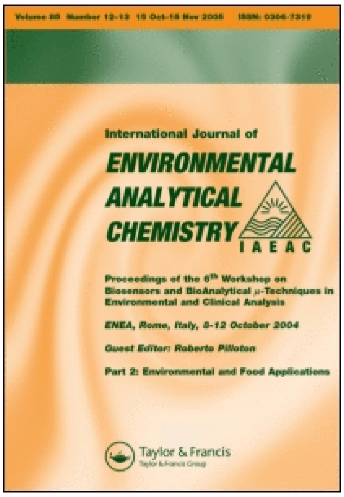

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Determination of phenolic compounds in the marine environment of Thermaikos Gulf, Northern Greece

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Determination of phenolic compounds in the marine environment of Thermaikos Gulf, Northern Greece

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Nitro- and chlorophenols were monitored at eight sampling sites along coast of Pieria province (northern Greece), from October 2003 to September 2004. The target compounds were 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2-chlorophenol, 3-chlorophenol, 2,4-dichlorophenol, and pentachlorophenol. Solid-phase extraction followed by high-performance liquid chromatography was used for the determination of the compounds. Among the selected phenolic compounds, the most frequently detected was pentachlorophenol, which was found to be present in all sampling sites. The maximum concentrations of chlorophenols were observed for pentachlorophenol ($8.04\,\mu g\,L^{-1}$) followed by 2,4-dichlorophenol ($6.11\,\mu g\,L^{-1}$). The geometric mean concentrations for pentachlorophenol during the 12-month survey ranged from non-detectable to $1.06\,\mu g\,L^{-1}$. The occasionally present levels of nitro- and chlorophenols in seawater of the Pieria province suggest that a continued monitoring study as far as toxic organic compounds are concerned is important for this area to maintain a clean environment and to remain attractive for tourism.

Keywords: Nitrophenols; Chlorophenols; Seawater; HPLC; Pieria

1. Introduction

Non-point-source contamination of surface waters has emerged as an important environmental problem in recent years. Although significant advances have been made in controlling point-source pollution, little progress has been accomplished in the area of non-point-source pollution of surface waters. This is because of the seasonality, inherent variability, and multiplicity of origins of non-point-source pollution [1].

Chemicals which are sufficiently resistant to degradation and are adequately soluble to be transported in water may reach the sea in significant amounts. Water runoff and river transport are the main processes involved in the land–sea transfer of chemicals [2].

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Sea water pollution is caused by several factors. The most important of these are human activities, such as the dumping of urban and industrial waste, but it can also be caused by natural activities. In this way, organic contaminants reach the marine environment and may be toxic to animal or plant species [3]. Among these organic contaminants, phenols play an important role.

Phenols are widely used as preservative agents, pesticides, antiseptics, and disinfectants, and in a variety of industrial applications. The phenolic compounds in the water environment can arise from industrial activities, agricultural practices, and natural substance degradation. The occurrence of phenols as industrial pollutants in surface waters is quite common due to the release of by-products in the petrochemical industry, coal liquefaction plants, and production of plastic and dyes, as well as in the pulp industry [4]. In agricultural practice, phenolic compounds are employed as herbicides and insecticides or can derive from the degradation of chlorophenoxy carboxylic herbicides (chlorophenols) and organophosphorus insecticides (nitrophenols) [5–8]. The source of contamination outbalances the natural formation pathways of phenols, i.e. farm waste, biodegradation of humic acids, tannins and lignins, as well as during decomposition of wood or leaves [9]. Moreover, nitrophenols are formed photochemically in the atmosphere mainly from automobile exhausts [10] and as by-products or degradation products of ammunition wastes [11]. Additionally, phenols might be produced from technical processes, i.e. the formation of chlorophenols during chlorination of natural humic substances in drinking water purification units.

