

## ORGANIC POLLUTANTS IN THE INDUSTRIAL AREA EAST OF KAVALA, NORTHERN GREECE

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### ABSTRACT

The occurrence and distribution of organic pollutants were studied at in an industrial area situated at the coastal zone east of Kavala, Northeastern Greece. The study focused especially on the area, where the oil facilities of Kavala Oil Co. are located. Three surface water samples were collected and investigated by means of non-target screening analyses to evaluate the level of organic pollution, as well as to reveal molecular markers representing the industrial emissions. The analytical procedure included a sequential extraction of the samples, GC-FID as well as GC/MS analyses (Franke et al., 1995). In the three water samples halogenated compounds, technical additives and synthetic fragrances, phosphates, phthalates, benzothiazoles, esters, ketones, phenols, ethers and PAH's were detected. Quantitative analyses of selected pollutants were additionally performed. Source-specific marker compounds were identified and used to trace different types of emissions throughout the affected environment.

### 1 INTRODUCTION

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 (Georgakopoulos et al., 1995). Three hydrocarbon reservoirs, the Prinos and Prinos-North Oil Fields and the South Kavala Gas Field, have been developed offshore, and 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. 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 natural gas liquids (N.G.L.) extraction facilities and storage for these products (Georgakopoulos, 1992; Speel, 1982). The mainland facilities are connected by submarine pipelines to the production treatment platforms and to a conventional spread mooring for shipment of crude oil by tankers. 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 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 Group Co., 1983; Reis, 1996). Many different potential pollutants (organic and inorganic) can be transferred to the environment from the petroleum installations. These industrial activities, also introduce severe changes in the regional landscape, drainage system, and infrastructures. Additionally, they generate significant volumes of solid and liquid wastes (Reis, 1996). The environmental importance of these features is a consequence mainly of the quality and quantity of the emissions. These waste

discharges can also introduce severe changes in the water and soil quality. The main economic activities of the area investigated are agriculture, fisheries, aquaculture, marble quarrying, oil production and refinery, trade and tourism (Euroconsultants, 2001). Furthermore, this area is characterized by intense maritime activities and is of enormous tourist interest.

In summary, the aim of our investigation included:

1. The identification of several organic pollutants in the area around Kavala Oil facilities.
2. The evaluation of their spatial distribution within the area investigated.
3. The quantitation of selected organic pollutants.
4. A linkage of qualitative and quantitative data of specific compounds with their usage, their risk for human health and their environmental concern.

## 2 EXPERIMENTAL

### 2.1 Samples

Sampling was performed in different distances from the main emission point (as illustrated in Fig. 1). Two surface water samples (KP<sub>w2</sub> and KP<sub>w4</sub>) have been taken directly from a canal in front of the Kavala Oil Co, in which liquid wastes were discarded. One further surface water sample was located in a swale, in which the uncontrolled discarding of solid waste was obvious (KP<sub>w1</sub>). The samples were collected in dark glass flasks that were filled free of air bubbles. The glass flasks were washed before the sampling with tap water, ultra pure water and acetone. The collected samples were stored in dark at temperatures of approx. 4°C and were extracted within two weeks.

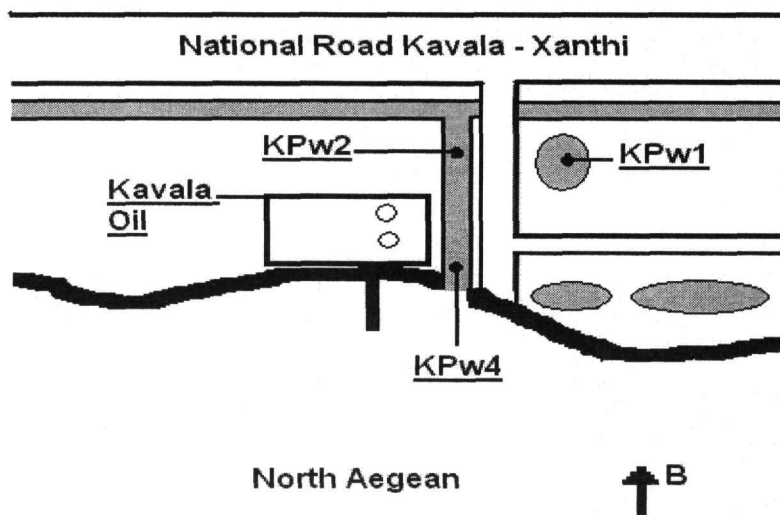


Figure 1. Sampling locations in the area of Kavala Oil Co. facilities.

