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Use of passive samplers in pollution monitoring: A numerical approach for marinas ☆

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ABSTRACT

Triolein-containing semipermeable membrane devices (SPMDs) and butyl rubber (BR) based sorbents were employed as passive samplers in 14 coastal stations of Turkey including shipyards and marinas to characterize time-integrated levels of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) and their relationship to potential pollution sources. Passive samplers of SPMDs and BR sorbents were deployed for 30 days in the spring of 2012. The maximum concentrations of total PAH and PCB compounds sequestered by SPMDs were 3338 ng g^{-1} SPMD and 4247 pg g^{-1} SPMD. (END)-I and DDT-related compounds were dominant OCP compounds for most of the sites in passive samplers. Total PAH concentrations in SPMDs were found 1.2 to 8 times higher than the concentrations in BRs. However, BR sorbents were able to sample some PAHs which could not be sampled by SPMDs. The concentrations of PCBs and OCPs in BRs were similar or higher than SPMDs. SPMD-data were used to estimate the average ambient water concentrations of the contaminants. Two existing theoretical approaches have been used to derive the concentrations of hydrophobic pollutants in the ambient waters. The results were found very similar and range from 7318 to 183864 pg L^{-1} for PAHs, from 2 to 186 pg L^{-1} for PCBs, and from 98 to 848 pg L^{-1} for OCPs. Furthermore, a simple numerical model was designed to estimate the boat-related water concentrations in marinas by using the seawater data supplied by SPMDs. The model was mainly built on the water concentration and the capacities of a particular marina and then applied to two sites in the second marina. A good correlation was found between the model outputs and SPMD-water data.

1. Introduction

Such hydrophobic pollutants as polycyclic aromatic compounds (PAHs) and persistent organic pollutants (POPs) have frequently been identified in several matrices of aquatic ecosystems (Cardellicchio et al., 2007; Okay et al., 2011; Perugini et al., 2007), their lipophilic character often causing their accumulation in sediments and organisms. However, knowledge of the actual concentrations of hydrophobic pollutants in ambient waters is essential for integrated water quality management. Primarily because of their very low, but toxicologically relevant levels in natural waters, direct determination of their water concentrations is almost impossible with normal analytical techniques. Therefore, several passive samplers such as polyoxymethylene (POM) strips (Cornelissen et al., 2005; Perron et al., 2013), silicone rubber (Jacquet et al., 2014; Smedes et al., 2013), low density polyethylene (LDPE) (Allan et al., 2012; Booij et al., 2003) and semi-permeable membrane devices (SPMDs) (Verweij et al., 2004; Wang et al., 2009) have been commonly used in monitoring of organic compounds in aquatic environment. The use of triolein containing SPMDs, spiked with performance reference compounds (PRCs), has been proposed to estimate the bioavailable and time-integrated water concentrations of hydrophobic pollutants (Booij et al., 1998; Huckins et al., 2002). Theoretically, when the SPMD is in equilibrium with its surroundings, the rate of PRC loss is proportional to the rate of contaminant uptake. The accumulation of organic pollutants in SPMDs is a diffusive and partitioning process similar to bioconcentration in marine organisms. However, SPMDs can also be installed to highly polluted waters where use of marine organisms for biomonitoring would be impossible.

In the present study, SPMDs were deployed at 14 stations in five main districts of coastal Turkey during the spring of 2012 and retrieved 30 days later. Furthermore, a butyl rubber (BR) based, polymeric, macroporous sorbent originally developed for oil spill clean-up (Ceylan and Okay, 2007; Doğu and Okay, 2008) was also installed at six of the stations. BR sorbents are hydrophobic, very tough with

☆ This research article is dedicated to the memory of Alec Gaines who passed away unexpectedly. We will all miss him; miss the great person and scientist.

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good resistance to aging and weathering, yet respond rapidly to pollutants (Ceylan and Okay, 2007; Doğu and Okay, 2008). It was recently reported that these sorbents provide a better alternative to the widely used polypropylene sorbents for oil spill clean-up (Ceylan et al., 2009) and remove PAHs efficiently from seawaters.