Phenols can be absorbed into the human body, whether dermally, orally, or via the airways [12, 13], and can produce many adverse effects on fish and aquatic ecosystems, when chronically exposed even at low concentrations [14]. Because most phenolic compounds exhibit a high degree of toxicity, several have been classified in the European Union (EU) legislation as priority contaminants. In EU countries, the determination of phenols in river and drinking water has become very important since the maximum admissible concentration was fixed at $0.5\,\mu g\,L^{-1}$ as total phenol amount and $0.1\,\mu g\,L^{-1}$ for the individual compounds [15], and in bathing water the maximum admissible value is $5\,\mu g\,L^{-1}$ [16]. Also, the US Environmental Protection Agency (EPA) has included phenols (Methods 604, 625, and 8041) in a list of priority pollutants [17–19].

The need for monitoring and controlling the presence of these compounds in the environment is now recognized, being essential for achieving good water-quality objectives. Analytical techniques used in the determination of phenols are mainly high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) in combination with ultraviolet detection (UV), fluorescence detection, electrochemical detection, or mass spectroscopy [20]. Also, gas chromatography (GC), usually after phenol derivatization, with flame-ionization detection (FID), electron-capture detection (ECD), mass spectroscopy (MS), or microwave-induced plasma atomic emission spectroscopy (MIP-AES), is a common tool for the analysis of phenols [21, 22].

An important step for chromatographic analysis of these compounds is the extraction mode and the extract pre-concentration, in order to comply with low permissible levels typical for phenols (a few micrograms per litre in surface waters). Solid-phase extraction (SPE) is the most frequently used pre-concentration technique for phenolic compounds [21, 23–25], because of its well-known advantages over liquid–liquid extraction (LLE), such as minimal sample manipulation and contamination, small volumes of solvent required, higher efficiency, good specificity with some polar adsorbent materials, etc.

This study presents investigations performed on seven representative phenols, included partly in the EU list and partly in the EPA list of priority pollutants, in the coastal area of Pieria (Thermaikos Gulf) located in northern Greece. Eight sampling points along the coastline of Pieria prefecture were selected for inclusion in this study.

2. Experimental

2.1. *Area description*

Pieria comprises a part of central Makedonia in northern Greece. The prefecture borders to the north with the prefecture of Imathia, eastwards there is a Thermaikos Gulf, west it borders with the prefectures of Kozane and Imathia, and south it borders with the prefecture of Larissa. It occupies an area of 1516 km^2 and has a population of more than 116,000. The population is distributed as agrarian (~45,000), rural (~24,000), and urban (~47,000).

The prefecture of Pieria runs across the Aliakmon River, in the northern section, whose delta consists of a wetland of the Thermaikos Gulf coast, which is protected by the Convention of Ramsar (1971). Moreover, Pieria crosses several other smaller rivers, such as Aisonas, Pelekas, Enipeas, Zliana, Toponitsa, Gerekas, and Mavroneri, which are the water sources for irrigation (figure 1).

The region's mild climate and abundant water, as well as the large percentage of land available for cultivation (38.1% of the total prefecture) makes agricultural production the primary sector of the area's economic activities. Of the total production, 34% is grain, followed by tobacco, corn, rice, potatoes, cotton, melon, grapes, and olives. Pastures cover the 17.5% of the prefecture, where goats, sheep, pigs, oxen, and chickens graze. The fishing industry of Pieria produces 60% of the total Greek mussel cultivation. Many units of mussel cultivation are located in an area of more than 600 ha. The most important light industrial activities, which represent the secondary section of the economy of Pieria, are: food products, wood and metal products, clothing, and textiles. An important part is also played by the drinks industry and several other local industries such as leather and fur, rubber, plastic, paper products, etc. Pieria is also one of the most important tourist prefectures in Greece, attracting a great number of visitors and offering a wide range of facilities (7000 rooms in hotels, 6000 rooms to let, and 35 camping sites).

2.2. *Sampling*

The study covers eight sampling stations (see figure 1) along the Pieria coastline, which extends over more than 70 km and receives internal water flow (rivers and streams). The following sampling sites within the area of the coastal waters of Thermaikos Gulf were chosen for the analyses: Agathoupoli (P1), Korinos (P2), Katerini bay (P3), Aisonas (river outflow) (P4), Litohoro (P5), Leptokarya (P6), Platamonas (P7), and Neoi Poroi (P8). The sampling sites (figure 1) are situated

