Assessing quality of an irrigation canal ecosystem, through water and sediment environmental parameters. A case study in Thessaly region, Greece

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Abstract: - This study aimed to record and evaluates the physicochemical parameters (Na^+, K^+, $C\ell^-$, Ca^{2+}, Mg^{2+}, electrical conductivity, SO_4^{2-}, total alkalinity, CO_3^{2-} and HCO^{3-}) and give heavy metals (Cr, Pd, Ni, Cu, and Cd) in sediment Asmaki canal in order to assess the quality of irrigation water used and the nature of pollution along the canal in relation the Sodium Absorption Radio (SAR), the percentage Sodium (Na %) with the help of the Piper diagram. Samples were collected and analyzed bimonthly in May, July and September, at twelve sampling sites along the irrigation-drainage Asmaki canal for two consecutive years (2008 – 2009). We observed increased concentrations of nutrients due to anthropogenic inputs, mainly because of the discharged contaminating waters from the large industrial and agricultural activity.

Key-Words: - Water quality, Sodium Absorption Radio, Sodium percentage, Piper diagramme

1 Introduction

This paper reveal the results of a two-year survey on specific water quality parameters of the Asmaki (Thessaly, Greece) irrigation canal in order to monitor changes caused by the seasonal hydrological cycle and assess the contribution of urban, agricultural and industrial activities.

For Pinios River and its tributaries, there are several studies which demonstrate the degradation of surface water due to extensive use of fertilizers and pesticides and the presence of heavy metals in some places [1,2,3]. With regard to Asmaki irrigation canal, which runs across part of the Thessaly basin, there are only few studies [4] showing the pollution of the surface waters.

The values of Sodium Absorption Radio (SAR) found by Stamatis (1999) [5], showed the water of Pinios river is suitable for irrigation Loukas (2010) [6]. They ranged around 0.3 and only in very few cases it reached up to 1.10. Conductivity values mostly ranged from 200 to 700 mS/cm and only in certain cases it was higher than 1000 mS/cm. This means that there is low salinity hazard by the use of such irrigation water. Papadopoulou-Mourkidou (2002) [7] found increased concentrations of sodium and SAR values in other rivers of Greece such as of Evros and Strimonas. Singh (2002) [8] evaluated the quality of both surface and underground waters of the Damodar river basin in India and found that taking into account both SAR values and the risk of sodium (Na%) the quality of surface waters of the basin found to excellent. Venugopal et al. (2008) [9], evaluated the water quality of Adyar River in India in two different seasons of the year and found that roughly most samples had high salinity levels. This involves a high or very high risk for crops. On the other hand the Na percentages (%) indicate a minimal use risk and this allows unrestricted use of that irrigation water in almost all types of soils with regard to development of high ESP values.

The values of heavy metals found by Fytianos et al. (2002) [2], shoed that the mean concentrations of the examined heavy metals (Cd, Cu, Pb, Cr, Ni) show little variations between different sampling sites, suggesting influence from geologic factors rather than from point sources. In general, dissolved metal concentrations at all sampling sites were low [10]. The values of heavy metals found by Calmano W. and Forstner, U. (1983) [11] showed the sediment of river in central Europe is there was not a significant burden of heavy metals. Venugopal et al. (2008) [9], evaluated the water quality of Adyar River in India in two different seasons of the year and found that heavy metals ranges (addition of Cu) to normal levels ranged.

2 Materials and Methods

2.1 Study area

The research area (Figure 1) extends from the north-eastern side of the city of Larissa, up to a region of the former and now in recovery Lake Karla. This is basically a flat area used for growing mostly one-year crops with cotton holding the first place with about 70%, corn in second place with about 20% and various seasonal and other tree crops holding the rest 10% (Pinios Local Land Reclamation Agency - T.O.E.V). Asmaki is the central canal (8T) and while it was designed as a drainage ditch, now it is primarily one of the main irrigation ditches in the area. According to available data, the Asmaki canal is supplied with water from Pinios River and the surrounding mountains and is connected to canal "1T" constructed in the period during which the Lake Karla was drained. The "1T" artificial canal leads to the tunnel opening that was created along with the drying of Lake Karla, the years 1961-62, to drain water in the Pagasetike Gulf.

For the purposes of this study 12 sampling sides were selected (S1 to S12) (Table 1, Figure 1), starting from the tunnel which drains the water to the Pagasetike Gulf (west of Lake Karla) (S2) and extending to the vicinity of the slaughterhouse of Gyrtoni village (S11) and Omorfochori village (S12). Asmaki is still the primary recipient of waste from industrial, agricultural, farming and urban activities. The sources of pollution of Asmaki river are distinguished in point, non-point and obscured sources creating α large-scale organic pollution and minor chemical pollution (eg. dyeworks, oily sludge, production waste, use of greases, soaps, disinfectants). The industrial units of the region are a factory of treatment of alcohol (near S7 station), a textile dyeworks (near to S8), a food production industry (near to spots S9 and S10) and the Slaughterhouses of Gyrtoni (near to S11). A lot of livestock farming units of the region manage their waste (eg. the waste of dairy plants and solid waste) to the method of direct dispersion in fields, or in streams. Significant pollution also occurs through the leaching of crops due to the use of pesticides and chemical fertilizers. The sampling side S1 was chosen because it is outside the Asmaki canal (Figure 1) but also because it is near to the cement factory "Hercules". Finally S12 sampling spot is the only one that receives water from Pinios River and the only one with a cemented sublayer.