### 2.2 Extraction and fractionation

A sequential liquid/liquid extraction procedure was applied to approximately 1L of the water samples using the solvents dichloromethane and dichloromethane after acidification to pH 2. Each extraction step was carried out in separating funnel with 50mL solvent. The second extraction was applied to the pre-extracted water samples after addition of 2mL of concentrated hydrochloric acid that was pre-cleaned by intense extraction with *n*-hexane. Subsequently, the organic layers were separately dried by filtration over 1g of granulated anhydrous sodium sulfate and 50µL of an internal standard solution containing 5,08ngµL<sup>-1</sup> of anthracene was added. Prior to gas chromatographic and gas chromatographic – mass spectrometric analyses the extracts were reduced to final volume of approximately 50µL by rotary avaporation at room temperature. Acidic compounds in the second extract were methylated with diazomethane. The analytical procedure is illustrated in Fig. 2.

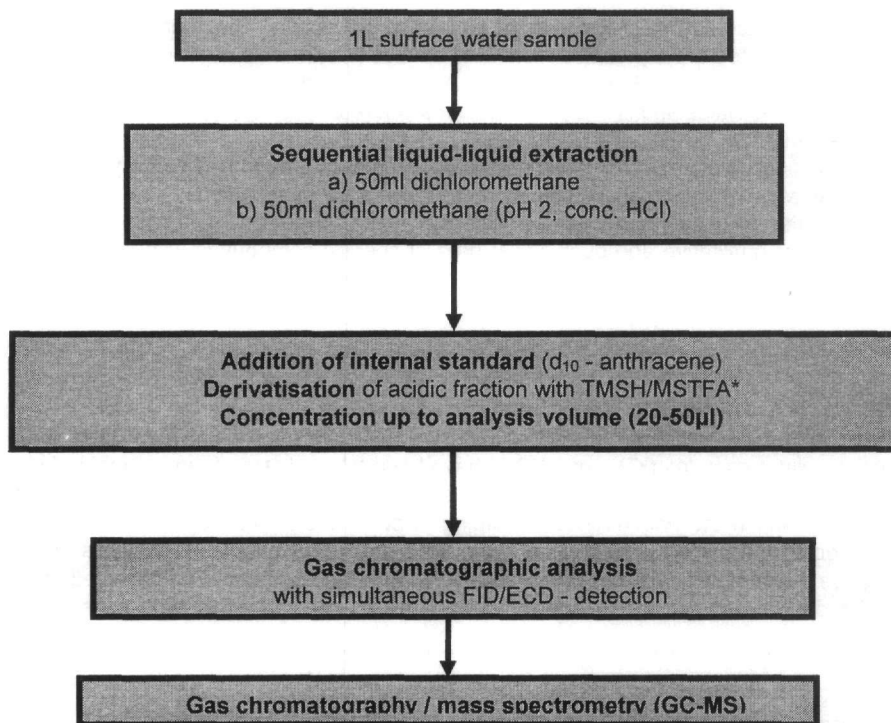


Fig. 2. Analytical procedure used for nontarget-screening analyses of surface water samples.

\* TMSH/MSTFA: Trimethyl-sulfonium-hydroxide/N-methyl-N-(trimethylsilyl)-trifluoro-acetamide.