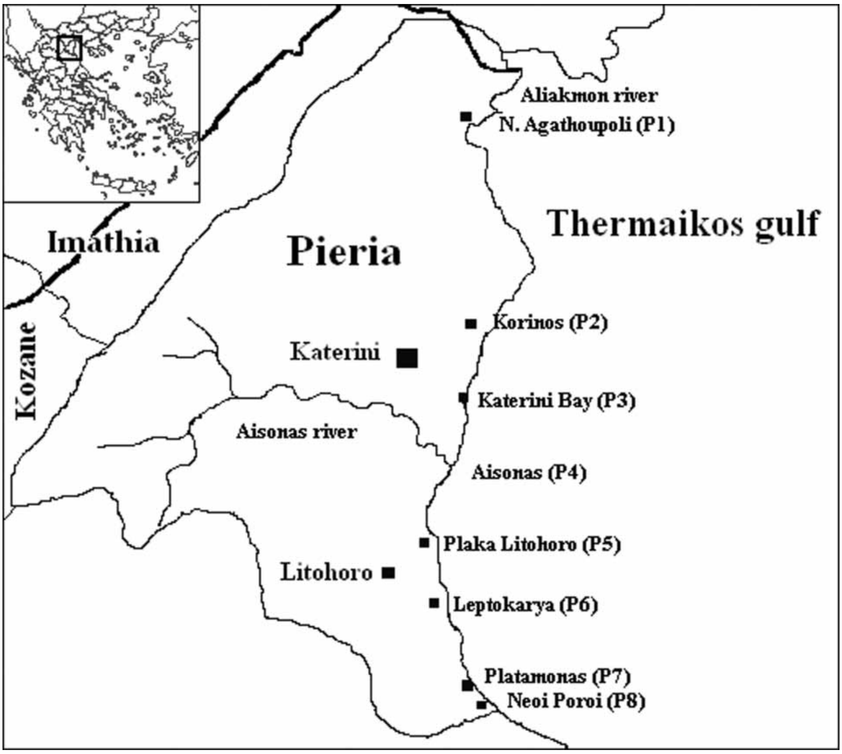

Figure 1. Sampling sites along the coast of the Pieria province chosen for the monitoring study.

along the seashore area of the gulf. Water samples were collected monthly between October 2003 and September 2004. The sampling was carried out at a depth of 1 m from the surface layer of sea water. Two 2.5 L volumes of water were collected in glass bottles from each sampling site. After filling with water, the bottles were sealed with screw caps lined with aluminium foil. These were transported in ice boxes (and reached the laboratory one day after sampling) and then stored at 4°C prior to extraction, normally within 48 h.

2.3. *Analytical techniques*

2.3.1. Chemicals. The tested compounds 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 2,4-dichlorophenol (2,4-DCP), pentachlorophenol (PCP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP) were purchased from Supelco (Bellefonte, PA). A stock standard solution of 1000 mg L^{-1} of each compound was prepared in methanol. Working standard solutions at various concentrations were prepared weekly by appropriate dilutions of the stock solutions in methanol. Stock and working standards were stored at 4°C in the refrigerator and were renewed every 2 months.

Solvents (methanol, acetonitrile, and water) of HPLC grade were purchased from Merck (Darmstadt, Germany). Orthophosphoric acid used for the acidification of water samples and acetic acid used in the preparation of the mobile phase were purchased from Riedel-de Haën (Seelze, Hannover, Germany).

2.3.2. Determination of seawater physicochemical parameters. The pH measurements were made with a PHM 82 Standard pH meter (Radiometer, Copenhagen), calibrated against two standard buffer solutions of known pH values (pH 3 and 10). Total dissolved solids, salinity, and conductivity were measured with a microprocessor-controlled conductivity meter (model LF 325) from WTW (Weilheim, Germany), equipped with a calibrated thermometer.

2.3.3. Solid-phase extraction. The selected phenols were pre-concentrated using an SPE method with SDB-RPS disks (manufactured by 3M under the trademark Empore). The disks used in this work were 47 mm in diameter and 0.5 mm thick, and contained sulphonated poly(styrenedivinylbenzene) as sorbent.