The principal objective of the present field study is to evaluate the concentrations of organic pollutants (PAHs, PCBs and OCPs) in Turkish coastal waters estimated from SPMD data using two similar methods devised by Huckins et al. (2006) and Booij and Smedes (2010). At the same time, this paper is the first report on the application of BR sorbents as passive samplers, their behavior as sequestering agents being compared with the performance of SPMDs. The results on the removal rates of model PAH compounds (acenaphthene and pyrene) in a research study performed by Ceylan et al. (2009) were very promising about the usage of those sorbents as passive samplers. The requirement to monitor organic compounds that are included in the European Water Framework Directive in natural waters for the European Union (EU) member states as well as candidate states to EU have been leading to the development of such passive samplers by different researches from several countries. This first study with BR sorbents, especially when the accumulation performance of organic pollutants were compared with SPMDs, encourages further research into the effectiveness of those sorbents to determine the water concentrations by PRC spiking.

Marinas and recreational boating are not one of the major pollution sources to coastal waters, however, there is still a strong potential for marina waters to become polluted with the chemicals produced from the various activities occurring at marinas. If the pollution prevention practices in marinas are poor or inadequate, the water quality might be deteriorated. The growth of recreational boating in coastal areas has led to an increased awareness of the need of our waterways—such as boat cleaning, fueling operations and marine head discharge—or from the entry of stormwater runoff from parking lots and hull maintenance and repair areas into marina basins. Monitoring and modeling studies in coastal areas together help to determine the present situation as well as to predict the changes that may occur in time. Therefore, in this study, a simple numerical model has been developed for marinas permitting estimation of the boat-related pollutant concentrations by using the monitoring data. The model may be used for management purposes by marina owners as well as governmental institutions.

The five main Turkish coastal sites investigated in this study consisted of two marinas, one in the Marmara Sea and the other in the Mediterranean, stations at Tuzla/Istanbul (the main shipyard region in Marmara Sea), Saros Bay (SB) (North Aegean Sea) and the Çanakkale Strait (ÇS). Shipyards and marinas may pose concerns because of the presence of several toxic chemicals generated by the various activities (Chiu et al., 2006; Kim et al., 2011; Marcus et al., 1988; US EPA, 1997). Both shipyards and marinas are generally located in semi-enclosed coastal areas, thereby generating a strong potential for pollutants to concentrate in their water and/or sediments. The shipbuilding industry and its main ship-repair sector are considered to be one of Turkey's most promising industrial sectors and have developed significantly in recent years (OECD, 2011). Boating and yacht tourism has been growing throughout the whole Mediterranean region (Cassi et al., 2008); marina capacity in Turkey has almost doubled during the past decade (Barlas, 2010; Genç and Güler, 2006).

2. Materials and methods

2.1. Study area

Pollution concentrations were determined during Spring 2012 at 14 stations in 5 major sites of coastal Turkey (Fig. 1): three stations in Saros Bay, SB, North Aegean Sea; one station in the Çanakkale Strait, ÇS, connecting the Aegean Sea to the Marmara Sea; four stations, S, near Tuzla, Istanbul, the major shipbuilding region in Turkey, and six marina stations in the Mediterranean, M1, and Marmara, M2, seas.

2.2. Passive samplers

SPMDs approximately 65 μm thick, were cut from 'lay-flat', low-density polyethylene tubing (VWR Ismaning, Germany) and then placed in a glove-box flushed with nitrogen to ensure the absence of air and all contaminants. The central 115 cm^2 area of each SPMD was filled with 700 μL of triolein (Sigma, Munich, Germany, 99%) spiked with a toluene solution (5 ng per μL) of the following isotopically labeled reference compounds, RC: Naphthalene-$^{13}C_6$, Acenaphthylene-$^{13}C_6$, Acenaphthene-$^{13}C_6$, Fluorene-$^{13}C_6$, Phenanthrene-$^{13}C_6$, Anthracene-$^{13}C_6$, Fluoranthene-$^{13}C_6$, Pyrene-$^{13}C_3$, Benz(a)anthracene-$^{13}C_6$, Chrysene-$^{13}C_6$, Benzo(b)fluoranthene-$^{13}C_6$, Benzo(k)fluoranthene-$^{13}C_6$, Benzo(a)pyrene-$^{13}C_4$, Indeno(1,2,3-cd)pyrene-$^{13}C_6$, Benzo(ghi)perylene-$^{13}C_{12}$, Dibenz(a,h)anthracene-$^{13}C_6$.

