

**INFLUENCE OF OIL FACILITIES IN SEAWATER QUALITY: TRACE ELEMENT DISTRIBUTION NEAR
KAVALA, NORTH AEGEAN SEA (GREECE)**

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ABSTRACT

The Prinos-Kavala sedimentary basin, located in the northern arc of the Aegean Sea, is, up to now, the most important hydrocarbon province in Greece. The distribution of seawater concentrations of Cd, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, and Zn, as well as the absence of abnormal color, mineral oils, surface-active substances, phenols, tarry residues and floating materials, indicate the absence of any damaging effect in the coastal environment of the city of Kavala related to the existing oil facilities nearby. The most evident anthropogenic effects are found only in the shoreline close to the coastline Philippos harbor-Phosphoric Fertilizer Industry (P.F.I.)-Oil Plant, which induce an increase in the concentration of phosphorous and, in a less degree, in the concentrations of iron and manganese, related mainly to the gypsum dump of the Phosphoric Fertilizer Industry (P.F.I.) and to the works carried out to build the new harbor of Kavala.

KEYWORDS: seawater, trace element, oil facilities, Kavala, North Aegean Sea

INTRODUCTION

The petroleum and petrochemical industries keep society supplied with large amounts of energy and organic chemicals, and like any other major industrial organizations they have an impact on the environment. In addition to the more known effects of accidental spills on the sea, the routine activities of coastal oil facilities could contribute to environmental damaging (Shell, 1983; Reis, 1996). Because of this, anti-pollution laws came into force in many countries. Such laws generally made emissions and discharges from industrial installations subject to permission from regulatory authorities. The petroleum and petrochemical industries now have to comply with a multitude of regulations aimed at protecting the health and safety of employees, of the local population, as well as with regulations aimed at protecting air, water and soil against pollution. Regulations vary significantly between countries, states and prefectures. In any case the control and prevention of environmental damaging are a priority in current legislation (API, 1997; 2000; CPA, 1990; EC, 1996; IOCC, 1990; USEPA, 1995). Many different potential pollutants (organic and inorganic) could be transferred to the environment from the petroleum installations. The aim of the present work is centered in those trace elements affecting mainly the bathing water quality: Cd, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, and Zn (EC, 1976). The Kavala coastal zone is located in Northeastern Greece and belongs to the East Macedonia - Thrace District. The extension of the Kavala Prefecture coast is of about 180 km. There are eleven municipalities in the Prefecture, six of them are coastal, where live approximately 150,000 inhabitants. The main economic activities are agriculture, fisheries, aquaculture, marble quarrying, oil production and refinery, trade and tourism (Euroconsultants, 2001). This area has intense maritime activities and is of enormous tourist interest. The present study was undertaken to assess the influence of the anthropogenic activities on the distribution of potentially hazardous trace elements, believed to be of a specific ecological, biological and health significance, in the central-western part of the Kavala coast, particularly in relation to the hydrocarbons operation facilities.

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GENERAL DESCRIPTION OF THE HYDROCARBONS EXPLOITATION PROJECT

Three hydrocarbon reservoirs, the Prinos and Prinos-North Oil Fields and the South Kavala Gas Field, have been developed offshore, in the area between the city of Kavala and the island of Thassos, North Aegean Sea, Greece. The Prinos Oil Field is located in 35 m of water, five miles west of Prinos Point on the island of Thassos and twelve miles southeast of the city of Kavala on the mainland, while the Prinos-North Oil Field is located approximately 1.8 km north of the Prinos Field. The oil fields produce a medium gravity, sour oil. The South Kavala Gas Field is located seven miles south of the Prinos Oil Field, in a water depth of 58 m (Georgakopoulos et al., 1995). The oil/gas traps are sealed by up to seven evaporitic layers with a total thickness, which, in some places, exceeds 350 m (Speel, 1982; Georgakopoulos, 1992). Operation facilities for producing, treating, pipelining, processing, sulfur treating, storing and shipping of the hydrocarbons are constructed and placed in the Gulf of Kavala. Principal areas for location of the facilities are the Prinos and Prinos - North Oil Fields, the South Kavala Gas Field, a mainland site near Kavala, and pipelines right-of-way (R.O.W.) between these sites. More specifically, the mainland site located approximately 13 km east of Kavala has a useable area of over 16 ha. It accommodates a crude oil treatment facility, sulfur and N.G.L. extraction facilities and storage for these products (Speel, 1982). The mainland facilities are connected by submarine pipelines to the Production Treatment Platform and to a conventional spread mooring for shipment of crude oil by tankers. The mooring is located adjacent to the mainland site in the Aegean Sea in a water depth of at least 20 m. The operating function of the mainland site near Kavala is the final processing of the oil and gas streams from the Prinos Production Treatment Platform into hydrocarbon liquids, elemental sulfur and natural gas to meet sales specifications. The companies responsible for the oil production (North Aegean Petroleum Company - NAPC in the beginning, and KAVALA OIL now), have adopted an attitude of environmental responsibility-not just comply with regulations but to actually protect the environment. The facilities operate so as to ensure complete safety and protection of workers, the public and the environment. A special attention was given in the prevention of sea pollution initially guided by the standards established by the International Conventions of London of May 12, 1954, and April 13, 1962 and ratified by Legislative Decree of Greece No 4529 of July 25, 1966, entitled "Prevention of Pollution of the Sea by Hydrocarbons". Other local legislations have been established since then, in order to prevent the seawater pollution by oil facilities.