Aqueous samples were acidified to pH 3 with orthophosphoric acid [25], and before usage each disk was conditioned with 10 mL of methanol and then with 10 mL of HPLC water pre-adjusted at pH 3 (with orthophosphoric acid). Disks were not allowed to dry out [26], and 500 mL of the seawater sample was passed through, by regulating the vacuum to give flow rates of 20–25 mL min^{-1}. Afterwards, a test tube of 40 mL was placed in the apparatus to collect the phenols trapped in the disk. The retained compounds were eluted with three 5 mL portions of an acetonitrile/methanol (1 : 1, v/v) mixture. Finally, the extracts were concentrated under a gentle stream of nitrogen to 50 μL, prior to injection in the HPLC system.

2.3.4. HPLC analysis. The LC system comprised a Shimadzu on-line DGU-14A degassing system coupled to an FCV-10AL controller unit and an LC-10AD high-pressure solvent-delivery pump, with a 20 μL sample loop injector and a Shimadzu SPD-M10A UV/diode array detector. The column material was a Discovery C18 (Supelco), with 5 μm particles (25 cm × 4.6 mm i.d.) with a guard column of the same material (8 mm × 3 mm).

The mobile phase consisted of HPLC water (containing 1% (v/v) acetic acid) as solvent A and acetonitrile (containing 1% (v/v) acetic acid) as solvent B [27]. The flow rate of the mobile phase was 1 mL min^{-1}, and the oven temperature was set at 30°C. The gradient composition of the eluent solvent is shown in table 1.

The separation and determination of the selected phenols were performed by injecting 20 μL of the extracts obtained into the liquid chromatograph, and the abundance of each compound, corresponding to the wavelength maximum, was measured. In particular, the UV/diode array detector was set at 278 nm for 2-CP, 2-NP and 2,4-DNP, at 283 nm for 3-CP, at 293 nm for 2,4-DCP, at 304 nm for PCP and at 319 nm for 4-NP. Representative HPLC chromatograms of a standard solution and a sample are shown in figures 2(a) and (b), respectively.

Table 1. HPLC gradient shape elution.

Time (min)	Solvent A (%) 1% acetic acid in HPLC water	Solvent B (%) 1% acetic acid in acetonitrile
0–10	70	30
10–28	20	80
28–29	70	30
29–35	70	30