The RC solution was added by capillary pipette as closely as possible to the heat-sealed bottom of the SPMD to give a final concentration of 0.32 μL per g of triolein. A second heat-seal, applied 23 cm from the first, ensured there could be no subsequent flow of spiked triolein. Loops for mounting the SPMDs were constructed from two further heat-seals at the empty ends of the tubing. The prepared SPMDs were placed in heat-cleaned 10 mL glass vials that were then tightly sealed with aluminum.

Sheets of passive sorbents, BR, having the same dimensions as the SPMDs were also cut from butyl rubber containing 2.3 mol% isoprene units (Butyl 365, Exxon Chemical Co.). The rubber was cross-linked with sulfur mono chloride, S_2Cl_2, according to the procedure described in Ceylan and Okay (2007) and Doğu and Okay (2008). These sorbents were wrapped in aluminum foil and stored at −20 °C similarly to the SPMDs. Performance reference compounds were not spiked in butyl rubber sorbents.

2.3. Deployment of passive samplers

At the stations, passive samplers were placed into stainless steel cages which were completely submerged vertically in the water column (0.5–1.0 m depth). The cages were secured to a fixed point on the shore or on the sea bottom using cables/ropes depending on the properties of the sites. A cage with passive samplers and deployment method can be seen in Fig. S1.

After 30 days, the samplers were collected and washed with ambient sea water to remove all obvious contaminants from their surface. They were then transferred to ice-filled boxes and stored in the laboratory at −20 °C until analysis. Transportation blanks from each site were stored in the dark in the absence of air.

2.4. Extraction analysis and quantification

Before analysis, passive samplers collected from the sites and blanks were cut into small pieces. SPMD pieces were extracted overnight with 100 mL of cyclohexane containing relevant concentrations of standards (Dr. Ehrenstorfer, Germany) in a 250 mL Erlenmeyer flask rotating at 200 rpm in a constant temperature shaker. The pieces of BR were mixed with diatomaceous earth (Separtis, Germany) and the standards are rapidly extracted (DIONEX ASE 200). The 10 minute extraction with 75:25 v/v hexane: acetone at 120 °C and 120 bar was repeated twice.

The quantification criteria included confirmation of retention times and isotope ratios of the labeled standards and respective analytes. Internal standards in nonane for PAHs were: PAHs: Naphthalene-D8, Acenaphthylene-D8, Acenaphthene-D10, Fluorene-D10, Phenanthrene-D10, Anthracene-D10, Fluoranthene-D10, Pyrene-D10, Benzo(a)anthracene-D12, Chrysene-D12, Benzo(b)fluoranthene-D12, Benzo(k)fluoranthene-D12,Benzo(a)pyrene-D12, Indeno(1,2,3-cd)pyrene-D12, Benzo(ghi)-perylene-D12, Dibenzo(a,h)anthracene-D14 PCBs: IUPAC nos. 28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 180, 189. OCPs: Pentachlorobenzene-$^{13}C_6$,

