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FATE OF OLIVE MILL WASTEWATER IN EVROTAS RIVER BASIN

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SUMMARY: Olive mill wastewater (OMW) is a significant environmental pollution problem in Mediterranean countries. In Greece, due to the existence of small and decentralized facilities, the treatment of OMW can't be achieved by a centralized large scale treatment plant. The most common practice is the use of evaporation basins after the pretreatment of wastewaters with calcium oxide. The main objective of this study is the evaluation of land and sediments characteristics amended with OMW. The research was focused on two parts: the fate of OMW (pretreated with calcite) to (a) a corn field and (b) to river sediments. The effect of OMW application to a greater scale (Evrotas river basin) was also evaluated.

1. INTRODUCTION

Olive mill wastewater (OMW) is a significant environmental pollution problem in Mediterranean countries. In Greece, due to the existence of small and decentralized facilities, the treatment of OMW can't be achieved by a centralized large scale treatment plant. The most common practice is the use of evaporation basins after the pretreatment of wastewaters with calcium oxide. The leachate in most of the cases is disposed to cultivations plants or to surface waters. The modern (centrifuge-type) Olive Mills (OM) produce 5 m^3 OMW per ton of olive oil produced (Kapellakis et al., 2006). OMW are characterized by high COD values about 45-170 gL^{-1}, high organic load mainly consisted of polysaccharides, sugars, polyphenols (0.5-24 gL^{-1}), polyalcohols, proteins, organic acids, lipids (0.3-23 gL^{-1}), suspended solids (1.5-190 gL^{-1}) and nutrients (Paraskeva and Diamadopoulos, 2006). The phenolics compounds can be either low molecular phenols and flavonoids or polymerization products of the simple phenols that are very difficult to biodegrade and can have a toxic effect. The study of OMW and their disposal practice is of significance since innovative, low-cost treatment methods are to be found.

The study area is Evrotas river basin and is located in the south-west part of Peloponesus. It includes a part of Arkadia prefecture and almost the major part of Lakonia prefecture. The basin area is 2410 km^2. Taygetos and Parnonas mountains cover the major part of the basin. The main activities in the area are agriculture, farming and tourism. The mountains are covered by forest and in the mainland the main plants are olive and orange trees, vineyards etc. Environmental pollutants are nutrients, organic matter, heavy metals and phenols, due to extensive use of herbicides, pesticides and the unmonitored disposal of OMW. In Lakonia prefecture operate 169 olive mills and 91 are located inside the boundaries of Evrotas river basin (Figure 1) which has resulted in the expansion of the pollution sources. Many mills dispose the wastes without pretreatment in the neighbor small streams or direct in Evrotas river and consequently create several important pollution problems (Figure 2) in the river and the riparian zone and the groundwater. Most common treatment practice in Lakonia is the disposal of OMW in evaporation reservoirs.

The question is what is the fate of this high pollution loads and whether they posse a real danger in the water quality of Evrotas river and in groundwater? The main objective of this study was to evaluate the effects of disposing OMW at (a) river basin scale and (b) plot scale (corn field-soil) and river reach scale-sediments). One the one hand we studied the effect of the OMW disposal by several mills in the water quality of Evrotas basin in the time scale of one hydrologic year and on the other hand the direct effect of OMW disposal in land. The direct effect can be assessed by the study of sediments amended with OMW that the disposal is completely unmonitored and by the study of soils sampled by a corn field that was regularly amended with OMW.