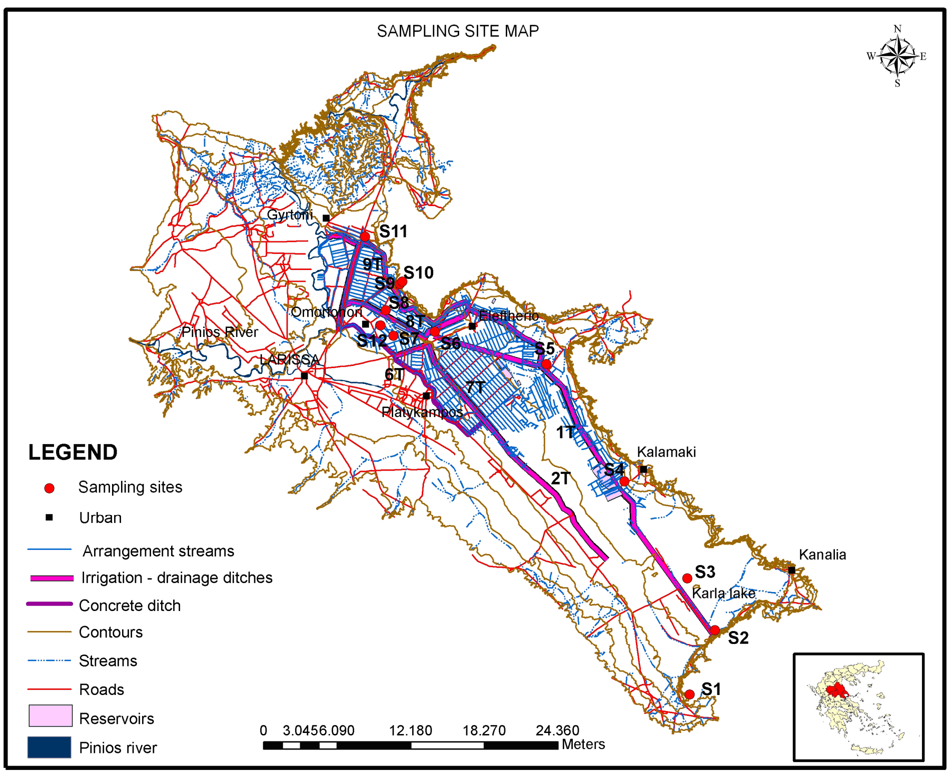


Fig. 1 - Map of study area with the sampling sites

Table 1 - Sampling sites

	Sampling sites	Latitude	Longitude
1	Near Hercules cement plant	39o 24΄.085	22o 46΄.951
2	Karla Tunnel (1T)	39o 27΄.044	22o 48΄.608
3	Bridge Stefanovikeio village(1T)	39o 28΄.825	22o 46΄.816
4	Kalamaki (1T)	39o 33΄.418	22o 43΄.390
5	Plasia (contribution 1T και 8T)	39o 38΄.539	22o 39΄.036
6	Bidge Eleftherio village (8T)	39o 39΄.756	22o 32΄.342
7	Near the alcohol industry (bypass 8T)	39o 39΄.627	22o 29΄.709
8	Near Pelasgis – washing, dyeing fabrics (bypass 9T)	39o 41΄.103	22o 29΄.424
9	Area of food industry (bypass 9t)	39o 41΄.814	22o 29΄.905
10	Gentiki 9T	39o 42΄.289	22o 29΄.987
11	Close slaughterhouse Gyrtoni (9T)	39o 44΄.288	22o 28΄.226
12	Omorfochorio (6T)	39o 39΄.897	22o 29΄.267

2.1 Water sampling - Chemical analysis

The water sampling was carried out bimonthly, during the irrigation season which lasts from May to September, for two consecutive years (2008 – 2009). The samples of water (1lt) were collected in PVC bottles from the middle of flow of the aquatic stream and as long as this was possible from its means of depth and was stored in refrigerator (at 4^oC), in the dark until chemical analysis that followed immediately after each sampling. The sampling and analytical protocols used were in accordance with Standards Methods for the Examination of Water and Wastewater [12].

Water temperature, pH, electrical conductivity (EC) and total alkalinity were measured by standard electrochemical methods [13]. The concentrations of sodium (Na^+) and potassium (K^+) cations were determined by flame photometry [14] while those of calcium (Ca^{2+}) and magnesium (Mg^{2+}) were measured by flame atomic absorption method, modified Varian solution in $CaCl_3$ environment [15]. To determine the concentration of chlorine anions ($C\ell^-$) Mohr method was applied [16] while for carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-) potentiometry was used [17]. The concentrations of ammoniac (NH_4) and sulphate (SO_4^{2-}) ions were evaluated according to Standards Methods for the Examination of Water and Wastewater [12,13].