### 2.3 Gas chromatographic/mass spectrometric analyses

Gas chromatographic analysis was carried out on a GC6000 gas chromatograph (Carlo Erba, Vega Series 2) equipped with a 30m x 0.25mm i.d. x 0.25 $\mu$ m film DB1 fused silica capillary column. Chromatographic conditions were: 1 $\mu$ L split/splitless injection at 60 $^{\circ}$ C, splitless time 60s, 3 min hold, then programmed at 3 $^{\circ}$ Cmin $^{-1}$  to 300 $^{\circ}$ C. Hydrogen carrier gas velocity was 40cm/s. GC/MS analyses were performed on a Finnigan Trace MS, Thermo Quest linked to a Carlo Erba, HRGC 5160 gas chromatograph, which was equipped with a 25m x 0.22mm i.d. x 0.25 $\mu$ m film BPX5 column. Chromatographic conditions were: 1 $\mu$ L split/splitless injection at 60 $^{\circ}$ C, splitless time 60s, 3 min hold, then programmed at 3 $^{\circ}$ Cmin $^{-1}$  to 300 $^{\circ}$ C. Helium carrier gas velocity was 2ml/min. The mass spectrometer was operated in electron impact ionization mode (EI $^{+}$ , 70eV) at a source temperature of 200 $^{\circ}$ C, a scanning from 35-500amu at a rate of 1s/decade, and an inter-scan time of 0.1s.

### 2.4 Identification of organic compounds

Identification of individual compounds was based on the comparison of EI $^{+}$  - mass spectra and gas chromatographic retention times with those of reference compounds. First evidence of identification derived from comparison of mass spectra with mass spectral databases (NIST / EPA / NIH Mass Spectral Library NIST98, Wiley / NBS Registry of Mass Spectral Data, 7<sup>th</sup> Ed., electronic versions). For correction of inaccuracies of injection time, the retention times of the internal standard compound were used.

## 2.5 Quantitative analyses

Quantitative data of selected target compounds were obtained by integration of specific ion chromatograms extracted from the TIC. Injection volume and sample volume inaccuracies were corrected by using  $d_{10}$ -anthracene ( $m/z$  188) as a surrogate standard. An external four-point-calibration curve generated from a mixture of reference compounds was used for quantification. The detection limit was approximately  $1\text{ngL}^{-1}$ . No attempts were made to quantify components at concentrations less  $10\text{ng}\mu\text{L}^{-1}$ .

## 3 RESULTS AND DISCUSSION

Qualitative analyses of the three water samples derived from the coastal area near Kavala Oil Co. facilities revealed a wide variety of organic substances, which were attributed to the groups of technical additives and metabolites, halogenated compounds, phosphates, phthalates, benzothiazoles, esters, polycyclic aromatic hydrocarbons, alcohols, phenols and ethers (Table 1). Several of these compounds are known contaminants of surface and waste waters as well as corresponding sediments (Franke et al., 1995; Schwarzbauer et al., 2002; Ricking et al., 2003; Labunska et al., 2000; Oros et al., 2002).

Table 1. Organic compounds identified in surface water samples near Kavala Oil Co facilities.

	KPw1	KPw2	KPw4
<b>Halogenated compounds</b>			
1,2,3 Trichloropropene	+		
Tribromomethane (Bromoform)			++
<b>Technical additives and metabolites</b>			
Carbamodithioic acid diethylmethyl ester (Disulfiram)	+	++	++
Carbamodithioic acid dimethylmethyl ester		+	0
1-(Hydroxycyclohexyl)phenylketone (Irgacure 184)	++	++	+
2,4,7,9-Tetramethyl-5-decine-4,7-diol (Surfynol)	++	+	+
2,6,6-Trimethyl-2-cyclohexene-1,4-dione (4-Oxoisophorone)	+	0	+
<b>Phosphates</b>			
Tris(chloropropyl)phosphate (PCF), (2 isomers)	++	0	
Tris(2-chloroethyl)phosphate	+		
Tri-n-butylphosphate	0	+	0
<b>Benzothiazoles</b>			
Benzothiazole	++	0	
2-(Methylthio)benzothiazol	+		
2(3H)-Benzothiazone	+		
<b>Ester</b>			
Hexanedioic acid dibutyl ester (Di-iso-butyl adipate)	++	++	+
Hexanedioic acid bis(2-ethylhexyl) ester			++
2-Ethylhexanoic acid 2-hydroxypropyl ester	++	++	++
2,4,4-Trimethylpentan-1,3-dioldi-iso-butyrate	+	++	+
Isopropylmyristate		0	0
<b>Ketones</b>			
2,6-Di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one	++	+	++
<b>Phenoles and ethers</b>			
2,4-Di-tert-butylphenol		+	0
3-tert-Butyl-4-hydroxyanisol	++	+	+
<b>Polycyclic aromatic hydrocarbons</b>			
Naphthalene			0
<b>Phthalates</b>			
Di-iso-butylphthalate	++	+	+
Di-n-butylphthalate	+	++	++
Butylphenylphthalate		+	++

