MONITORED NATURAL ATTENUATION OF NUTRIENTS AT RIVER BASIN SCALE – THE CASE OF EVROTAS RIVER BASIN

Katerina Valta[a], Fotini Stamati[a], Daniel Moraetis[a], Andrianaki Maria, Ourania Tzoraki[a1], Papadoulakis Vassilis[b], Nikolaos P. Nikolaidis[a]

[a]Technical University of Crete, Department of Environmental Engineering, University Campus, 73100 Chania, Greece.

[b]Water resources services of Lakonia Prefecture, Sparta, Greece

[1]Tzoraki Rania (rania.tzoraki@enveng.tuc.gr)

ABSTRACT

Monitored Natural Attenuation is a technology that until now has been used for the remediation of contaminated soils and groundwater. In this study, is presented the first step for the application of Monitored Natural Attenuation for the whole basin of Evrotas river. The main pollutants that are studied are nutrients. The results of the six field campaign that were conducted until provide the first evidence that there are mechanisms of natural attenuation.

Keywords: Monitored natural attenuation, MNA, River Basin, Evrotas, nutrients.

1. INTRODUCTION

Monitored Natural Attenuation (MNA) is a remediation technology based on understanding and quantitatively documenting naturally occurring processes that "destroy" or immobilise contaminants at a contaminated site in order to protect humans and ecological receptors from unacceptable risks of exposure to hazardous contaminants. It must be stressed that MNA is a "knowledge-based" remedy because, instead of imposing active controls, as in engineering remedies, scientific and engineering knowledge is used to understand and document naturally occurring processes (EPA, 2001). MNA has been used in the past for the remediation of small scale plumes contaminated with sites contaminated with oils and heavy metals (Hellerich and Nikolaidis, 2005, Palmer and Puls, 1994), fuels and chlorinated solvents (Wiedemeier et al., 1999) and since nowadays hasn't been used at catchment scale (TNO-Nicole project, 1999

The main objective of this study is the application of MNA at a river basin scale. The study area is Evrotas river basin, located on the south-east of Peloponnesus of Laconia Prefecture, Greece. The pollutants studied are nutrients, organic load and total phenols due to the main activities (intense agriculture, olive oil mills and orange juices factories) undertaken at the area. MNA methodology was developed based on the three basic steps field, laboratory and molelling each of which includes specific actions (EPA, 2001). The combination MNA with sustainable use of water resources helps to the creation of effective management plants and results the long term protection of the water resources.

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 river flows from Taygetos Mountain and ends up, after 90 km, in to the Lakonian Gulf. 61.2% of the basin is covered by forest, 37.85% by agricultural areas, 0.7% by urban and only 0.2% by water bodies. The main activities in the area are agriculture (olive and orange trees, vineyards), farming and services. Unfortunately, during the last decade, its ecological quality has deteriorated due to the intensive agricultural practices that utilize fertilizers and agrochemicals, thus creating non-point pollution of metals and organics and nutrients. In Lakonia prefecture operate 169 olive mills and 91 are located inside the boundaries of Evrotas river basin which has resulted in the expansion of the pollution sources. Also two orange juice factories operate in Evrotas basin and the municipality of Sparta is serviced by a central wastewater treatment plant.

The mean annual precipitation value ranges 450-500 mm. Main characteristic of the river is that during the summer its main part becomes dry. The main tributaries are Oinountas (temporary flow), Mariorema (episodic flow), Xerias, Magoulitsa, Gerakaris, Kakaris, and Rasina. In Evrotas river basin the water mass balance is positive and the needs for irrigation and drinking water are covered. In contrast in the south-east part of the prefecture (Glikovrisi, Githio and

Neapoli Vion) the water needs area higher than the available water resources and due to overexploitation occurs the groundwater quality degradation and the penetration of seawater to the groundwater basin

2. METHODOLOGY

In order to apply MNA at a basin scale, field (collection of samples that would indicate that pollutants are being reduced as they follow their path to the river and eventually to the sea) and laboratory evidence (lab studies of the processes that attenuate pollutants and quantification of the kinetic rates of reactions) as well as modeling studies (modeling of the site that would illustrate how the pollutant behaves in nature and that the attenuation will continue to occur over geologic times) are needed. For the case of Evrotas river basin historic data for the water quality of Evrotas River were taken from the Ministry of Agriculture, the MEDSPA90 project and Mr. Antonakos study (1997), presenting the first evidences for the reduction of contaminants in the study area. From these data it was obvious that concentrations of pollutants at the outflow of Evrotas were less than those observed along the river. These observations were the first evidences that MNA is taking place because if it wasn't, concentrations in the estuaries should exceed all the others due to intermediate pollution of diffuse (agriculture, livestock etc.) and point sources (olive mills, juice producing factories, towns).

