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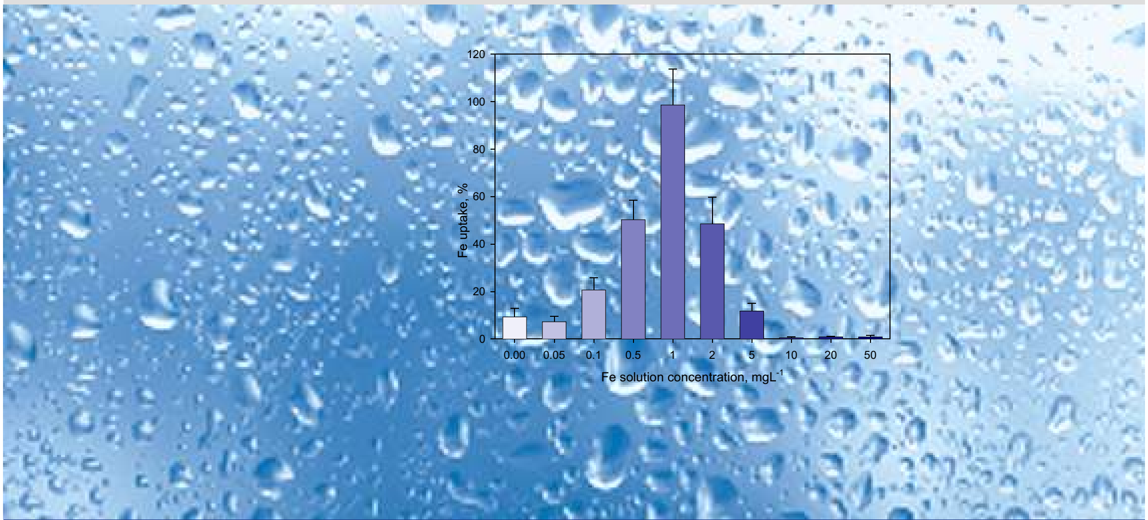
Trace Elements and Isotopes in Geochemistry – Fluids and Solids



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Trace Elements in the Waters of Troy

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Hydrogeological investigations were conducted within the Historical National Park Troia in north-western Anatolia (Turkey). 131 springs, wells, caves, and surface waters have been sampled and 44 representative samples were analyzed in the laboratory. It was possible to deduce three water types which differ in their main ions and especially in conductivity. Some trace elements and main parameters in waters used for drinking exceed the EU standards which might need future actions. No clear indication for the source of the water in the Troyan spring cave and for the other waters in the area investigated could be found by now, which might be due to a lack of geological information.

1 Introduction

Troy (Troia, Troja, Truva, Illios, Illium) in Western Anatolia (Turkey) belongs to the most intensively investigated archaeological sites in the world. Since the time of Heinrich Schliemann, though not being the first one who excavated at the site, four archaeological teams excavated Troy and in 1988 Manfred Korfmann of Tübingen University and Brian Rose of Cincinnati University started the latest period of investigations. Besides the archaeological investigations, natural sciences were always an integral part of the research at the Hisarlık hill, were Troy is located (ARCHÄOLOGISCHES LANDESMUSEUM BADEN-WÜRTTEMBERG et al. 2001).