0 = low concentrations as compared to the internal standard

+ = similar concentrations as compared to the internal standard

++ = high concentrations as compared to the internal standard

Several compounds were pre-selected for quantitative analyses (Table 2). The selection was focused on the availability and source specificity of the compounds. In the following we present and discuss all compounds identified with respect to their source specificity.

Table 2. Quantitative data of selected contaminants in surface water samples near Kavala Oil Co facilities (ng/L).

	KPw1	KPw2	KPw4
<b>Halogenated compounds</b>			
Tribromomethane (Bromoform)			98400
<b>Technical additives and metabolites</b>			
1-(Hydroxycyclohexyl)phenylketone (Irgacure 184)	1700	2100	400
2,4,7,9-Tetramethyl-5-decine-4,7-diol (Surfynol)	460	120	150
2,6,6-Trimethyl-2-cyclohexene-1,4-dione (4-Oxoisophorone)	110	39	78
<b>Phosphates</b>			
Tris(chloropropyl)phosphate (PCF), (2 isomers)	1650	30	
<b>Benzothiazoles</b>			
Benzothiazole	690	50	
2-(Methylthio)benzothiazol	1300		
<b>Ester</b>			
Hexanedioic acid dibutyl ester (Di-iso-butyl adipate)	1200	670	120
Hexanedioic acid bis(2-ethylhexyl) ester			490
Isopropylmyristate		55	17
<b>Phenoles and ethers</b>			
3-tert-Butyl-4-hydroxyanisol	690	140	98
<b>Polycyclic aromatic hydrocarbons</b>			
Naphthalene			32
<b>Phthalates</b>			
Di-iso-butylphthalate	950	150	67
Di-n-butylphthalate	640	2000	1500
Butylphenylphthalate		83	660

### 3.1 Kavala Oil Co. specific compounds

Several organic compounds representing anthropogenic contamination were identified in the surface water sample KP<sub>w4</sub> taken in front of Kavala Oil facilities. Due to their limited spatial distribution, they might characterize Kavala Oil waste discharges. This point source emission was reflected in particular by industrial markers including halogenated compounds, PAHs, as well as plasticizers.

In the present study bromoform was detected at a concentration of 98.4 µg/L. Small amounts of tribromomethane (bromoform) can be formed naturally by plants in the oceans. But most of the bromoform detected especially in the terrestrial and coastal environment is introduced anthropogenically, as by-product of chlorine based drinking water production. Additionally, bromoform was used in the past as solvent, flame retardant, or synthesis material, but nowadays it is used mainly as laboratory reagent. Interestingly, bromoform was also detected formerly as a contaminant from oil facilities (N.P.D.E.S., 2003). In water, this chemical will evaporate to the air and/or be broken down slowly by bacteria and it does not build up in the food chain. Several recorded cases indicate that high doses affect the central nervous system causing unconsciousness, loss of reflexes, shallow breathing, erratic heart rate, and respiratory failure. Milder cases resulted in rapid breathing, constricted pupils, and tremors. There is evidence that ingestion of bromoform causes intestinal cancer in rats, but the International Agency for Research on Cancer (IARC) stated that the human carcinogenicity of bromoform is not classifiable. The Environmental Protection Agency (EPA) has set a Maximum Contaminant Level (MCL) of 1µg/L for bromoform that occur in chlorinated drinking water (A.T.S.D.R., 1990). It has to be noted, that our results exceeded this value by a factor of approx. 100.