Despite the existing data, it was necessary to carry out intensive field campaigns to introduce new field evidence and account for all major ecotopes in the basin. The pollutants studied are nutrients, organic load and total phenols. The collection of these aimed at tracking the foot print of contamination (the way contaminants travel from pollution sources to underground and surface water). Evrotas river basin has a complex hydrogeology and hydrographic network while pollution sources are both point and diffuse. To this end, it was necessary to develop a sampling network based on the hydrology of the region, the geology, the relief, slopes and land uses. The basin was separated into seven sub-basins presented in Figure 1. The selection of the position of each Sampling Point (SP) was based on the typology of the basin which was presented as maps created in ArcView 9.3 environment.

The selection of the sampling points (SPs) was based on the separation of the basin to the 7 sub-basins, as described above. Surface water sampling points were chosen throughout the length of the river and in order to cover all the sub-basins. As far as ground water is concerned, the majority of sampling points were selected to be in sub-basins 5 and 7, at Sparti and Skala regions. In these regions many point sources of pollution exist and agricultural activities are extensive. Additionally, in sub-basin 5 are located the most important tributaries of Evrotas and the groundwater aquifers at the region of Sparti and Skala, where ground water is used for irrigation and water supply. Based on the above considerations the sampling network consists of 64 sampling points: 32 for surface water and 32 for underground water (Springs: 10, Shallow Wells: 10, Deep Wells: 12). To date, six sampling campaigns have been conducted on: 1st/ 9-12 of May 2006, 2nd/8-12 of September 2006, 3rd/ 12-17 of January 2007, 4th/26 of May – 1 of June 2007, 5th/26 September -2 December 2007, 6th/3-5 of March 2008. During those field campaigns psychochemical parameters of the samples were measured in situ while water samples were taken to the laboratory for chemical analysis.

3. RESULTS

Comparing surface and ground water samples (Figure 3a) there are significant reductions between ground water concentrations and surface water concentrations for nitrates, while COD and the total phenols are not statistically different. Phosphates are higher in surface water and in deep wells. It can also observe that the variability of COD in the surface water samples is large while in the ground water is low indicating localized pollution. Finally, it is of concern the similarity of Total phenol concentrations in all water bodies suggesting that the parameter is not a good indicator of pollution since there are naturally occurring phenols that are being measured.

