Assessing quality of an irrigation canal ecosystem, through water and environmental parameters (temperature, total hardness, pH, D.O, EC, BOD_5, COD, N, P, Na^+, NO_3^-, $C\ell^-$, PO_4^{3-}, NH_4^+ and SO_4^-). A case study in Thessaly region, Greece

AVGOUSTINOS AVGOUSTIS[a], SAVVAS PAPADOPOULOS[b], DIMITRIOS KATERIS[a], ANASTASIOS GEORGIADIS[a], IOANNIS GRAVALOS[a], PANAGIOTIS XYRADAKIS[a], ZISIS TSIROPOULOS[a]
[a] Department of Biosystems Engineering, Technological Education Institution of Larissa
41110 Larissa, GREECE
avgoustis@teilar.gr
[b] PEGEAL Central Greece Prefecture of Larissa
Ioanninon and Avlonos, 41334 Larissa, GREECE

Abstract: This study aimed to record and evaluate the physicochemical parameters (temperature,total hardness, pH, D.O., EC, BOD_5, COD, N, P, Na^+, NO_3^-, $C\ell^-$, PO_4^{3-},NH_4^+ and SO_4^-) in sediment Asmaki canal in order to assess the quality of water used and the nature of pollution along the canal. Samples were collected and analyzed bimonthly at twelve sampling sites along the irrigation-drainage Asmaki canal (Thessaly, Greece) and a total of 12 samples was made (every two months) for two consecutive years (2008 – 2009). We observed increased concentrations of, pH, D.O., EC, BOD_5, COD_5, N, P, Na^+, NO_3^-, PO_4^{3-}, $C\ell^-$, SO_4^- and NH_4^+due to anthropogenic inputs, mainly because of the discharged contaminating waters from the large industrial and agricultural activity.
Specifically, in many cases (especially in the area of Karla) the values of electrical conductivity (EC) were too high (which is apparently due to leaching of saline soils), high total hardness, elevated concentration of Na^+ions, very high values of BOD_5, COD, low prices D.O.and high eutrophication. The "Asmaki" presented at many points apparent industrial pollution, high intense anoxic conditions and high organic pollution. The findings of the study do not show that the parameter values are not affected greatly by the time of year (winter and summer) and this is due to an uncontrolled pollution from point and non-point sources.

Key-Words: Physicochemical parameters, industrial pollution, organic pollution, eutrophication.

1 Introduction

In the study of a natural ecosystem, many variables simultaneously change due to time so continuous water quality monitoring is essential for efficient management of urban rivers and for the prompt control of pollution. Due to the rapid responses of urban rivers to intensive land use and/or diverse pollution sources, the deterioration of the water quality may be accelerated, posing immediately a direct or indirect threat to human health and aquatic ecosystems [1-3]. The degree of organic pollution which occurs due to an excessive amount of organic matter, has typically been monitored by measuring BOD_5 and COD values in rivers. A high level of BOD_5 deteriorates river water quality by rapid decomposition of biodegradable organic matter and the subsequent depletion of dissolved oxygen, while COD traditionally represents the total organic matter. However, both concentrations are quantified by the amount of oxygen consumed for a particular chemical oxidation of organic compounds in samples. Enrichment of total nitrogen in urban rivers may result in excessive growth of algae and macrophytes, decreased biodiversity, and odor problems [3-5].

The 5-day biochemical oxygen demand (BOD_5) has been used as a water quality indicator in rivers worldwide [6-11]. In Japan, BOD_5 has been employed as a standard method for estimating the water quality of rivers since the Water Despite of the improvement of water quality, it is currently estimated that about 13% of rivers nationwide still exceeded the maximum acceptable BOD_5 value set by the environmental quality standard for rivers established by the Japanese Ministry of the Environment in 2005 [12].

There are several studies concerning Pinios River and its tributaries, which demonstrate the degradation of surface water due to extensive use of fertilizers and pesticides [13-15]. With regard to Asmaki irrigation canal, which runs across part of the Thessaly basin, there are only few studies [16, 17] showing the pollution of the surface waters. Reduced rateD.O. was found in various rivers of Europe [5], in Pinios River [15] and in River Turvo Brazil [19]. Generally, throughout the length of the trench (with few exceptions), the values of BOD_5 and COD were consistently higher than physiological, which are the maximum permissible limit values for living cyprinid throughout the year (EU Directive 98/03/EC - EU Directive 75/440/EEC - Quality of surface waters). Similar conclusions reached by Papadopoulou-Mourkidou (2002) [19] for the Axios and Evros, the Boskidis et al. (2010) [20] for the Vorvosi, the Surindra et al. (2010) [21] for Hindon river of India and Ali et al. (2011) [22] for the Nile. On the contrary, the findings according to Kyritsaki (2010) [23] are different forPiniossince values are almost normal.Remarkable, however, was the fact that the concentrations of ammonium ions in a few points remain on an annual basis higher than the limit of 1 mg/ℓ.

The "Asmaki" in its entirety can be considered a eutrophic recipient. In high eutrophication, based always on concentrations of nutrients N, P, is the portion extending from the sampling sites S5 to S12 and the station where the averages of PO_4^{3-} show the variation 0.57 mg/ℓ - 2.76 mg/ℓ, a small downward deviation in sampling site S8 (0,37 mg/ℓ). About the same results for "Asmaki" given by Bakopoulou and Kungolos (2004) [16] and Argyropoulos and Samara (2008) [17]. Similar results were found by Dassenakis et al. (1998) [13] for the Lithaio (tributary of Pinios), the Bellos et al. (2003) [4] for Pinios and Bowes et al. (2010) [24], for British rivers.

2 Materials and Methods

2.1 Study area

The research area (Fig. 1) extends from the northeastern side of the city of Larissa, up to the 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 at about 70%, corn in the second place at about 20% as well as 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 though 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 canaln"1T" made 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 to the Pagasetike Gulf. For the purposes of this study12 sampling sides were selected (S1 to S12) (Table 1, Fig. 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).

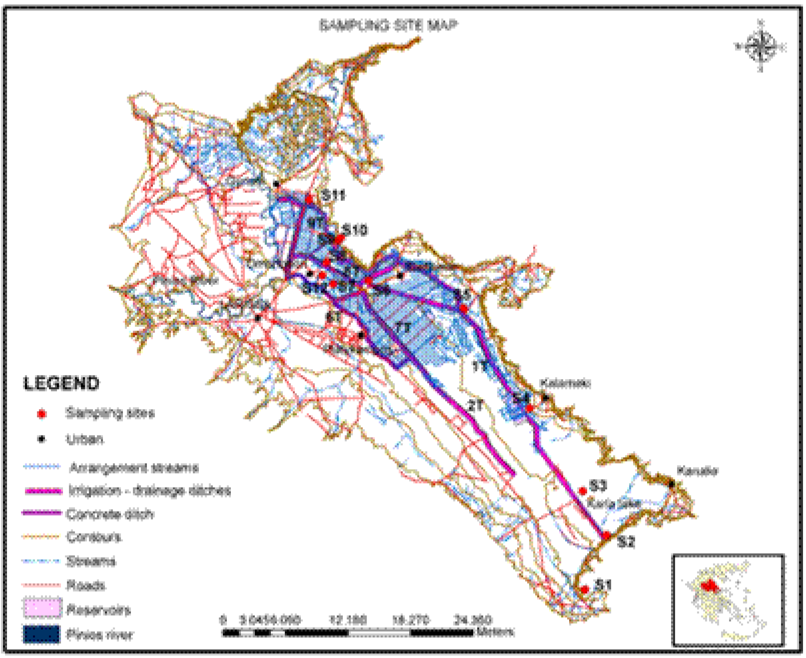

Fig. 1 - Map of study area with the sampling sites

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 alarge-scale organic pollution and minor chemical pollution (e.g.dyeworks, oily sludge, production waste, use of greases, soaps, disinfectants). The industrial units of the region are a factory of alcohol treatment (near S7 sampling site), a textile dye works (near the sampling site S8), a food production industry (near the sampling sites S9 and S10) and the Slaughterhouses of Gyrtoni (near to sampling site S11). A lot of livestock farming units in the region manage their waste (e.g. the waste of dairy plants and solid waste) with 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 the cementfactory "Hercules". Finally sampling site S12 is the only one that receives water from Pinios River as well asthe only one with a cemented sub layer.