A sediment sample was taken once to determine the organic matter concentration and five heavy metals (cadmium, chromium, lead, nickel, copper) in the sediment. These samples were held on July 29, 2009 at 11 out of 12 sampling spots because in station S12 the substrate is concrete. Three samples of surface sediment were taken (to a depth of 5 cm) from each spot, quantity of 100 - 200g. Stones and foreign matter were removed from the samples before the later being transported to the laboratory. Air drying of samples followed, with periodic shaking to constant weight and final moisture content from 0 to 7%, drying in an oven at 40°C to constant weight. Then after the three samples of each sampling sides were mixed, grinding and sieving followed (sieve of 2 mm^2) in accordance with ASTM C 999 (2010) [18]. Samples were placed in polyethylene containers and stored in a desiccator. Organic matter was determined using Walkley and Black method. For the determination of metals the samples were treated with 4M HNO_3 [19]. Total metals Cd, Cr, Pb, Ni and Cu, were determined by using atomic absorption (VARIAN 220 FS). All water and sediment tests were conducted in the laboratories of Regional Laboratory of Agricultural Extension and Fertilizer Analysis [20].

For all water samples SAR value (Sodium Absorption Ratio) was calculated which expresses the activity of sodium ions and determines their ability to rotate with cations such as Ca and Mg adsorbed by soil colloids. Based on S.A.R. value four categories of risk of salinisation of irrigation water are distinguished for electrical conductivity 100mmho cm^{-1}, according to the classification of US Salinity Laboratory, (1954) [21]. When the index takes values:

<10, Category 1 (low risk of sodium)
10 - 18, Category 2 (sodium average risk)
18 - 26, Category 3 (high risk of sodium)
> 26, Category 4 (very high risk of sodium)

Another classification was made according to the classification of US Salinity Laboratory, (1954) [21] and took into account the measured values of EC (electrical conductivity) and SAR (Sodium Absorption Ratio) focusing on the irrigation period. The % Na content in irrigation water was determined as the ratio of Na^+ to the sum of cations (sodium, potassium, calcium and magnesium) expressed in meq ℓ^{-1} :

Water quality	Na%	Conductivity (μs/cm)
Excellent	<20	<250
Good	20-40	250-750
Acceptable	40-60	750-2000
Doubtful	60-80	2.000-3.000
Unsuitable	> 80	> 3.000

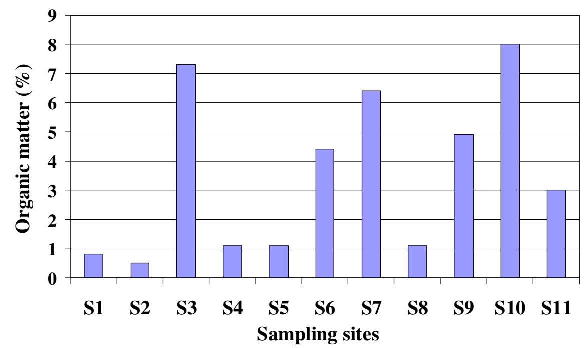
To further investigate the hydrochemical condition and the origin of water from aquifers in the study area it was considered appropriate to make Piper diagram in order to evaluate hydrochemical phase of water [22].

3 Results and Discussion

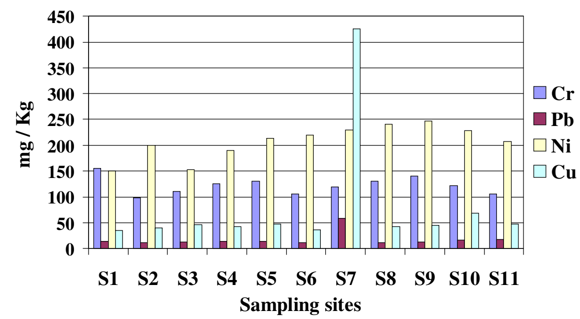
Increased organic matter (Figure 2a) in the sediment was found at sapling sides 10, 3 and 7, while at the S1 and S2 the proportion of organic matter was much lower. Higher value (8.0%) was found at SS 10 which is associated with organic pollution, as this sampling site is located in an area where the textile dyeing plant is operating while the lower value was found at S2 (0.5%) indicating that the soil near Lake Karla is poor in organic matter.

The concentrations of 5 heavy metals (cadmium, chromium, lead, nickel copper) in the sediment were low (Figure 2b, 2c). The levels of heavy metals found at 11 sampling sites are well below the allowed limits set by the European legislation for agricultural use [23]. This was largely expected as there aren't any large units in the area producing wastes containing significant concentrations of heavy metals.

