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# Chemical quality of groundwaters in the deltaic plain of Pinios river: Preliminary results after a year of monitoring

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**Abstract**

In this contribution we present some preliminary findings on the chemical quality of groundwaters of the deltaic plain of R. Pinios (Thessaly), as part of the implementation of the project THALIS-DAPHNE. Samples were obtained from 13 groundwater drillings on a seasonal basis during the hydrological year 2012 - 2013 and analyzed for major ions, nutrients, dissolved organic carbon and trace metals. Temperature, pH, conductivity and salinity were measured *in situ*. In order to evaluate the groundwater quality, we compare the data obtained against the Hellenic legislation threshold values and FAO guidelines for irrigation waters. Conductivity ranged from 230 to 9180 μS/cm. Exceedance of the 700 μS/cm threshold (Type I water FAO) in 71% of the samples suggests slight to moderate restrictions in irrigation. In two drillings (No 10, 13) maximum permissible limits of conductivity, sodium and chloride concentrations were exceeded particularly in summer and autumn. Some exceedances of guidelines were also identified for nitrates and ammonium. Concentrations of dissolved trace metals, were generally below the limits, with the exception of Zn, however some concern has been raised in terms of increased levels of total dissolved Cr in drilling No. 15 (8.3 - 37.9 μg/L). On the basis of our results degradation of groundwater quality was identified together with seasonal salinization; these two factors corroborate to the need for sustainable groundwater use especially in months with increased demands for water supplies.

*Keywords: trace metals, nutrients, dissolved organic carbon, major ions*

## 1. INTRODUCTION

Groundwater quality is often degraded due to natural processes and anthropogenic activities as recorded in many coastal areas of Greece [1, 2]. In the present work, the chemical quality of groundwaters in the area of the Pinios River Delta (Thessaly) was studied in the framework of the project Thalis – Daphne, whose general scope is to investigate the consequences of climate change on deltaic plains, as one of the most vulnerable coastal and wealth-producing ecosystems.

The Pinios river delta, located in the region of Thessaly (Greece) has been selected as a case study, since it is one of the largest Greek rivers with very limited flow controls. The Pinios deltaic plain is approximately 62 $km^2$, consisting of alluvial (Holocene) sediment deposits and characterized by vertical and lateral heterogeneity. Despite the fact that the deltaic plain is part of the NATURA network, human interventions continue to occur at an increasing rate. At least two major activities, i.e. extensive agricultural land use and expansion of touristic settlements, substantially increase the demands for water [3, 4]. The water needs for irrigation are covered by the use of the river/canals network and the exploitation of the shallow aquifer through an extended number of drillings. A few deeper drillings in the area supply water to summer vacation housing settlements built along the coastal front of the delta. Therefore, groundwater quality is very important and should be monitored in order to ensure compliance with established guidelines.

## 2. MATERIALS AND METHODS

The first year of sampling, commenced in October 2012 and a total number of 49 samples were collected from 13 groundwater drillings (for location see Figure 1) on a seasonal basis, i.e. October 2012, January 2013, April 2013 and July 2013.