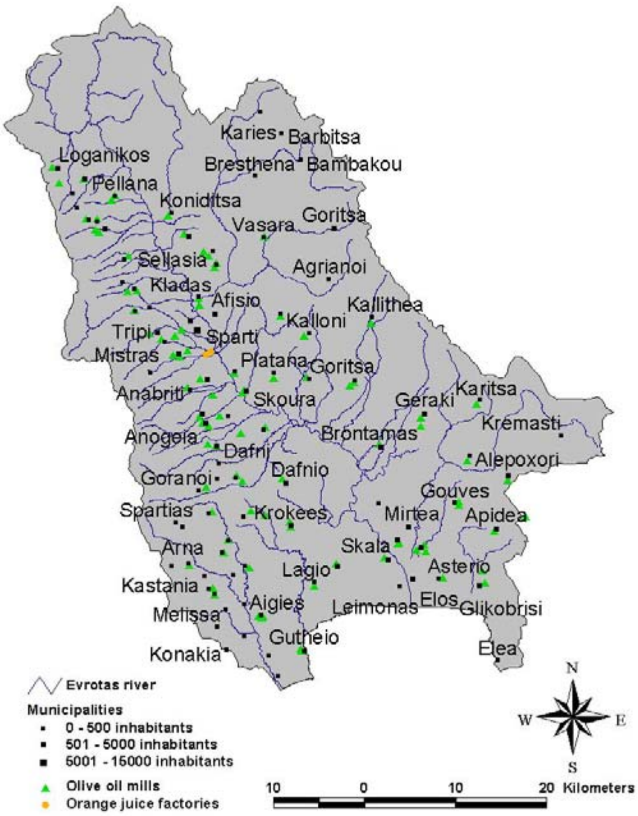

Figure 1. Evrotas river basin and the main point sources (inhabitants, olive oil mills and orange juice factories).

Figure 2. OMW disposal effect in Evrotas river and riparian zone.

2. METHODOLOGY

The study was focused in two different spatial and temporal scales. First spatial scale is Evrotas river basin and the main goal is to understand the effect of OMW by the several dispersed mills in Evrotas river water quality during a hydrologic year. In order to study the effect of OMW in Evrotas river basin a sampling network was established. The watershed was delineated into 7 subbasins according to the main geologic formations, landuses, the slopes, the elevation and the point sources (using ArcGIS 9.2). The sampling network covers the 7 subbasins and concerning the surface water covers the whole hydrologic network of Evrotas river (31 sampling points). The groundwater samples were taken by Sparta and Skala region (Figure 1) that are both more intensive cultivated and the point sources are very dense (32 sampling points). Five field campaigns took place (05/2006-12/2007) and water samples were taken for analyzing in the laboratory and soils amended by OMW.

The water samples were analyzed using phasmatophotometer of Hack company for Nitrate Nitrogen (NO3-N) (Cadmium Reduction Method, 8039), Nitrite Nitrogen (NO2-N) (Diazotization {Chromotropic Acid} Method, 8507), Ammonia (NH4-N) (Salicylicate Method, 10023), Dissolved Inorganic Phophorous (DIP) (PhosVer3 Method, 8048, Total Organic Carbon (TOC) (Direct Method, Low Range, 10129), Chemical Oxygen Demand (COD) (Low Range, 8048), phenols (Folin Ciocalteu method). The physicochemical parameters pH, Eh, Dissolved Oxygen and conductivity were measured in situ using the following electrodes: Orion 9107 pH meter, Orion 081010 D.O. meter, and Orion 011050 Conductivity meter.

A sediment sample from Skoura river bottom was taken during the second field campaing (September 2006) and it was analysed for its physicochemical charactaristics (pH, water content, porosity, dry bulk density, grain size distribution)(Method ISO 11277:1998 + Corr. 1:2002 (without destruction of carbonates)), metal determination (XRF), Total Kjeldahl Nitrogen (Nessler Method, 8075) and Total Organic Carbon (Walkley Black Method). A release kinetic experiment was conducted in the laboratory and the purpose was to study the rate of release of nutrients and phenols from the sediment affected by OMW. The experiment was carried out in 100 ml bottles using 2.5g of sediment samples (< 2 mm fraction), 2.5g sand (fraction 0.5-2 mm) and adding 100 ml synthetic river water as release solution. The release solution composition had similar geochemistry to Evrotas river water in Skoura (without nutrients): KCl 0.056 mM, $MgSO_4$*7$H_2$0 0.893 mM, Na(HCO_3) 2.522 mM, CaF_2 2.545, HCl 2.5 mM. The pH of the solution was regulated 7.7 (by adding HCl 1.2 mM) and the ionic strength 1.2 mM. All samples were placed on a shaking table in 20^{o}C. The samples were analyzed in duplicate at 12 hours, one day and one sample every day for 68 days. The supernatant was filtered through a 0.45 μm Nylon filter and analyzed using a Hack spectrophotometer 2010 for TOC (Direct Method Patent Pending, 10129), COD (COD

Reactor Digestion Method), NH3-N (Salicylicate Method, 10023), NO3-N (Cadmium Reduction Method, 8039), NO2-N (Diazotization Method, 8507), Total Nitrogen (TNT Persulfate Digestion Method, 10071) and phenols (Folin Ciocalteu).

