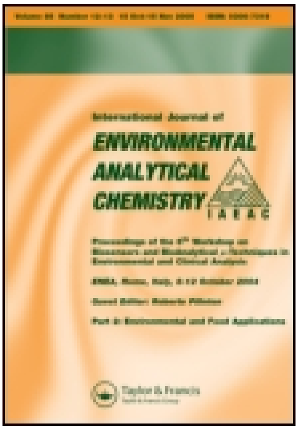

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Polybrominated diphenyl ether (PBDE) concentrations were determined in marine sediment samples collected from 7 different locations around Thermaikos Gulf in north Greece. PBDEs were detected in all sampling sites and their average total concentration (ΣPBDEs) ranged from 0.26 to 4.92 ng g^{-1} d.w. Concentrations were an order of magnitude higher in locations outlining the inner part of the Gulf, which were also closer to industrial areas, sewage treatment plant discharges, the city's harbour and landfill area. These findings suggest pollution in the aquatic ecosystem from industrial and urban activities in the area. Congener profiles exhibit predominance of BDE-209, while concentrations of other PBDE congeners were usually lower, when compared to similar studies from other countries globally, indicating that Thermaikos Gulf is among the low-polluted areas. Statistical analysis showed significant differences among the higher polluted sampling stations. Statistically significant differences also existed between sampling stations with high and low PBDE concentrations. Correlations between congeners suggested local contamination sources; however, specific point sources of pollution were not established.

Keywords: brominated flame retardants, BFR; aquatic ecosystem; environmental pollution; BDE-209

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a chemical group of substances of anthropogenic origin, which belong to a larger group of chemicals used as flame retardants. These substances are incorporated in various products such as plastics, textiles, paints, electrical equipment and building materials in a percentage range from 5 to 30 w/w [1–8] to reduce flammability and lower the combustion probability of the polymeric materials.

PBDEs are found to be highly lipophilic, persistent in the environment and resistant to degradation, as their structural similarity to already known persistent organic pollutants (PCBs, PCDDs, PCDFs) suggests [9,10]. Entry sources to the environment can be through air, soil or water, directly from PBDE manufacturing or from leaching and volatilisation during the use of products or after their disposal [7]. Analysis of sediment can illustrate

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possible recent pollution sources of PBDEs in an aquatic environment [11]. Due to their physico-chemical properties, they are quickly absorbed by sediment and thus enter into the aquatic food chain through benthic organisms. They have been traced in a large number of different organisms in aquatic ecosystems, whether they were located near cities and industrial areas or rural and remote areas [12–15]. The toxicity of these chemicals to organisms, although less potent than other persistent organic pollutants (i.e. PCBs), constitutes through bioaccumulation and biomagnification an accountable risk associated with the endocrine system [16]. There have been indications of adverse effects in the immune and reproductive systems [9,17–18]. Human exposure to PBDEs is constant through food intake, with fish and shellfish as the food groups of interest [19–21].

In Europe, there has been a ban on penta- and octa-BDE production since 2006 [22]. Thereafter, deca-BDE has been the main PBDE product, covering over 80% of PBDE worldwide production, while penta- and octa-BDE represent 12% and 6% [4]. Although there is still no directive in Europe against the production and use of deca-BDE, the European Court of Justice recently annulled the Commission Decision on the exemption of deca-BDE from the directive. The use of BDE-209 formulation has also been prohibited in Europe since July 2008 [23]. A number of studies were performed in Europe analysing PBDE congener patterns. Congeners included in penta-BDE, octa-BDE and deca-BDE were detected. [12,24]. The latest studies in sediment indicate a significant increase in the presence of BDE-209 in comparison to other congeners, constituting in many cases over 90% of the ΣPBDE (sum of polybrominated diphenyl ether compounds) levels. Photo- and bio-degradation of BDE-209 is viewed by some authors as the main source of tetra- and penta-BDEs in the marine environment [25–28]. There are so far no official data on amounts of PBDE production, import or usage in Greece.

The objective of this study was to evaluate PBDE concentrations in marine sediment from Thermaikos Gulf, congener profile and spatial distribution, compare them with reported worldwide data on marine sediment and identify possible point or non-point sources of pollution. According to our knowledge, this is the first study reporting levels of these compounds in the region of Thermaikos Gulf.

