7
BAY	8.23	26.0	1467	6.77	84.2
BAZ	7.78	20.9	1264	2.35	26.7
BBA	7.45	17.7	2681	2.79	29.9
BBB	8.56	18.3	605	0.30	3.1
BBE	7.49	24.8	1028	5.08	62
BBF	7.06	17.4	1523	7.60	80.2
BBF	7.06	17.0	1508	6.12	63.9
BBF	7.06	17.4	1523	7.6	80.2
BBG	7.60	23.0	1560	7.68	90.6
BBK	7.04	17.2	3749	6.83	71.7
BBL	7.50	23.3	968	13.2	155.8
BBM	6.87	19.1	2832	0.42	4.6
BBN	6.87	16.6	1936	0.21	2.3
BBO	6.87	18.0	1965	0.26	2.7
BBP	7.65	16.1	7135	0.09	0.9
BBS	7.19	17.7	1147	1.60	16.7
BBT	7.18	18.2	1369	7.03	75.5
BBU	7.36	17.6	2424	1.17	12.4
BBV	7.42	17.6	2066	8.03	84.9
BBW	7.22	18.0	1895	4.96	52.7

**Tab. 7 (cont.): Main on-site parameters measured in Troian waters**

<b>Measuring point</b>	<b>pH</b>	<b>T [°C]</b>	<b>EC [μS/cm]</b>	<b>O<sub>2</sub> [mg]</b>	<b>O<sub>2</sub> [%]</b>
<b>BBX</b>	7.22	16.1	966	4.95	50.2
<b>BBY</b>	8.05	21.4	1450	8.05	92.1
<b>BBZ</b>	7.82	16.8	1301	8.66	90.4
<b>BC1</b>	7.13	18.7	1155	6.81	73.8
<b>BCC</b>	6.67	16.9	2197	0.48	5.1
<b>BCD</b>	6.73	20.8	1125	0.06	0.7
<b>BCG</b>	7.26	18.6	953	8.70	94.4
<b>BCH</b>	6.81	19.0	2368	2.63	28.7
<b>BCI</b>	7.09	19.1	2419	0.51	5.5
<b>BCK</b>	6.88	18.3	2187	5.01	53.6
<b>BCL</b>	7.37	21.1	1391	6.20	70.5
<b>BCN</b>	7.26	18.2	1413	0.14	1.4
<b>BCO</b>	7.17	19.4	1626	1.80	19.7
<b>BCQ</b>	8.54	27.9	1978	20.00	200
<b>BCR</b>	7.26	18.4	986	0.18	21
<b>BCS</b>	7.06	22.3	1350	6.77	78.4
<b>BCT</b>	6.99	19.5	886	7.67	84.5
<b>BCU</b>	6.89	17.1	950	7.58	79.2
<b>BCV</b>	7.08	17.0	1023	0.40	4.1
<b>BCW</b>	6.99	17.1	843	2.13	22.5
<b>BCX</b>	7.05	24.3	1855	5.63	67.9
<b>BCY</b>	7.18	25.2	1614	5.08	62.2
<b>BCZ</b>	7.23	19.7	1204	2.17	24.3
<b>BDD</b>	7.81	30.2	1259	6.18	83.2
<b>BDF</b>	7.16	17.0	967	1.08	11.4
<b>BDG</b>	7.41	21.2	866	8.13	92.6
<b>BDH</b>	7.43	20.8	867	8.09	91.5
<b>BDN</b>	7.50	23.1	1735	5.82	69.5
<b>BDO</b>	7.42	21.5	1328	6.02	69.1
<b>BDQ</b>	7.02	21.7	1808	3.44	39.4
<b>BDR</b>	6.98	18.4	2217	5.81	62.6
<b>BDS</b>	7.03	23.5	1807	4.01	47.9
<b>BDT</b>	6.94	16.9	1948	3.31	31.3
<b>BDV</b>	6.99	18.5	2509	0.70	7.5
<b>BEA</b>	7.41	16.9	1953	0.14	1.4
<b>BEC</b>	7.51	18.2	1079	8.47	90.9
<b>BED</b>	7.35	19.6	747	5.58	61.3
<b>BEE</b>	7.29	17.7	1363	7.38	78.2
<b>BEF</b>	7.17	18.1	2348	0.96	10.2