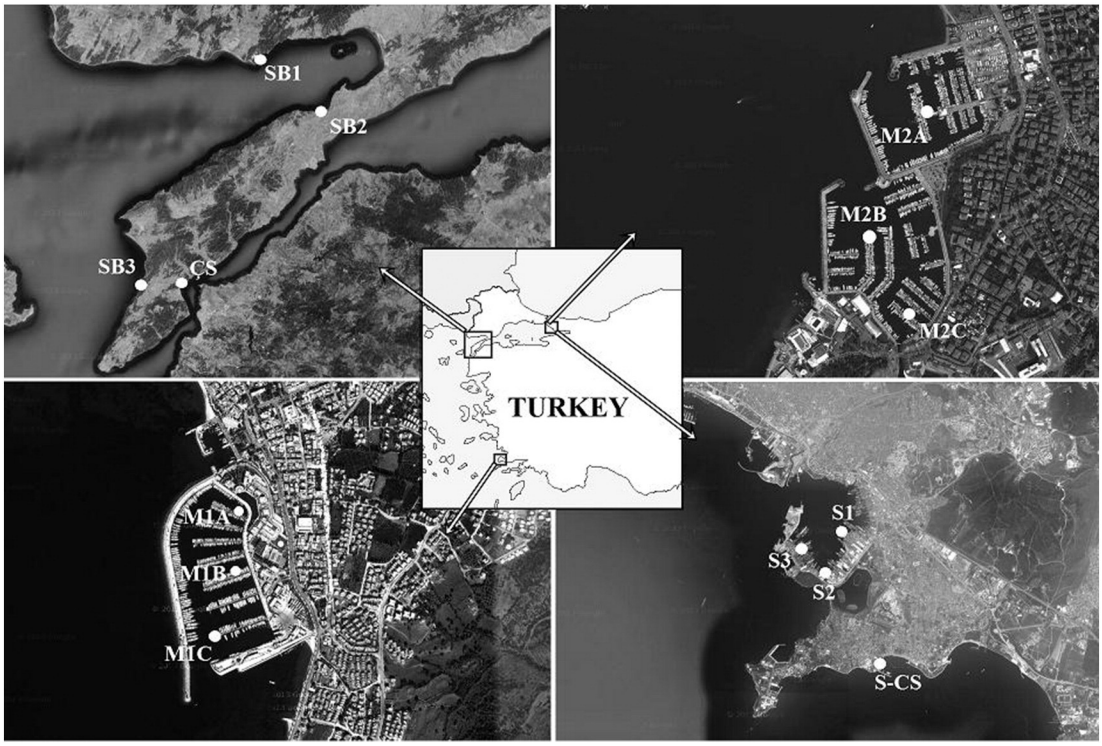

Fig. 1. Sampling stations; SB Saros Bay; CS Çanakkale Strait; M1 Marina-Mediterranean; M2 Marina-Marmara Sea; S Shipyard area.

alpha-HCH-$^{13}C_6$, gamma-HCH-$^{13}C_6$, beta-HCH-$^{13}C_6$, delta-HCH-$^{13}C_6$, Pentachloroanisole-$^{13}C_6$, Hexachlorobenzene-$^{13}C_6$, Heptachlor-$^{13}C_{10}$, Aldrin-$^{13}C_{12}$, Octachlorostyrene-$^{13}C_6$, *oxy*-Chlordane-$^{13}C_{10}$, Heptachlorepoxide-$^{13}C_{10}$, 2,4′-DDE-$^{13}C_{12}$, 4,4′-DDE-$^{13}C_{12}$, *trans*-Chlordane-$^{13}C_{12}$, Endosulfan-I-$^{13}C_9$, Endosulfan-II-$^{13}C_9$, 4,4′-DDD-D8, Dieldrin-$^{13}C_{12}$, 2,4′-DDT-$^{13}C_{12}$, 4,4′-DDT-$^{13}C_{12}$, Methoxychlor-$^{13}C_{12}$, Mirex-$^{13}C_{10}$.

To obtain a calibration by using PRC compounds, first, PRC concentrations in SPMD-production blank and in deployed SPMDs were quantified, then the PRC concentration in the deployed SPMDs was corrected by using the production blank PRC data. A two-point derivation was used to calculate the elimination rate assuming first order kinetics (Eq. (1)) (Huckins et al, 2002)

$$k_{e-PRC} = \ln(C_{SPMD-0}/C_{SPMD})/t \quad (1)$$

where, $k_{e\text{-}PRC}$ is the elimination rate for the PRC, $C_{SPMD\text{-}0}$ is the initial PRC concentration in SPMD (concentration in the production blank), C_{SPMD} is the PRC concentration in deployed SPMD corrected by using production blank in the retrieved SPMD, and t is the exposure time in days.