Table 1 - Sampling sites

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

2.2 Water sampling - Chemical analysis

The samples of water (ℓ) were collected in PVC bottles from the middle of flow of the aquatic stream and as far as this was possible from the middle of its of depth and was stored in refrigerator (at 4^{o}C), in the dark until the 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 [25]. Water temperature, D.O., pH, electrical conductivity (EC) and total alkalinity were measured by standard electrochemical methods [26]. The concentrations of sodium (Na^+) cation, were determined by flame photometry [28]. The concentrations of ammoniac NH_4^+, N, P, NO_3^-,

PO_4^+, CL^- and SO_4^- were evaluated according to Standards Methods for the Examination of Water and Wastewater [26,27]. The $B.O.D_5$ was calculated by the manometer method and the COD by spectrophotometer method.

3 Problem Solution

The D.O. concentration appears low, especially in the area covered by the sampling sites S7 and S11 (average D.O = 2.40 mg/ℓ< 4 mg/ℓ), indicating the existence of reducing conditions, which is consistent with the relatively high values of concentrations of ammonium ion for the same field (average NH_4^+ = 1.85 mg/ℓ), compared to the average of NH4+ for the remaining field (S2 - S6) which were 0.38 mg/ℓ, the event that highlighted the D.O. measurements is that they are particularly low in active industries in the region (S6 - S11). Although the number of measurements was not large enough, it is clear that throughout this length, anoxic conditions prevail ($[O_2]$ < 4 mg/ℓ), which are prohibitive for the safety of living fish, even cyprinid Zanakia (2001) [28]. In this region, there is a clear correlation of three parameters (NH_4^+, NO_3^-, D.O.), that briefly indicate the existence of such conditions (Fig. 2 to 13) as:

1. Low concentration of D.O. (average = 3.16 mg/ℓ).
2. Low concentration of nitrate, NO_3^- (average = 2.08 mg/ℓ).
3. Relatively high concentration of NH_4^+ (average = 2.05 mg/ℓ).

Specifically, acceptable values of the concentration of ammonium ions in the Greek Law (MD 46399/1352/86 - FEK43V/1.v/3-7-86) are:

1. Desirablelimit 0.2 mg/ℓ.
2. Supreme permissible 1 mg/ℓ.

The above situation can be attributed to the following factors acting synergistically:

1. Low flow rate
2. High turbidity
3. Improper Operation of wastewater industries
4. Scraping of sediments in the waste stream industries.
5. “Pirates” waste, e.g. unloading silos.
6.Eutrophication in the second phase, the degradation of algae.
7. Large volume of waste in relation to the provision of the recipient.

In contrast, high concentrations of D.O. occurred where there was considerable industrial activity, but there were other imponderables related to pollution of surface water with high organic waste load (S2 - S5), where the average D.O. was 7.82 mg/ℓ, suggesting low organic load which partially agrees with the values of biochemical oxygen demand (BOD_5) (average = 13 mg/ℓ). While that is prohibitive for living cyprinid (desirable than 6 mg/ℓ), it is an indicator of high organic pollution. Similar results were found by Zissis (2005) [29] in Litheon River (tributary of Pinios), which also fall within the scope of the legislation.

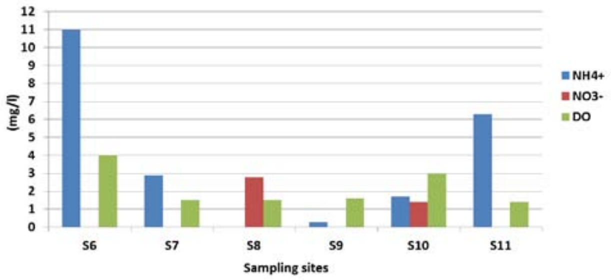

Fig. 2 - The concentration of NH_4^+, NO_3^-, DO, at sampling sites S6 - S11 (22/01/2008).

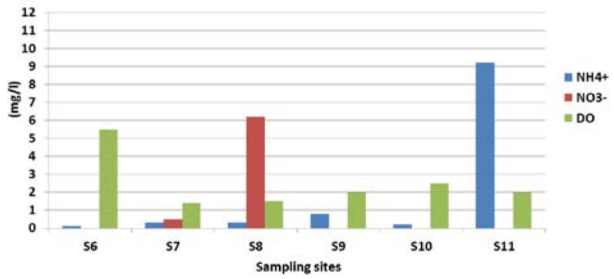

Fig. 3 - The concentration of NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (18/03/2008).

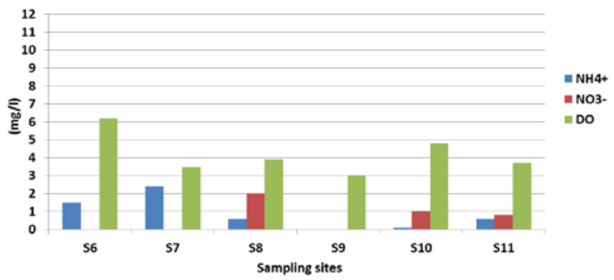

Fig. 4 - The concentration of NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (20/05/2008).

A. Avgoustis, S. Papadopoulos,
D. Kateris, A. Georgiadis, I. Gravalos,
P. Xyradakis, Z. Tsiropoulos

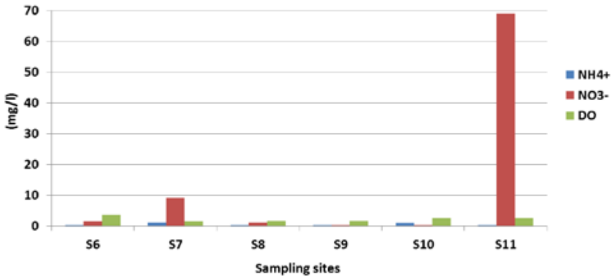

Fig. 5 - The concentration of NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (29/07/2008).

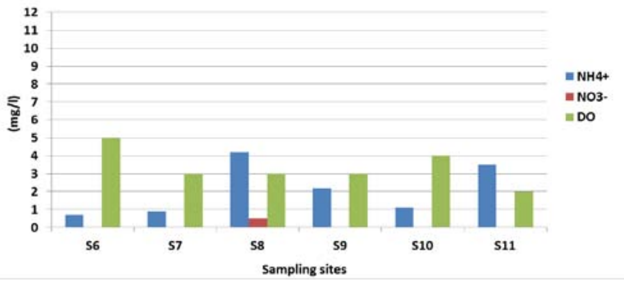

Fig. 6 - The concentration of NH_4^+, NO_3^-, D.O., at sampling sites Σ6 – Σ11 (23/09/2008).

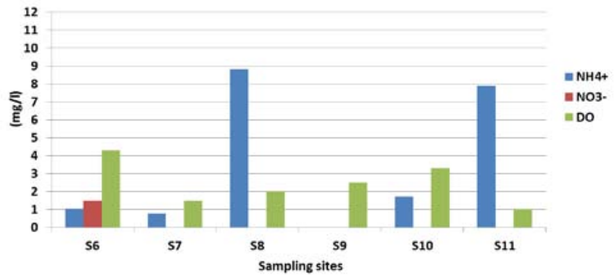

Fig. 7 - The concentration of NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (21/11/2008).