MATERIALS AND METHODS

Surface seawater samples were collected from fourteen coastal and eight offshore (at a distance between 500 and 1000 m from the coast) points in Kavala coast, covering a coastline of about 45 km length (Figure 1). Intensive recreational activities are located from Nea Peramos to Kavala and also at the easternmost area of the studied coastline (Keramoti area). The industrial activities are concentrated east of the city of Kavala, the oil installations and a Phosphoric Fertilizer Industry (P.F.I) being the most important. Seawater samples were collected in pre-cleaned (2% HNO₃) high-density polyethylene bottles (HPDE), 250 mL at each sampling point. In addition, a visual and/or olfactory verification of the absence of abnormal color, mineral oils, surface-active substances, phenols, tarry residues and floating materials was carried out. Seawater concentrations of Cr, Cu, Fe, Ni, P, and Zn were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), while the concentrations of Cd, Hg, Mn, and Pb were determined by Flow Injection-Inductively Coupled Plasma Mass Spectrometry (FI-ICP-MS).

RESULTS, DISCUSSION AND CONCLUSIONS

Seawater concentrations of the analyzed trace elements are shown in Table 1. The concentrations of the trace elements Cd, Cr, Hg, Ni and Pb were lower than the corresponding analytical detection limits, in all samples. For the elements Cu, Zn, P and Mn, detectable concentrations (above detection limit), were only measured in sampling points along the coastline of Philippos harbor-Phosphoric