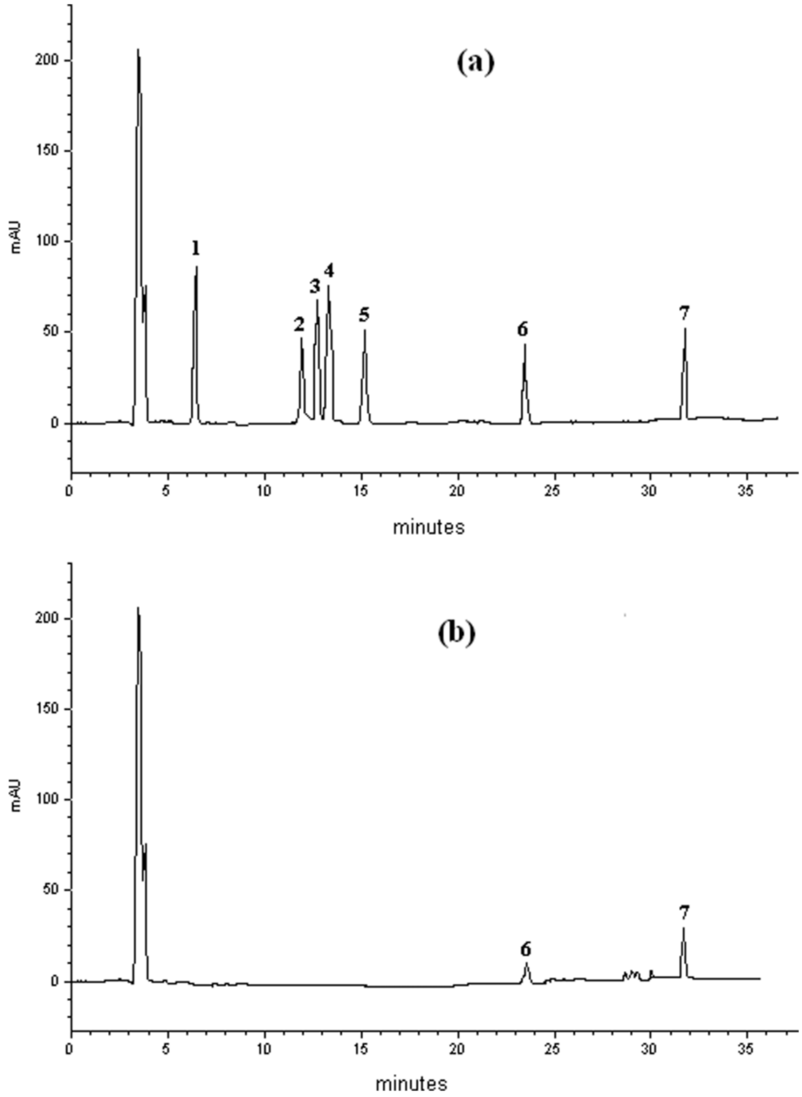

Figure 2. (a) HPLC chromatogram of a standard solution of phenolic compounds. Peaks: (1) 4-NP (6.45 min), (2) 2-CP (12.00 min), (3) 2,4-DNP (12.82 min), (4) 2-NP (13.36 min), (5) 3-CP (15.18 min), (6) 2,4-DCP (23.64 min), (7) PCP (31.73 min). (b) Chromatogram obtained from analysis of a seawater sample.

3. Results and discussion

Four chlorophenols (2-CP, 3-CP, 2,4-DCP, PCP) and three nitrophenols (2-NP, 4-NP, 2,4-NP) were monitored in sea waters of the Pieria coastline (northern Greece) for a 12 month period by means of an SPE-HPLC method. The phenols and major method performance characteristics are given in table 2. In table 3, the mean values and range of physicochemical characteristics of samples, during the period from October 2003 to September 2004, are presented. The validation of the analytical method used has been performed with Thermaikos Gulf water (open sea).

Table 2. Recoveries (%) and detection limits ($\mu g\,L^{-1}$) of phenolic compounds in sea water obtained from the SPE-HPLC method.

Compound	Recovery (%)[a]	Limit of detection ($\mu g\,L^{-1}$)
2-NP	87.4	0.1
4-NP	87.8	0.1
2,4-DNP	89.6	0.09
2-CP	88.6	0.1
3-CP	89.0	0.1
2,4-DCP	88.1	0.15
PCP	87.2	0.1

[a] Spiking level $2\,\mu g\,L^{-1}$ for each analyte. Sample volume: 500 mL.

Table 3. Mean values and range of physicochemical characteristics determined in water samples from eight sampling sites of the Pieria coastline during October 2003 to September 2004 ($n = 96$).

	pH		Conductivity		TDS[a] ($g\,L^{-1}$)		Salinity (‰)	
Sampling site	Mean	Range	Mean	Range	Mean	Range	Mean	Range
P1	7.71	7.13–8.41	46.9	40.9–56.1	33.8	26.1–46.9	31.8	26.1–36.6
P2	7.85	7.26–8.37	48.7	42.3–55.9	35.9	29.8–43.3	34.4	30.0–36.6
P3	7.87	7.46–8.38	48.5	43.4–53.4	40.4	31.0–53.2	34.3	30.5–36.6
P4	7.96	7.48–8.62	50.1	42.3–58.4	37.8	29.7–49.1	35.0	31.1–37.0
P5	7.88	7.30–8.41	50.0	42.2–57.2	38.5	33.8–47.7	34.8	30.4–37.5
P6	7.96	7.34–8.30	49.6	42.8–56.6	39.6	27.1–50.6	34.6	29.9–36.6
P7	7.91	7.35–8.37	49.2	41.9–56.7	37.7	32.3–49.3	33.7	27.2–36.6
P8	7.94	7.35–8.25	49.1	44.2–56.5	36.6	28.9–47.0	33.7	26.8–36.7

[a] TDS: Total dissolved solids.

Recoveries at the low- to sub-$\mu g\,L^{-1}$ level, for the compounds tested, were higher than 87%. The detection limits for all the compounds that are under examination range between 0.09 and $0.15\,\mu g\,L^{-1}$ (table 2). For the diode array detector, the limit of detection for a compound was calculated as the lowest fortification level at which the compound was detected with a signal-to-noise (S/N) ratio above three.