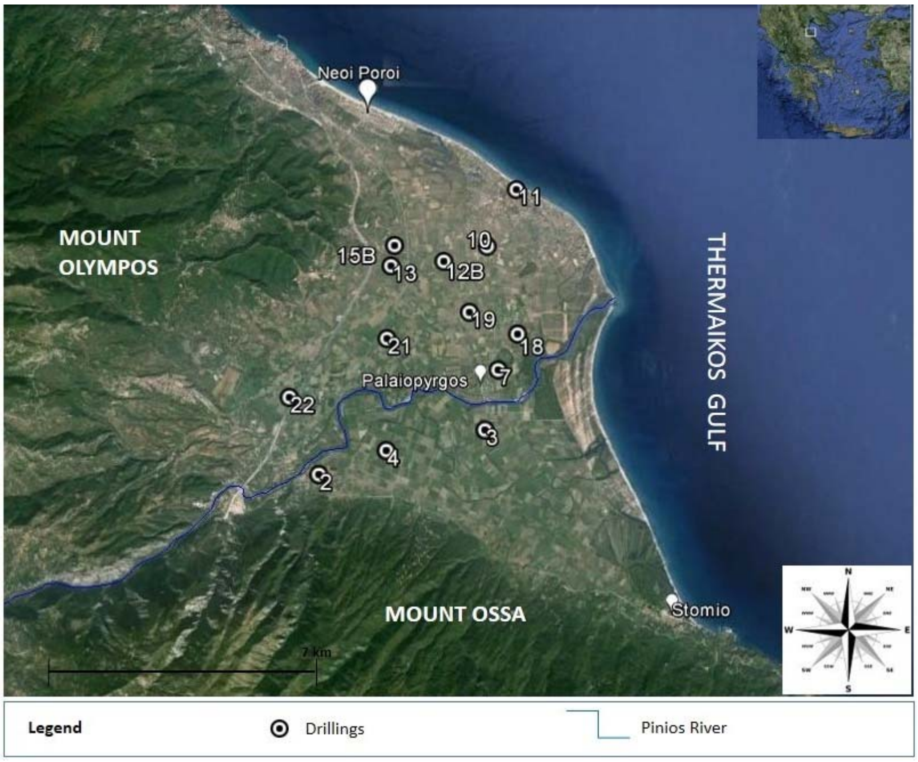


**Figure 1.** Map of the Pinios deltaic area and location of the drillings

The groundwater samples were collected from private and public drillings. Water samples were stored in thoroughly cleaned 2L Nalgene bottles. *In situ* measurements of temperature, pH, conductivity and salinity were performed with a YSI 63 portable multimeter. The samples were filtered within 24 hours and refrigerated until filtration; the latter was conducted using a Nalgene filtration apparatus and Millipore membrane filters (mixed cellulose esters types with 8μm and 0.45 μm pore diameter). Subsamples were divided and the physico-chemical parameters, listed below, were determined in the laboratory. The analytical precision of the chemical analyses ranged from below 5 % for the main constituents to 10% for the nutrients and DOC and up to 15% for some of the trace elements (Cd, Pb). These levels of precision are usual for measurements of environmental samples.

-***Main constituents (Ca, Mg, K, Na, $Cl^-$, $SO_4^{2-}$)*** – The cations were determined using flame emission atomic spectrometry (FAAS, Varian SpectrAA 200) or titrimetrically [5] and the anions using ion chromatography (Metrohm 820 IC Separator Center, 819 IC Detector)

-***Nutrients ($NO_3$, $NO_2$, $NH_4$, $PO_4$)*** – nutrients were measured spectrophotometrically with a Varian Cary 1E UV-visible spectrophotometer [6].

-***Dissolved trace metals (Cd, Cu, Fe, Mn, Pb, Ni, Zn)*** – aliquots of the filtered water samples were pre-concentrated using Chelex 100 resin [7, 8] and measured with atomic absorption spectrometry (FAAS Varian SpectrAA 200, Graphite Furnace AAS Varian GTA 100-Zeeman 640Z with

autosampler). The Chelex procedure allows a) the separation of the trace metals from other chemical elements that cause significant interference during measurement and b) their simultaneous pre-concentration ensuring more accurate quantification of the very low natural concentrations [9].
***-Dissolved Cr species*** – The main dissolved Cr species (VI and III) were also determined. Upon receipt to the laboratory, all samples were measured for total dissolved Cr with Graphite Furnace AAS (Varian GTA 100-Zeeman 640Z). Samples in which total dissolved Cr was detectable (> 0.6 μg/L) were also analyzed within 2-4 days for Cr (VI) [10].
***-Dissolved Organic Carbon (DOC)*** was measured with an automatic analyzer (Shimadzu TOC/5000).