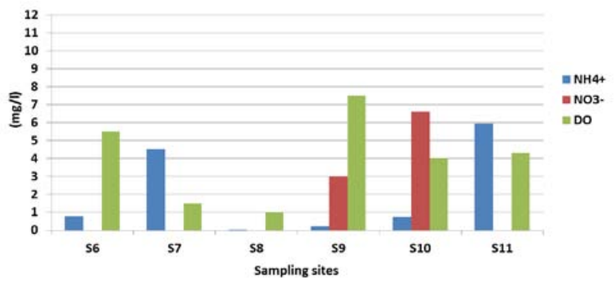

Fig. 8 - The concentration of NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (22/01/2009).

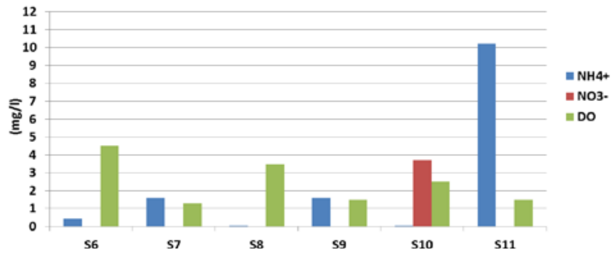

Fig. 9 - The concentration of NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (18/03/2009).

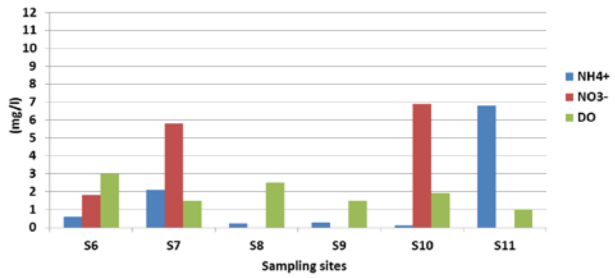

Fig. 10 - The concentration of NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (18/05/2009).

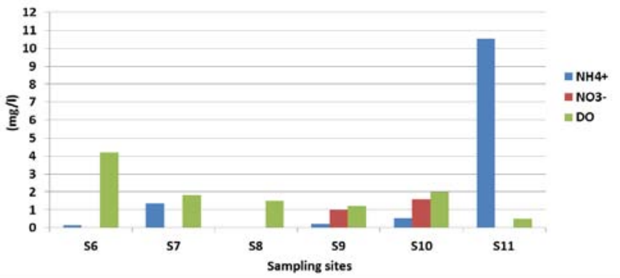

Fig. 11 - The concentration of NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (21/07/2009).

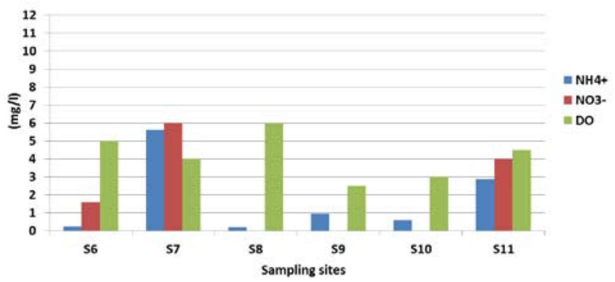

Fig. 12 - The concentration NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (21/09/2009).

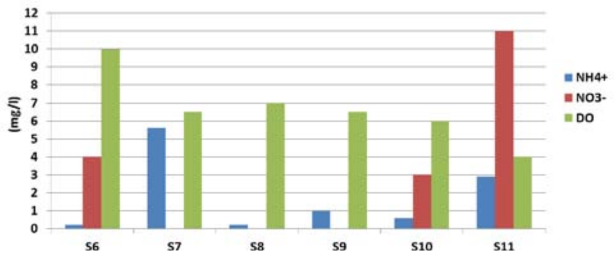

Fig. 13 - The concentration NH_4^+, NO_3^-, D.O., at sampling sites S6 – S11 (17/11/2009).

3.1 Dissolved oxygen (D.O.)

The concentration of D.O. (Fig. 14) appears low, especially in the area covered by the sapling sites S7 and S11 (Chatzidima distilleries and slaughterhouses of Gyrtoni) with an average D.O. = 2.4 mg/ℓ ± 1.692 < 4 mg/ℓ, a factor which indicates the existence of reducing conditions and in line with the lowest values of concentrations of nitrate (NO_3^-) concentrations (Fig. 15). High concentrations of D.O. appeared at the parts where there was considerable industrial activity as well as other imponderables of surface water pollution with high organic waste load (stations S2 - S5), where the average D.O. was 7.82 ± 1.582 mg/ℓ, an evidence indicating low organic load and is partly consistent with the values of biochemical oxygen demand (BOD_5) with an average = 13 mg ± 7.642 O_2/ℓ, which is prohibitive for living cyprinid (desirable 6 mg O_2/ℓ) (98/03/EC EU Directive - EU Directive 75/440/EEC - Quality of surface waters).

3.2 Biochemical Oxygen Demand (BOD_5)

The values of BOD_5 (Fig. 16) showed a clear split by segments:

Industry Sector (I.S.) - large industrial density.
Agricultural Sector (A.S) - a small industrial density.

At sampling sites S6 - S11 there was high industrial activity and relatively large ranching operation. There even were unpredictable and isolated incidents of pollution due to the easy access of tankers and other heavy vehicles in the area.

I.S. - Average BOD_5 = 41.7 mg/ℓ (sampling sites S6 - S11).
A.S. - Average BOD_5 = 13 mg/ℓ (sampling sites S2, S3, S4, S5, S12).

Indicative rates are measured downstream of certain industries, such as the sampling site S8, where during the period 23/09/2008 - 18/05/2009 (about 8 months) very high concentrations were found (average = 137 mg/ℓ), which can be attributed, apart from the misapplication of environmental conditions in the industry to the substantial reduction of water and low flow velocity. The extremely high value of 17/11/2009, BOD_5 = 360 mg/ℓ can be attributed only to channeling raw or semi-processed industrial wastes to the recipient. High values of BOD_5, were measured at sampling sites S8 and S11, where the average was 94.17 and 69.42 mg/ℓ. Probable cause of massive channeling waste in the recipient, which at that time had very little flow, while sampling site S11 showed extremely high values which may be due to channeling blood and flushing fluids from the slaughterhouses to the recipient. As it is known, the blood is of very high organic load. The fact is testified eloquently through the image of the recipient during the visits for samples. Generally, throughout the length of the trench (with few exceptions), the values of BOD_5 were consistently at the highest limit of 6 mg/, which is the maximum allowed for living cyprinid throughout the year. (EU Directive 98/03/EC - EU Directive 75/440/EEC - Quality of surface waters).

3.3 Chemical Oxygen Demand (COD)

The values of COD (Fig. 17), showed almost the same variance with the one that showed the values of BOD_5, for the same sampling points. Specifically:

Sampling site S8: average C.O.D. = 202.17 mg/ℓ. For the same period, BOD_5 = 94.17mg/ℓ. The rate COD/BOD_5 = 2.15 is normal for industrial waste.On 17/11/2009 the values C.O.D. showed exacerbation (COD = 646 mg/ℓ), which, as mentioned before, is due to a recent, prior to sampling, bulk waste channelling to the recipient, having at that time very little flow.

Sampling site S9: Values ranged generally at lower levels than the ones for the station S8. The average value was 67 mg/ℓ and the corresponding ground COD/BOD_5 = 2.42 was normal for industrial waste (r = 2.00 to 2.50) (Decree 1180/81 (Gov. 293/A/6-10-1981).