2. Experimental

2.1 *Sampling area*

The study area of Thermaikos Gulf is located at the north-west corner of the Aegean Sea with a width of 15 km at its maximum opening between the river delta on the west, and a residential area in the east around sampling station S7 (Figure 1). The maximum 'height' of the gulf, from north to south, is 45 km and its total surface 473 km^2. Its depth reaches 90 m at the southern part of the gulf, the only open side that allows access to the Aegean Sea. It constitutes the discharge basin for one main river (Axios) and three minor rivers in terms of flow rate (Aliakmon, Loudias, Gallikos). All rivers carry water year-round, with flow rates varying between 10 m^3 s^{-1} and 400 m^3 s^{-1} from summer to winter. The flow rates also vary greatly due to irregular drainage from agricultural irrigation. In addition, the sewage water from the town of Thessaloniki (1–1.5 million inhabitants) is also discharged into the gulf after a second degree wastewater treatment. There is an industrial zone located on the northern part of the gulf. In the eastern part, a stream runs not far from the city's landfill and discharges into the sea by the airport [29].

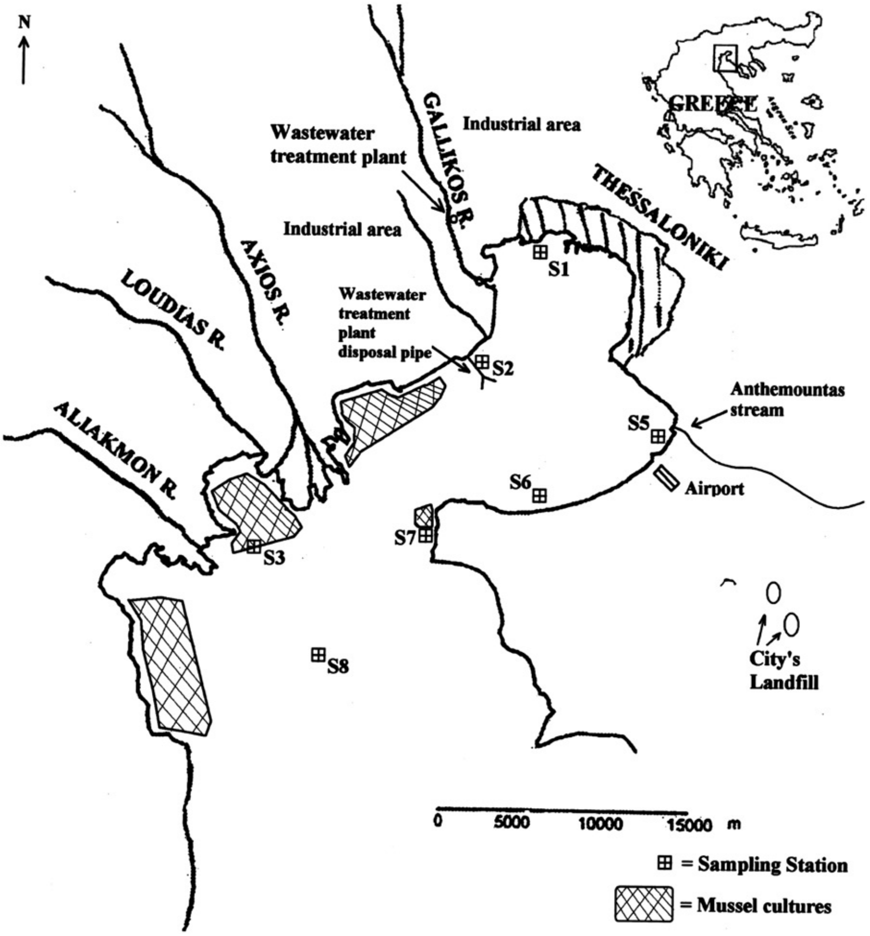

Figure 1. Area map of Thermaikos Gulf with the sampling locations indicated S1–S8.

2.2 *Sample collection*

A total of 56 surface marine sediment samples (depth 0–10 cm) were collected from 7 locations (8 samplings from each station) in Thermaikos Gulf during a two year period (Spring 2005–Spring 2007) (Figure 1). Table 1 gives information about the location and depth of the sampling sites. The samples were collected using a Van Veen sediment grab device deployed from a research vessel. During every sampling, three samples were collected from each station in a 10–20 m radius and were pooled together for chemical analysis. There were four annual samplings. Sampling sites were selected according to effluent discharges (domestic, urban and rural), anthropogenic impact sources in general and natural watersheds of Thermaikos Gulf. One of the sampling stations (S8) was the reference station in the open southern part of the gulf. Sampling station S1 was located in the city's passenger and trade harbour entrance, station S2 is in front of the industrial area of Thessaloniki, including the discharge outlet of the city's wastewater treatment plant and also discharge outlet of industrial solid waste and wastewater. Station S3 is located near

Table 1. Depth/GPS/humidity data of sampling stations and mean levels of ΣPBDEs concentration in sediment.