## 3. RESULTS AND DISCUSSION

The ranges and averages for selected parameters (main constituents, i.e. anions and cations and some trace elements) in each sampling point are presented in Table 1; the data refer to a total of 49 samples, collected during the 4 campaigns of the first year. Subsequently, the identified values are compared to those proposed by the Food and Agriculture Organization [11, 12] for the quality of irrigation water (Table 2). Additionally, they were also compared to the maximum acceptable concentrations of selected chemical parameters in groundwaters established in Greek legislation [13], which are: pH (6.5-9.5), Conductivity 2500 μS/cm, Nitrates 50 mg/L, Ammonium 0.5 mg/L, Chloride 250 mg/L, Sulphate 250 mg/L, Cadmium (Cd) 5 μg/L, Lead (Pb) 25 μg/L, Nickel (Ni) 20 μg/L and total Chromium (Cr) 50 μg/L. For Zinc (Zn) and Chromium (VI) there exist only surface water guidelines which are 125 μg/L and 3 μg/L respectively [14].

The pH values were normal, in the 6.5-9.5 range in all samples. Conductivity ranged from 230 to 9180 μS/cm. Exceedance of the 700 μS/cm threshold (Type I water FAO) in 71% of the samples suggests slight to moderate restrictions in irrigation. Drilling no 10 exceeded the limit of 2500 μS/cm in three out of four samplings. According to FAO guidelines severe immediate problems to irrigated plants may arise. Problems may also arise, due to the increased concentrations of sodium and chloride, apart from drilling No 10 also in drilling No 13, particularly in summer and autumn. Some exceedances of guidelines were also identified for nitrates and ammonium (Table 1). The levels of sulphates ranged from below 0.5 mg/L to 161 mg/L.

S.A.R. was also calculated for the evaluation of groundwater quality and possible infiltration problems in conjunction to conductivity levels. The calculated SAR ranged from 0.26 to 18.3 (Table 1). According to Wilcox diagram (1955), that is widely used and is especially implemented to classify groundwater quality for irrigation, water can be grouped into sixteen (16) classes. The conductivity (horizontal axis) is classified into low (C1), medium (C2), high (C3) and very high (C4) salinity zones; these zones (C1–C4) are associated with EC values of <250, 250–750, 750–2250 and >2250 μS/ cm, respectively. The SAR (vertical axis) is subdivided into four classes, with decreasing limiting values as EC increases: low (S1), medium (S2), high (S3) and very high (S4) sodium hazard. The results show that the majority of the samples from the study area is classified as suitable for irrigation use (classes C1S1, C2S1 and C3S1) (Figure 2) with some caution required with regards to sensitive crops and heavy soils, while sampling sites 10 and 13 (October 2012) are classified as unsuitable for use (classes C4S3 and C4S4).

**Table 1**. Ranges, mean values for major ions and selected trace metals in each of the sampled drillings in Pinios Delta