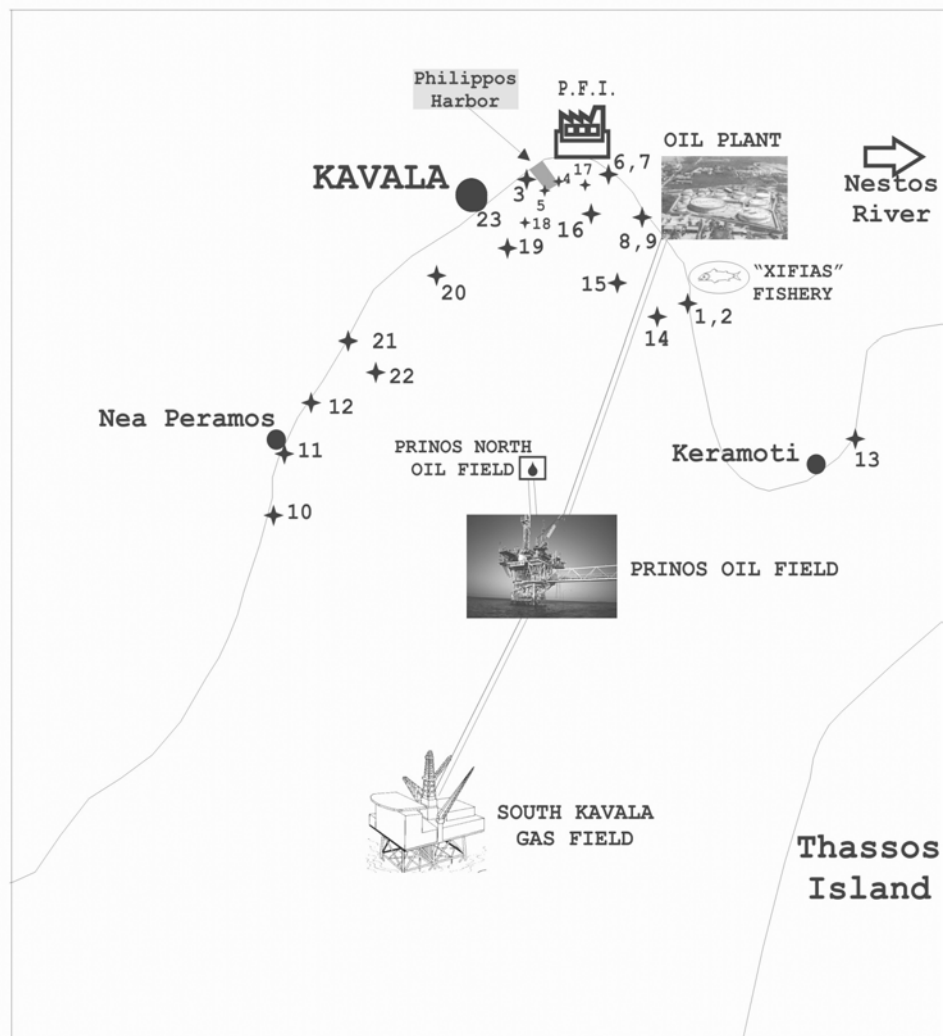


Figure 1. Map of the Gulf of Kavala, North Aegean Sea, showing offshore and onshore oil facilities and surface seawater sampling points. P.F.I.- Phosphoric Fertilizer Industry, ★ sampling points.

Fertilizer Industry-Oil Plant (samples No. 4, 6, 7, 9 and 16). Copper and zinc were detectable only in one sample each (No. 9 and No. 4, respectively). Sample No. 9 contains 64 $\mu\text{g/L}$ of copper, while sample No. 4 contains 82 $\mu\text{g/L}$ of zinc. Both samples were collected in the industrial area, east of the city of Kavala. Two samples (No. 6 and 7) show phosphorous concentrations exceeding 1000 $\mu\text{g/L}$. These samples were collected in the shoreline close to the gypsum dump area of the fertilizer industry. Manganese was detectable in the same samples (No. 6 and 7) and showed concentrations of 11.1 and 3.5 $\mu\text{g/L}$ respectively, as well as in the sampling points No. 9 (1.5 $\mu\text{g/L}$) and No. 16 (0.6 $\mu\text{g/L}$).

Table 1. Trace element concentrations ($\mu\text{g/L}$) determined in seawater from the coastline of the city of Kavala, Northern Greece.

Sample No.	Cd	Cr	Cu	Fe	Hg	Mn	Ni	P	Pb	Zn	Location
10	<0.05	<3.9	<15.8	79	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Sand Dunes (cst)
11	<0.05	<3.9	<15.8	81	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Nea Peramos (cst)
12	<0.05	<3.9	<15.8	80	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Nea Iraklitsa (cst)
21	<0.05	<3.9	<15.8	90	<0.10	<0.5	<1.5	<26	<0.1	<5.5	"Palio" area (cst)
23	<0.05	<3.9	<15.8	87	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Kavala-Rapsani (cst)
5	<0.05	<3.9	<15.8	103	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Philippos harbour (cst)
4	<0.05	<3.9	<15.8	98	<0.10	<0.5	<1.5	<26	<0.1	82.2	Philippos harbour (cst)
3	<0.05	<3.9	<15.8	91	<0.10	<0.5	<1.5	<26	<0.1	<5.5	P.F.I* (cst)
6	<0.05	<3.9	<15.8	104	<0.10	11.1	<1.5	1358	<0.1	<5.5	P.F.I* (cst)
7	<0.05	<3.9	<15.8	102	<0.10	3.5	<1.5	1403	<0.1	<5.5	P.F.I* (cst)
8	<0.05	<3.9	<15.8	75	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Mainland oil facilities (cst)
9	<0.05	<3.9	64.1	81	<0.10	1.5	<1.5	<26	<0.1	<5.5	Mainland oil facilities (cst)
1	<0.05	<3.9	<15.8	29	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Xifias Fisheries (cst)
2	<0.05	<3.9	<15.8	<7	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Xifias Fisheries (cst)
13	<0.05	<3.9	<15.8	86	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Keramoti (cst)
22	<0.05	<3.9	<15.8	92	<0.10	<0.5	<1.5	<26	<0.1	<5.5	"Palio" area (500 m)
20	<0.05	<3.9	<15.8	91	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Biological Treatment Effluent (west)
19	<0.05	<3.9	<15.8	86	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Kavala harbor (500 m)
18	<0.05	<3.9	<15.8	93	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Biological Treatment Effluent (east)
17	<0.05	<3.9	<15.8	87	<0.10	<0.5	<1.5	<26	<0.1	<5.5	P.F.I* (500 m)
16	<0.05	<3.9	<15.8	94	<0.10	0.6	<1.5	<26	<0.1	<5.5	P.F.I* (1000 m)
15	<0.05	<3.9	<15.8	86	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Mainland oil facilities (1000 m)
14	<0.05	<3.9	<15.8	78	<0.10	<0.5	<1.5	<26	<0.1	<5.5	Xifias Fisheries (500 m)

*P.F.I.: Phosphoric Fertilizer Industry (cst): Coastal sampling point.