For analysis, all extracts were diluted with a 100 mL of 1:1 n-hexane and dichloromethane mixture and then reduced to 1 mL. These residues were further purified by acetonitrile elution through a C18 SPE cartridge. After adding a recovery standard, extracts were concentrated to 20 μL using a gentle flow of nitrogen. The dried (anhydrous sodium sulfate and cyclohexane) organic phase of the SPMD extracts was removed in a vacuum rotary evaporator so as to isolate the triolein residues. The triolein was re-dissolved in 1–2 mL of a (1:1) *n*-hexane: dichloromethane mixture. Solutions from both SPMD and BR passive samplers were purified using a mixed column (silica gel from Wesel Germany, grade 60; 3 cm diameter column containing, from the bottom upward, 10 g silica, 5 g alumina with 3% H_2O, and 5 g anhydrous sodium sulfate).

The purified extracts were analyzed by gas chromatography (Agilent GC6890; Agilent Technologies, Palo Alto, California)–high resolution mass spectrometry (Finnegan MAT 95S; Thermo Electron Gmbh, Bremen, Germany) using ^{13}C isotope dilution for quantification of the concentrations of extracted chemicals. The analyses followed accredited DIN EN ISO/IEC 17025 procedures, all operations being regularly validated by analysis of standard reference compounds which were confirmed by inter-laboratory comparison. Mass fragments possessing the highest intensities of the molecular or fragment ion cluster were used for quantification. Concentrations were calculated by comparison of the signal height of the analyte with its respective labeled analog. Laboratory blanks and control samples, QC, were analyzed between every 5–10 samples. The results of the blanks were subtracted from the environmental samples. Concentrations less than the blanks by a factor of about 2 were abandoned. The recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD for PCB, Pentachlorotoluene and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD for OCP and PAH) was used for the calculation of the recoveries of the labeled internal standards. The mean recoveries for PAH, PCB and OCP were in the ranges of 25%–110%, 30%–90% and 30%–130%, respectively. The three-time signal/noise ratio was set as the limit of detection.

3. Results and discussion

3.1. Pollutant concentrations in passive samplers

3.1.1. PAHs in SPMDs

Tables 1a, 1b and 1c show the individual concentrations of PAHs, PCBs and OCPs respectively collected in 30 days by SPMDs in the 14 stations in the five coastal regions. No station showed significant differences between duplicate SPMDs. All the PAH concentrations confirm the importance of the local anthropogenic activity in determining their magnitude. Total PAH concentrations (Table 1a) varied between 36 and 3338 ng g^{-1} SPMD and, consistent with an earlier study (Karacık et al., 2009), the maximum total PAH concentration, approximately 8 to 90 times greater than total PAH concentrations determined at the other 13 stations, was observed at a busy shipyard, station S3. Conversely, the lowest total PAH concentrations, between 36 and 72 ng g^{-1} SPMD, were observed far from any extensive

Table 1a
Mean concentrations of organic compounds in SPMDs deployed to the Turkey coastal waters for a 30-day exposure period; (PAHs; pg g^{-1} SPMD; C-PAH: Carcinogenic PAHs; TEQ_{BaP}: BaP based Toxic Equivalent Value).

PAH[a]	SB1	SB2	SB3	CS	M1A	M1B	M1C	M2A	M2B	M2C	S1	S2	S3	S-CS
NaP	nd[b]	3333	4991	3435	6132	18,263	13,921	33,455	28,651	38,169	3247	36,984	62,582	35,385
ACL	496	690	192	792	4910	6795	8449	4863	7720	19,493	2280	3735	2073	7648
AC	327	454	339	746	979	3313	2145	2050	3043	4551	24,795	18,982	14,1757	4074
FL	4746	6115	4717	5138	8199	16,787	14,126	4480	11,025	19,127	18,949	14,671	11,4004	19,818
PHE	15,324	26,768	17,159	28,973	27,283	57,372	54,522	33,971	66,116	86,233	57,162	51,708	41,9844	84,227
AN	571	1591	721	1733	2411	6408	5411	8926	8527	10,908	14,277	12,452	97,815	3739
FA	9560	16,988	10,582	22,551	13,769	17,098	27,670	146,337	107,841	91,407	140,625	104,624	844,430	42,728
PY	1458	8008	1642	12,872	9379	18,517	17,600	120,243	71,133	61,607	99,274	104,688	925,267	13,116
BaA	274	770	590	2039	483	574	1305	8955	5722	4465	7357	13,743	139,595	794
CHR	2312	4440	2572	5918	2421	3278	4368	17,433	11,551	8864	19,139	43,285	218,378	2975
BbFa/BjFA	597	1098	979	2390	468	389	1371	8621	3583	4040	3721	9453	72,751	569
BkFA	386	658	586	1633	396	390	1310	2975	1779	1223	2862	6082	47,293	275
BaP	177	349	309	1028	201	172	1173	2682	1344	987	1935	3960	201,543	89
IP	256	379	457	750	238	140	931	1069	895	477	376	1088	17,722	495
BghiP	215	328	404	648	255	167	772	2782	1940	911	120	826	27,258	631
DBahA	49	51	97	143	38	26	196	223	117	45	133	227	5785	110
Total PAH	36,747	72,021	46,339	90,790	77,561	149,689	155,271	399,064	330,986	352,508	396,253	426,507	333,8098	216,672
C-PAH	4050	7745	5591	13.902	4244	4969	10.653	41.959	24,991	20,101	35,524	77,838	703,068	5306.6
C-PAH %	11	11	12	15	5.5	3.3	6.9	11	7.6	5.7	9.0	18	21	2.4
TEQ_{BaP}	356	689	606	1783	388	357	1728	5040	2669	2101	3571	7452	232,041	343