Sampling site S11: The average value was 147.67 mg /ℓ and the rate was COD/BOD_5 = 147.67/69.42 = 2.13 which is also acceptable for industrial waste. It is notable that at the station there is a seasonal variation in values of COD which presented remarkable bouts, including:

1st month average = (279 +169) : 2 = 224 mg/ℓ
11th month average = (294 +250) : 2 = 272.00 mg/ℓ
3rd month average = (265 +99) : 2 = 182.00 mg/ℓ
7th month average = (36 +45) : 2 = 40.50 mg/ℓ
9th month average = (129 +50) : 2 = 89.50 mg/ℓ
5th month average = (115 +41) : 2 = 78.00 mg/ℓ

The values cannot be attributed solely to the low flow of water, but to the fact of the likely diversion of poorly treated or untreated plants waste in the region. More specifically, during the 11th month when the flow is minimized, the channelling of such waste to the water body is equivalent to the death of the recipient.

An important finding is the fact that, in general, for the industries of the region, the recognized environmental conditions in terms of the quality standards of their waste, provide as follows: BOD_5 = 30 - 40 mg/ℓ, COD = 120 -180 mg/ℓ.The average of the values of these parameters (except sampling sitesS1 and S12 tsimentavlakas) were:

$B.O.D_5$ = 30.72 mg/ℓ and C.O.D. = 75.07 mg/ℓ.

That is, the water quality of "Asmaki" is akin to that of the industrial waste. Consequently, the question arises whether an irrigation ditch with the features presented, has the potential to be used as a recipient of industrial waste with an unsafe and ineffective control system while its irrigation and ecological mission, has to be fulfilled with reliability.

3.4. Ammonium ions (NH_4^+)

The increased concentration of ammonium ions present clear or anoxic conditions, if accompanied by low concentrations of O_2, or pollution from animal waste. A typical example is the sampling site S11, where the average values of ammonium ion NH_4^+ were 5.57 mg/ℓ,a much higher value than1 mg/ℓ, which is the maximum allowed for the welfare of cyprinid, while the mean D.O. was 2.37 mg/ℓ, below the safety limit of 4 mg/ℓ (EC Directive 2000/60/E.C.). Many cyprinids can survive in concentrations of D.O. which is less than 3 cc/ℓ even at very low concentrations D.O. (Up to 0.5 cc/ℓ, such as the Butterfly (carassinuscarassius) (Neofytou 1997) [30]. The highest average concentration of ammonia, appeared in March (average, 2008, 2009 = 9.7 mg/ℓ), but the value seems rather momentary or more likely, typical of the time, since it presents itself throughout the year but peaks normal variation. There were significant differences between the low values (mean = 1.99 mg/ℓ), the average values (5.57 mg/ℓ) and high values respectively (average = 9.46 mg/ℓ). Remarkable however, was the fact that the concentrations of ammonium ions remain at the higher limit of 1 mg/ℓ, yearly.

At the other sampling sites, average of concentrations of NH_4^+ (Fig. 18) ranged normally for superficial recipient levels [0.15 -1.0 mg/ℓ (there are 2 extremes S6 22/01/2008 11mg/ℓ and S8 8.33 mg/ℓ 22/11-2008) except S7 sapling site, where high values occurred from 2.9 to 5.6 mg/ℓ (average = 2.43 mg/ℓ), which can be interpreted by the qualitative characteristics of the waste industry and the low flow rate and stagnation to the recipient at that point. Note that the liquid waste industry from the condensation tank washes the organic waste industry having a high concentration of nitrogen.

NH_4^+ -pH - T - NH_3^-

The measured pH values (<9), show that ammoniac nitrogen is almost completely in the form of NH_4^+ + NH_3. Based on the above equation, the values pH 8.0, result to very low or to negligible values regarding the concentration of NO_3^-. The ammonia is in equilibrium with the ammonium ions, according to the equation:

$NH_4^+ + H_2O \leftrightarrow NH_3^- + H_3O^+$ which shows the relationship:

pCb = pH - pCa - pka, wherein:

Cb = concentration of NH_3^- (moℓ/ℓ)

Ca = concentration of acid, NH_4^+

Ka = constant ionization of the acid, pKa = 9.20.

Based on the above equation, for values pH 8.0 resulting very low to negligible values the concentration of NH_3^-.

3.5. Electrical conductivity (EC), pH, Na^+, total hardness, CL^- and SO_4^-

Sampling sites S2, S3, S4, S5 presented too high electrical conductivity values S2 (6176 mS/cm), S3 (5740 mS/cm), S4 (2959 mS/cm), S5 (2037.55 mS/cm) (Fig. 19), which may be due to leaching of saline soils in the area [31]. In general, these three sampling sites appeared and elevated Na^+ ions concentration (Fig. 20), and total hardness (Fig. 21). Higher pH values (Fig. 22) were found at sampling sites S2, S6, S8 and S4 while the values were lower at sampling sites S10 and S4. The highest value 9.20 (21/07/2009) were observed at sampling site S2 and the lowest 5.7 (29/07/2008) at sampling site S10.The smallest average (7.39) was observed at sampling site S9 and the largest (8.52) at sampling site S2. What is discovered directly from the measurements been performed is the fact that there is a potential relationship of electrical conductivity (EC) with the chlorine ions Cl^- and sulphate ions SO_4^-.Very high concentrations of sulphates were measured at sampling sites S2 and S3, throughout the year, with averages of 1166.09 mg/ℓ and 901.25 mg /ℓ, a fact is consistent with the high conductivity values and chlorine for the corresponding area. The value remains high at the sampling sites S4, while it is diminishing at the other sampling sites, with some intermediate peaks at sampling site S7 (18/03/2009 - 768 mg/ℓ and 18/05/2009 - 10 mg/ℓ). The values can be attributed to runoff of neighbouring fields, due to fertilizing with sulphate fertilizers or and low flow. Periodic increase occurs and the sampling site S11 (slaughterhouse of Gyrtoni) due to industrial waste during the month 7^{th} to 11^{th} of the year 2008 and the year 2009.

3.6 Part with prominent industrial pollution

The section that displays remarkable industrial pollution is recognized primarily by two key parameters: BOD_5, COD The first parameter is booming at sampling sites S8 and S11, which have some form of stability (average, 94.17 mg/ℓ and 69.42 mg/ℓ respectively). Slight downward deviation occurs at sampling site S9 (average = 27.67 mg/ℓ). In all three cases there is industrial activity upstream of the sampling point. Sampling site F8 during sampling of 17/11/2009 showed particularl elevated values of both parameters, especially the COD (640 mg/ℓ) which is explained only by the channelling of massive waste in the recipient and the stagnation of water.

3.7 Part with heavy eutrophication

The "Asmaki" in its entirety can be considered a eutrophic recipient (Table 2). In high eutrophication, based always on concentration of nutrients N, P, (Figs 25 and 26) is the part extending from the sampling site S5 to S12 and the sampling site where the averages of PO_4^{3-} (Fig. 27) show the variation 0.57 mg/ℓ - 2.76 mg/ℓ, a small downward deviation in sampling site S8 (0.37 mg/ℓ).

Thus the recipient has two parts, visible enough, based on the concentration of phosphate ions:

1. Part with moderate to heavy eutrophication (S2, S3, S4) (average PO_4^{3-} = 0.22 mg/ℓ - expressed as [P] = 0.07 mg/ℓ.

2. Part with very high eutrophication (S5 - S12) (average PO_4^{3-} = 1.18 mg/ℓ expressed in P = 0.38 mg/ℓ.

Table 2 - The concentrations of P which characterize the degree of eutrophication of surface waters (Dillon an Rigler 1975) [32].