Tab. 7 (cont.): Main on-site parameters measured in Troian waters

Measuring point	pH	T [°C]	EC [μS/cm]	O <sub>2</sub> [mg]	O <sub>2</sub> [%]
BEG	6.85	23.6	946	4.34	52.5
BJB	7.63	26.4	712	8.85	111
BJC	7.08	27.2	719	3.80	50
BJD	6.77	18.2	1062	5.97	63.9
BJE	7.07	17.1	3104	1.08	11.5
BJG	6.97	19.3	1163	0.17	1.6
BJL	6.96	18.2	1423	5.58	59.5
BJM	6.99	18.3	1995	0.18	1.9
BJQ	7.06	19.7	1628	1.61	17.7
BJR	7.3	16.6	948	2.00	20.8
BJS	7.46	19.8	1530	0.07	0.7
BJT	6.82	16.4	807	4.09	47.3
BK1	7.15	17.9	1731	7.50	79.5
BK4	7.76	23.8	1079	8.92	106
BK9	7.57	27.1	1045	8.29	106
BNK	7.25	17.3	1221	8.19	85.5
BSC	7.03	16.4	2278	0.21	2.1
BT2	7.06	19.1	2675	7.52	82.1
BT3	7.37	22.1	1645	8.30	95.7
BT4	6.76	18.4	1027	4.81	51.3
BT5	6.68	17.5	3316	3.18	33.6
CTB	7.06	19.3	1814	4.11	45.1
DAF	7.24	23.6	1113	2.44	29.4
FAA	7.97	23.0	609	-	-
FAB	6.8	17.1	804	4.88	51.4
FAC	6.9	17.6	775	-	-
FAD	8.13	23.2	1014	1.37	16.1
FAE	7.46	24.3	525	2.56	30.8
FAF	7.93	24.4	489	6.96	83.7
FAG	7.62	23.5	472	3.32	39.1
FAH	8.22	25.2	451	8.54	103.8
FAI	7.57	23.9	479	2.54	30.2
FAK	7.62	23.9	476	2.98	35.7
FAL	7.69	24.9	540	4.40	53.4
FAN	8.13	26.9	444	8.84	111.5
FAO	7.82	27.3	447	6.25	79.5
FED	7.29	19.7	1076	7.20	80.2
FKK	8.17	25.9	503	8.66	108.1
GHW	7.31	26.8	1003	8.88	110.9
HS1	8.33	17.9	664	-	-
HS3	7.78	16.4	734	9.51	97.4

**Tab. 7 (cont.): Main on-site parameters measured in Troian waters**

<b>Measuring point</b>	<b>pH</b>	<b>T [°C]</b>	<b>EC [μS/cm]</b>	<b>O<sub>2</sub> [mg]</b>	<b>O<sub>2</sub> [%]</b>
<b>PAA</b>	7.12	17.9	699	3.28	35
<b>PAB</b>	7.05	16.9	1818	7.60	79.2
<b>PB1</b>	7.33	18.0	747	3.42	36.2
<b>QCF</b>	7.55	25.1	509	7.44	91
<b>QEA</b>	6.60	25.3	2580	4.56	56.5
<b>QEE</b>	7.25	17.6	2730	8.44	88.1
<b>QEG</b>	7.03	22.0	1380	4.00	46.4
<b>QET</b>	7.58	17.0	1874	8.80	91.6
<b>QHC</b>	7.35	25.4	2308	8.80	109.3
<b>QJA</b>	7.18	15.8	1235	2.50	25.9
<b>QJE</b>	6.85	21.5	826	8.39	98.1
<b>QKE</b>	7.49	17.4	557	4.55	48.2
<b>QNT</b>	7.47	18.2	2072	8.92	95.8
<b>QPA</b>	7.18	17.5	566	3.68	38.8
<b>QPB</b>	7.18	17.7	566	3.84	40.5
<b>QPC</b>	7.18	17.7	565	3.65	38.8
<b>QPT</b>	7.03	20.7	1441	4.15	45.9
<b>QRB</b>	7.55	19.6	693	8.49	93.2
<b>QRW</b>	7.24	18.0	701	7.03	75.8
<b>QS2</b>	8.11	16.6	1100	9.62	99.5
<b>QWD</b>	7.45	18.8	1058	-	-
<b>QWK</b>	6.90	18.2	903	5.31	57.1
<b>QWO</b>	6.99	18.4	928	2.12	23.2
<b>QWT</b>	8.03	22.5	2731	12.8	152.1
<b>R30</b>	7.18	20.2	2157	6.12	68.4
<b>SB3</b>	6.93	17.8	999	0.41	4.4
<b>SK1</b>	7.04	16.3	1449	0.12	1.2