[a] Naphthalene: NAP; Acenaphthylene: ACL; Acenaphthene: AC; Fluorene: FL; Phenanthrene: PHE; Anthracene: AN; Fluoranthene: FA; Pyrene: PY; Benzo(a)anthracene: BaA; Chrysene: CHR; Benzo(b)fluoranthene, Benzo(j)fluoranthene: BbFA, BjFA; Benzo(k)fluoranthene: BkFA; Benzo(a)pyrene: BaP; Indeno(1,2,3-c,d)pyrene: IP; Benzo(g,h,i)perylene: BghiP; Dibenzo(a,h)anthracene: DBahA.
[b] nd: not detected.

anthropogenic activity at stations SB in Saros Bay. Higher total PAH concentrations were observed at station M1 on the Mediterranean coast than at site M2 by the Marmara Sea. The Marmara Sea, close to İstanbul, is generally polluted (Karacık et al., 2009; Okay et al., 2011) more highly polluted than the eastern Mediterranean, due to the anthropogenic activities in nearby İstanbul. Station M2, however, is situated in a marina of a small town of summer houses and there is no industrial activity close to the marina.

Table 1a shows the greatest contributions to the PAH concentrations observed in the SPMDs at all stations to have been made by phenanthrene, fluorene, pyrene, fluoranthene and chrysene.

Commonly, anthropogenic sources of PAHs in the marine environment are either petrogenic or pyrogenic. Pyrogenic PAHs are generated by incomplete combustion of organic matter (Wang et al., 1999) whereas petrogenic PAHs arise in marine environments from oil spills, municipal and urban runoff, tanker operations etc. Pyrogenic and petrogenic PAHs may be distinguished by the ratios of the molecular concentrations of PHE/AN, FA/PY and BaA/CHR (Barakat et al., 2011; Benlahcen et al., 1997; Soclo et al., 2000). PAHs generated by pyrolysis of organic matter have generally been formed at higher temperatures than petrogenic PAHs. Accordingly pyrolytic PAHs have been found to have lower PHE/AN ratios and higher FA/PY and BaA/CHR ratios than petrogenic PAHs. Thus, Table 1a reveals PHE/AN ratios of between 17 and 27 in PAHs in SPMDs from SB stations, between 9 and 11 in PAHs derived from M1 stations, between 4 and 8 for PAHs from M2 stations and ~4 for S stations. These values suggest the source of the PAHs

Table 1b
(PCBs; pg g^{-1} SPMD; TEQ; Toxic Equivalent Value).