| Drilling | Conductivity | Ca | K | Na | Mg | SAR | $Cl^-$ | $HCO_3^-$ | $NO_3^-$ | $NH_4^-$ | DOC | Zn | Total Cr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (μS/cm) | (mg/L) | | | | - | (mg/L) | | | | | μg/L | |
| 2 | 706–856 | 48.4–91.8 | 3.1–12.1 | 9.6–32.4 | 11.6–35.6 | 0.27-0.86 | 8.9–27.1 | 211–267 | 16. 8–18.0 | 0.008–0.20 | 0.27–2.8 | 12.1–64.8 | <0.64–6.1 |
| | 761 | 75.6 | 5.7 | 19.8 | 19.4 | 0.52 | 17.6 | 239 | 17.4 | 0.12 | 1.4 | 41.5 | 3.5 |
| 3 | 294–884 | 26.5-90.0 | 14.7–21.9 | 8.5–34.5 | 10.6–38.7 | 0.35-0.77 | 5.4–17.6 | 350 | 6.1–15.2 | 0.12–2.3 | 14.5–21.1 | 31.6-1862 | <0.64–6.1 |
| | 618 | 58,2 | 17.6 | 19.3 | 24.4 | 0.51 | 10.8 | | 10.6 | 0.87 | 16.8 | 1171 | 3.6 |
| 4 | 817-1134 | 41.2-66.8 | 12.1-13.6 | 25.4–37.2 | 28.6–38.0 | 0.65-1.0 | 8.0–13.2 | 240–364 | <0.5 | 35.8–89.7 | 2.6–8.2 | 5.4–25.0 | <0.64–0.66 |
| | 1030 | 52.1 | 12.8 | 31.6 | 34.1 | 0.84 | 11.8 | 302 | | 60.0 | 5.9 | 14.0 | |
| 7 | 230-1230 | 22.9–101 | 6.3–9.7 | 6.1–25.5 | 10.9–37.9 | 0.26-0.55 | 5.3–21.2 | 168–300 | <0.5.5 | 0.01–1.8 | 0.95–11.6 | 17.0-1341 | <0.64 |
| | 685 | 70.5 | 7.8 | 15.6 | 28.7 | 0.38 | 13.2 | 234 | | 0.52 | 5.8 | 563 | |
| 10 | 408-9180 | 65.6-80.3 | 46.8-62.7 | 445–1375 | 149–215 | 6.4-18.3 | 12.0->3000 | 670–695 | <0.5 | 0.1–15.4 | 3.3–13.4 | 8.5-677 | <0.64–0.69 |
| | 5849 | 73.8 | 56.2 | 871 | 179 | 12.3 | | 683 | | 9.7 | 7.0 | 180 | |
| 11 | 479–1010 | 45.5–90.2 | 3.2–7.4 | 9.5–73.2 | 12.2-22.4 | 0.32-1.8 | 11.6–81.3 | 191–220 | 10.6–30.6 | 0.29–1.13 | 1.9–3.1 | 10.6–105 | <0.64 |
| | 711 | 70.0 | 5.6 | 32.3 | 18.1 | 0.85 | 38.9 | 206 | 20.6 | 0.65 | 2.5 | 40.4 | |
| 12B | 826-1084 | 71.2–87.2 | 2.3–3.7 | 48.3–78.8 | 38.3–45.6 | 1.0-1.7 | 40.9–66.8 | 332–406 | <0.5–2.1 | 0.48 – 0.78 | 1.2–3.8 | 3.1–34.4 | <0.64 |