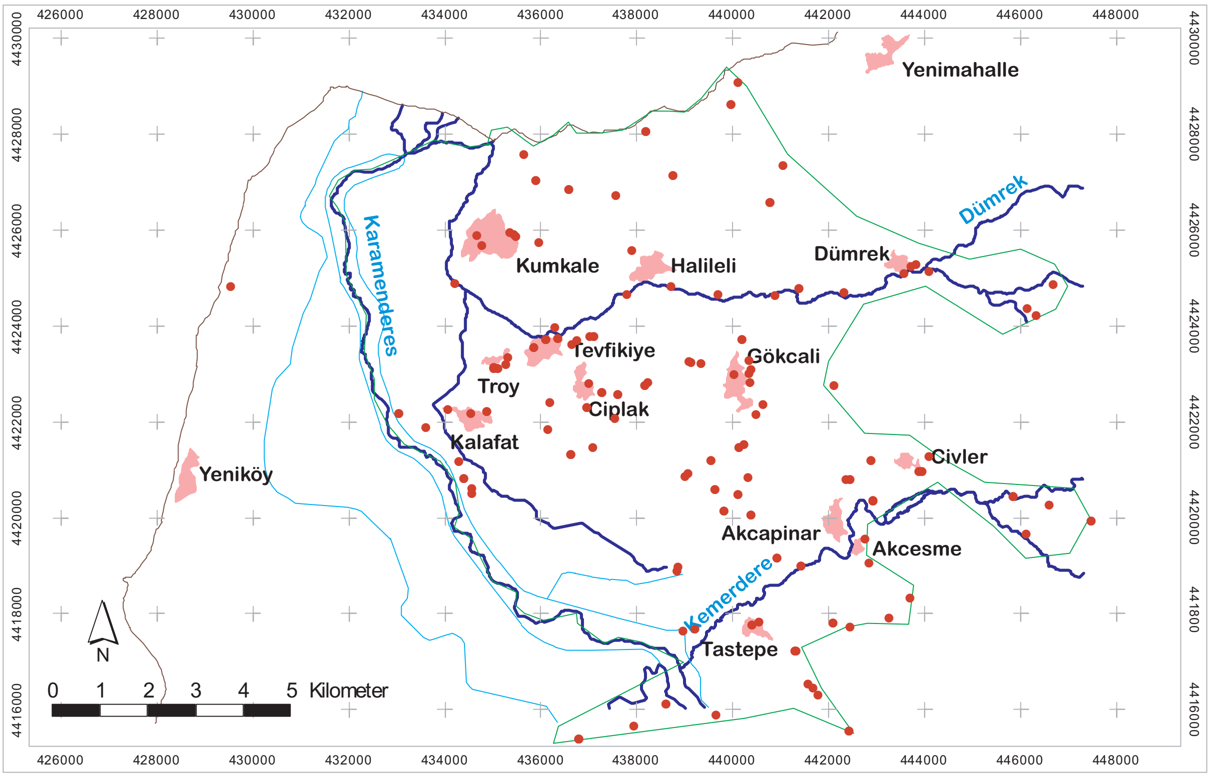

Figure 1: Area of the "Historical National Park Troia" and the locations sampled in 2001 and 2002 (darker dots). Map based on IKONOS data provided by the Troia-Team. Co-ordinates: UTM, WGS84.

Troy's importance dates back to the 8th century B.C., when Homer wrote down the Iliad and Odyssey, where he described the myths and the war that was fought in Troy's vicinity. Starting in the 17th century A.D. travellers and scientists tried to locate the place of the Troyan war and in 1863 Frank Calvert, after having studied Homer's descriptions, concluded that the Hisarlık must be the site of the historic Troy. Heinrich Schliemann, who visited the Troas at that time, started to excavate the hill in 1870 and he soon stated, that Hıssarlık was the place were the Troyan war took place. To understand the ongoing discussion of Troy's importance, three things must be distinguished: the place where the Troyan war happened, the place where Homer located his epic poem, and the place of today's Troy. Though the latter two are commonly seen to be identical, this must not necessarily be the case for all three of them. Therefore, every investigation should make clear which of the three Troys is meant. In this paper, Troy is seen as the place of the present archaeological excavations of the Tübingen/Cincinnati teams.

An important question about Troy is where the cold and hot springs described by Homer could have been located (Iliad, XXII v. 147). A set of springs which meet Homer's characteristics can be found near Pınarbaşi, but not only two, but more then eight water outlets near Miocene conglomerates can be found there – all of them bearing more or less the same hydrogeological parameters. One of the first systematic hydrogeological investigations to locate Homer's cold and hot springs was conducted by Rudolf Virchow in 1879. He measured the temperatures of several springs and rivers in the north-western Troas and discussed his findings (VIRCHOW 1879).

Since then no regional hydrogeological investigations were conducted in the National Park, though two deep wells are located north-east of Pınarbaşi: Pınarbaşi and Kokarna with average yields of 600—1500 and 50 Ls^{-1}, respectively (Yüzer 1997). Both wells are used for the water supply of Pınarbaşi and for irrigation purposes. Unfortunately, no more data is given for this water. Intensive hydrogeological and geothermal investigations are reported from the Çanakkale and the Ezine geothermal fields (e.g. MÜTZENBERG et al. 1992; BATTOCLETTI 1999). KAYAN (2000) focuses on the water supply of Troy without investigating the hydrogeological situation in the broader vicinity and the hydrogeochemical properties of the waters at all.