Sampling stations	Average humidity %	Depth (m)	GPS data	ΣPBDEs
S1	52	4–5	40°37′52″ N 22°52′90″ E	$1.100^{a,c} \pm 0.327$ [0.342]
S2	49	7–9	40°34′68″ N 22°50′70″ E	$4.917^{b} \pm 1.937$ [2.513]
S3	51	13–15	40°28′89″ N 22°41′34″ E	$0.503^{c} \pm 0.117$ [0.305]
S5	49	12–14	40°32′32″ N 22°58′26″ E	$2.533^{a,b} \pm 1.344$ [1.442]
S6	45	15–17	40°30′69″ N 22°53′53″ E	$0.305^{c} \pm 0.078$ [0.288]
S7	36	17–19	40°29′50″ N 22°48′66″ E	$0.406^{c} \pm 0.121$ [0.171]
S8	52	32–35	40°25′96″ N 22°44′55″ E	$0.259^{c} \pm 0.080$ [0.124]

Notes: ΣPBDEs values are expressed as mean values ± standard error of the mean value.

[a,b,c] Mean values with the same index bear no statistically significant difference ($p > 0.05$).

Square bracket values stand for geometric means.

the estuaries of the main rivers Axios and Aliakmonas, with extensive mussel cultures (*Mytilus galloprovincialis*) around the estuaries. The mussel cultures are modern longline spread across the northwestern/western part of the gulf and older pole/stake cultures in more shallow water estuaries. The river delta is protected by the Ramsar Convention treaty [30]. Station S5 represents the area outside the airport, with the estuary of Anthemountas Stream, a stream steering in the vicinity of the city's main landfill site. The area in front of station S6 is a highly populated residential area. Station S7 is also located in a residential area, where there are some mussel cultures and the city's main fish-wharf. The samples were immediately transferred into amber glass jars, previously cleaned and rinsed with solvent (acetone and n-hexane). The jars were sealed with aluminum foil, in order to avoid sample contamination, stored in isothermal bag and transported as quickly as practical to the laboratory, where they were kept in deep freeze (−20°C) prior to analysis.

2.3 *Chemicals and reagents*

Organic solvents and water used in this study were of LC-grade or pesticide-grade, purchased from Merck and Riedel de Haën. All other chemicals were of analytical grade. N_2 gas (99.99%) was obtained from Linde Hellas. Silica gel 60 (0.063–0.200 mm) was purchased from Merck and used for chromatography columns. Silica gel was activated by heating over night, at 250°C, and allowed to cool to room temperature prior to use. Analytical standards were synthesised in-house (Department of Environmental Chemistry, Stockholm University) [31]. The PBDE mix consisted of BDE 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209. Concentration levels ranged from 3.35 to 13.5 $\mathrm{ng\,mL^{-1}}$.

In order to choose the appropriate internal standards, pilot studies were performed to identify congeners not present in the samples. The internal standards used were BDE-77 as surrogate standard and BDE-138 as injection standard, which were also synthesised in house.

2.4 *Extraction and analyses*

Humidity percentage was assessed by drying 3–5 g of sediment at 100°C overnight,. Average humidity percentages per sampling station are shown in Table 1.

A cold extraction method was applied according to the Jensen method [32], slightly modified for sediment.

In detail, 20 g of homogenised sediment were weighed and centrifuged for 10 min at 3500 rpm. Excess water was discarded. Using a solvent mixture (isopropanol 25 mL and diethylether 10 mL) the sediment was transferred into a 100 mL conic flask and spiked with 50 μL of BDE-77 with a concentration of 2.86 ng mL^{-1}. Stirring for 10 min followed. The overhead organic phase was transferred through a Wattman filter into a separatory funnel (500 mL), which contained 50 mL of 0.1 M H_3PO_4 in an aqueous 0.9% NaCl. The sediment was re-extracted twice, first with a mixture of 25 mL n-Hexane : diethylether (9 : 1) and 10 mL isopropanol and then with 25 mL n-Hexane : diethylether (9 : 1). All organic phases were collected into the separatory funnel. To avoid formation of an emulsion, the funnel was not shaken but turned upside down 30 times. After phase separation, the lower aqueous phase was transferred to a 100 mL beaker. To avoid water presence in the organic extract, the funnel was rotated and any additional water was transferred into the beaker. The organic phase was decanted into another 100 mL beaker. The aqueous phase was returned into the funnel and re-extracted with 10–15 mL of n-Hexane : diethylether (9 : 1) as described above. The combined organic phases in the beaker were evaporated in a cupboard overnight at room temperature.