Metals enter into river water through a variety of sources, such as chemical weathering of rocks and soils, dead and decomposing vegetation and animal matter, wet and dry fallout of atmospheric particulate matter and from man's activities including the discharge of various domestic and industrial effluents [9]. Sampling sites 7 (Figure 2b) where extensive farming is practiced shows high Cu values and it is expected that Cu may enter into the aquifers through agrochemicals. The value obtained was lower than the permissible limits and hence adverse effects from domestic use are not expected as far as this metal is concerned. The S7 site is found in an area where a factory producing alcohol is operating which probably relates to the additional $CuSO_4.5H_2O$. At this station increased organic matter which strongly retains Cu was observed (Figure 2a). Organic matter is one of the main factors responsible for strong retention of elements in the soil, because it forms stable soluble and insoluble compounds [24].



(a)



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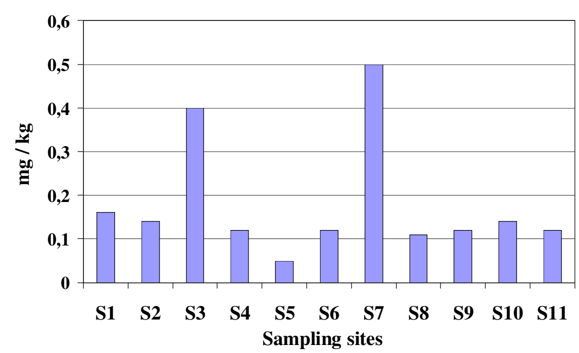


(c)

Fig. 2 - a) The organic matter (%) in the sediment, b) measured values (copper, cadmium, lead nickel) core of heavy metals in sludge chromium and c) Cadmium (Cd) on September 21, 2009.

All measured chemical parameters of the sampled waters taken from the 12 sampling spots are presented in Figures 3 to 6. The EC values and the ions concentrations showed variation both between seasons and stations. The pH values did not show remarkable differences neither between sampling sites nor between sampling periods and the mean values for each site ranged from 5.7 in S10 to 9 in S2. Conductivity also showed temporal and spatial variation ranging between 414 and 11.700 μS cm^{-1}. Sulphates showed remarkable annual variation at most sampling spots with higher concentrations being recorded during 2009. The highest values were observed at sampling spots S2, S3, S4 and S11 while at the other sites the fluctuation was smaller. The maximum value (1890 mg L^{-1}) was observed in S2 in May 2009 and the minimum value (11 mg L^{-1}) in S1 in September 2008. Statistical difference among sampling sites was found only for the total alkalinity, (Analysis of variance, F = 3.16 df =5 p <0.001).

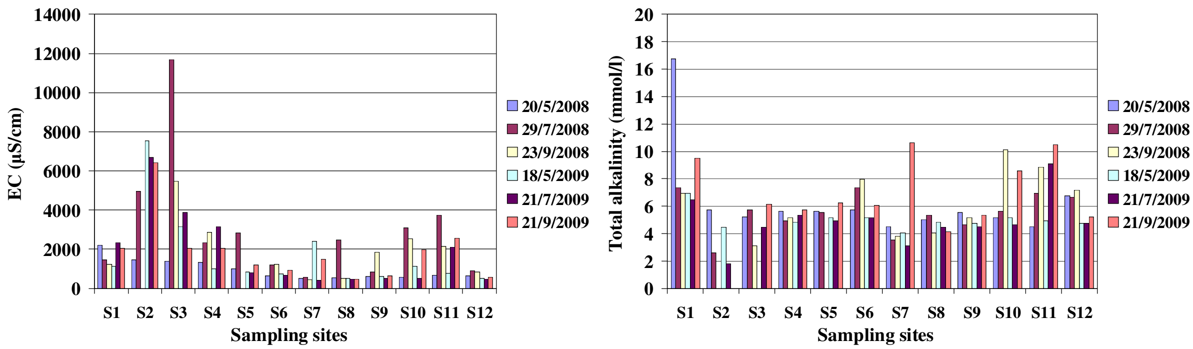


Fig. 3 - The variation of electrical conductivity (EC), total alkalinity, at the sampling sites in years 2008 and 2009

