

## Groundwater quality of Assini and Iria Valleys in Peloponnese Region, Greece

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### Abstract

The degradation of groundwater quality is mainly related to the intensification of agriculture, the use of fertilizers and the overexploitation of groundwater aquifers which in coastal areas leads to sea water intrusion. An assessment of groundwater quality was conducted in Assini and Iria valleys. Groundwater samples was collected in the beginning (May) and in the end (October) of the irrigation season and subjected to chemical analyses for the main anions and cations. Groundwater was classified using the Piper diagram. Chloride and E.C. (electrical conductivity) contour maps of the regions were obtained in order to evaluate the extent of sea water intrusion. The main cultivated crops in the regions are irrigated citrus and high amounts of nitrogen fertilizers are used. Nitrate concentration of groundwater was found often to exceed the value of 50 mg/l. A comparison was made with the situation that was prevailing in the region eight years ago. The suitability of groundwater for irrigation was evaluated.

**Keywords:** nitrate, sea water intrusion, fertilizer movement, nitrate

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### Introduction

The quality of groundwater is influenced by natural and anthropogenic factors including climate, geology, land use, irrigation practices. Groundwater in coastal areas is vulnerable to salinization by the intrusion of seawater. Especially in the Mediterranean countries degradation of groundwater quality is a common problem due to multiple pressures on the aquifers, excessive pumping in relation to low natural recharge, return flow from irrigation water with intense use of agrochemicals, leakage from urban areas, land fills, septic tanks (Barraque, 1998; Fornes et al., 2005). Irrigated agriculture is the main consumer of water in the Mediterranean and its expansion in the last half of the century has been remarkable. In coastal areas urbanization and tourism place also pressures on groundwater resources leading to unsustainable overexploitation (Iglesias et al., 2007). In Greece many coastal aquifers are affected by salinization (Petalas, et al. 2009, Voudouris and Daskalaki, 1998; Stamatis and Voudouris, 2003, Lambrakis, 1998).

The purpose of this study is to determine the chemical characteristics of groundwater in two coastal aquifers in Greece, to examine the processes and chemical reactions involved and also to evaluate suitability of groundwater for irrigation and domestic use.

### Study area

Assini and Iria valleys are situated southeast of the city of Nafplio and belong to Argolis Prefecture (Figure 1). Iria valley is a coastal plain open towards the Argolis gulf. It is shaped as an isosceles triangle with a direction from east to west the base of which forms the coastal zone.

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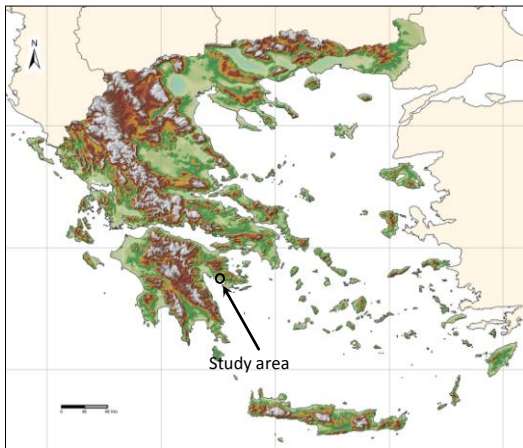


Figure 1. Study area

It is run through by Karnazeikos torrent by the erosive action of which it was formed. The watershed of the torrent covers an area of around 200 km<sup>2</sup> and Iria valley, of an area of about 3500 ha, lies in the end part of the watershed close to the sea. The plain lies between the mountainous complexes of Mavrovouni to the north and Didymon to the south. The flat area of the valley lies between 0 and 20 m, the area near the village of Karnezaika extends between 20 to 40 m. In the mountainous area of the watershed elevations more than 800m are encountered. The area falls into the geotectonic zone of Eastern Greece. The limestone formations of "Pantokrator" is surrounded the valley. The more recent deposits of sand and clay of Quaternary covering the lower area is of small or moderate permeability and in some areas they become more coarse and of greater permeability (Figure 2).