Identification of phenols was accomplished on the basis of the retention times and by comparison between the UV spectrum of the reference compound in the library and the UV spectrum of the detected peak in the sample.

Table 4 contains a summary of the occurrence and concentrations of nitro- and chlorophenols detected in samples collected during the 12 month study period at eight coastal sampling points. Mean values were not calculated because the occurrence of the phenolic compounds was lower than 50% of the samples for all the phenols, except for PCP. The results of the analyses of the samples have shown the presence of a number of phenolic compounds in some water samples. The compounds detected were 2-NP, 4-NP, 2,4-DNP, 3-CP, 2,4-DCP, and PCP. The highest concentrations of phenolic compounds detected in coastal waters were $1.32\,\mu g\,L^{-1}$ for 2-NP, $2.54\,\mu g\,L^{-1}$ for 4-NP, $0.72\,\mu g\,L^{-1}$ for 2,4-DNP, $1.05\,\mu g\,L^{-1}$ for 3-CP, $6.11\,\mu g\,L^{-1}$ for 2,4-DCP, and $8.04\,\mu g\,L^{-1}$ for PCP. The appearance of targeted phenols in different coastal regions changes significantly. Phenols were detected in all sampling sites, appearing more frequently at P5 (Litohoro).

Among the compounds, nitrophenols are presented in a restricted number of areas, mainly at P5. 2-NP especially was detected twice at sampling site P5 at a concentration

Table 4. Range and percentage detection of phenolic compounds in the coastal waters of Pieria during October 2003 to September 2004 ($n = 96$).

Phenolic compound	Concentrations ($\mu g\,L^{-1}$) P1	P2	P3	P4	P5	P6	P7	P8	Detection (%)
2-NP	nd[a]	nd	nd	nd	nd–0.40	nd–1.32	nd	nd	3.1
4-NP	nd	nd	nd	nd	nd–2.54	nd	nd	nd	1.0
2,4-DNP	nd	nd–0.72	nd–0.29	nd	nd–0.28	nd	nd	nd	3.1
2-CP	nd	nd	nd	nd	nd	nd	nd	nd	0
3-CP	nd–0.45	nd–0.34	nd	nd–0.65	nd	nd–1.05	nd–0.48	nd	10.4
2,4-DCP	nd–0.48	nd	nd–6.04	nd–6.11	nd	nd	nd–2.63	nd–1.52	8.3
PCP	nd–0.76	nd–6.64	nd–2.51	nd–1.42	nd–8.04	nd–0.32	nd–6.60	nd–1.99	62.5

[a] nd: not detected.

of 0.33 $\mu g\,L^{-1}$ (October) and 0.40 $\mu g\,L^{-1}$ (September), as well as at sampling site P6 at a concentration value of 1.32 $\mu g\,L^{-1}$ (October). 4-NP was detected once at sampling site P5 at a concentration of 2.54 $\mu g\,L^{-1}$, and finally 2,4-DNP appeared at sampling sites P2, P3, and P5 at concentrations of 0.72, 0.29, and 0.28 $\mu g\,L^{-1}$, respectively, in the same month (November). Although these values seem to appear occasionally, they cannot be considered negligible. The concentrations found could be explained by several factors concerning mainly human and natural activities.