Naphthalene is a well-known organic contaminant, which was identified in sample KP<sub>w4</sub> and determined at a concentration of 32ng/L. It belongs to the group of the high hazardous compounds for the human being (E.C.L., 1996). It is found naturally in fossil fuels, and as pyrolytic product e.g. of tobacco, fuels and wood. The major commercial use of naphthalene is the technical synthesis of

polyvinyl chloride plasticizers (PVC). Additionally, it is used as constituent of moth repellents and toilet deodorant blocks as well as paints additive. Naphthalene is also detected as a contaminant from oil facilities and also commonly found in heavy fuels, such as diesel (N.P.D.E.S., 2003).

Exclusively in sample KP<sub>w4</sub>, we determined hexanedioic acid bis(2-ethylhexyl) ester [bis(2-ethylhexyl) adipate] at a concentration of 490 ng/L. It is a liquid of low volatility, widely used as a plasticizer in flexible poly(vinyl chloride) products (notably food films), and further plastics as well as in a number of other minor applications, such as lubricants and cosmetics (bath oils, eye shadow, cologne, foundations, etc.). It is also known as a contaminant derived from oil facilities (Spectrum, 2003). However, food is the major source for human uptake of this plasticizer as a result of migration from poly(vinyl chloride) packaging, particularly, into fatty foods such as cheese and meat. Additionally, it is released into the environment during its manufacture and distribution, during PVC blending operations and from commercial and consumer use of finished product sand subsequent emissions from waste deposit. As a result, concentrations of 130 ng/L and 35 ng/L were detected in Mississippi River water, collected from Lake Itasca, Minnesota (source of the river), and from New Orleans, LA, respectively (Spectrum, 2003).

### 3.2 Specific compounds

Another group of contaminants, identified in higher concentrations exclusively in sample KP<sub>w1</sub>, represent another source of pollution. The pollution in this specific point is probably due to the uncontrolled discarding of solid wastes in the area. A wide variety of anthropogenic substances including 1,2,3-trichloropropene, benzothiazoles, 2,4-di-*tert*-butylphenol and phosphates were detected.

1,2,3-trichloropropene is a halogenated compound, which is toxic, corrosive, and can readily absorbed through skin (Sigma-Aldrich, 2003). This compound is referred as a byproduct formed during epichlorohydrin synthesis. Epichlorohydrin is mainly used for the manufacture of glycerine and unmodified epoxy resins. It is also used in the manufacture of elastomers, glycidil ethers, cross-linked food starch, wet strength resins for the paper industry, water-treatment resins, surfactants, ion-exchange resins, plasticizers, dyestuffs, pharmaceutical products, oil emulsifiers, lubricants, and adhesives. It may also be used as a solvent for resins, gums, cellulose, esters, paints, and lacquers, and as a stabilizer in chlorine-containing substances such as rubber, pesticide formulations, and solvents (Strizhakova et al., 2000). Hence, the widespread use of epichlorohydrin might also cause the emission of its technical byproduct 1,2,3-trichloropropene.

Tris(chloropropyl)phosphates (2 isomers) (Fyrol PCF) appeared in the samples KP<sub>w1</sub> and KP<sub>w2</sub>, in the first one at a concentration of 1650ng/L and in the second one at a concentration of 30ng/L. It is a common xenobiotic, used as PVC plasticizer and as component in fertilizers, additive in nitro-based paint, hydraulic fluids, gasoline and as flame-retardants. It may also be used in thermoset and thermoplastic materials as well as for textile finishes. However, it is not recommended either for direct application to, or use in, formulations which will be applied to fabrics intended for apparel uses (Saeger et al., 1979). Tris(2-chloroethyl)phosphate, mainly used as a flame retardant appeared only in sample KP<sub>w1</sub>. Also tris-*n*-butylphosphate, a common plasticizer, occurred only in this sample (Table 1).