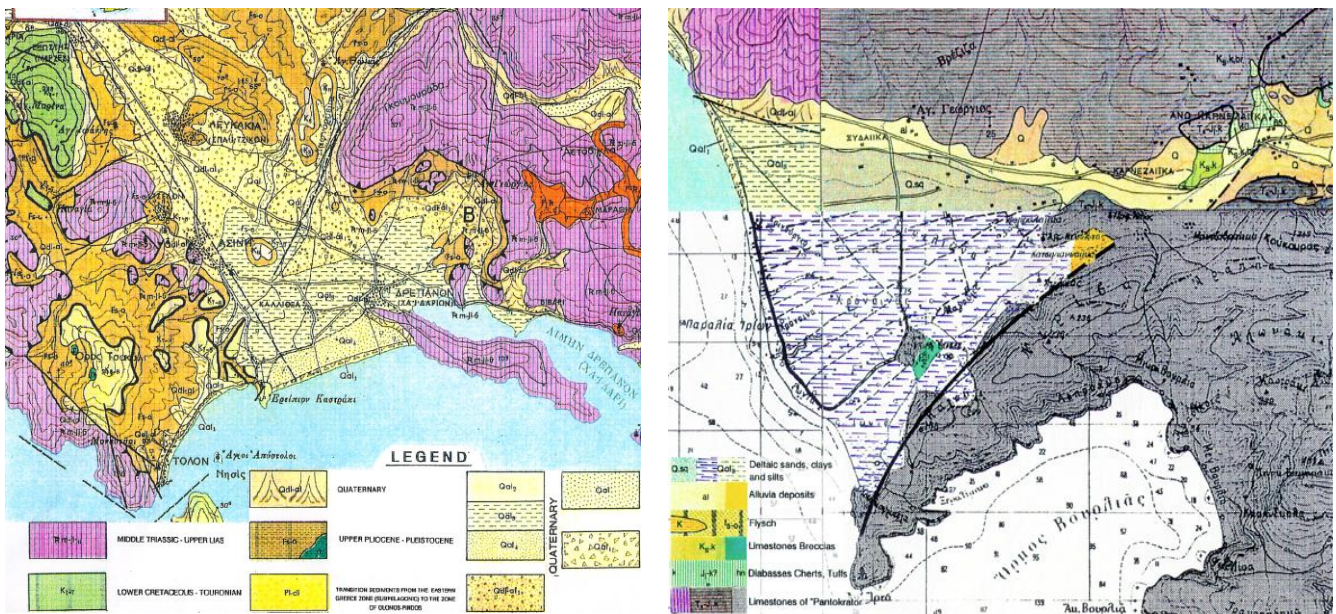


Figure 2. Geological Map of Assini (left) and Iria (right)

Upstream of the plain and mainly in the bed of Karnazeikos river coarse grained materials are encountered mainly boulders of different sizes and high permeability. This zone of coarse grained materials is the main recharging zone of the aquifer of the plain. Across the plain a gravel layer has been created and in some areas the depth of this layer is less than 1 m from the soil surface creating soils with moderate depth. Groundwater was the only source of irrigation water and the aquifer of the plain is seriously degraded quantitatively and qualitatively by the intensive and long overexploitation of groundwater.

Irrigation agriculture has been expanded in these areas during the last 40 years and the main crops cultivated in Iria regions are vegetables, especially the salt tolerant artichokes that have replaced the cultivation of citrus. A small proportion of the total cultivated area is covered by citrus and olive trees. In Assini citrus trees are the main cultivation, covering 95% of the total cultivated area.

## Materials and Method

For the assessment of groundwater quality water samples were collected from 40 boreholes in Iria valley and from 25 boreholes in Assini. Groundwater samples were collected in June and October 2009 after the end of the rainy season and of irrigation period respectively. In all collected samples EC, pH and the main anions and cations were determined. Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations were measured by the EDTA titrimetric method, K<sup>+</sup> and Na<sup>+</sup> by flame photometer, CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> by titration, SO<sub>4</sub><sup>2-</sup> by the turbidimetric method, NO<sub>3</sub><sup>-</sup> by the cadmium reduction method and Cl<sup>-</sup> by potentiometric titration with silver nitrate (APHA, 1989).