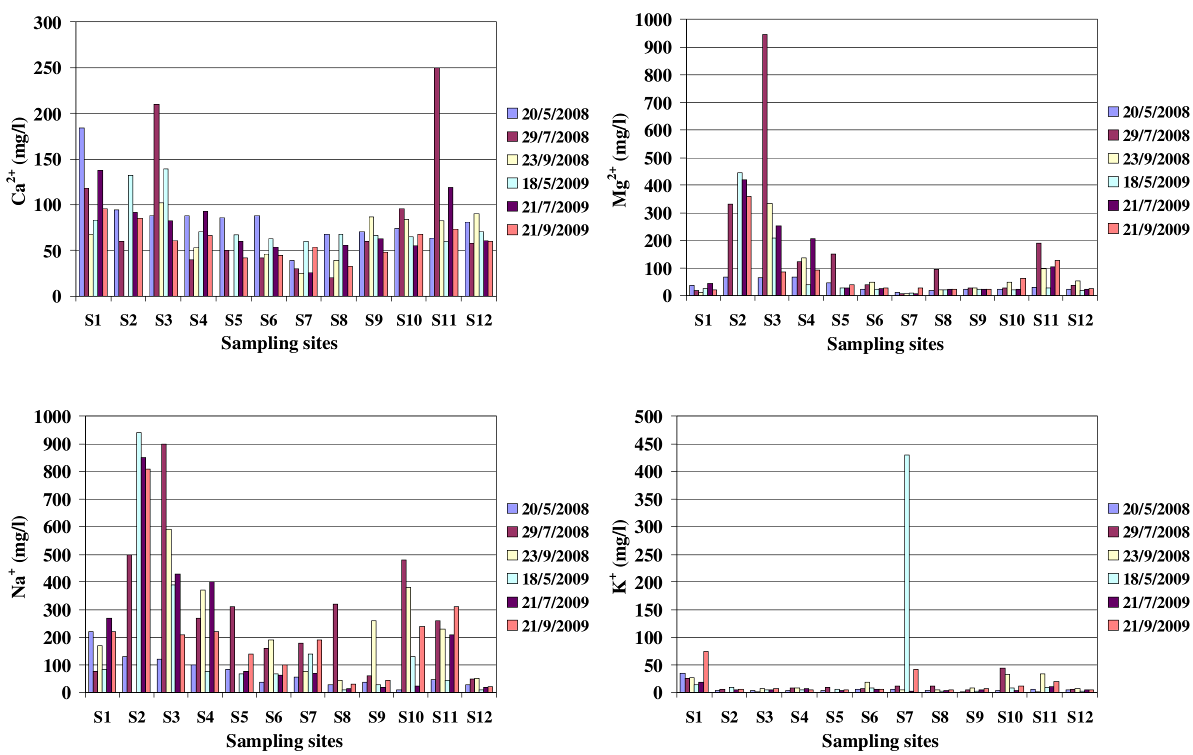


Fig. 4 - The calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), at the sampling sites in years 2008 and 2009

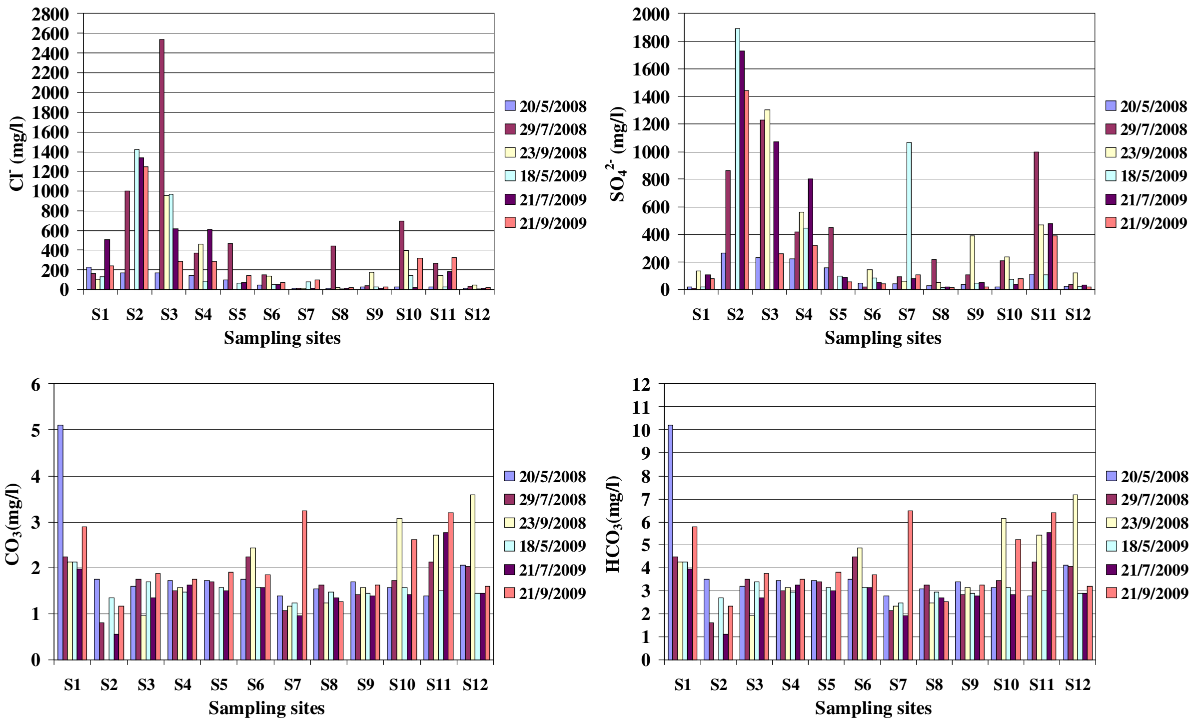


Fig. 5 - The Chlorine ($C\ell^-$), sulphates (SO_4^{2-}), carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-), at the sampling sites in years 2008 and 2009