The whole investigation area is drained by two rivers: the Karamenderes, flowing from south to north, and the Dümrek flowing in an east—west-direction. Both rivers flow into the Çanakkale Boğazi (Dardanelles) north-west of Kumkale. YÜZER (1997) gives a catchment area of 1,584 km² and an average discharge of 12,900 $m^3 s^{-1}$ for the Karamenderes. A mean temperature of 15 °C and a mean annual precipitation of 600 mm is given for Çanakkale and the observation period 1990—2001 (pers. comm. Jeff Masters). Typical for the area is an extensive agricultural use by which the groundwater table was lowered to about 5 — 15 m below surface.

This paper describes the first findings of the hydrogeological investigations of the TU Bergakademie Freiberg. Since 2001 a total of 131 springs and surface waters were measured and 44 water samples taken to be analysed in the laboratory. Yet, no indication for a hot and cold spring near Troy could be found – which might not be surprising, as Strabo 2000 years ago describes in his Geographica, that the hot spring had already disappeared at the time of his visit (Geographica XIII 1,43).

2 Investigations

In summer 2001 and 2002 a total of 131 springs, bore holes and surface streams in an area of approximately 120 km² within the "Historical National Park Troia" have been visited, most of them twice (fig. 1). At each site the on-site parameters temperature, conductivity, redox-potential, oxygen, and pH-value were evaluated with a Myron P6 multi-parameter probe and the flow measured. Based on these results 44 representative locations including the historical sampling sites of Virchow were selected for water sampling. At each of those sampling points, four water samples were taken to be analysed for base- and acid-capacity (sample 1: 250 mL), NO_3^{2-}, NO^{2-}, PO_4^{2-}, and $Fe^{2+/3+}$ (sample 2: 250 mL, filtered through Sartorius 0.45 cellulose nitrate filter), main ions (sample 3: 250 mL, filtered through Sartorius 0.45 cellulose nitrate filter) and trace elements (sample 4: 50 mL, filtered through Sartorius 0.45 cellulose nitrate filter and acidified with ultra-pure HNO_3). Samples 1 and 2 were analysed on-site with a Hach Photometer DR 890 and a Hach Digital Titrator. Samples 3 and 4 were stored in a cool place within the Excavation House and analysed at the TU Bergakademie Freiberg for main anions (IC, photometry, ion selective probe) and TU Dresden – Tharandt for trace elements (ICP-MS).

As the investigations described here were the first hydrogeological investigations of this kind in the National Park, we measured as many trace elements as possible, to find out, which of them could be used as natural tracers in the area: Li, Ni, Zn, Sr, Ba, Co, U, Rb, Tl, Sb, Ce, Cu, Mo, Eu, As, Sn, Cd, Pb, Bi, In, Cs, Mn, La, Tm, Lu, Cr, Nd, Ho, Ag, Er, Zr, Sm, Dy, W, Be, Pr, Hf, Gd, Tb, Yb, Th. In future studies this list will be reduced to the important parameters only (fig. 4).

In addition to the chemical parameters, three conductivity, pressure, and temperature probes were installed within the research area during the field investigations (fig. 3). Two of them still measure the parameter changes at Düden Spring near Calvert's Farm and at the outflow of the cave spring (squares tu 14/15). Furthermore, two tracer tests, one with sodium chloride, the other one with Na-fluorescein were conducted between shaft 4 and the cave spring's entrance.

3 First Results and Conclusions

All the waters in the National Park have a pH between 6.5 and 8.5 and are therefore well buffered in the range of the $CaCO_3$-buffer. Their temperature is between 16.4 and 31.9 °C, whereas the higher temperatures are an indication for shallow waters with lower residence times and the lower temperatures indicate ground water of deeper strata. Conductivity ranges between 360 and 5,560 µS cm^{-1} (fig. 2). Redox-potentials of natural waters are within a range of 60 and 430 mV, and the chlorinated waters from the deep well near Halileli between 710 and 900 mV (used as public water supply in Troy).

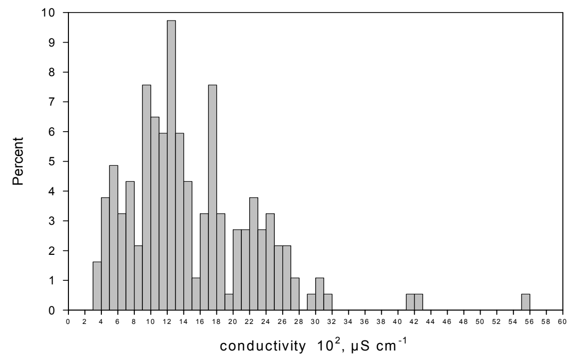

Figure 2: Histogramm of the conductivities in the Historical National Park Troia area (185 data sets).