| | 994 | 78.5 | 2.9 | 57.5 | 41.8 | 1.3 | 55.3 | 369 | 1.1 | 0.62 | 2.4 | 12.3 | |
| 13 | 1342–2412 | 73.9-108 | 3.3-4.6 | 142–1407 | 45.0–58.3 | 3.2-27.8 | 294-439 | 326 | <0.5 | 0.01–0.05 | 1.2–1.6 | 18.9-322 | <0.64 |
| | 1868 | 96.7 | 4.2 | 575 | 51.6 | 11.5 | 366 | | | 0.03 | 1.4 | 127 | |
| 15B | 1323-1760 | 134–140 | 1.3-1.7 | 29.1-60.6 | 34.5–43.1 | 0.57-1.1 | 8.2–153 | 206–429 | 25.6–30.6 | 0.004–0.10 | 1.3-2.4 | 5.1–18.7 | 8.3–37.9 |
| | 1472 | 138 | 1.5 | 40.6 | 37.5 | 0.78 | 108 | 318 | 28.0 | 0.05 | 1.8 | 14.2 | 26.6 |
| 18 | 264-1106 | 20.8–85.3 | 4.2–4.4 | 8.9-44.9 | 6.3–37.9 | 0.44-1.0 | 16.6–104 | 91–448 | - | 0.37–0.46 | 7.7–11.5 | 100-298 | <0.64–2.9 |
| | 685 | 53.0 | 4.3 | 26.9 | 22.1 | 0.73 | 60.4 | 270 | | 0.42 | 9.6 | 199 | |
| 19 | 672-1230 | 63.1–92.3 | 1.9–4.9 | 24.1–58.7 | 33.9–61.8 | 0.61-1.2 | 28.1–109 | 350–352 | 0.86-3.8 | 0.10–0.25 | 1.7–4.6 | 6.5-876 | <0.64 |
| | 1067 | 76.1 | 3.3 | 38.1 | 50.1 | 0.82 | 76.2 | 351 | 2.3 | 0.18 | 3.2 | 343 | |
| 21 | 512 - 955 | 63.5–108 | 0.8–1.8 | 11.5–35.4 | 35.4–46.8 | 0.25-0.88 | 13.6–15.9 | 295–386 | <0.5–1.7 | 0.01–0.29 | 1.6–5.8 | 6.5-35.6 | 0.7–4.0 |
| | 760 | 80.9 | 1.2 | 19.1 | 42.5 | 0.44 | 14.7 | 341 | 0.86 | 0.10 | 2.9 | 20.7 | 2.2 |
| 22 | 708 - 985 | 44.1–83.9 | 6.4 – 20.8 | 38.0–57.6 | 29.1–35.6 | 1.0-1.4 | 5.4–95.6 | 180–230 | <0.5 | 0.74–2.1 | 4.3–6.9 | 2.4–22.3 | <0.64 |
| | 849 | 64.9 | 11.3 | 45.7 | 32.0 | 1.2 | 56.9 | 205 | | 1.3 | 5.9 | 9.5 | |
| ***Limits*** | ***700//2500*** | ***-*** | ***-*** | ***69//207*** | ***-*** | ***See Fig.2*** | ***250*** | ***-*** | ***5//30//50*** | ***0.5*** | ***-*** | ***125*** | ***50*** |