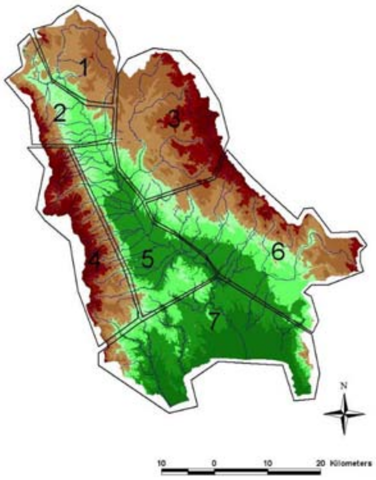

Figure 1. Su b-basins of Evrotas River Basin

Figure 2. Main point pollution sources

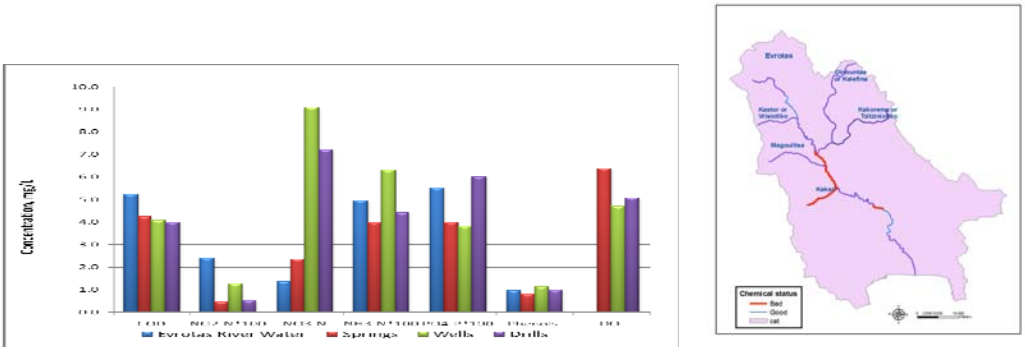

Figure 3: (a) Water Quality in Evrotas water resources (average value of 2006-7sampling), (b) Chemical status of surface waters.

Evidences of Natural Attenuation in surface water. In order to further enforce the existence of natural attenuation at Evrotas River samples along the river were analyzed. COD value at the Estuaries of Evrotas was below detection limit. At Vrondamas the COD concentration decreases significantly potentially due to in-stream attenuation processes and dilution from unpolluted streams. The same applies to the concentration of nitrate nitrogen. The concentration of phenols is low at Evrotas springs while at Skoura and Vrondamas the concentration is almost the same. The same trend seems to be observed for the other pollutants as well. Highest concentration of NO_2-N, NO_3-N and Total phenols are observed at Skoura, while after Skoura moving downstream concentration of pollutants is reduced. Phosphates have a peak close to the biological treatment of Sparta and afterwards follow a decline. This peak is due to the outflow of the treatment plant._Considering the above results it is quite obvious that evidence concerning natural attenuation of pollutants of surface water exists.

Evidence of Natural Attenuation in Ground Water. The main ground water aquifer is the plain of Sparta. Ten shallow ground water wells and twelve deep ground water wells have been sampled. The results indicate that there is a high concentration of nitrates in the Sparti region and a gradual decrease from Sparti towards the Vrodamas area. The same can be seen for the case of phenols. Results concerning COD and nitrate nitrogen concentrations from groundwater deep wells showed that pollution load is reduced following the direction of ground water flow. As a conclusion, evidences for natural attenuation in groundwater exist. Five heavy metals were analyzed (Cu, Cd, Zn, Pb and Ni) for 12 surface and ground water samples to examine potential pollution. In general results suggest that either there is little heavy metal pollution (the metals measured only) or the metals are being retained well in the environment and do not appear in the aquatic phase.

4. CONCLUSION

Some pollutants appear higher concentration in surface water, whereas, other in groundwater. COD concentration is higher in surface water in comparison to groundwater. The highest values COD were observed in wells than in surface water. Concerning phosphate higher concentration were measured in bores and surface water. The water physicochemical paremeters don't indicate any pollution. An exception is the DO conc. in Skoura that ranges from 1.67 up to 7.70 mg/L that is affected by the point sources outflow into the river. In Skoura were observed also the highest phosphate, TOC and nitrite content. Concerning phenols the highest concentration was observed upstream where operate many olive mills. The groundwater physicochemical paremeters don't indicate any pollution. Again in bores and wells in Skoura region are measured higher COD and phenols values. The main pollution problem in Evrotas basin is created by the point sources. The olive oil mill wastewater even after pretreatment with calcite contains high COD and phenols concentration. Also the outflow of the municipal wastewater treatment plant amends the river water with nutrients and organic load.

The chemical data obtained in each water body were compared against the respective criteria of surface and ground waters (Nikolaidis et al., 2008 and using a probabilistic method each water body was classified as good status (quality below the criteria) or bad status. Figure 3b presents the chemical quality of surface waters. 87% of the length of surface water has good quality. Only the river segment from Sparti up to Skoura can be characterized as bad quality. Also Kakaris tributary appears to be of bad chemical quality due to extensive agricultural activities. Regarding the groundwater bodies, 100% of them have good quality status, even though the probability of exceedance is relatively high (49%). Good water quality status since 2015 (according to WFD) can be achieved for Evrotas river, if the MNA technology is combined with effective management technologies to reduce both point and non-point sources pollution. Overall, this study todate has provided significant evidence that mechanisms of natural attenuation exist.

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