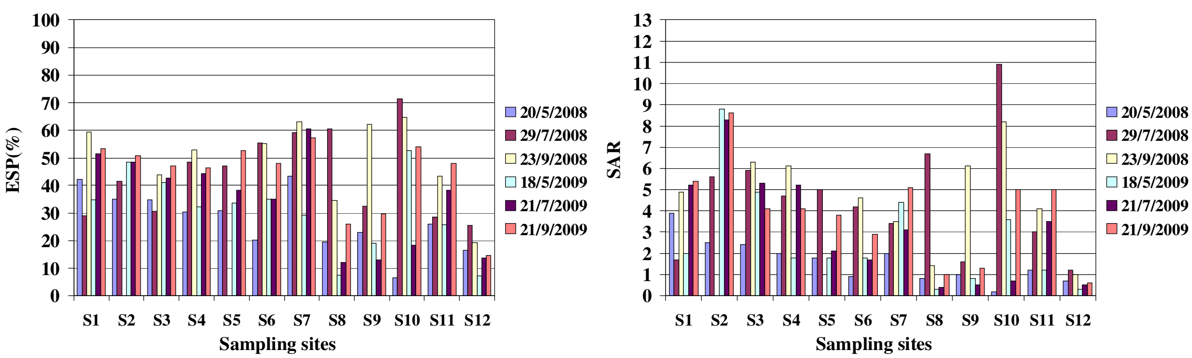
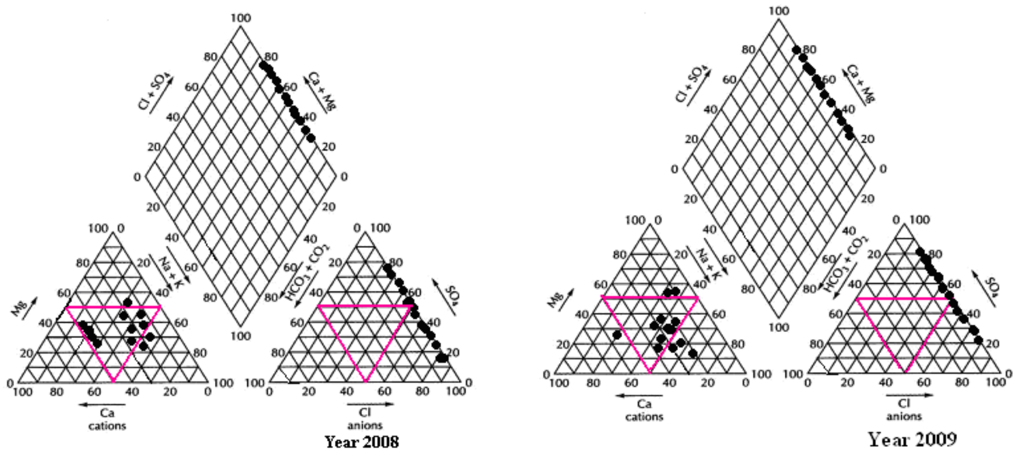


Fig. 6 - The Percentage Alternative Solution (ESP), Sodium Absorption Radio (SAR), at the sampling sites in years 2008 and 2009

Measured values show considerable variation from year to year, mainly due to large differences in climatic conditions that occurred both between 2008 and 2009, and between months, but also due to a number of other factors, such was the influx of water from the Pinios, the fertilization of crops, the hydraulic characteristics of the recipient.

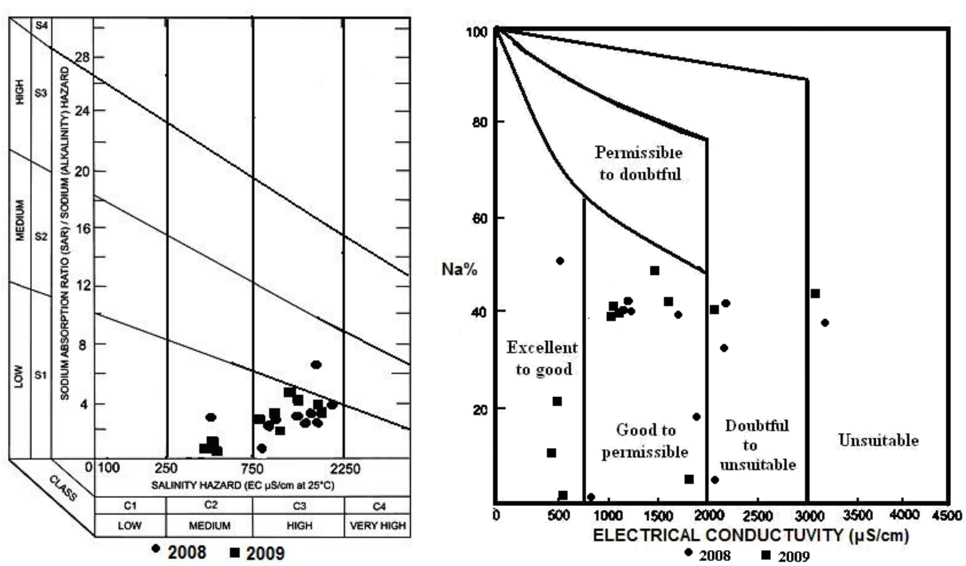
The nature and type of water can be evaluated by plotting the concentration of major cations and anions in the piper diagram (Figure 7). As for the anions sampling sites were classified into two categories in year 2008, the chloride, where 8 sampling sites belong (S1, S2, S3, S4, S5, S6, S8 and S10) and the sulphuric where the 4 remaining sites are included. The same results apply to the irrigation season of 2009 with the difference that station 4 was classified into the sulphuric. As far as the cations are concerned 4 stations were classified in Na-K waters in 2008 and 3 stations in 2009 as shown in the diagram. The magnesium cations prevailed in 2 sampling stations and in both irrigation seasons. Most sampling spots (9 in 2008 and 6 in 2009) were classified in the fourth category, in which no ion is predominant. As for the cations only sampling sites S1 and S9 were classified similarly in both years.