PCB	SB1	SB2	SB3	ÇS	M1A	M1B	M1C	M2A	M2B	M2C	S1	S2	S3	S-CS
PCB #28	42	68	91	336	22	14	57	487	454	370	973	637	937	475
PCB #52	37	50	88	133	22	12	43	252	192	198	462	419	891	188
PCB #101	nd[a]	nd	nd	nd	21	nd	2.9	128	102	79	130	222	570	104
PCB #138	4.9	nd	nd	nd	4.3	15	nd	72	40	25	90	205	385	nd
PCB #153	nd	36	nd	27	14	32	29	70	25	nd	111	328	471	31
PCB #180	nd	nd	104	26	19	75	nd	nd	nd	nd	64	94	139	nd
T-Indicator PCB	**84**	**155**	**283**	**523**	**102**	**148**	**133**	**1009**	**813**	**672**	**1831**	**1905**	**3393**	**798**
PCB #77	nd	nd	10	nd	12	7.7	23	30	32	24	44	36	83	34
PCB #81	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB #126	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB #169	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
T-non-ortho PCB	**nd**	**nd**	**10**	**nd**	**12**	**7.7**	**23**	**30**	**32**	**24**	**44**	**36**	**83**	**34**
PCB #105	nd	nd	37	23	13	8.6	5.0	37	23	12	39	70	206	18
PCB #114	nd	nd	nd	nd	nd	nd	nd	nd	6.0	2.3	5.7	nd	11	9.1
PCB #118	8.0	27	nd	75	0.8	0.3	14	55	49	25	104	177	467	103
PCB #123	4.9	nd	nd	nd	6.5	nd	nd	16	5.9	9.0	6.8	9.6	nd	8.9
PCB #156	nd	1.9	6.4	9.3	2.3	nd	5.7	6.5	nd	nd	17	25	41	5.7
PCB #157	nd	nd	nd	13	nd	nd	nd	nd	1.5	nd	4.2	5.4	6.9	nd
PCB #167	nd	nd	nd	10	2.7	nd	nd	1.1	nd	nd	18	25	39	23
PCB #189	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
T-mono-ortho PCB	**13**	**29**	**43**	**131**	**26**	**9.0**	**25**	**117**	**85**	**48**	**195**	**312**	**771**	**168**
T- PCB	**97**	**184**	**336**	**654**	**139**	**164**	**181**	**1156**	**930**	**744**	**2070**	**2253**	**4247**	**1000**
TEQ (WHO 1998)	0.001	0.004	0.008	0.021	0.004	0.002	0.007	0.017	0.015	0.008	0.033	0.045	0.105	0.024
TEQ (WHO 2005)	0.000	0.001	0.002	0.004	0.002	0.001	0.003	0.006	0.006	0.004	0.010	0.013	0.031	0.008

[a] nd: not detected.

Table 1c
(OCPs pg g^{-1} SPMD).

OCP[a]	SB3	M1A	M1B	M1C	M2A	M2B	M2C	S1	S2	S3	S-CS
α-HCH	158	nd[b]	nd	36	320	360	362	371	385	367	286
β-HCH	875	nd	nd	74	1182	1468	1545	1218	1230	1317	1010
γ-HCH	nd	nd	nd	nd	nd	nd	nd	28	26	28	38
δ-HCH	nd	nd	nd	8.0	nd	nd	nd	nd	nd	nd	nd
ε-HCH	17	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PeCB	92	87	123	813	159	226	156	582	nd	32	8.0
HCB	371	204	232	438	285	398	308	585	300	856	187
PCA	nd	36	21	42	57	49	60	102	92	95	51
OCS	nd	nd	nd	nd	nd	nd	14	nd	nd	nd	nd
4,4′-DDT	201	97	71	45	333	288	239	87	125	572	17
2,4′-DDT	nd	21	24	14	nd	nd	nd	56	54	224	nd
4,4′-DDD	164	29	44	37	1140	1350	1300	2501	1980	2817	534
2,4′-DDD	55	11	26	28	338	505	419	667	557	809	181
4,4′-DDE	152	101	99	157	502	561	436	588	454	1238	238
2,4′-DDE	10	10	7.0	17	17	43	24	52	42	96	14
t-CHL	nd	nd	nd	nd	20	nd	nd	18	nd	nd	nd
c-CHL	nd	nd	nd	18	25	nd	nd	15	nd	nd	49
OXC	nd	nd	nd	nd	nd	nd	nd	38	nd	nd	21
Heptachlor	nd	nd	nd	nd	4.0	nd	nd	nd	nd	nd	nd
c-HE	85	45	53	46	17	7.0	5.0	63	nd	nd	20
t-HE	nd	nd	nd	nd	28	nd	nd	nd	nd	nd	13
Aldrin	nd	nd	nd	nd	63	40	49	61	21	24	21
Dieldrin	296	63	nd	nd	207	261	238	279	263	230	177
Endrin	nd	nd	nd	48	14	nd	32	31	nd	nd	26
(END)-I	nd	2005	2966	3197	1758	6139	7580	278	1906	356	140
(END)-II	nd	205	596	385	226	732	823	70	259	nd	nd
(END)-S	nd	nd	40	33	14	72	75	22	nd	nd	nd
MOC	24	nd	nd	nd	3.0	nd	nd	40	7.0	198	77
Mirex	nd	nd	nd	nd	3.0	nd	9.0	3.0	nd	nd	nd