Release of 2- and 4-NP into the environment occurs primarily as emissions into, air, water, and soil from diffuse sources such as vehicle traffic and hydrolytic and photolytic degradation of the respective pesticides [6, 10]. 2-NP and 4-NP have been detected in the exhaust gases of light-duty gasoline and diesel vehicles [10]. Cloud-water model experiments have shown that 2- and 4-NP are also formed from the reaction of phenol with nitrogen pentoxide or monochloronitrogen dioxide, especially under alkaline conditions [28]. Significant releases of 4-NP into the hydrosphere may occur from the hydrolytic degradation of the insecticides methyl parathion and ethyl parathion [5]. Furthermore, a considerable portion of airborne nitrophenols, especially 4-NP, can be released to the hydrosphere by wet and dry deposition [29, 30]. Experimental results have shown that the major transformation pathway for airborne 2-NP, which has less tendency to adsorb on particles than 4-NP, should be rapid nitration to 2,4-DNP [29, 30]. From valid test results available on the toxicity of the 2- and 4-NP to various aquatic organisms, nitrophenols can be classified as substances exhibiting moderate to high toxicity in the aquatic compartment. The lowest observed effect concentrations (LOEC) found in chronic studies with freshwater organisms were 40-to-50-fold higher than the maximum levels determined in a densely populated and highly industrialized Asian river basin (7.2 $\mu g\,L^{-1}$ for 2-NP and 19 $\mu g\,L^{-1}$ for 4-NP) [31]. These values are also much higher than those determined in our study for nitrophenols. Therefore, nitrophenols emitted could pose some risk to sensitive aquatic organisms, particularly under surface water conditions not favouring their known elimination pathways. In all cases, the concentrations detected were lower than the maximum EU values for bathing waters [16].

Within the monitoring period, chlorophenols were detected in all sampling sites. Among these compounds, 2-CP was not observed in the seawaters of the Pieria coastline. 3-CP was detected in most sampling sites, with the highest concentration (1.05 $\mu g\,L^{-1}$) at sampling site P6. This compound was also detected twice at sampling site P2 (0.31 and 0.34 µg L^{-1}, respectively) and once at sampling points P1, P4, and P7 with the corresponding values of 0.45, 0.65, and 0.48 µg L^{-1}. The highest concentration of 2,4-DCP was detected at sampling site P4 (6.11 µg L^{-1}), followed by sampling site P3 (6.04 µg L^{-1}) in the same month (November). Similar concentrations of 2,4-DCP (6 µg L^{-1}) have also been reported recently along the Polish coastline (Gulf of Gdańsk) [32]. This chlorophenol was also detected twice at sampling site P7 (2.63 and 1.55 µg L^{-1}) and two other times at sampling point P8 (1.52 and 0.62 µg L^{-1}).

The principal use of monochlorinated phenols is as intermediates in the synthesis of the higher chlorinated congeners and certain dyes and pesticides. The main use of 2,4-DCP is as an intermediate in the production of 2,4-D and other herbicides, as well as an ingredient in antiseptics [33]. Besides the discharges from plants manufacturing the compounds or from plants using them as intermediates in the production of higher phenols, these compounds can enter the environment as discharges from paper mills; as by-products of the bleaching process; as a result of the disinfection of sewage, industrial waters, and drinking water with chlorine; and from the microbial breakdown of herbicides (2,4-D) and subsequent runoff of the products [33]. The appearance of these compounds along the coast of Pieria is mainly due to random, temporal, and spatial inputs from all the aforementioned sources that are present in the area.

Residues of chlorophenol isomers have also been detected in other aquatic systems, mainly in discharges from such sources [34]. 2-CP, 3-CP, and 4-CP have been detected at µg L^{-1} levels in effluents from European sewage-treatment plants and cooling water from power stations as a result of disinfection by chlorination [34], while in coastal areas and in rivers flowing through industrial regions of the Netherlands, concentrations of monochlorophenols have been reported to range from non-detectable to 20 µg L^{-1} and dichlorophenols from non-detectable to 1.5 µg L^{-1} [34]. The concentrations of monochlorophenols detected in Pieria coastal line were significantly lower than those values, but 2,4-DCP provided a maximum concentration value approximately four times higher.

Most of the available data on the aquatic toxicity of these chlorophenols include more studies on saltwater organisms than on freshwater organisms [33]. Long-term exposure data available for saltwater organisms relate to a study conducted under field conditions in which a 2,4-DCP concentration of 1.0 µg L^{-1} was found to cause severe inhibition of growth and biomass of natural phytoplankton communities [35]. Among the lowest reported toxicity data for 2,4-DCP were a 96 h LC_{50} and 72 h EC_{50} (growth) of 2.55 and 0.6 mg L^{-1} for the grass shrimp *Palaemonetes pugio* and diatom *Phaeodactylum tricornutum*, respectively [34, 36]. Toxicity values for 2- and 3-CP for fish provided a 96 h LC_{50} of 6.6 and 4.0 mg L^{-1} for *Solea solea* and flounder *Platichthys flesus*, respectively [37]. According to these toxicity data, it seems that the detected levels of mono- and dichlorophenols, in Pieria coastline waters, should not represent a risk to the marine environment in this region.