In order to assess the water suitability for irrigation, sodium percentage, SAR and Wilcox diagrams (Figure 8) are evaluated. Wilcox (1955) [25] used % sodium and electric conductivity in evaluating the suitability of water for irrigation. For each station Na% and averaged SAR of the 3 seasonal samplings are given in Table 2. During 2008, 9 of 12 sampling sites (75%) appear to be good to permissible for irrigation; only S4 are classified between doubtful and unsuitable and two sampling sites (S2 and S3) fall under the unsuitable level. The results for 2009 irrigation period show that the sampling site S8 has excellent to good classification, S8 of S12 sites (66.67%) have good to permissible for irrigation, the S4 is characterized doubtful to unsuitable; and two sampling sites (S1 and S2) are classified under the unsuitable level. The results for both years demonstrate that 75% of the water show good to permissible quality; 8% are between doubtful and unsuitable; 17% of the water is unsuitable for irrigation. The results reveal that the water near the Pinios River is good for irrigation while contamination occurs higher near Karla Lake. This may be due to the increased values of electrical conductivity due to soil composition in the particular [2].



(a) (b)

Fig. 7 a,b - Piper diagram representing hydrochemical types [22]



(a) (b)

Fig. 8 – a) Rating of water samples in relation to salinity and SAR [21] and b) Specific conductance and Na% relation for rating irrigation water [25]

Table 2 - Evaluation of irrigation water based on Na%, electrical conductivity (EC) [20], SAR, electrical conductivity (EC) and U.S. Salinity Laboratory Staff (1954) [21]

Sampling sites	Year	EC (μS/cm)	Na (%)	SAR	Quality category (Na % - EC)	Quality category (SAR – EC)
S1	2008	1677	43,53	3,5	Good to permissible	High risk
	2009	1533	45,53	4,16	Unsuitable	High risk
S2	2008	3200	38.35	4,05	Unsuitable	Very High risk
	2009	6893	49,17	8,57	outside the scope (Unsuitable)	Very High risk
S3	2008	6186	43,53	4,87	outside the scope (Unsuitable)	Very High risk
	2009	3026	43,53	4,77	Unsuitable	Very High risk
S4	2008	2183	43,97	4,33	doubtful to unsuitable	High risk
	2009	2076	40,90	3,70	doubtful to unsuitable	High risk
S5	2008	1920	38,96	3,40	Good to permissible`	High risk
	2009	951	41,53	2,57	Good to permissible`	High risk
S6	2008	1041	43,60	3,23	Good to permissible`	High risk
	2009	794	39,30	2,47	Good to permissible`	High risk
S7	2008	506	55.10	2,97	Good to permissible	Medium risk
	2009	1448	48,97	4,20	Good to permissible`	High risk
S8	2008	1172	38.13	2,97	Good to permissible	High risk
	2009	491	15,10	0,57	excellent to good	Medium risk
S9	2008	1108	39,20	2,90	Good to permissible`	High risk
	2009	585	20,57	0,87	Good to permissible`	Medium risk
S10	2008	2065	7,53	6,43	Good to permissible`	High risk
	2009	1209	41,70	3,10	Good to permissible`	High risk
S11	2008	2194	32,63	2,70	Good to permissible`	High risk
	2009	1823	7,23	3,23	Good to permissible`	High risk
S12	2008	95	0,97	0,97	Good to permissible`	High risk
(cement- furrow)	2009	532	0,47	0,47	Good to permissible`	Medium risk

Another important tool commonly used to assess the degree of suitability of water for irrigation is SAR. It has been found that the magnitude of absorption of Na^+ by soils has a direct relationship to SAR. The SAR concentrations (Table 2) ranges from 0.2 (in sampling site S10) to 10.9 (again in S10) with a mean of 3.58 (n=34) for 2008 and from 0.3 (in sampling site S8) to 8.8 (in sampling site S2) with a mean of 3.18 (n=36) in 2009 irrigation period. The results show that 6 samples in 2008 (one sample in S3, S4, S8, S9 and two in S10) and 3 samples in 2009 irrigation period (in sampling site S2) show SAR values >6. Water containing SAR values >6 contains higher concentration of Na^+ compared to the concentration of Ca^{2+}, reflecting that this water is not suitable for irrigation [9].