2.4.1 *Sulphuric acid treatment*

The organic extract was dissolved in 4 mL n-Hexane (doses of 1–2 mL at a time) and transferred into a centrifugal tube, where it was partitioned with 2 mL of conc. H_2SO_4, turning the tube upside down 30 times and centrifuged for 5 min at 3000 rpm. The overhead organic phase was transferred into a test tube using a Pasteur pipette. A quantity of 3 mL of n-Hexane was added into the centrifugal tube for re-partitioning as described above. The new overhead organic phase was added to the test tube and volume was decreased with gentle N_2 flow to 0.5–1 mL approximately.

2.4.2 *Silica gel/sulphuric acid column*

Conc. H_2SO_4 was mixed with activated silica gel (1 : 2, w/w) by rotating until no lumps were left. A quantity of 1 g of this mixture was transferred into a Pasteur pipette, containing silylated glass wool in the bottom. Approximately 2 g of recently activated Cu were added on top of the column (Copper powder was activated with HCl and rinsed subsequently with H_2O, acetone and dichloromethane, and placed in a 60°C oven to dry). The column was then washed with 5–10 mL of n-Hexane. The extract from the sulphuric acid treatment was transferred onto the column, using a Pasteur pipette. A quantity of 1–2 mL of n-Hexane was added into the test tube and after vortex mixing, it was added into the column as well.

The compounds were eluted with 10–15 mL n-Hexane and collected into a test tube. Volume was once more decreased with gentle N_2 flow to 0.5–1 mL approximately. A second Pasteur pipette column, containing only activated silica gel, was prepared and washed as described above. The extract was transferred to the column as above and eluted with 3–4 mL n-Hexane collected as first fraction and 6–7 mL dichloromethane (DCM) as second fraction. The solvent of the second fraction was changed to n-Hexane; volume was reduced to 50 µL, spiked with BDE-138, sealed in vials and analysed in GC-MS.

For clearer and faster phase separation a Hettich zentrifugen Universal 16A centrifuge was used. For solvent evaporation a centrifugal concentrator was used, Buchi rotevaporator R-3000 & Vacuum controller B-720.

2.5 *Instrumental analysis*

Analysis was performed with gas chromatography/mass spectrometry (GC/MS) utilising a Finnigan MAT SSQ710 instrument (Thermo Fischer Scientific, San Jose, CA, USA) connected to a Varian 3400 gas chromatograph equipped with a CTC A200S autosampler. The transfer line temperature was set to 290°C, and the ion source temperature was maintained at 200°C. Automated injections of 1 µL were made on a septum-equipped temperature-programmable injector (SPI) fitted with a high-performance insert directly connected to a DB-5 HT capillary column (15 m × 0.25 mm i.d., 0.1 µm film thickness, J&W Scientific, Folsom, CA, USA) with helium as the carrier gas, at a head pressure of 5 psi. The GC oven was programmed as follows: 85°C (1 min), 15°C $\min^{-1}$ to 300°C and then 2°C $\min^{-1}$ to 320°C (5 min). The injector was temperature-programmed from 85°C (0.5 min) to 300°C at 150°C $\min^{-1}$ (20 min).

The PBDE congeners were analysed by the negative ions formed by electron capture reaction at chemical ionisation (ECNI) in the selected ion monitoring (SIM) mode by scanning for the bromine ion isotopes m/z 79 and m/z 81 and for the perbrominated PBDE-209 only, the fragment ions m/z 484.6 and m/z 486.6 corresponding to $[C_6Br_5O]^-$.

Methane (5.0, AGA, Stockholm, Sweden) was used as the electron thermalisation buffer gas at 5.6 Torr and a primary electron energy of 70 eV.

All chromatographic data were collected, analysed, and quantified using the proprietary ICIS2 software from Thermofinnigan.

2.6 *QA/QC*

An analytical blank was processed for every ten samples under the same conditions and procedure for evaluation of possible contamination in the samples. Blank samples were extracted and analysed simultaneously to the environmental samples. The correction of sample concentrations was deemed unnecessary according to blank samples, which presented no significant problems. Sample peaks are reported only if the signal exceeded three times the baseline noise. Limits of detection for individual PBDE congeners (tri- to deca-BDE) ranged from 0.0001 to 0.01 ng g^{-1}, dry weight. A calibration curve was produced by analysis of PBDE standards solutions at 3 concentration levels ranging from 3.35 to 13.5 ng mL^{-1}, in order to calculate relative response factors of the different congeners. Average recovery for surrogates spiked in samples was at 94% (±29.5 SD) for BDE-77. All concentrations are reported in a dry weight basis (dw).

2.7 *Statistical analysis*

For the statistical analysis and evaluation of the experimental data, both parametric and nonparametric methods were applied. As all forms of parametric tests are based on the assumptions that the within-groups data are samples drawn from normally distributed populations with equal variances, both formal tests and graphical displays were performed for assessing departures form normality, while variances were tested for homogeneity using the Levene's test. For accessing the assumptions of normality and stability of variances, data were also transformed to $\log_e$, $\log_{10}$ or sqrt [33].