Benzothiazole appeared in samples KP<sub>w1</sub> (690ng/L) and KP<sub>w2</sub> (50ng/L). It is the major leachate compound of automobile tires (Suwanachaichinda et al., 2002). Biotransformation by fungies forms 2-(methylthio)benzothiazole, but this compound is also a byproduct of rubber production processes (Kind et al., 2000). 2-(methylthio)benzothiazole also appeared exclusively in the sample KP<sub>w1</sub> with a high concentration of 1300 ng/L. Both benzothiazoles are associated with automobile tire residues and exhausts. Therefore, their occurrence can be attributed mainly to urban runoff from the nearby national road or rubber waste discharge.

2,4-di-*tert*-butylphenol, also was identified in the highest concentration in sample KP<sub>w2</sub>, is an intermediate for antioxidants and other products (in solid samples of the most frequently used rubber) (O'Malley et al., 1988). It is also known as byproduct from the phenolic hydrolysis (Haider and Karlsson, 2002).

### 3.3 Non-specific contaminants

The distribution of numerous compounds including technical additives, fragrances, personal care products and plasticizers indicated no source specificity due to their occurrence in all samples investigated.

Phthalates are well-known and ubiquitous pollutants as a result of their persistence and long-range transport. They have been developed in the last century and they are used mainly as plasticizers (P.I.C., 2003). The compounds di-*iso*-butylphthalate and di-*n*-butylphthalate appeared in all samples investigated. The highest concentrations of di-*iso*-butylphthalate and di-*n*-butylphthalate were determined in sample KP<sub>w1</sub> (950ng/L) and sample KP<sub>w2</sub> (2000ng/L), respectively. On the contrary, butylphenylphthalate appeared in the samples KP<sub>w2</sub> (83ng/L) and KP<sub>w4</sub> (660ng/L). Di-*iso*-butyl adipate occurred in all samples with concentrations between 120 and 1200 ng/L. It is a plasticizer for imparting low temperature flexibility to various polymers, with a good balance of salvation and low temperature properties. Di-*iso*-butyl adipate is also a constituent in fingernail enamel, nail enamel remover, hair spray, adhesives and coatings. It is particularly recommended for plasticizing resinous and polymeric coatings that are intended for direct contact with foodstuffs.

Carbamodithioic acid dimethylmethyl ester was detected in all samples with very high concentrations in samples KP<sub>w4</sub> and KP<sub>w2</sub>. It is a component of fungicides, parasiticides and insecticides. The corresponding carbamodithioic acid diethylmethyl ester appeared in two samples (KP<sub>w2</sub> and KP<sub>w4</sub>) and is the major metabolite of Thiram. Thiram is a dimethyl dithiocarbamate based compound used as a fungicide to prevent crop damage in the field and to protect harvested crops from deterioration in storage or transport. Thiram is also used as a seed protectant and to protect fruit, vegetable, ornamental, and turf crops from a variety of fungal diseases. In addition, it is used as an animal repellent to protect fruit trees and ornamentals from damage by rabbits, rodents, and deer (Glauser et al., 1993). Thiram is moderate toxic by dermal adsorption. Another major use of thiram is as an accelerator and vulcanization agent in the rubber industry (EX.TOX.NET., 2004).