**Table 2** Irrigation water quality criteria in terms of hazard for plants according to FAO [11, 12]

| Chemical Parameter | **Water Type - I** Irrigation causes no problems | **Water Type II** Continuous use for irrigation may cause gradual increasing problems | **Water Type III** Irrigation may cause immediate development of severe problems |
|---|---|---|---|
| Conductivity (μS/cm) | <700 | 700-3000 | >3000 |
| Sodium (Na mg/L) * | <69 | 69-207 | >207 |
| Chloride (Cl mg/L)* | <142 | 142-355 | >355 |
| Ammonium and Nitrates ** ($NH_4$-$NO_3$ mg/L) | <22 | 22-133 | >133 |
| Nitrates ($NO_3$ mg/L) ** | <5 | 5-30 | >30 |
| pH** | Normal Range 6,5-8,4 | | |

*Root intake toxicity, ** Special problems for sensitive plants

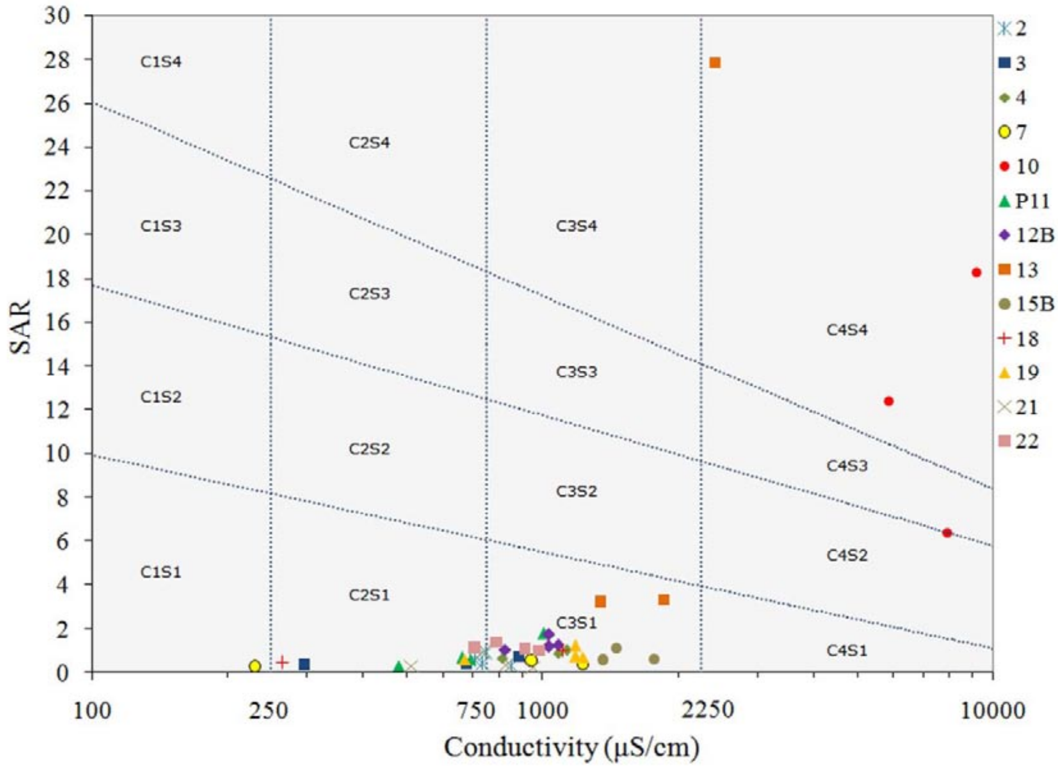


**Figure 2.** Assessment of groundwater suitability for irrigation purposes based on Wilcox diagram

Dissolved trace metals ranged from 0.006 to 0.06 μg/L for Cd, 0.02 to 1.4 μg/L for Cu, 1 to 278 μg/L for Fe, 0.28 to 423 μg/L for Mn, 0.04 to 5.2 μg/L for Ni, 0.02 to 0.63 μg/L for Pb and 2.4 to 1862 μg/L for Zn. The large variations in the concentrations of trace metals are not easily explained without knowledge of the redox potential, that controls the distribution between the dissolved and particulate phases, especially for the redox sensitive metals. This parameter was not measured in the first year of samplings but will be included in future samplings. In groundwater, the behaviour of metals is more complicated than in surface water, since it is controlled by the pH, Eh, dissolution - sorption –precipitation and redox reactions, as well as by the variability of inputs by the pollution sources [15]. Therefore, it is not uncommon for trace metals to exhibit large variations between sampling campaigns, especially when the physicochemical parameters such as conductivity and redox potential display significant short-term variations. The concentrations of dissolved trace metals were in all cases lower than the maximum limits, except for Zn. For this metal there is no established guideline for groundwaters intended to be used for irrigation. In some of the drillings dissolved Zn exceeded the surface water guideline of 125 μg/L, indicating a possible source of pollution, which needs to be identified.

In the case of chromium the maximum total dissolved concentrations did not exceed 50 μg/L, which is the limit set by Hellenic and EU legislation. However, in three samples (No 2, 3 and 15B) relatively high concentrations of total dissolved chromium were determined. In drilling No15 total Cr was found to be increased at the three latest samplings (i.e. 30.2 – 30.0 and 37.9 μg/L) compared to the first one (8.3 μg/L). The origin of chromium in groundwaters may ascribe both to human interferences (e.g. small metal frames manufacturing facility) and to natural sources related to the presence of rock strata rich in Cr (III)-bearing minerals, such as those of mafic, ultramafic and serpentinite rocks [16] that also outcrop in the Pinios catchment [17]. Motivated by the relatively high concentrations of total Cr, speciation was carried out from which we found that Cr (VI) in drilling No 15 also followed the same trend, from below 0.5 μg/L in October 2012 to 13.3, 24.3 and finally, 37.1 μg/L in July 2013. In drillings No2 and No3 Cr (VI) ranged from below 0.5 μg/L to 2.2 μg/L; these findings are of some concern and impose continuation of monitoring of Cr levels and species in the area.

A well-defined seasonal variability was associated with only the conductivity values. Thus, in drillings closer to the coastline (No. 10, 11, 19 & 21) a significant decrease in conductivity that took place in January indicates the presence of a seasonal salinization process. On the contrary, in drillings at increased distances from the coastline (No 2, 22) there was almost no seasonal variability (Figure 3).