## Results and Discussion

In Table 1 the maximum and minimum values of E.C., pH and ion concentrations of groundwater samples in May and October 2009 are presented for Iria and Assini valleys. Also for Iria valley the values of ion concentrations prevailing in October 2004 are shown. In Iria groundwater was seriously affected by sea water intrusion, EC values varied between 0.737 dS/m and 8.48 dS/m with a mean value of 3.68 dS/m in October 2009. In the majority of water samples (56%) EC values were greater than 3 dS/m. Cl<sup>-</sup> dominates the anionic composition of water samples, its values fluctuated from 1.36 meq/l to 70.36 meq/l and with 36% of the samples presented values greater than 30 meq/l. The dominant cations are Mg<sup>2+</sup> and Na<sup>+</sup> with mean values of 14.01 meq/l and 13.85 meq/l respectively followed by Ca<sup>2+</sup> with a mean value of 8.24 meq/l.

Table 1: Hydrochemical data of groundwater in the study areas (min and max values).

	IRIA			ASSINI-DREPANON	
	Oct 2009	May 2009	Oct 2004	Oct 2009	May2009
E.C. (dS/m)	8.48 - 0.74	7.43 - 0.72	11.28 - 1.46	3.76 - 1.72	3.92 - 0.48
Ca <sup>2+</sup> (meq/l)	14.9 - 2.2	15.6 - 1.8	35.4 - 4.0	16.9 - 8.5	15.9 - 3.1
Mg <sup>2+</sup> (meq/l)	40.5 - 3.5	33.6 - 2.8	61.0 - 7.6	17.3 - 5.1	14.3 - 1.2
Na <sup>+</sup> (meq/l)	42.78 - 1.27	41.48 - 1.15	47.92 - 0.81	10.16 - 3.33	11.21 - 0.27
HCO <sub>3</sub> <sup>-</sup> (meq/l)	11.0 - 1.2	9.6 - 2.0	13.2 - 3.2	5.2 - 1.8	5.2 - 1.4
Cl <sup>-</sup> (meq/l)	70.36 - 1.36	57.50 - 1.32	99.2 - 7.60	21.31 - 9.67	21.50 - 0.92
SO <sub>4</sub> <sup>2-</sup> (meq/l)	12.80 - 0.84	11.22 - 0.01	9.38 - 1.06	8.32 - 2.01	11.60 - 0.46
NO <sub>3</sub> <sup>-</sup> (mg/l)	192.44 - 0.62	235.75 - 17.16	317.6 - 6.57	430.1 - 18.75	365.50 - 7.66
SAR	19.73 - 0.66	18.02 - 0.65	16.22 - 0.27	3.17 - 0.91	3.36 - 0.23

In Assini valley EC values of groundwater are lower than in Iria, varied from 1.72 to 3.76 dS/m with a mean value of 2.70 dS/m in October 2009. The dominant cations of groundwater in Assini are Ca<sup>2+</sup> and Mg<sup>2+</sup> followed by Na<sup>+</sup>. The dominant anion is Cl<sup>-</sup> with a mean concentration of 14.77 meq/l, its concentration varied from 9.67 meq/l to 21.31 meq/l. In Figures 3 and 4 the spatial distribution of EC values and Cl<sup>-</sup> concentration of groundwater are presented for October 2009 in Iria and Assini regions respectively.