PCP was detected in all of the sampling sites and every month appeared in almost one sampling point. Its highest concentration was found at sampling point P5 (8.04 µg L^{-1}) followed by sampling sites P2 (6.64 µg L^{-1}) and P7 (6.60 µg L^{-1}). Figure 3 illustrates the geometric mean annual concentrations (µg L^{-1}) of PCP at the different sampling points.

There are currently three principal areas of use for PCP-containing chemicals in the EU: as anti-sap stain agents in green timber; as a fungicide in the treatment of

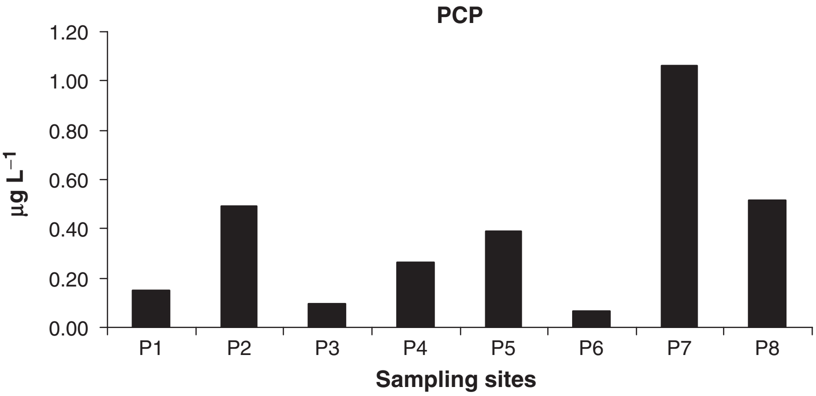

Figure 3. Geometric mean annual concentrations of PCP (μg L^{-1}) detected along the coast of Pieria.

timber and masonry; and as a preservative against fungal and bacterial attack in heavy-duty textiles [38]. In coastal waters and estuaries, the concentrations are reported as either average (mean) or median PCP concentrations. Data are mainly available for The Netherlands, UK, and Germany. According to these surveys, the maximum PCP concentrations of 1.10, 5.80, and 0.10 μg L^{-1}, respectively, have been reported [39–41]. The maximum concentration values determined in our study were 50% higher than the above references. However, the geometric mean annual concentrations ranged from undetectable to 1.06 μg L^{-1}, thus providing results comparable with these studies. A review of the available acute toxicity data for marine aquatic organisms reveals that the acute LC_{50} values for fish ranged from 38 to 440 μg L^{-1} and for invertebrates 84 to >10,000 μg L^{-1}. For marine aquatic plants, short-term EC_{50} values ranged from 280 to 300 μg L^{-1} PCP [42]. Taking into account these toxicity data, the PCP concentrations in the tested seawaters have a low potential to have a significant effect on the aquatic environment of the Pieria coastline. Among the tested chlorophenols, only 2,4-DCP and PCP exceeded (in some cases) the maximum admissible level decreed by the EU for bathing waters [16].

4. Conclusions

The occurrence of phenolic compounds (nitro- and chlorophenols) was studied in the seawaters of the Pieria coastline (northern Greece) for a period of one year. The compounds detected were 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 3-chlorophenol, 2,4-dichlorophenol and pentachlorophenol. In some cases, the concentrations detected were higher than the levels set by the EU for bathing waters, especially for pentachlorophenol and 2,4-dichlorophenol. Urban, industrial, and agricultural contaminations, as well as natural loading, are the main accountable factors for the presence of these phenolic compounds, taking into account the dominant activities in this prefecture. The concentrations detected for all the phenolic compounds do not seem to pose a threat to the aquatic environment of the area. The low concentrations found in seawater indicate that this natural system is very stable and has a great 'auto-purification' ability. Nevertheless, permanent control is necessary, and improvements in investigations have to be continued to provide more information on phenolic compounds in Greek coastal waters and to help ensure their quality is maintained.

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