S/N	Scale Concentration	Eutrophication DP in mg/ℓ
1	Natural ecosystem	D.P $\leq$ 0,01
2	Low eutrophication	0.01 < D.P $\leq$ 0.05
3	Significant eutrophication	0.05 < D.P $\leq$ 0.10
4	High eutrophication	0.10 < D.P $\leq$ 0.15
5	Very high eutrophication	0.15 < D.P $\leq$ 0.20
6	Super - Eutrophication	D.P > 0.20

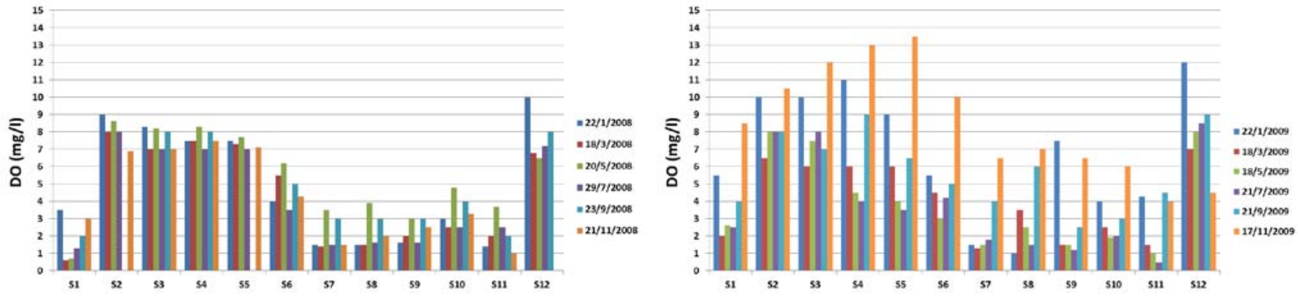

Fig. 14 - The variation of (D.O.), at the sampling sites in years 2008 and 2009.

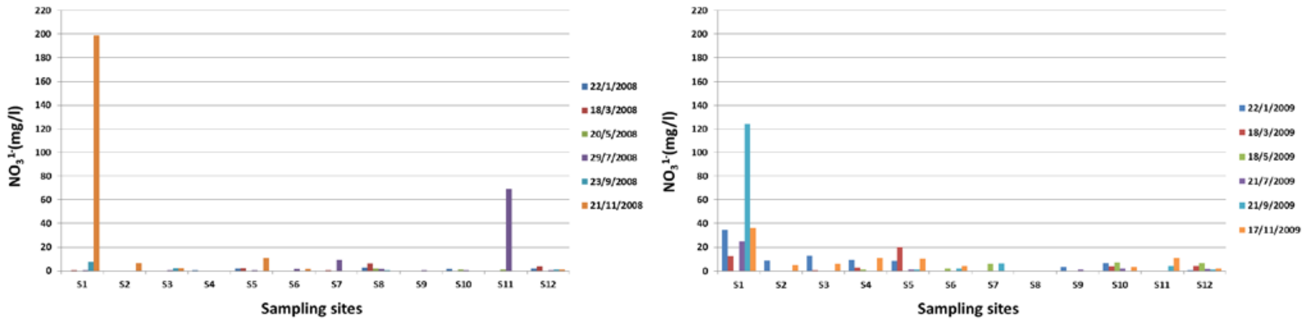

Fig. 15 - The variation of NO_3^-, at the sampling sites in years 2008 and 2009.

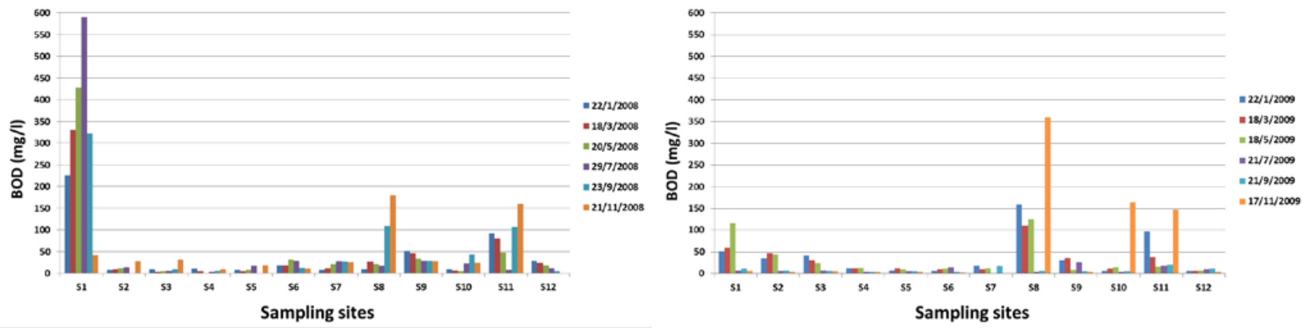

Fig. 16 - The variation of BOD_5, at the sampling sites in years 2008 and 2009.

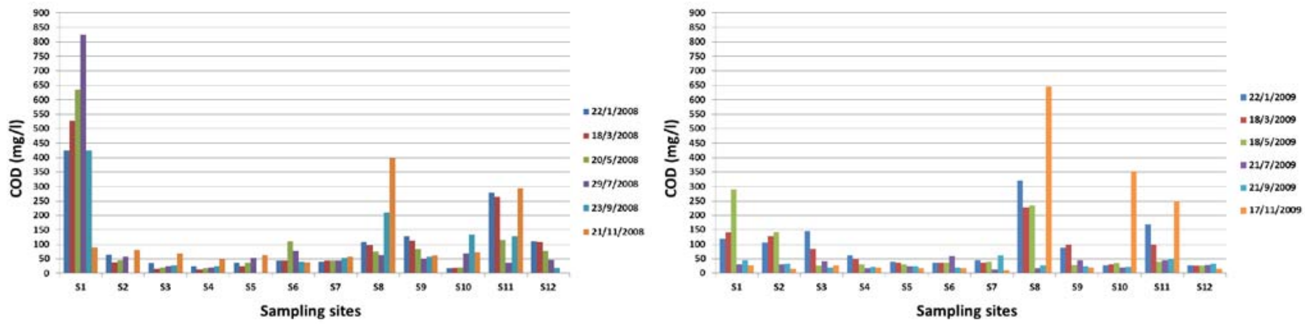

Fig. 17 - The variation of COD, at the sampling sites in years 2008 and 2009.

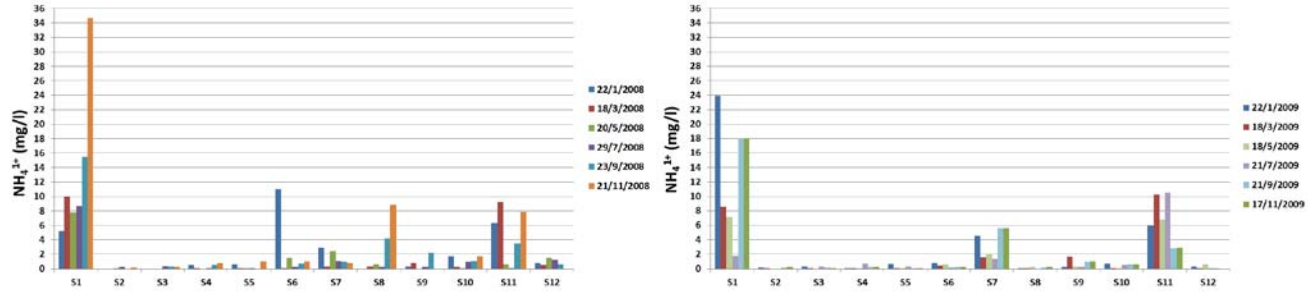

Fig. 18 - The variation of NH_4^+, at the sampling sites in years 2008 and 2009.