Electric conductivity (EC) is a good indicator of salinity hazard to crops as it reflects the TDS in water. Representation (Figure 8) of the chemical data on the irrigation suitability diagram [26] clearly brings out the seasonal variation and the suitability of the water for irrigation. During the 2008 irrigation period, the US salinity diagram demonstrates that the Asmaki water samples fall in the fields of C2S1, C3S1 and C4S1. About 91,67% of the samples fall in the field of C3S1 and C4S1 reflecting high salinity and low sodium in water which can be used for irrigation on almost all types of soil with only a minimum risk of exchangeable sodium._The water of this type can be used for plants having good salt tolerance [27]. Only one sample (8%) showed medium salinity- low sodium (C2S1).In the case of 2009 irrigation period, US salinity diagram illustrates the same results: 75% of the samples show high salinity-low sodium (C3S1, C4S1) and the remaining 25% belong in the C2S1 classification, clearly demonstrating the seasonal variation and the adequate drainage required for irrigation. In September 2008 there was no flow at sites S2 and S5, so no water at all. 2008 was a year of drought while 2009 was a rainy season, there was more flow and more dilute, so the salinity showed lower values. Overall, in 2009 water quality is presented better than in 2008.

Based on the Na% irrigation water was suitable for farming. The combination, however, Na% and salinity has about 10% water Excellent to good, 50% Good to permissible, and 20% water Doubtful to unsuitable and unsuitable respectively. The rates shall be divided equally for the years 2008 and 2009. The Na% showed lower rates in 2009.

The evaluation of water quality was carried out in order to identify its suitability for irrigation purposes. The major factors that define the quality of the water in the study area are agricultural activities, anthropogenic activities and the leaching of saline soils in the region. At sampling sites S2, S3, S4, excessively high values of electrical conductivity, were presented which may be due to leaching of saline soils in the region. Increased concentration values of Na^+, ions, SAR and grade of alkaliosis. (30.45% - 57.92%) occurred at the same sites. High values of $C\ell^-$, sulfate (SO^{4-}). Ca^{2+}, and Mg^{2+} ions were also present in this field. In this part of the ditch the above mentioned parameters classify water as unfit for irrigation use. Berkant et al. (2010) [28] also found similar results in the Rivers Tigris and Euphrates. Conclusions are different for the Pinios River [8], showing evidence acceptable for irrigation purposes. Loukas, (2010), also found that the SAR value for Pinios was <0.3 and only in few cases reached up to 1.1 and the conductivity ranged from 200 to 700 mS cm^{-1}, in few cases was greater than 1000 mS cm^{-1}, which means that water has a low probability on the occurrence of salinity, if used for if it is used for irrigation purposes. If the increased demand for irrigation water require its use in future, in this section, leaching of soil should be prevented along with any other method that contributes to the phenomenon of salinization.

4 Conclusion

Taking into account the Hydrochemical classification of waters by Piper, the measured conductivity values (EC), sodium adsorption ratio in SAR (Sodium Absorption Ratio), the hazard of sodium (Na%), chlorine (Cl), sulfate (SO_4^-), Ca^{2+}, and Mg^{2+} ions and five basic heavy metals (Cd, Cr, Pb, Ni and Cu), and focusing on irrigation season, which is determined by the 5th to the 9th month of each year, yields the following conclusions:

In regard to (EC) water and for two years was found unsuitable for irrigation at a rate exceeding 90%, in the vicinity of Lake Karla in fact the rate of salinity was very high. The SAR was a very large percentage levels for irrigation. The combination, however, salinity and SAR gave water to a large extent unsuitable for irrigation. Based on the Na% irrigation water was suitable for farming. The combination, however, Na% and gives salinity water suitable for irrigation by 50% for both years.

High values of $C\ell^-$, sulfate (SO_4^-). Ca^{2+}, and Mg^{2+} ions were also present in this field in most sampling sites where the mentioned parameters classify water as unfit for irrigation use. As regards heavy metals (Cd, Cr, Pb, Ni and Cu), the results of measurements showed that concentrations of heavy metals in the sediment was significantly lower than the limits for use of sludge in agriculture.

In terms of water quality it tends to become prohibitive even for conventional crops, particularly for high-quality crops especially in terms of salinity and chlorine. Consequently, the pollution of Asmaki is not only a cutting-edge environmental issue, but mainly a problem of development and character, if not only fails to support a reliable agricultural production, but rather undermines it. Consequently, if we need to explore the future of agricultural production, in the existence and operation of the Asmaki we may need to revise some issues, such as: i) The Asmaki should be left an open pipeline? ii) Should it serve as an irrigation ditch, drainage ditch and recipient of industrial waste all at the same time? iii) Is it a reliable ecological function?

Acknowledgements

We would like to thank Dr. Vassilia Artemiadou from Department of Agricultural Development Region of Thessalia and Dr Zisis Argyropoulos for their comments on an earlier draft of this paper.

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