Finally the direct effect of OMW application can be assessed by the study of soils sampled by a corn field that was regularly amended with OMW. "Tzinakos" OM produces annually 2400 m^3 OMW. The OMW after preatreatment with calcite are used during the summer period (July and August) for the irrigation of a corn field that covers an area of 3 hectares. The OMW are diluted four times with irrigation water. Fifteen soil samples were taken during the fifth sampling campaign (November 2007) and analysed for Total Kjeldahl Nitrogen (Nessler Method, 8075), Total Organic Carbon (Walkley Black Method), Total Phenols, Ph, Conductivity.

3. RESULTS AND DISCUSSION

Lakonia prefecture produces annually 20445 ton olive oil (mean value 2000-2004 production) (Nikolaidis et al., 2006). It is estimated that in Evrotas river the 169 OM produce 11.7 m^3hr^{-1} OMW. That means that in Evrotas river are produced annually 57384 ton COD, 24285 ton TOC, 6337 ton total phenolic compounds. The monitoring of Evrotas river basin indicated that the natural attenuation processes are active (Nikolaidis et al., 2006). As it is shown in Figure 3 the COD, phenols and nutrients levels in Evrotas river are very low and satisfy the limits for the water quality criteria (criteria of EPA, WHO) (Table 1). In general springs water indicates low nutrients values, in contrast to the groundwater (wells and bores) that are enriched to nitrate and ammonia. The mean phenols concentration in Evrotas water bodies varies up to 1 mg/L that means that there is high attenuation.

As it is shown if Figure 4 the phenols concentration along Evrotas river is increased in Skoura and Vrontamas station due to the olive mills that operate nearby and decrease near the estuaries of the river. The decrease of phenolic compounds insist a strong evidence of attenuation, since the loads that are deposited are very high. In one OM in Anogia village was estimated COD, TOC and phenols concentration in the raw wastewater to be 57384, 24285 and 6337 mgL^{-1}, and in the outflow of the evaporation pond (after calcite preatreatment) 4621, 1796 and 175 mgL^{-1}. That means, that 92% of COD load, 93% of TOC and 97% of the phenolic compounds were retained during wastewater treatment in the evaporation pond. In most of the cases the outflow of the evaporation ponds are disposed directly onto the soils. For that reason studies have been conducted in to soils amended by OMW in order to determine the fate of pollutants. A release kinetic experiment was conducted in the laboratory and the purpose was to study the rate of release of nutrients and phenols from the sediment. The COD, TOC and phenol concentration in the sediments leachate (Figure 5) estimated to be 30.3, 20 and 2.0 mgL^{-1}. By the leaching experiments was resulted that Evrotas river sediments appear high load attenuation capacity (the phenols concentrations were reduced to from 2.0 to 1.0 mg/L and COD from 30.3 to 6.3 mg/L in a period of 68 days). If the sediments that are amended by OMW remain anaerobic have the capacity to degrade the pollution load.

The attenuation capacity that is estimated by the leaching kinetic experiment (COD 6.3 mg/L, Nitrate-N 4 mg/L) is verified in situ in the water quality of Evrotas river (Figure 3). The final COD concentration of the leachate after 68 days estimated to be 5 mg/L, thus in the river water 6.3 mg/L, the Nitrate-N 4 in leachate and 1.4 in the river, Ammonia-N 0.05 mg/L in both and phenols 0.069 mg/L in the leachate and 1 mg/L in the river (river values are the mean values 2006-7). Other point sources of pollution were recognized like orange juice factories and diffuse point sources like animal farming, agriculture loads, wet and dry deposition loads that can explain this small difference (Andrianaki et al., 2007).

The main conclusions of the aforementioned studies are:

i. There is a significant pollution load by the operation of OMW mills
ii. This load is also significantly attenuated naturally.
iii. The toxic phenols are the ones degraded first and they are gone within 20 days.
iv. The OMW present a toxic problem to the biota in the stream and an aesthetic problem to the people nearby.
v. Simple, low cost technologies need to be found.