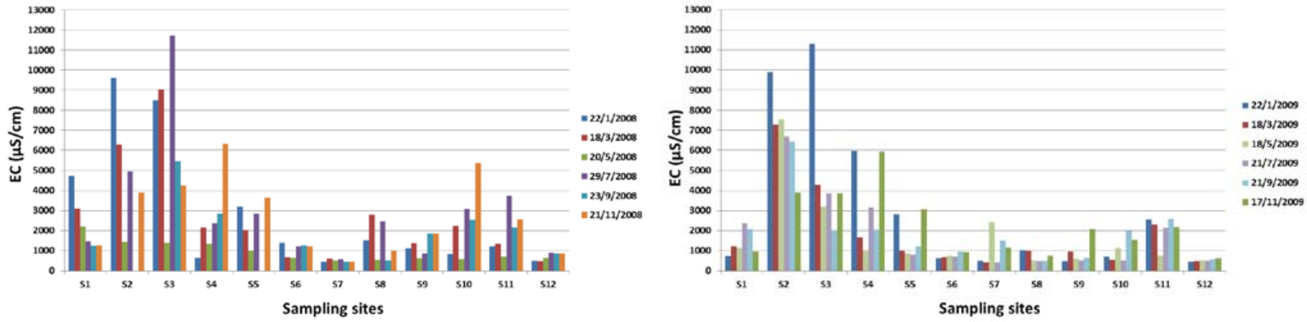

Fig. 19 - The variation of electrical conductivity (EC), at the sampling sites in years 2008 and 2009.

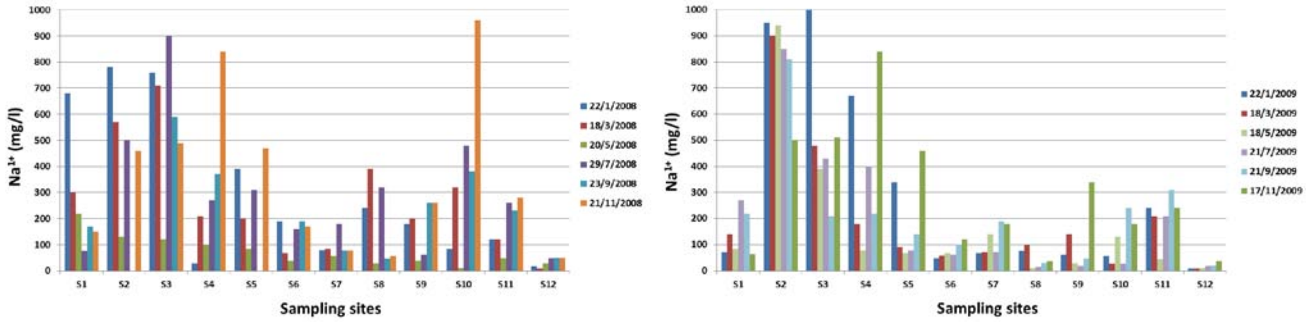

Fig. 20 - The variation of Na^+, at the sampling sites in years 2008 and 2009.

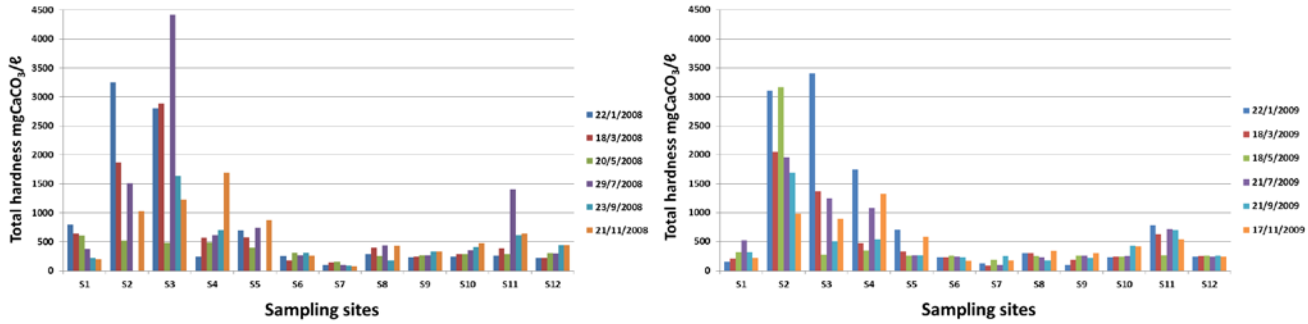

Fig. 21 - The variation of total hardness, at the sampling sites in years 2008 and 2009.

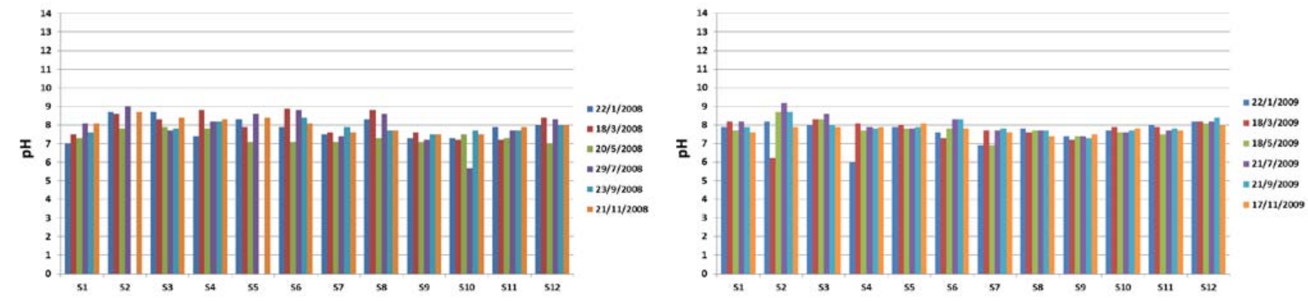

Fig. 22 - The variation of pH, at the sampling sites in years 2008 and 2009.

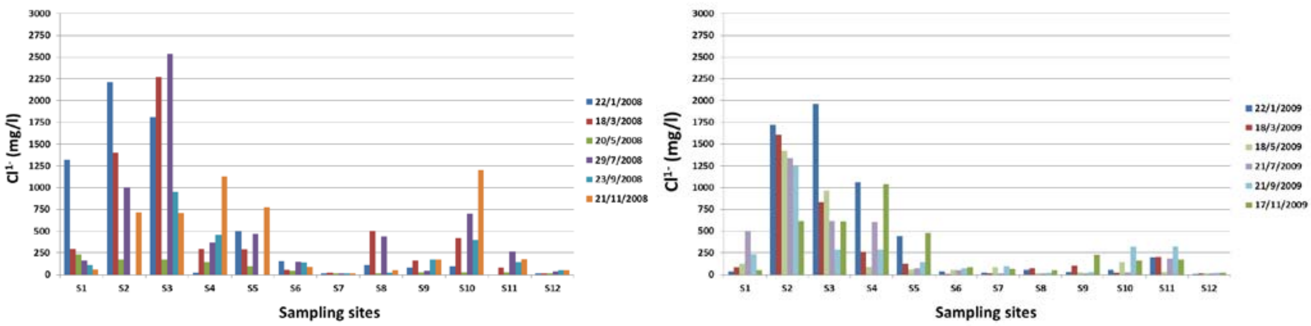

Fig. 23 - The variation of Cl^{-}, at the sampling sites in years 2008 and 2009.

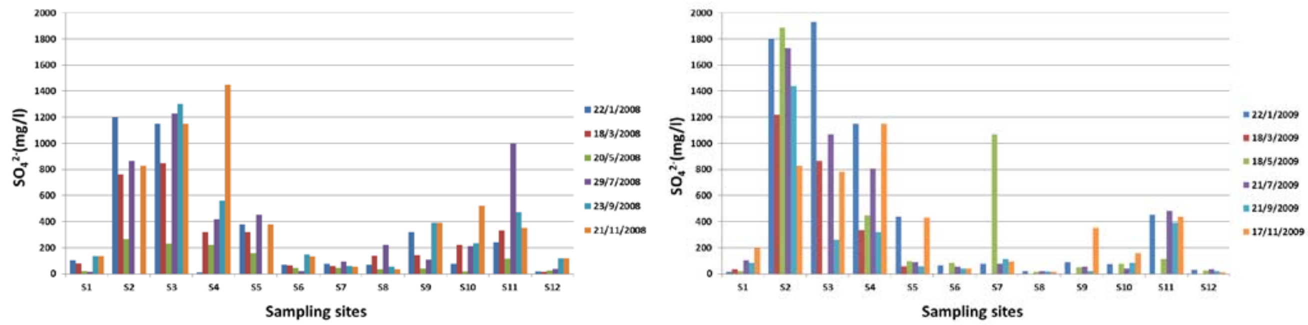

Fig. 24 - The variation of SO_4^{-}, at the sampling sites in years 2008 and 2009.