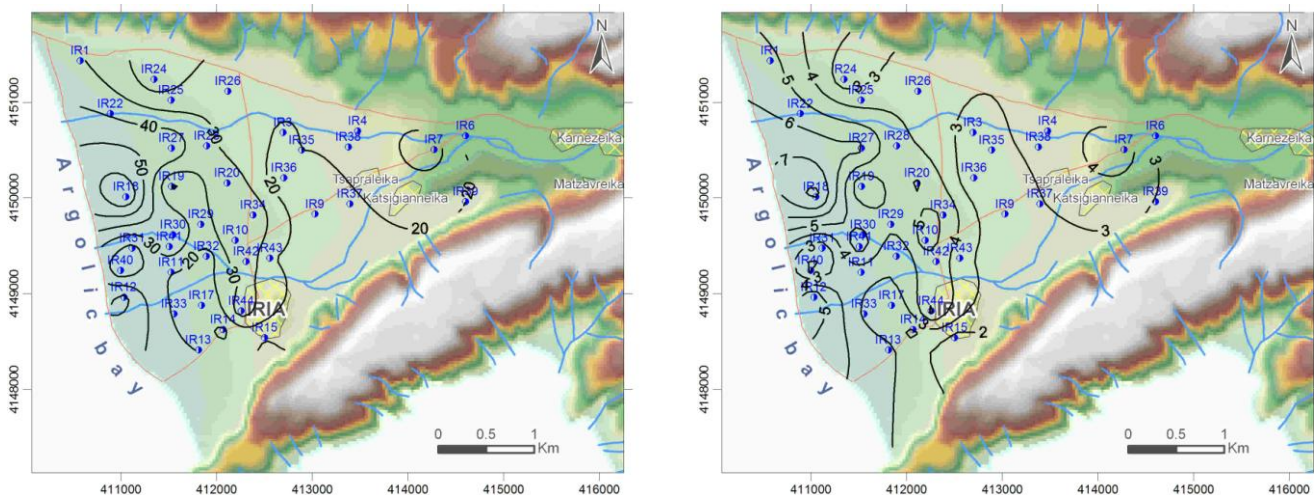


Figure 3. EC (left) and Cl (right) contours in Iria region for October 2009.

EC and chloride contours are clear evidence of saline intrusion in the two regions since higher values are observed in the coastal zones in the Gulf of Argolis. The area by the sea is consisted of highly permeable materials allowing the intrusion of sea water and the deterioration of groundwater quality. The phenomenon is more pronounced in Iria valley where also in the centre of the valley, high values of EC and Cl<sup>-</sup> are prevailing. Groundwater quality in Iria valley was more degraded some years ago (Poulovassilis et al., 1994) as it can be seen from the range of ion concentrations in Table 1, but the transfer of water from Kiveri springs as an additional irrigation source relieved to some extent the pressure in the aquifer from the intense agricultural practices in the region and there is an obvious amelioration of groundwater quality.