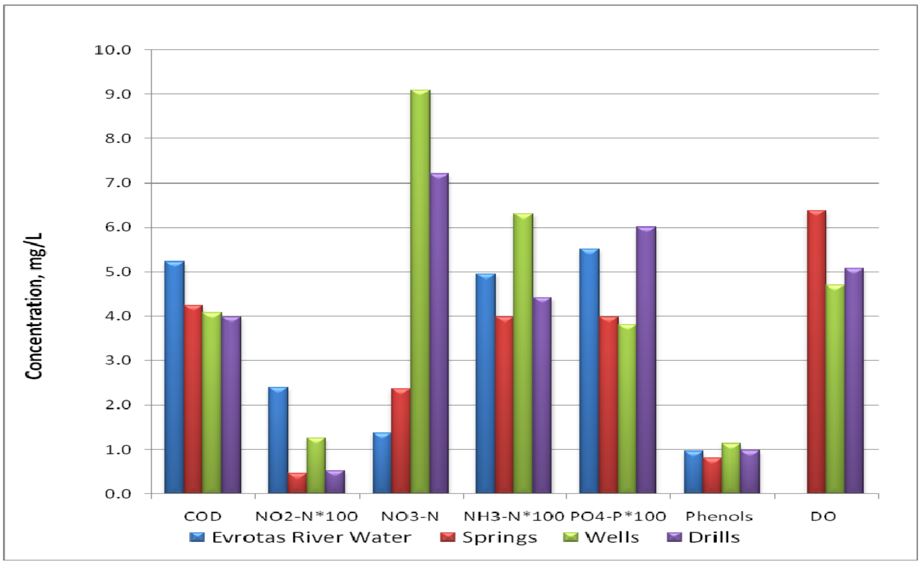

Figure 3 Water Quality in Evrotas water resources (average value of 2006-7sampling