One-way analysis of variance was used to evaluate possible significant effects of sampling station on the ΣPBDEs, while differences between mean values of specific stations were evaluated using Duncan's new multiple range test.

Spearman rank correlation was also applied to test associations of various congeners.

All analyses were conducted using the statistical software program SPSS for Windows (v. 15.0). Significance was declared at $P \leq 0.05$, unless otherwise noted. Back-transformed mean values are reported in the results.

3. Results and discussion

3.1 *PBDE concentrations – potential point sources*

The analysis of all sediment samples collected showed that PBDEs were present in all of the aforementioned sampling sites, attesting that these pollutants are not foreign to the northern Greek marine environment. Mean ΣPBDE (sum of 9 BDE congeners, namely BDE-28, −47, −99, −100, −153, −154, −183, −190 and −209) concentrations ranged from 0.259 to 4.917 ng g^{-1} calculated on dry weight basis (Table 1). Higher concentrations were observed in stations S2 and S5, followed by station S1. These three locations outline the internal part of Thermaikos Gulf, the one more heavily affected by human activity. The highest concentrations of ΣPBDEs were measured in sampling station S2 (4.917 ± 1.937 ng g^{-1}). It is a location where Thessaloniki's industrial zone, in combination with the municipal wastewater treatment plant's disposal pipe shows a considerable impact on PBDE levels. It should be noted that the disposal pipe originates from a second degree urban wastewater treatment plant. Moreover, the existence of textile and dyes factories in the area could suggest the use of deca-BDE formulations. Relatively high concentrations were observed in station S5 (2.533 ± 1.344) as well. These concentrations strengthen the suspicion of a possible direct influence from the city's non-sanitary landfill (Table 1). It is possible, that waste material is washed out with rainwater, causing leakage through small streams, ending up in Anthemountas Stream, which flows into the gulf. Sampling station's S1 concentration (1.100 ± 0.327), although lower than S2 and S5, underlines the effects of the harbour activities, as well as urban activities of the city of Thessaloniki. Sampling station S3 shows low concentrations (0.503 ± 0.117), influenced primarily from polluted solid material produced by rural activities and transferred through the rivers of Axios and Aliakmonas to reach their estuaries and be deposited into the gulf. As already noted, in the area surrounding station S3 there are extensive mussel cultures, which could potentially affect sediment concentrations. According to other studies [34,35], there could be a connection between bivalve and sediment pollution with PBDEs. Stations S6 and S7 are also showing low concentrations (0.305 ± 0.078 and 0.406 ± 0.121 respectively). They are locations surrounded by suburban areas, with less human activities than the inner part of the gulf area. S8 has the lowest concentrations (0.259 ± 0.080), yet the presence of PBDEs does not qualify Station S8 as a reference station, as was originally intended. Explanation lies in gulf currents transporting solid material, especially from the river estuaries.

Statistical analysis demonstrates statistically significant differences between sampling stations. Table 1 marks these differences in concentrations between the stations. Station S2 shows no significant difference with S5, unlike with all other stations. Subsequently, station S5 shows no significant difference with station S1. The rest of the stations (S1, S3, S6, S7, and S8) bear no statistically significant difference between them.