Tab. 8: Major cations and anions of water samples from Troia

Sampling point	Ca [mg/l]	Mg [mg/l]	Na [mg/l]	K [mg/l]	Cl [mg/l]	SO <sub>4</sub> [mg/l]	NO <sub>3</sub> [mg/l]	HCO <sub>3</sub> [mg/l]
BAF	52.9	136	340	4.44	412	1.64	0.67	1025
BAH	252	238	206	1.11	1043	117	13.3	592
BAL	165	129	147	1.76	424	78.9	101	603
BAO	161	48.4	42.5	0.85	152	47.5	125	423
BAT	150	61.2	47.1	1.95	145	58.9	116	452
BAU	55.7	104	107	1.32	134	81.8	60.0	574
BAZ	20.4	204	16.2	0.66	34.7	7.81	0.48	930
BBF	110	107	87.3	3.58	157	153	128	543
BBP	130	161	1316	225	1865	594	11.0	1054
BBT	84.9	85.7	105	4.06	105	92.6	66.1	415
BBV	102	141	157	2.34	356	272	67.9	493
BBW	103	145	129	6.73	258	231	38.7	609
BBX	68.6	94.8	24.2	1.04	55.2	41.9	25.4	508
BBZ	82.9	84.3	78.4	1.09	154	136	147	278
BCL	107	87.1	72.9	2.86	213	51.1	64.3	430
BCR	49.1	79.2	71.5	2.49	41.6	56.1	41.4	549
BCT	137	30.3	26.8	0.98	44.8	39.5	76.0	416
BCX	211	74.3	112	1.12	325	95.3	109	499
BCZ	66.3	137	35.5	<0.5	71.5	25.6	10.1	793
BDF	114	57.1	39.3	1.64	73.4	62.6	55.4	447
BEA	177	124	98.6	1.58	219	453	125	360
BED	90.6	38.3	32.7	2.18	59.1	29.5	19.3	351
BSC	152	138	144	7.07	332	129	134	517
FAF	58.8	18.2	27.8	1.82	38.6	30.0	1.33	209
FKK	61.4	17.5	27.2	0.92	48.5	13.0	0.16	243
HS3	98.6	29.4	30.2	1.42	65.6	33.6	8.00	305
QCF	56.8	21.9	29.2	2.19	36.8	23.2	2.23	221
QEE	152	188	167	2.43	492	208	237	523
QEG	93.8	111	63.2	2.63	153	52.7	31.2	566
QET	118	119	88.3	3.96	287	110	144	384
QNT	156	127	96.3	7.22	279	132	325	415
QPB	79.3	23.1	24.6	2.47	38.2	27.0	4.74	252
QPT	131	79.6	64.2	35.2	189	79.3	136	444
QRW	121	13.3	24.3	1.02	41.4	20.8	0.67	391
QS2	91.4	58.6	46.4	52.7	103	49.7	84.7	403
QWK	60.2	84.1	19.2	0.76	36.5	15.1	1.60	540
QWO	-	-	-	-	39.8	12.6	0.05	609

**Tab. 9: Tritium ( $^3\text{H}$ ) levels in water samples from Troia**

<b>Sampling point</b>	<b><math>^3\text{H}</math> (TU)</b>	<b><math>^3\text{H}</math> error (TU)</b>
BAF	4.4	0.5
BAH	3.7	0.7
BAL	3.1	0.7
BBF	3.2	0.7
BBP	5.8	0.5
BBV	5.1	0.8
BCL	3.5	0.4
BCR	4.1	0.5
BCT	5.7	0.5
BCZ	5.8	0.5
BEA	3.0	0.5
BED	4.1	0.4
QCF	3.0	0.7
QEE	3.1	0.7
QEG	4.2	0.5
QET	2.5	0.6
QPT	4.2	0.4
QRW	4.2	0.5
QS2	5.3	0.5
QWK	3.9	0.5
QWO	3.1	0.4