Additional compounds associated with fragrance and cosmetic products were identified in all water samples. 2,4,7,9-Tetramethyl-5-decine-4,7-diol, appeared at concentrations between 39 and 110 ng/L. It is a multifunctional surfactant (Surfynol 104). Due to its volatile nature, it evaporates from a system under used conditions. Therefore, it is useful in applications like silicon water and glass cleaning. This compound is also a constituent of perfumes and cosmetics (S.F.S., 2001). Further on, 2,6,6-trimethyl-2-cyclohexen-1,4-dione (4-oxoisophorone) is also a constituent of perfumes and cosmetics. It is produced by a direct oxidation of isophorone (Papa et al., 1981). It appeared in all samples in the range between 460ng/L (sample KP<sub>w1</sub>) and 120ng/L (sample KP<sub>w2</sub>). 2,6,6-Trimethyl-2-cyclohexen-1,4-dione has been recently reported as a contaminant in surface sediments (Ricking et al., 2003). 3-*tert*-Butyl-4-hydroxyanisole appears in all samples with highest concentration of 690ng/L in KP<sub>w1</sub> and lowest in KP<sub>w4</sub> (98ng/L). This compound is also added to perfumes and cosmetics. It is an antioxidant known to promote renal and bladder carcinogenesis in the rat, although the mechanisms of these effects are unclear (Peters et al., 1996). Isopropyl myristate is widely used in cosmetics, but also as a pesticide and for topical medicinal preparations, where good absorption through the skin is desired.

1-(Hydroxycyclohexyl)phenylketone (trade name: Irgacure 184) is a highly efficient non-yellowing photoinitiator which is used to initiate photopolymerisation of chemically unsaturated prepolymers – e.g. acrylates – combined with mono- or multifunctional vinyl monomers (S.F.S., 2001). It was determined in all samples between 400ng/L (sample KP<sub>w4</sub>) and 2100ng/L (sample KP<sub>w2</sub>).

For the compounds 2(3H)-benzothiazone, 2-ethylhexanoic acid 2-hydroxypropionic acid ester, 2,2,4-trimethylpentan-1,3-dioldi-*iso*-butyrate and 2,6-di-*tert*-butyl-4-hydroxy-4-methyl-2,5-cyclohexadienone, information is very limited and they are rarely reported as environmental contaminants.

## 4 SUMMARY AND OUTLOOK

A wide variety of organic compounds were determined in surface waters in the area near Kavala Oil facilities by detailed screening analyses. Specific organic markers were isolated and

characterized in terms of their spatial distribution indicating the contribution of emissions derived from different anthropogenic activities.

The disposal of liquid wastes from Kavala Oil facilities is probably the main cause of the presence of a first group of organic pollutants such as tribromomethane, naphthalene, and of hexanedioic acid bis(2-ethylhexyl) ester, all detected exclusively in water sample KP<sub>w4</sub>.

A second group of contaminants defined different point source pollution. The presence of the compound 1,2,3-trichloropropene as well as phosphate based plasticizers is possibly due to the uncontrolled disposal of solid wastes, plastic and synthetic. The presence of pollutants of the benzothiazole group is possibly caused by surface runoff derived from the nearby Kavala-Xanthi highway.

On the other hand, with respect to the third group as non-specific contaminants, diethyldithiocarbamodithioic acid, dimethyldithiocarbamodithioic acid (both detected as methyl esters), were identified. These compounds are components of fungicides, parasiticides and insecticides. They possibly constitute drainage material from the surrounding agricultural areas.

The compounds di-*iso*-butylphthalate and di-*n*-butylphthalate as well as, adipic acid di-*iso*-butyl ester are also present in all water samples. These compounds, found in large quantities, are probably derived from widespread and uncontrolled solid wastes disposal in the area.

In all water samples we also detected compounds which are constituents of perfume and cosmetics, and probably are emitted by sewage water emissions in the surrounding areas [e.g. (1-hydroxycyclohexyl)phenylketone, 2,4,7,9-tetramethyl-5-decine-4,7-diol, 2,6,6-trimethyl-2-cyclohexene-1,4-dione, 3-*tert*-butyl-4-hydroxyanisole, 4-oxoisophorone].

In summary, this study evaluated specific marker characterizing specific source point emissions in the area where the Kavala Oil facilities are located. In the future, a comprehensive overview on the pollution in the coastal zone of the industrial area of Kavala in terms of pollution level and spatial distribution can be estimated.

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