3.2 *PBDE congener profile*

Table 2 shows the congener profiles and concentrations of the PBDE congeners. Congeners that were not detected (under limit of detection) are not included in calculations. Dominance of BDE-209 in all sampling stations is evident; its contribution in ΣPBDEs ranges from 58% to 97%. The resemblance between ΣPBDEs and BDE-209 is apparent in Figure 2. In theory, such a distribution could be attributed to production and/or usage of industrial deca-BDE mixtures focused on deca-BDE formulations. However, given the lack of heavy industrial presence in the area, only a small part of BDE-209 concentrations could tentatively be attributed to usage of industrial deca-BDE mixtures. Commercial products (i.e. plastics, textiles, electrical equipment) usage and/or disposal possibly accounts for the major part of BDE-209 concentrations. As sediment is considered the end-reservoir of pollutants in the environment, individual congener levels can also be affected by numerous processes that occur during the transfer of PBDEs from source to the marine environment. Such processes could be evaporation, photolysis, biodegradation, atmospheric deposition, sedimentation, water mixing, etc. It has been reported that over 95% of the atmospheric removal of BDE-209 derives from wet and dry deposition, while photolysis in the presence of UV light leads to degradation and lower brominated BDEs and brominated dibenzofurans [26,36]. Photolytic processes are also responsible for ~90% of the removal of gas-phase congeners such as BDE-47 [37]. Taking into account the different physicochemical properties of the various congeners, that lead to different effects from environmental processes, it is apparent that their composition profiles may be significantly altered compared to their initial source. The remaining congeners without BDE-209 are in fairly low concentrations. BDE-209 concentration was higher at stations S2, S5 and S7 compared to other stations. However, the lower levels in stations S1 and S3, in comparison to S6, S7 and even S8, which originally was intended to be a reference station, should be noted. In nearly all sediment samples there is a decrease in concentration levels, which follows the pattern BDE-209 ≫ BDE-47 > BDE-99 > BDE-100 > BDE-28 > BDE-153/BDE-154 > BDE-183. It is already known that heavily brominated congeners tend to associate with sediment and organic matter. On the other hand, less brominated congeners are more volatile and more susceptible to dissolve in water than the heavily brominated ones [38,39]. BDE-47 contribution ranges from 1.3% to 28.6%. This could pinpoint the use of commercial penta-BDE mixtures as the part in these products of BDE-47 is around 37% [40]. BDE-99 percentages are between 0.6% and 9.9%, far lower than the corresponding commercial product (45%). A percentage of the lower brominated analytes, such as tetra- to hexa-BDEs, can also be attributed to gradual debromination of higher brominated congeners in the environment, as pointed out in other studies [27,41]. However, the complexity of the congener patterns attest to multiple potential factors affecting PBDEs concentrations. Such factors can be environmental

Table 2. PBDE congener profile and mean concentration levels (ng g^{-1} d.w.) in sediment.

Sampl. St.	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-190	BDE-209	ΣPBDEs	ΣPBDEs (BDE-209 excl.)
S1	0.005	0.053	0.018	0.004	0.002	0.001	0.002	0.001	1.015	1.100	0.085
	(0.4%)	(4.8%)	(1.7%)	(0.4%)	(0.2%)	(0.1%)	(0.1%)	(0.1%)	(92.3%)		(7.7%)
	[0.001]	[0.009]	[0.005]	[0.002]	[0.001]	[0.001]	[0.001]	[0.000]	[0.302]	[0.342]	[0.027]
S2	0.005	0.065	0.030	0.015	0.007	0.012	0.013	0.000	4.770	4.917	0.147
	(0.1%)	(1.3%)	(0.6%)	(0.3%)	(0.1%)	(0.2%)	(0.3%)	(0.0%)	(97.0%)		(3.0%)
	[0.002]	[0.034]	[0.018]	[0.008]	[0.002]	[0.003]	[0.001]	[0.000]	[2.390]	[2.513]	[0.078]
S3	0.003	0.034	0.010	0.004	0.001	0.001	0.001	0.000	0.449	0.503	0.055
	(0.7%)	(6.8%)	(2.0%)	(0.8%)	(0.2%)	(0.2%)	(0.2%)	(0.1%)	(89.1%)		(10.9%)
	[0.001]	[0.010]	[0.005]	[0.002]	[0.001]	[0.001]	[0.000]	[0.000]	[0.261]	[0.305]	[0.024]
S5	0.008	0.070	0.061	0.009	0.003	0.003	0.003	0.001	2.376	2.533	0.157
	(0.3%)	(2.8%)	(2.4%)	(0.4%)	(0.1%)	(0.1%)	(0.1%)	(0.0%)	(93.8%)		(6.2%)
	[0.003]	[0.029]	[0.040]	[0.003]	[0.001]	[0.001]	[0.002]	[0.001]	[1.134]	[1.442]	[0.100]
S6	0.004	0.065	0.033	0.008	0.001	0.002	0.001	0.001	0.218	0.334	0.116
	(1.3%)	(19.5%)	(9.9%)	(2.5%)	(0.4%)	(0.5%)	(0.5%)	(0.2%)	(65.3%)		(34.7%)
	[0.001]	[0.037]	[0.020]	[0.006]	[0.001]	[0.001]	[0.001]	[0.001]	[0.132]	[0.288]	[0.073]
S7	0.004	0.050	0.018	0.005	0.004	0.002	0.073	0.002	0.215	0.372	0.157
	(1.1%)	(13.5%)	(4.7%)	(1.2%)	(1.2%)	(0.6%)	(19.5%)	(0.4%)	(57.7%)		(42.3%)
	[0.001]	[0.013]	[0.006]	[0.002]	[0.001]	[0.001]	[0.005]	[0.001]	[0.091]	[0.171]	[0.039]
S8	0.006	0.074	0.018	0.005	0.002	0.001	0.001	0.000	0.152	0.259	0.107
	(2.5%)	(28.6%)	(6.8%)	(1.8%)	(0.6%)	(0.5%)	(0.5%)	(0.1%)	(58.7%)		(41.3%)
	[0.002]	[0.018]	[0.005]	[0.002]	[0.001]	[0.001]	[0.001]	[0.000]	[0.072]	[0.124]	[0.037]