Cluster analyses (average linkage) show, that the Troyan waters can be classified into three water types, with a total of eight subtypes. The detailed interpretation of those types is still under way, but the three main types can be interpreted as follows: Type 1 are waters with a conductivity range of 0.4—1.9 mS cm^{-1} (75 %), Type 2 waters range between 1.9 and 4 mS cm^{-1} (23 %),

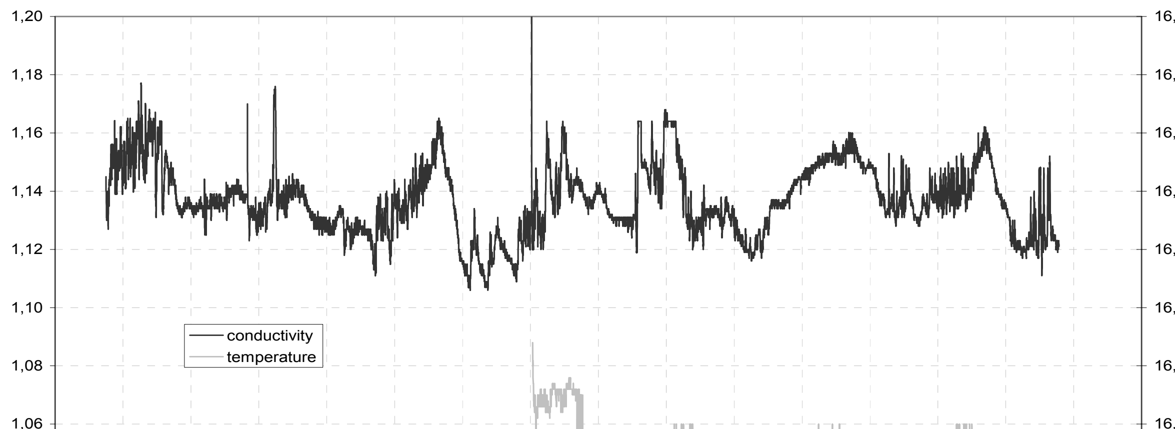

Figure 3: Temperature and conductivity distribution within the Troyan spring cave (conductivity: left scale, upper graph; temperature: right scale, lower graph).

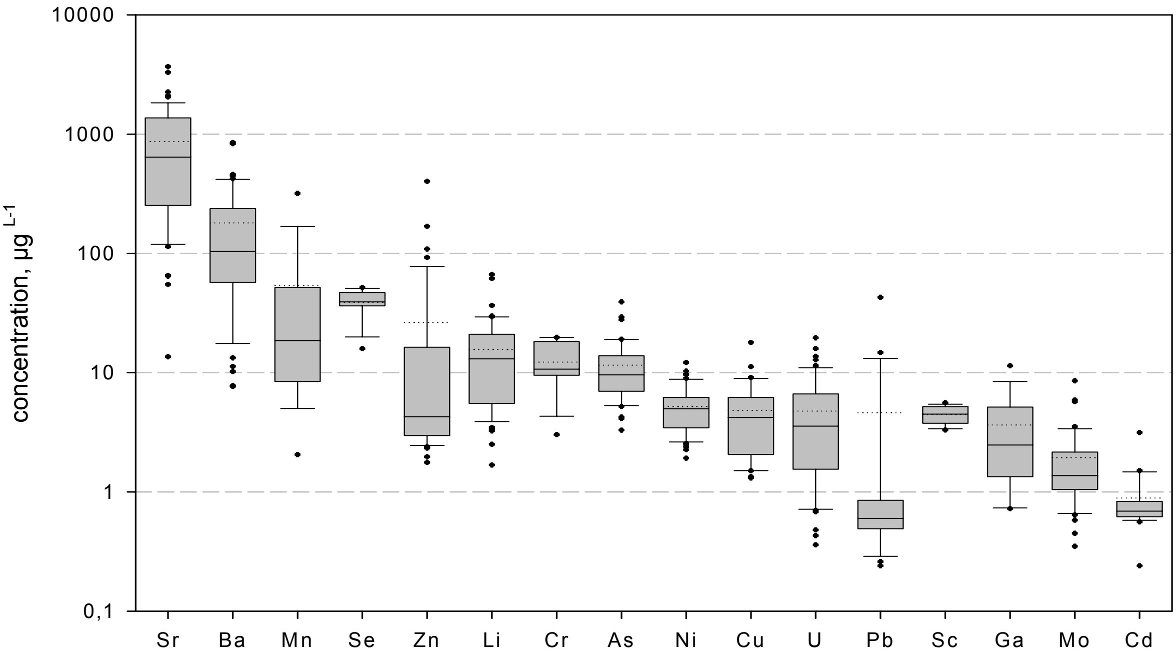

Figure 4: Box plot graph of trace elements in the Troyan waters. Dotted horizontal line: mean; solid horizontal line in box: median; 10th, 25th, 75th, and 90th percentiles. Outliers are given as crosses.