Concentrations of iron exceed the detection limit ($7 \mu\text{g/L}$) in all seawater samples, with the exception of sample No. 2 showing a concentration lower than $7 \mu\text{g/L}$. This sample was collected in the mouth of a channel, with an important contribution of fresh-water. The mean concentration of iron in the analyzed seawater samples is $86 \mu\text{g/L}$. Maximum concentration was found in sample No. 6 ($104 \mu\text{g/L}$) and minimum concentration was found in sample No. 1 ($29 \mu\text{g/L}$). The latter was collected close to sample No. 2. The absence of abnormal color, mineral oils, surface-active substances, phenols, tarry residues and floating materials was evidently noticed in all sampling points and no effects from the oil facilities were detected in seawater. On the other hand, the higher

concentrations of iron (Figure 2), phosphorous and manganese were detected in the coastline close to the phosphoric fertilizer industry (P.F.I.). This kind of industrial activity produces large quantities of wastes (mainly gypsum - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), as a result of the processes used in the treatment of phosphates in order to generate fertilizers for agricultural uses (USEPA, 2000). The results of the analyses evidence that there is transference of matter from the gypsum dump of the fertilizer industry to the seawater. However, this effect is only perceptible in the closest seawater, while, offshore, the dilution factor makes undetectable this transference. The works for the construction of the new harbor of Kavala in this area could also contribute to increase the iron concentration.

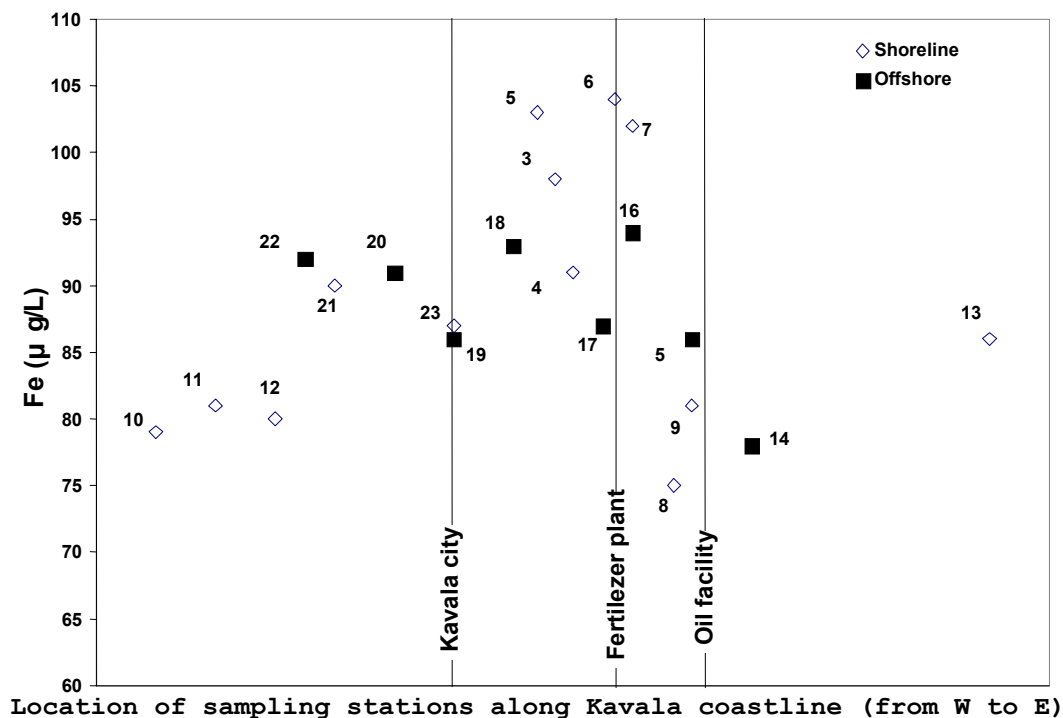


Figure 2. Longitudinal sampling profile along Kavala coastline showing the iron concentrations of seawater and the location of the city of Kavala and the main industrial facilities in the area. Samples No 1 and 2 have not been included because of the relative low iron concentrations.

The iron concentrations observed in seawater are higher than the average in seawater ($0.06 \mu\text{g/L}$; Taylor and McLennan, 1985) but are in the same order of magnitude with the average for stream water ($40 \mu\text{g/L}$; Taylor and McLennan, 1985). This fact reflects the influence of the regional geology on water composition. The studied coastline is located west of the mouths of Nestos river, which produce an important input of sediments and water from the continent into the studied area. The high rate of sediment transport of the Nestos River is evidenced by the large surface of its delta. Also, due to the asymmetric growth of river networks in the area during the Neogene-Quaternary, the fluvial, marine and deltaic deposits were affected of rocks and mineralizations from mountain chains at NW-N-NE of Kavala (Perissoratis et al., 1988; Psilovikos, 1990; Filippidis et al., 1996).

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