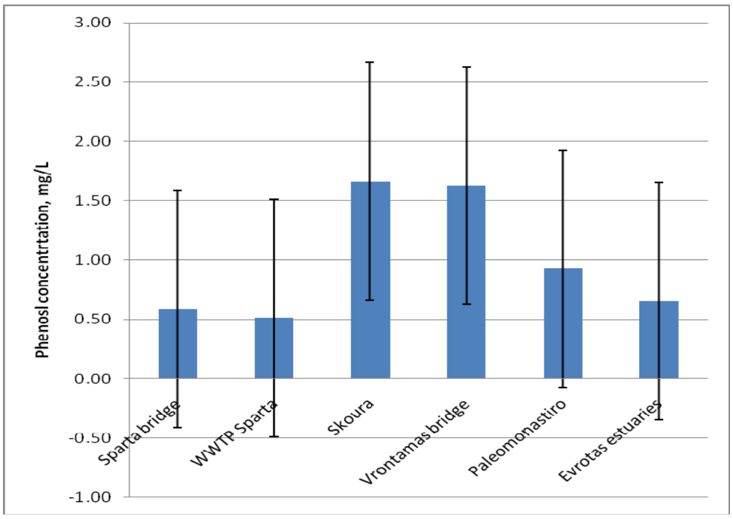

Figure 4 Phenols concetration along Evrotas river main stream

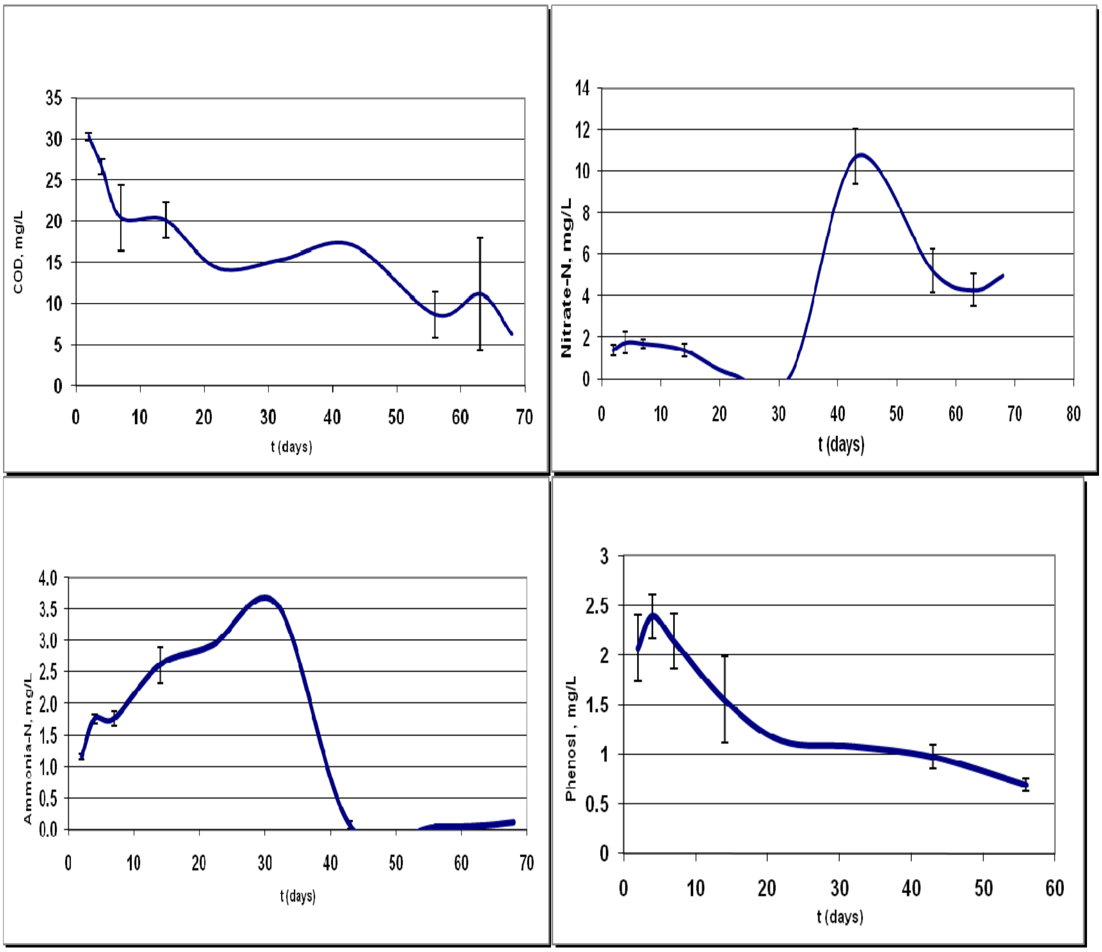

Figure 5 Leaching kinetic results phenols, COD, Nitrate-N, Ammonia-N, Phenols.

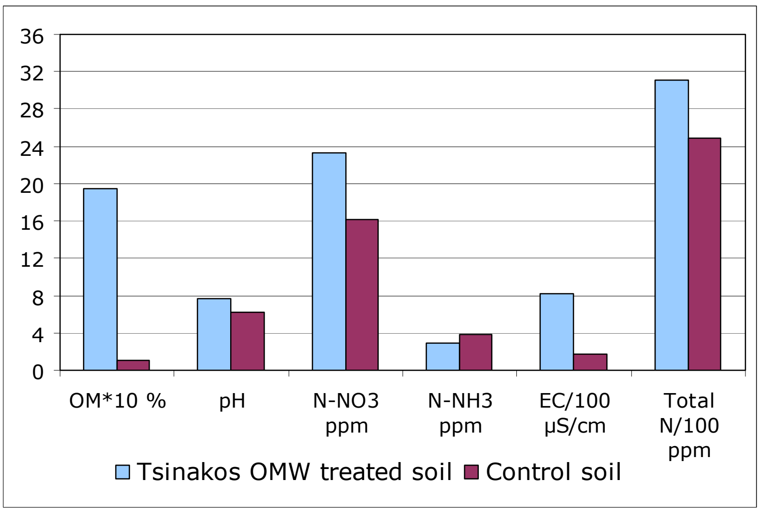

Figure 6 “Tzinakos” OMW ammended soil characteristics in comparison to control soil.