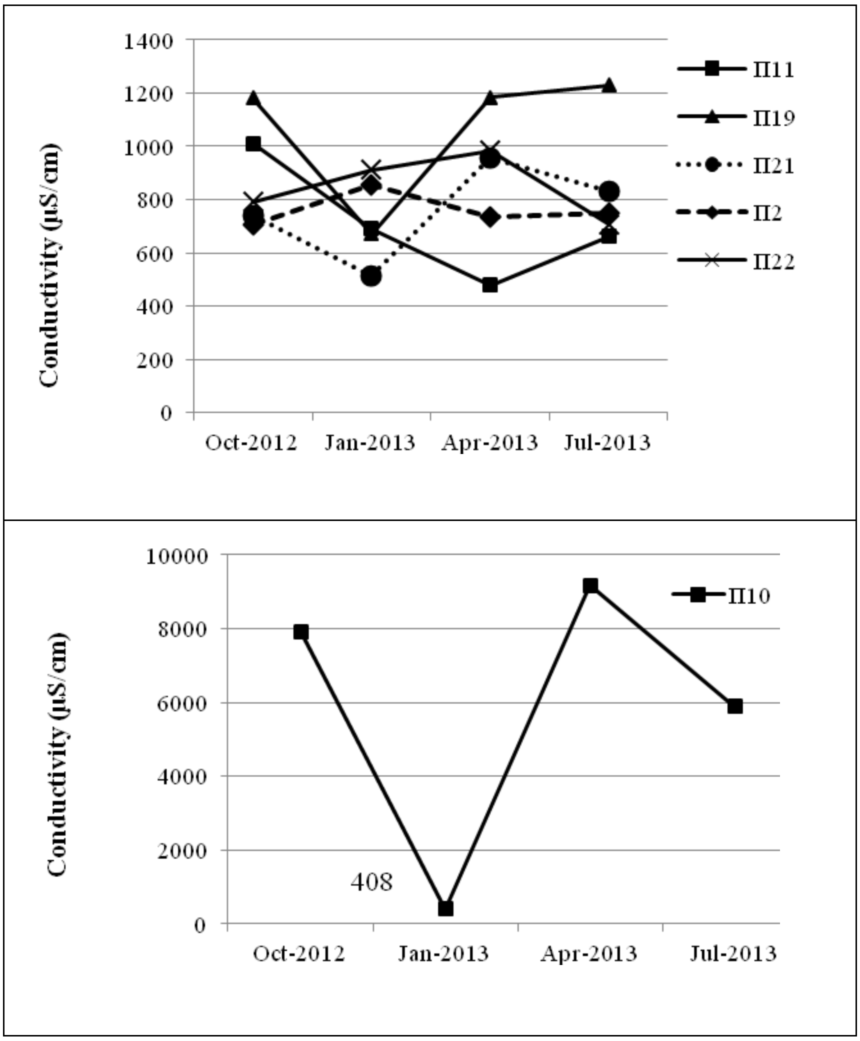


**Figure 3.** Seasonal fluctuation of conductivity in selected drillings

Moreover, the continuation of monitoring (Oct. 2013-Sept 2014) will permit a better evaluation of the chemical status of groundwaters, especially in the cases of quality limits exceedances and a more definite depiction of seasonal trends and implied salinization. A detailed mapping of all activities in the deltaic area that is currently materialised will contribute to the identification of possible pollution sources. Furthermore, an overall statistical processing of chemical parameters is scheduled upon completion of all the sampling campaigns in association with hydrogeological flow measurements, which along with the application of contaminant transport models will permit identification of pathways and sources (both natural and anthropogenic) of groundwater contamination. Finally, the water quality data (chemical parameters) need to be combined with quantitative information of water abstraction (e.g. level of water table, actual volumes of water pumped seasonally), which are currently under investigation.

## 4. CONCLUSIONS

This contribution presents the chemical quality status of the Pinios deltaic plain area groundwaters based on one year seasonal campaigns. Preliminary findings of degradation of groundwater quality were identified especially in some of the drillings; additionally our data indicates groundwater salinization towards the deltaic coast. More concrete conclusions will be drawn upon the completion of the second year sampling campaigns. However, our results so far, corroborate to the need for measures that would ensure sustainable groundwater use, especially in months with increased water demands, such as the application of more effective irrigation systems, that would minimize water losses, and raising of public awareness on prudent water use practises.

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