Notes: Percentages in parentheses are of mean values.
Square bracket values stand for geometric means

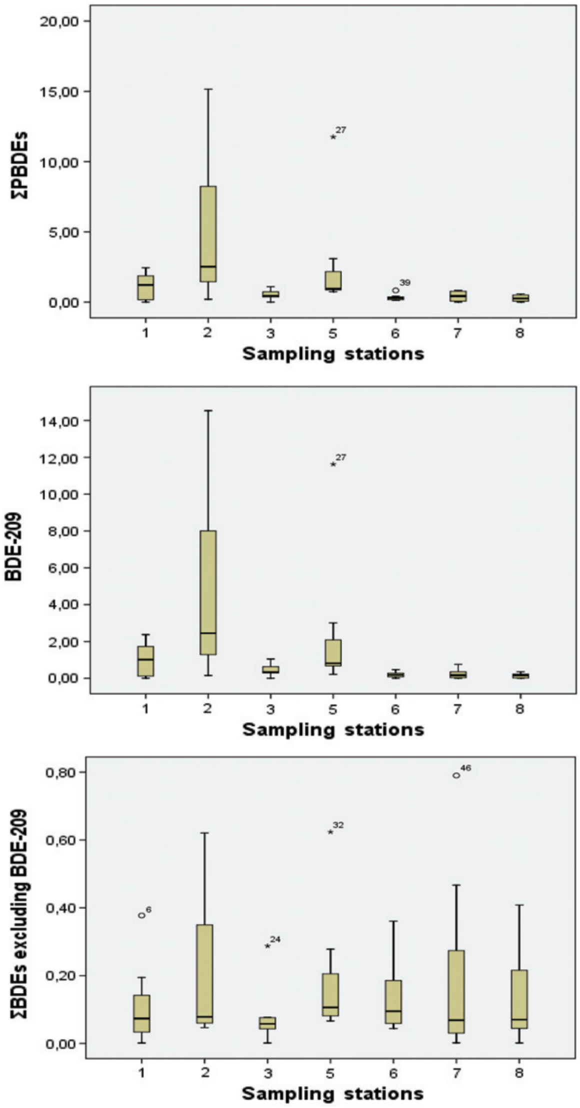

Figure 2. Boxplots of ΣPBDEs, BDE-209 and ΣPBDEs excluding BDE-209 respectively, according to sampling stations.

degradation as mentioned above, accumulation and/or dispersion patterns of PBDEs in marine sediment, metabolism by benthic organisms and different source compositions.

Spearman correlation analyses are performed for all PBDE congeners of different sediment sample intervals, to investigate potential sources and spatial distribution, also taking into account geographical data, e.g. distance to potential sources, water current circulation. The Spearman correlation coefficients among these congeners are shown in Table 3. Significant correlations exist among BDEs 47, 99, 100, 153 and 154. High correlations are recorded also between BDE-183 and BDE-154 ($r = 0.382$, $p < 0.01$), BDE-190 and BDE-183 ($r = 0.456$, $p < 0.01$), and interestingly between BDE-209 and BDE-99

Table 3. Spearman correlation coefficients among PBDE congeners in sediment.

	BDE28	BDE47	BDE99	BDE100	BDE153	BDE154	BDE183	BDE190	BDE209
BDE28	1								
BDE47	0.203	1							
BDE99	0.260	0.819[b]	1						
BDE100	0.135	0.815[b]	0.720[b]	1					
BDE153	0.133	0.696[b]	0.668[b]	0.656[b]	1				
BDE154	0.130	0.505[b]	0.536[b]	0.680[b]	0.729[b]	1			
BDE183	0.070	0.191	0.269[a]	0.135	0.314[a]	0.382[b]	1		
BDE190	−0.281[a]	0.074	0.111	−0.007	0.033	−0.044	0.456[b]	1	
BDE209	−0.109	0.242	0.442[b]	0.328[a]	0.206	0.217	0.070	0.059	1

[a] Correlation is significant at the 0.05 level (2-tailed).
[b] Correlation is significant at the 0.01 level (2-tailed).