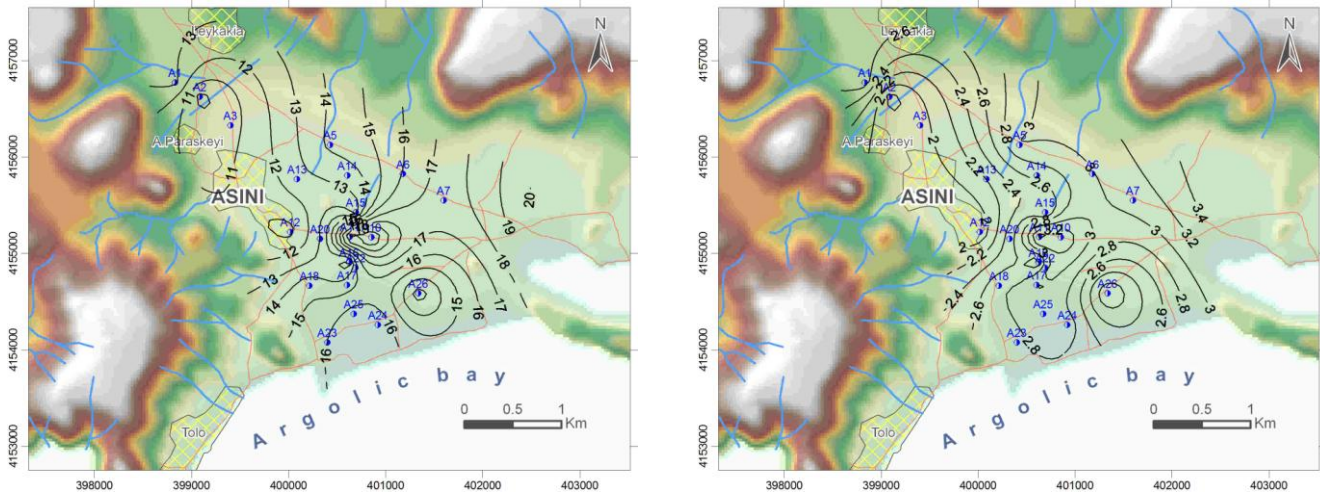


Figure 4. EC (left) and Cl (right) contours in Assini region for October 2009.

In order to examine the relationship between the different ionic species correlations between major ions were performed using Spearman's coefficient analysis. Relative strong correlations, significant at  $p=0.05$  level, were found between EC and  $\text{Cl}^-$  ( $r=0.098$ ),  $\text{Mg}^{2+}$  (0.885),  $\text{SO}_4^{2-}$  (0.838),  $\text{Na}^+$  (0.776) and  $\text{Ca}^{2+}$  (0.72) for Iria groundwater samples in October, implying that groundwater chemistry was mainly controlled by these ions. The EC values in Assini valley are strongly correlated with  $\text{Cl}^-$  (0.933),  $\text{Ca}^{2+}$  (0.832) and  $\text{SO}_4^{2-}$  (0.789). To classify the groundwater and to identify the hydrochemical processes the Piper diagram is used (Figure 5) (Piper, 1944).

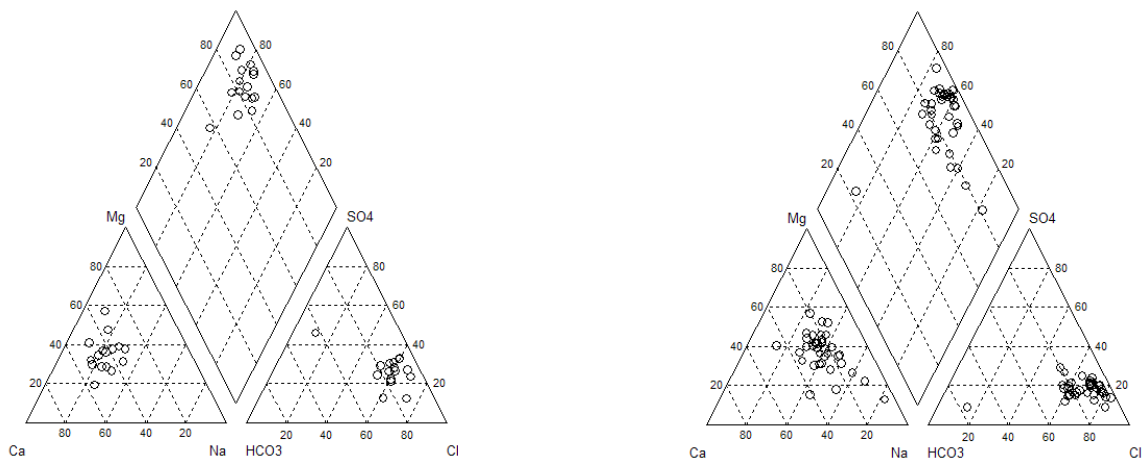


Figure 5. Piper diagram for groundwater in Iria (left) and Assini (right) regions