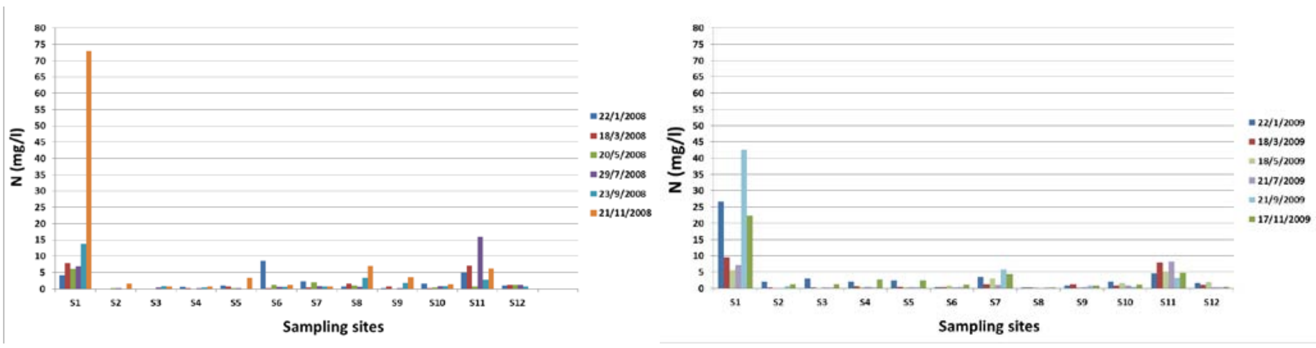

Fig. 25 - The variation of N, at the sampling sites in years 2008 and 2009.

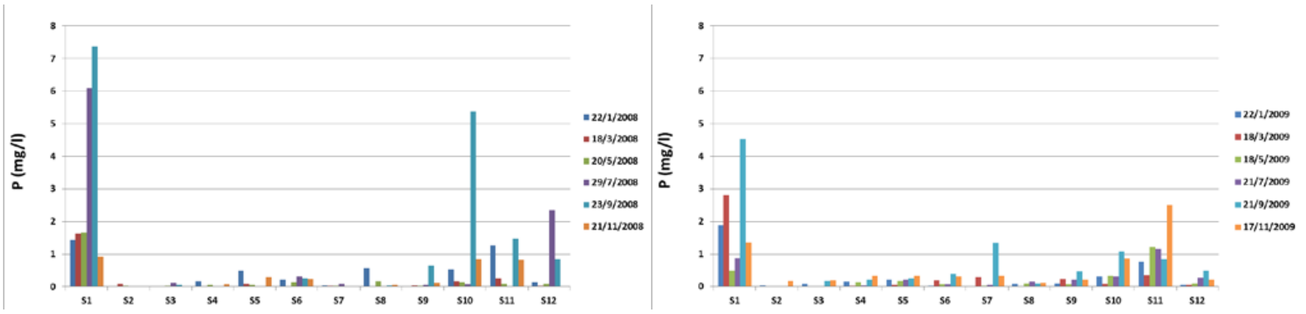

Fig. 26 - The variation of P, at the sampling sites in years 2008 and 2009.

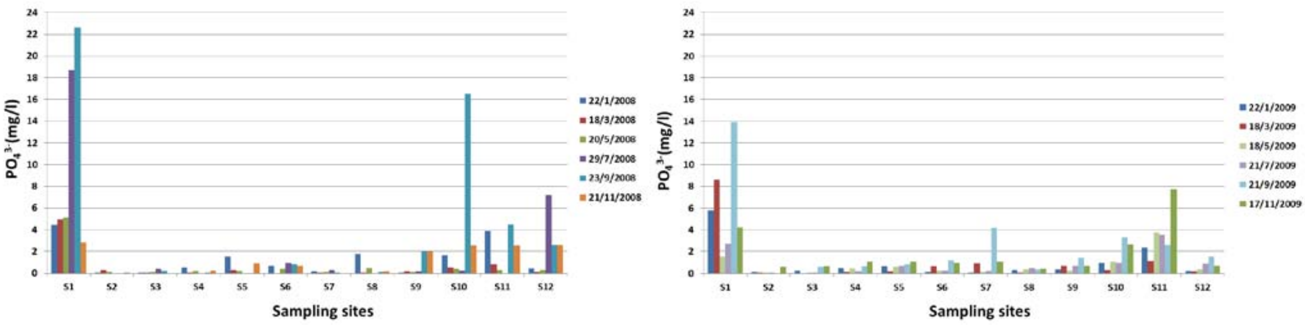

Fig. 27 - The variation of PO_4^{3-}, at the sampling sites in years 2008 and 2009.

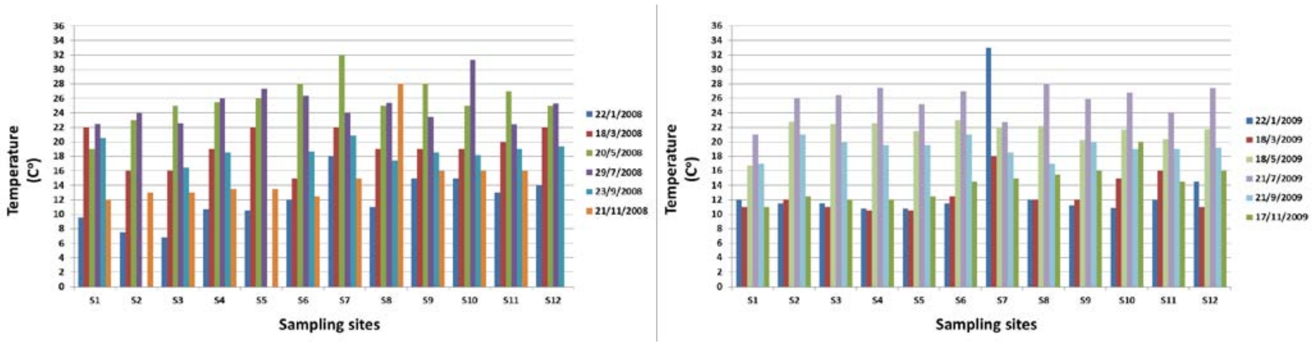

Fig. 28 - The variation of temperature (^oC), at the sampling sites in years 2008 and 2009.

4 Conclusion

The findings of this study showed that the "Asmaki" is a heavily modified water body that requires immediate and concerted effort to make it very useful and serve its mission. More specifically it was found that eutrophication prevails throughout the length of the channel. Eutrophication was the dominant effect of the water of the moat, which was evident in almost all its length, especially during the summer. The part that extends from sampling sites S5 to S12, where there are industries operating in the area, was in heavy eutrophication. On the contrary the degree of eutrophication was much lower in the agricultural sector.

The concentration of D.O. appears low, especially in the area covered by the sampling sites S7 and S11 with averageD.O. = 2.4 mg/ℓ ± 1.692 < 4 mg/ℓ, a factor which indicates the existence of reducing conditions and is consistent with the lowest values of concentrations of nitrate (NO_3^-), for the same field, despite the nitrate fertilizer runoff (average NO_3^- = 0.69 mg/ℓ) and the relatively high rates of ammonium ion concentrations on the same field (average NH_4^+ = 1.85 ± 1.975 mg/ℓ, compared with the average of NH_4^+ for the remaining area (stations S2 - S6: 0.38 mg/ℓ ± 0.812).