and Type 3 waters have conductivities above 4 mS cm^{-1} (2 %). Investigating the spatial distribution of those waters shows, that the volcanic and Mesozoic rocks in the south east of the area investigated, the surface waters and the wells in the alluvial plain mainly belong to type 1, while Type 2 and 3 waters are concentrated at the Troy ridge. A connection to the geological formations could not yet be established, but cannot be excluded from the first results. Very similar is the pH-distribution, with the lower pH-values generally related to higher and the higher pH-values related to lower conductivities.

Characteristic for many waters analysed in the National Park are the high NO_3^--contents of up to 330 mg L^{-1}. Most of those waters are used for drinking purposes, not necessarily as public water supply, and more than half of them exceed the recommended EU drinking water standard of 25 mg L^{-1}. A clear interpretation can be given for the extreme high NO_3-contents of the springs north of Tevfikiye and this situation might be seen as an indicator for the other height NO_3^--contents in the area as well. Above the springs the inhabitants have small farm lands with chicken, cattle, and goats. As the protective layer above the springs is only about 20 m thick and consist of limestone, sandstone, and siltstone, the animals' excrements pass through those sediments very quickly, resulting in the extreme NO_3^{2-}-mass concentrations.

One of the most important trace elements in the Troyan waters is Sr (fig. 4), as it is strongly liked to the three Troyan water types. Sr mass concentrations range between 14 and 3,690 µg L^{-1} with higher mass concentrations between Kumkale and Yenimahalle and south of a line between Gökçali and Çiplak. Rb/Sr ratios are not very selective, as they show a strong log-normal distribution, with the highest values at the spring cave and Düden spring. Interestingly, this shows that the rock's source for the Sr and Rb waters seems to be of a common origin, which can not be deduced from the mass concentrations of those two elements alone.

Zn, Cu, and Pb can easily be used to trace back tab waters. No correlations between the 3 water types and those heavy metals can be found, but to metal water pipes used. In the case of a well south of Çiplak, which was sampled in 2001 and 2002, this situation can be studied exemplified: in 2001 the well had a well head made of metal and a pipe containing Pb. In 2002 the well head was removed and the mass concentrations of Zn, Cu and Pb decreased significantly (Zn: 400 to 50; Cu: 18 to 7; Pb: 10 to 1 µg L^{-1}).

Arsenic seems to be a problematic element in the Historical National Park, because nearly 50 % of the analysed waters exceed the EU drinking water limit of 10 µg L^{-1}. Those waters are used for irrigation, and cattle watering tanks. KNACKE-LOY (1994) already noticed that Troyan pottery contains unusually height arsenic contents. Thus, the arsenic in the Troyan water might reflect this local anomaly, too. Because there is no correlation between the three Troyan water types and the arsenic content, the sources for the arsenic in the water are not clear, yet.

Due to the high pH-values, most of the REEs analyzed are below the detection limit. With the sampling and analyzing technique used, they are therefore not selective for the Troyan waters. From the data presented above, it can be deduced, that future hydrogeological studies must include environmental isotopes, such as $\delta^{18}O$, $\delta^{2}H$, or $\delta^{14}C$ or Sr-isotope ratios. Such studies were not possible within the framework of these first investigations.

As a first result, it can be concluded, that some of the Troyan waters should not longer be used as drinking water due to the height NO_3^{2-} or metal contents. Furthermore, three different water types can be found in the Historical National Park Troia, which seem to be connected to the different geological strata of the Neogene, Quaternary and Palaeozoic as well as volcanic rocks. It is not clear yet, from where the water at the archaeological site of Troy (spring cave) comes from, but due to the low conductivity of the Troy waters, the source must be different from the shallow waters of the Troy ridge. Waters similar to those of the spring cave can be found near Paşa Tepe, north of Gökçali, and Düden spring.

4 Acknowledgements

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