The most obvious indication of seawater intrusion is the high increase in Cl concentration. The dominance of chloride ions in relation to carbonate ions indicates secondary pollution from sea water intrusion (Todd, 1980). All samples (except one) in Iria had values of the ratio  $\text{Cl}^-/\text{HCO}_3^-$  much greater than 1 and 60% of the samples have values greater than 5 reaching also very high values greater than 15, thus indicating significant saltwater encroachment. In Assini region all samples present values of  $\text{Cl}^-/\text{HCO}_3^-$  higher than 1 and 40% of samples have values between 5 and 10. The existence of Ca-Cl or Mg-Cl or Ca-Cl,  $\text{SO}_4$  facies, as the water types of the study areas, in a coastal aquifer indicates the existence of inverse ion exchange (Appelo and Postma, 1994; Lloyd and Heathcote, 1985). The  $\text{Na}^+/\text{Cl}^-$  ratio is also used as an indicator of seawater intrusion. The  $\text{Na}^+/\text{Cl}^-$  ratio in all samples is significantly lower (0.57 in average) compared to the seawater ratio (0.858) indicating reverse ion exchange processes.

Nitrate contamination of groundwater has become an issue of growing concern since intense agricultural practices; high rates of nitrogen fertilizers generally result in low N use efficiency and high N loss through leaching rendering the water of the aquifer unsuitable for drinking (Keeney, 1986). Nitrate concentration

ranged from 17.66 to 430.1 mg/l in Assini region and from 0.62 to 235.62 mg/l in Iria region during the two sampling periods. The distribution of NO<sub>3</sub><sup>-</sup> for the two study regions is shown in Figure 6.

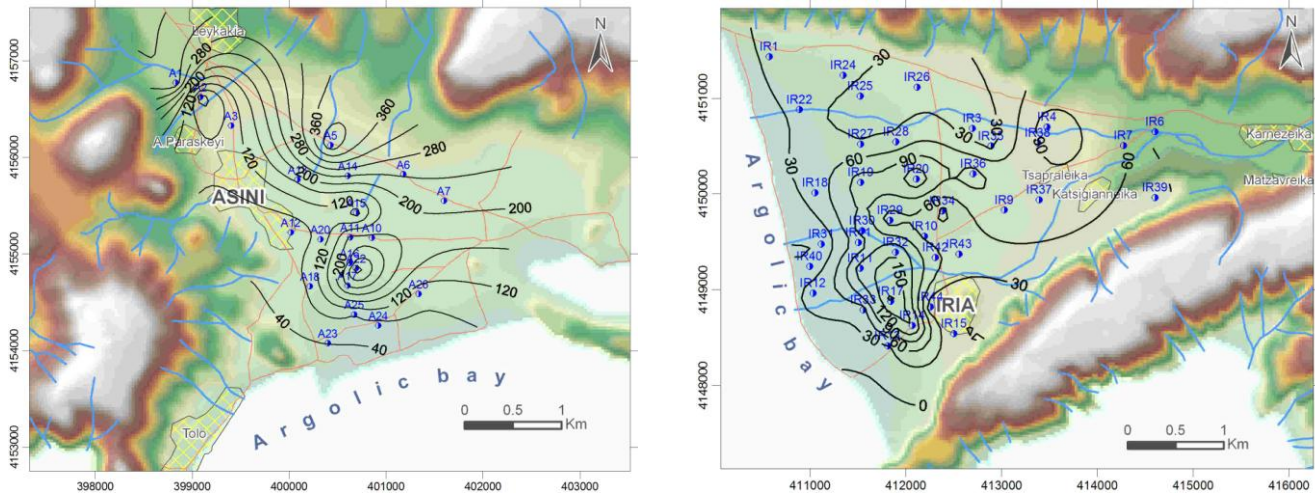


Figure 6. NO<sub>3</sub><sup>-</sup> contours in Iria (left) and Assini (right) regions in October 2009

In October 2009, nitrate concentration of groundwater exceeded the limit of 50 mg/l set for drinking water (EC, 1998; WHO, 2006) in 42% and 80% of the water samples for Iria and Assini respectively. Groundwater in the two regions is heavily contaminated by nitrates since it is a common agricultural practice the addition of large amounts of nitrogen fertilizer, in an effort to counter the adverse effects of irrigation water salinity on crop yields. Shallow unconfined aquifers as the aquifers in Iria and Assini valley present a high contamination risk of nitrates. Additionally the increased rates of leaching imposed to tackle with the soil salinity and the existence of gravel layer across the valley especially in Iria enhance the leaching and the transfer of NO<sub>3</sub><sup>-</sup> to groundwater.