**Tab. 10: Water discharge at selected measuring points, 2002-2006**

<b>Measuring point</b>	<b>Discharge [l/min]</b>			
	<b>2002</b>	<b>2003</b>	<b>2004</b>	<b>2006</b>
BAH	1.68	1.91	1.68	1.47
BAN	0.05	4.26	4.07	4.01
BAO	13.9	19.4	19.7	23.3
BAP	18.8	21.7	24.8	24.8
BAT	7.42	20.4	24.6	90.5
BAU	1.32	1.77	2.11	2.40
BAZ	0.19	1.14	1.84	1.45
BBG	0.42	1.16	1.43	2.05
BBS	5.60	5.41	2.27	2.79
BBV	2.93	3.10	3.13	3.28
BBW	1.32	2.75	3.14	3.50
BCX	1.70	11.1	3.21	6.77
BDQ	3.82	4.55	3.50	3.82
BDS	16.6	12.2	15.5	29.9
BEE	3.50	4.13	4.64	4.61
BT2	0.30	0.50	1.34	2.01
BT3	0.46	0.16	0.51	1.02
QEG	1.80	1.80	2.67	3.09
QET	10.8	14.1	16.3	18.8
QNT	7.80	8.09	9.65	8.28
QS2	1.02	1.94	3.09	3.42

**Tab. 11: Level of the groundwater table below the well top at selected measuring points in Troia**

<b>Measuring point</b>	<b>Water table below top of well [m]</b>			
	<b>2002</b>	<b>2003</b>	<b>2004</b>	<b>2006</b>
<b>BAF</b>	3.89	3.93	3.85	3.76
<b>BAK</b>	2.31	2.16	2.00	1.98
<b>BAL</b>	2.81	2.44	2.38	2.48
<b>BBA</b>	11.2	10.6	10.0	9.62
<b>BBK</b>	5.94	5.94	4.61	5.23
<b>BBM</b>	4.09	4.26	3.93	3.98
<b>BBO</b>	5.07	4.81	4.54	4.64
<b>BBP</b>	3.40	3.40	2.83	2.90
<b>BBU</b>	1.91	2.65	1.48	2.77
<b>BBY</b>	2.34	2.20	1.76	1.99
<b>BC1</b>	3.83	3.80	3.81	3.58
<b>BCD</b>	2.40	2.31	2.10	2.10
<b>BCH</b>	2.24	2.39	1.91	1.91
<b>BCI</b>	3.50	2.93	2.34	1.37
<b>BCV</b>	2.90	2.42	1.85	1.98
<b>BCW</b>	2.82	2.03	1.48	1.55
<b>BDF</b>	5.73	3.40	3.15	3.69
<b>BEA</b>	2.95	3.93	3.52	3.22
<b>BEC</b>	5.85	5.52	5.13	5.04
<b>BSC</b>	3.67	3.75	3.45	3.34

**Tab. 12: Nitrate concentrations at selected measuring points in Troia, 2001-2006**

Sampling point	Nitrate (NO <sub>3</sub> <sup>-</sup> ) [mg/l]			
	2001	2002	2003	2006
BAF	-	40.5	0.50	0.67
BAH	-	9.70	15.0	13.3
BAL	-	169	194	101
BAO	-	92.9	94.0	125
BAT	-	130	133	116
BAU	-	61.3	58.0	60.0
BAZ	-	1.70	0.50	0.48
BBF	-	124	108	128
BBT	-	55.8	66.0	66.1
BBV	-	21.0	40.0	67.9
BBW	-	29.3	34.0	38.7
BBX	-	19.3	18.8	25.4
BBZ	-	124	115	147
BCL	-	60.6	57.0	64.3
BCR	-	35.4	24.0	41.4
BCT	-	85.3	82.0	76.0
BCX	-	76.3	105	109
BCZ	-	6.40	12.3	10.1
BDF	-	53.4	60.0	55.4
BEA	-	174	91.0	125
BED	-	14.5	20.0	19.3
BSC	48.0	99.7	125	134
FAF	-	0.90	0.25	1.33
FKK	-	1.60	0.25	0.16
HS3	-	11.0	10.0	8.00
QCF	1.10	1.50	2.70	2.23
QEE	145	135	187	237
QEG	21.5	26.5	26.8	31.2
QET	120	123	140	144
QPB	1.40	2.00	2.80	4.74
QNT	330	330	360	325
QPT	67.0	65.8	81.0	136
QRW	-	0.80	0.25	0.67
QS2	81.0	86.8	87.0	84.7