($r = 0.442$, $p < 0.01$). BDE-28 shows no correlation to any other congener, except a moderate one with BDE-190 ($r = -0.281$, $p < 0.05$). Higher brominated BDEs, like BDE-209 show no significant correlation with lower brominated congeners, except BDE-99 and a moderate correlation with BDE-100 ($r = 0.328$, $p < 0.05$), while BDE-190 correlated well with BDE-183. BDE-183 shows moderate correlations with BDE-153 ($r = 0.314$, $p < 0.05$) and BDE-99 ($r = 0.269$, $p < 0.05$), and high correlations with BDE-154 and BDE-190. The pattern leads toward the conclusion that the sources for the pollution of the aquatic environment with lower brominated BDEs and the higher brominated ones are not the same. Another reason could be the differences in partitioning and environmental behavior between these congeners. Such patterns are in accordance with other studies [35,42].

3.3 *Comparison with other international studies*

A comparison of the concentrations found in the present study and concentrations reported from several other countries in sediment around the globe is presented in Table 4. The number of congeners analysed varies in each study, and there are other factors such as analytical techniques or sampling procedure that may affect the final outcome, and thus restrict the comparison between studies. However, certain BDE congeners, such as 47, 99, 100, 153, 154, 190 and 209 are included in most studies.

The predominance of BDE-209 over the rest of the BDE congeners is reported in several other surveys around the world as shown in Table 4. This probably lies on the fact that most PBDE products and usage around the globe are industrial deca-BDE mixtures [6,43]. Stations S2, S5 and S1 exhibit the highest BDE-209 concentrations and percentages among all other congeners. However, they are still the lowest compared to most other studies, except Romania where BDE-209 was not detected, or certain sampling sites in China, Hong Kong, Korea where there were similarly low concentrations. The sum of PBDE concentrations, excluding BDE-209, are likewise on the lowest level compared to nearly all other studies.

According to de Wit [4] there is an influence of heavily industrialized and urban areas on contamination of marine and river sediment. Congener profiles are in accordance with most other studies. When BDE-209 is excluded, congeners BDE-47, −99, and −100 account for higher percentages than the rest. Small fluctuations in congener concentrations

Table 4. Comparison of PBDE concentrations (ng g^{-1} d.w.) in sediment measured in this study with concentrations from other locations worldwide.

Location. Country	n	ΣPBDE excl. 209	BDE209	Sampling year	References
Thermaikos Gulf	9	0.06–0.16	0.15–4.77	2005–2007	This study
The Netherlands	5	0.6–17.6	4–510	2001	[48]
Pearl River Delta. China	9	0.04–94.7	0.4–7341	2002	[11]
Japan	7	0.013–2.39		2000	[49]
China and Hong Kong	14	7.9–9322.9	6.0–35.9	2004	[50]
Hong Kong	14	0.96–58.5	nd–2.92	2004	[34]
Korea	20	0.03–6.87	0.22–2253	2003–2004	[35, 42 and 47]
Niagara River. USA	9	nd–148		2003	[51]
Spain	11	0.24–3.94	2.46–132	2002	[27]
Australia	26	800[a]	305[a]	2002–2003	[52]
Romania		nd	nd	2001	[53]
Laizhou Bay. China	11	1.3–24.7	nd–1800	2007	[54]
Kuwait	3	0.08–3.7			[55]
Portugal	17	0.5–20		2000	[56]
Lake Superior. Great Lakes. USA	9	0.5–3.0	4–17	2001–2002	[46]
Lake Michigan. Great Lakes. USA	9	1.7–4.0	43.9–95.6	2002	[57]
Lake Huron. Great Lakes. USA		1.0–1.9	21.5–36.0	2002	[57]
Lake Ontario. Great Lakes. USA	9	4.85–6.33	211–242	2002	[58]
Lake Erie. Great Lakes. USA	9	1.83–1.95	50.2–55.4	2002	[58]

n = number of PBDE congener analysed in sediment samples.
nd = not detected.
[a] = median concentration.

between different studies could be attributed to different types of commercial BDE formulations used in different locations, or fractionation of the congeners which occurs during their transport in the environment and partitioning in environmental media or surfaces due to their different physicochemical properties [44].

In general, PBDEs levels found in this study are considered to be low and Thermaikos Gulf is among low-polluted areas in comparison with other studied areas from around the world, concerning PBDEs. Atmospheric deposition is considered to be an important route of aquatic sediment pollution with PBDEs [45–47]. The low levels of PBDEs measured in this study could suggest atmospheric deposition to be one of the main input sources. However, uneven spatial distribution and congener profiles of PBDEs concentrations show influence from terrestrial input sources. Specific ongoing point sources of pollution could not be established; future studies of possible point sources will hopefully lead towards a more definite source apportionment of PBDEs in the area. Correlations between congeners suggested non-point sources of contamination. The actual reasons for the low concentrations may be due to small usage of these substances in the area. This research is ongoing and will be extended to living organisms such as mussels and benthic species of fish.

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