Different schemes for the evaluation of water for irrigation have been proposed (USSL, 1954, Ayers and Westcot, 1988). In Figure 7 the classification of groundwater for irrigation purpose is shown according to USSL, 1954 based on EC and SAR (sodium adsorption ratio) values. SAR (Sodium adsorption ratio) is used to evaluate the sodicity hazard of irrigation water. Excess exchangeable sodium in soils can lead to soil swelling and/or dispersion causing water infiltration, aeration and root penetration problems.

From the evaluation of water quality for irrigation according to USSL, 1954 it is obvious that the quality of groundwater is deteriorated and its use for irrigation is severely restricted. Most of the samples are characterized as C4S1 for Assini and C4S2 for Iria regions (Figure 7) presenting a severe danger to develop high levels of soil salinity and important reduction in crop yields. The adverse effects of salts on plants are generally related to the decrease of the osmotic potential of the soil solution reducing the availability of water to plants and thus affecting plant growth and its productivity (Shainberg and Shalhevet, 1984, Tanji, 1990).

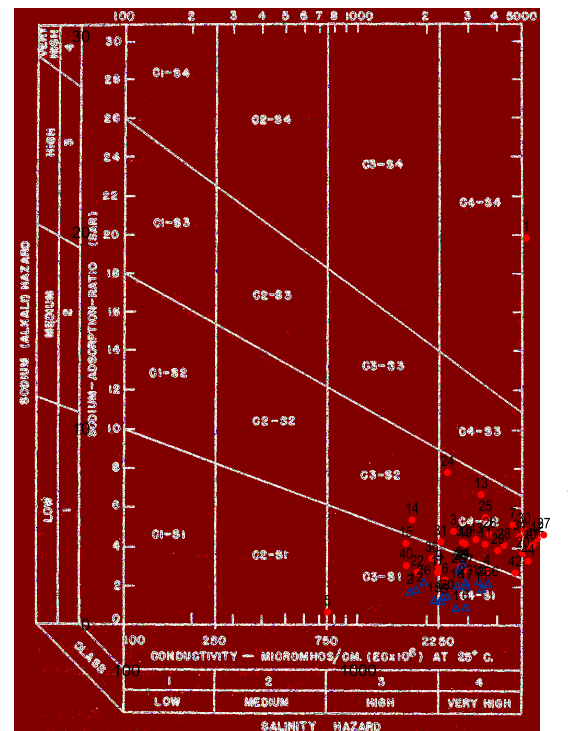


Figure 7. USSL diagram for irrigation water quality classification (USSL, 1954) (red circles: Iria, blue triangles- Assini).

Excessive concentrations of Cl<sup>-</sup> and Na<sup>+</sup> cause also specific toxicities to the crops. Citrus trees are sensitive to salinity and the use of groundwater for the irrigation of citrus trees leads to reduced yields (Maas, 1993). The low to medium levels of SAR value in the majority of samples indicate that soil alkalization problems of dispersion or reduction of the infiltration rate in the soil could not be expected by the use of these waters.

## Conclusions

Groundwater quality in both areas due to over-pumping and intrusion of sea has been seriously degraded. The higher values of EC and Cl<sup>-</sup> are prevailing in the coastal zones but also extent to the central areas of the regions. Cl<sup>-</sup> dominates the anionic composition of water samples and is strongly correlated with EC values. EC is also positively correlated with Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup> and Ca<sup>2+</sup>. Ionic ratios and water hydrochemistry show that groundwater degradation is due to extensive seawater intrusion. Hydrochemical facies of groundwater and the low ratio of Na/Cl prevailing in the area reflect reverse ion exchange processes. Groundwater in both regions is also heavily contaminated by nitrates due to intense use of fertilizers.

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