In contrast, high concentrations of D.O. were present where there was a considerable industrial activity, as well as other imponderable factors of pollution of surface water with a high organic waste load (sampling sites S2 - S5), where the mean D.O. was 7.82 ± 1.582 mg/ℓ,an evidence that indicates low organic load and partially agrees with the values of biochemical oxygen demand (BOD_5) in average = 13 mg ±7.642 O_2/ℓ, which is prohibitive for living kyprinid (desirable limit 6 mg O_2/ℓ) (98/03/EC EU Directive - EC Directive 75/440/EEC - Quality of surface waters). The values of COD, showed almost the same variation with that showed by values of BOD_5, for the same sampling sites.

It is noteworthy that the concentrations of ammonium ions (NH_4^+) remain on an annual basis the highest limit of 1 mg/ℓ. Furthermore, there is only one significant concentration of nitrate (NO_3^-) from all sampling points (69 mg/ℓ - 29/07/2008 – sampling site S11). There was a proportionalrelationship between conductivity (EC) and the concentration of sodium ions (Na^+) and (SO_4^-) which were found by the measurements. Very high concentrations of sulphate were measured in sampling sites S2 and S3, throughout the year, with averages 1166.09 mg/ℓ ± 512 and 901.25 ± 456 mg/ℓ, which are consistent with the high conductivity values for the respective area.

Acknowledgements

We would like to thank Mr ZisisArgyropoulos and Nicolaos Kokkinos for his comments on an earlier draft of this paper.

References:

[1] Henderson, R.K., Baker, A., Murphy, K.R., Hambly, A., Stuetz, R.M., Khan, S.J. Fluorescence as a potential monitoring tool for recycled water systems: A review,*Water Res.*,Vol.43,2009, 863–881.

[2] Su, S., Li, D., Zhang, Q., Xiao, R., Huang, F., Wu, J., Temporal trend and source apportionment of water pollution in different functional zones of Qiantang River, China,*Water Res.*,Vol.45, 2011, 1781–1795.

[3] Mouri, G., Takizawa, S., Oki, T., Spatial and temporal variation in nutrient parameters in stream water in a rural-urban catchment, Shikoku, Japan: Effects of land cover and human impact,*J. Environ. Manag.*,Vol.92, 2011, 1837–1848.

[4] Bellos, D., Sawidis, T., Tsekos, I., Nutrient chemistry of River Pinios (Thessalia, Greece),*Environ. Int.*,Vol.30, 2004, 105–115.

[5] Gerda M. V.D., Louis L., Wim A., Bert A. B., Jan J. C., Present state of the water quality of European rivers and implications for management,*The Science of the Total Environment*,Vol.145, 1994, 187-195.

[6] Morimoto, K.,Nobuso, M., & Kondo, Y., Studies on river pollution by cattle wastes: River pollution by pig farm waste and self-purification, *The Journal of Hygienic Chemistry*,Vol.15, No.6, 1969, 335–341.

[7] Ajayi, S. O. and Osibanjo, O., Pollution studies on Nigerian River II: water quality of some Nigerian Rivers,*Environmental Pollution (Series B)*, Vol.2, No.2, 1981, 87–95.

[8] Ramjeawon, T. and Baguant, J., Evaluation of critical BOD loadings from Mauritian Sugar Factories to streams and standards setting,*Journal of Environmental Management*,Vol.45, 1995, 163–176.

[9] Amisah, S. and Cowx, I. G., Response of the fish populations of the River Don in South Yorkshire to water quality and habitat improvements,*Environmental Pollution*,Vol.108, 2000, 191–199.

[10] Jonnalagadda, S. B. and Mhere, G., Water quality of the Odzi River in the Eastern Highlands of Zimbabwe,*Water Research*,Vol.35, No.10, 2001, 2371–2376.

[11] Chung, S. W., Ko, I. H., Kim, Y. K., Effect of reservoir flushing on downstream river water quality,*Journal of Environmental Management*, 2007.

[12] Japanese Ministry of the Environment,*Annual report on the environment and the sound material-cycle society in Japan 2007*, Tokyo, Japan: Japanese Ministry of the Environment, 2007.

[13] Dassenakis, M., Scoullos, M., Foufa, E., Krasakopoulou, E., Pavlidou, A., Kloukiniotou, M., Effects of multiple source pollution on a small Mediterranean river,*Applied Geochemistry*,Vol.13, 1998, 197–211.

[14] Fytianos, K., Siumka, A., Zachariadis, G., Beltsios, S., Assesment of the quality characteristics of Pinios River, Greece,*Water*

*air and soil pollution,*Vol.136, 2002, 317-329.

[15] Bellos, D., Sawidis, T., Tsekos, I., Nutrient chemistry of river Pinios (Thessalia, Greece). *Environment International,*Vol.30, No. 1, 2004, 105–115.

[16] Bakopoulou, S., Kounkolos, A., *Waste management in Larissa prefecrive Greece,* In 2nd International Conference on Waste Management and the Environment, 2004, 549-558.

[17] Argyropoulos G. and Samara T., Study of Sanitation Rehabilitation of irrigation-ditch T813 - "Asmaki", 2009, 160.

[18] Jordao C. P., Ribeiro P. R. S., Matos A. T., Bastos R. K. X., Fernandes R. B. A., Fontes R. L. F., Environmental assessment of water courses of the Turvo River basin at the Minas Gerais State, Brazil. *Environmental Monitoring and Assessment,* Vol.127, 2006, 316-326.

[19] Papadopoulou-Mourkidou E.,*Checklist for Surface Water Quality in Macedonia-Thraci-final report of results',* Aristotle University, 2002, 133.

[20] Boskidis I., Gikas G., Pisinaras V., Tsihrintzis V., Spatial and temporal changes of water quality, and SWAT modeling of Vosvozis river basin, North Greece. *Journal of Environmental Science and Health part A, Toxic/Hazardous substances and Environmental Engineering,* Vol.45, No.11, 2010, 1421-1440.

[21] Surindra S., JitenderS., Mayuri C., Arvind N., Water quality assessment of river Hindon at Ghaziabad, India: impact of industrial and urban wastewater. *Environmental Monitoring and Assessment,*Vol.165. No.1-4, 2010,103-112.

[22] Ali S.M., Sabae S.Z., Fayez M., Monib M., Hegazi N.A., The influence of agro-industrial effluents on River Nile pollution. Journal of Advanced Research, Vol.2, 2011, 85-95.

[23] Kyratsakis G.,*'Report conclusions month of August - September - October - November 2010 arising from the results of the sampling and testing conducted in three defined sampling stations of river Peneus,*2010, 95.

[24] Bowes M., Neal C., Jarvie H., Smith J., Davies H., Predicting phosphorus concentrations in British rivers resulting from the introduction of improved phosphorus removal from sewage effluent. *Science of the Total Environment,* Vol.408, No.19, 2010, 4239–4250.

[25] Eaton, D. A., Ganson, H. M., *Standard Methods for Examination Water and Wastewater*, 21th Edition, 2005,1917.

[26] EN 27888:1993, Water quality. Method for the determination of electrical conductivity.

[27] ISO 9964-3:1993. Water quality - Determination of sodium and potassium – Part 3: Determination of sodium and potassium by flame emission spectrometry.

[28] Zanakia K.,*Water Quality Control.* Ion Publications, 2001, 508.

[29] Zissis S. E., "Environmental factors and quality control river water Lithaiou." Thesis, 2007. 62.

[30] Neophytou Ch., *Ichthyology,*1997, pp. 290.

[31] Floras, S., Sgouras I., Pateras D., Zerva-Kapetanaki, G., Makrides H.,*Soil study of Southeast Zone 2 works part diversion Achelous River (region of dried lake Karla).* National Institute for Agricultural Research, Institute of Soil Mapping, 1997, 108.

[32] Dillon J. and Rigler H., A simple method for predicting the capacity of a lake for development based on lake trophie status. *Canadian Journal of Fisheries and Aquatic Sciences,* Vol.32, 1975, 1519-1531.