Physical and chemical parameters of soil of “Tzinakos” crop are presented in comparison to background values of control soil sample which was not irrigated with OMW (Figure 6). Higher Electrical Conductivity (E.C.) was observed for the amended soil compared to the non treated soil, in addition pH appeared also higher for the OMW treated soil. Siera et al. (2007) observed also higher pH for soils treated with OMW, however pH lowered to background values two months after OMW application. In the present study pH remains high and this probably related to the short time period from the last OMW application. Total Nitrogen (mg/kg), Nitrate-N, Organic Matter levels are higher to OMW treated soil in comparison to control soil (Figure 6). However, Ammonia-N appears lower to OMW treated soil and this probably related with low nitrogen mineralization due to high C/N in the OMW. The irrigation rate in “Tzinakos” crop field is 323.7 m^3/acre (or 809.3 m^3/ha) per annum and the soil characteristics are similar to those mentioned by Mekki et al. (2007) in soils after the 7^{th} consecutive irrigation year by OMW. Total phenols appeared higher for our OMW treated soil (48.1 mg/kg) whereas, for Mekki et al. (2007) total phenols were lower and this is related with the lower application rate of OMW. Comparing total phenol content of our sample (48.1 mg/Kg) with those of Sierra et al. (2001) (9926 mg/kg), is obvious that the pretreatment of OMW in our case, decreases the phenolic burden in soil. The groundwater below “Tzinakos” crop field has been affected with phenolic compounds (0.85-3.12 mg/L), TOC (0.61-30.88 mg/L) and COD (23.5-366.9 mg/L) varying according to the sampling period. Groundwater quality values are much higher than the river water, thus this suggest a leaching of loads from the surface to the groundwater. Also the high phenol content in groundwater is responsible for the high ammonia values (0.046-0.800 mg/L) because affect in a toxic way chemolithotrophic ammonia-oxidizing bacteria (AOB).

4. CONCLUSIONS

Evrotas river basin indicates high attenuation capacity. In a longer time scale and spatial scale (hydrologic year-watershed scale) the water quality satisfy the water quality criteria. COD, TOC and phenols annual fluxes are 358, 158 and 69 tonnes for mean river flow 2.17 m^3/s (Vrontamas station flow data for 2006-7). Assuming that the loads are coming from the OM almost 0.6% of the COD 0.65% of the TOC and 1.1% of the phenols are coming into the karst in Vrontamas.
Also the use of OMW for irrigation purposes indicates a very easy and environmental friendly technology. OMW is not any more toxic after their pretreatment, contain nutrients that fertilize the soil and is viable solution if the olive mill can irrigate with it (after dilution) large areas.

The problem is focused what happened during the small time scale (minutes) when the raw or the outflow of the evaporation pond come in contact to the soils and the sediments. For example solution containing even 40 mg/L phenols is toxic for *Gambusia affinis* and the invertebrate *Daphnia magna* for 15 minutes expose time (Angus R.A., 1983, Mekki et al., 2007)). The phenol concentration in the evaporation pond is estimated to be 175 mg/L, that impose an environmental threat to the environment. However future studies should take under consideration the toxic effect of the OMW in the bacterial and the invertebrates (during some minutes) of the soil/sediment ecological life.

The OMW land application modify the soil physical and chemical characteristics which could affect cultivation after long-term application. Until now, nothing has proved that long-term accumulation of OMW in soil makes it much more phytotoxic. The successive load of acidic and salt effluent would cause the salinisation of the soil which, in long term could impair its cation exchange capacity and affect its fertility.

AK NOWLEDGEMENT

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Table 1. Water quality parameters of Evrotas water resources

Evrotas basin monitoring 2006-8		COD (mg/L)	NO2-N (mg/L)	NO3-N (mg/L)	NH3-N (mg/L)	PO4-P (mg/L)	T.phenols (mg/L)	DO (mg/L)
Evrotas river	mean value	5.2	0.024	1.4	0.049	0.055	1.0	6.8
	standard deviation	5.7	0.040	1.5	0.044	0.046	0.7	2.0
Springs	mean value	4.3	0.005	2.4	0.040	0.040	0.8	6.4
	standard deviation	1.1	0.002	2.9	0.022	0.029	0.4	2.8
Wells	mean value	4.1	0.013	9.1	0.063	0.038	1.1	4.7
	standard deviation	0.9	0.025	6.4	0.087	0.026	0.3	1.3
Drills	mean value	4.0	0.005	7.2	0.044	0.060	1.0	5.1
	standard deviation	0.8	0.005	13.7	0.026	0.045	1.1	1.1

Good quality of surface waters	<7.5	<0.009	<2.3	<0.039	<0.065		>5