[a] Hexachlorocyclohexane (HCH); pentachlorobenzene (PeCB); hexachlorobenzene (HCB); pentachloroanisole (PCA); di-chlorodi-octachlorostyrene (OCS); di-chlorodi-phenyl-trichloroethane (DDT); trans-CHL (t-CHL); cis-chlordance (c-CHL); oxychlordane (OXC); cis-heptachloroepoxide(c-HE); trans-HE (t-HE); endosulfan (END)-I; endosulfan (END)-II; endosulfan sulfate (END)-S; methoxychlor (MOC).
[b] nd: not detected.

observed at each group of stations to have been different and the proportion of pyrolytic PAHs to have increased from SB stations to S stations. Indeed, it is suggested that petrogenic PAHs predominated at the SB, Saros Bay stations and pyrolytic PAHs were clearly dominant in the shipyard, S, stations. It also appears that the PAHs observed at the Mediterranean coast, station M1, contained a higher "petrochemical content" than those from the Marmara marina, stations M2. This would support the contention that the relative absence of industrial activity near the marina has reduced the expected total PAH concentration. Care is needed before accepting these interpretations of the PAH data since the obtained ratios are sometimes inconsistent.

3.1.2. PCBs in SPMDs

Table 1b shows, not surprisingly since PCBs derive more or less directly from human activity, the total concentrations of PCBs in the SPMDs to have been largest where anthropogenic activity was greatest in a similar manner to total PAH concentrations. Thus the total concentrations of PCBs varied markedly from 97 to 4247 pg g^{-1} SPMD and notably, the highest total concentrations were again observed at stations, S, in the active shipyards and the lowest total concentrations were found in the SPMDs situated in Saros Bay, stations SB. Total PCB concentrations were observed to be higher at stations M2 in the Marmara Sea than at stations M1 in the Mediterranean coast, suggesting that the PCB concentrations are more directly linked to anthropogenic activity, notably the anthropogenic activity associated with nearby Istanbul, than the PAH concentrations. At all stations, concentrations of indicator PCBs were higher than the concentrations of either non-ortho or mono ortho-PCBs. Generally the dominant congeners of indicator PCBs were PCB 28 and 52. Among the non-ortho PCBs, only PCB 77 was detected and the dominant congener of mono ortho-PCBs was PCB 118.

3.1.3. OCPs in SPMDs

Table 1c shows the distribution of OCPs differed at each sampling location suggesting different local histories at each site and making it difficult to draw generalized conclusions.

α-HCH and β HCH were the dominant HCH-isomers observed at all stations other than those along the eastern Mediterranean coast, M1, where no HCH isomers were detected. The β-isomer has the highest bioconcentration factors and high resistance to biodegradation among the HCH isomers (Ramesh et al., 1991). HCH and DDT related compounds together contribute for 32–57% at the M2 stations and for 63–81% at the S stations. 4,4′-DDD was the major pollutant detected at shipyard stations. DDT can be biodegraded to DDE and DDD which are not present in technical DDT. 4,4′-DDD and 4,4′-DDE are more stable and persistent than their parent compound. Confirmation of the historical usage of DDT is provided by the values of the (DDD + DDE)/DDT ratio being in excess of 0.5 (Hites and Day, 1992). Δ-HCH, ε-HCH, OCS, t-CHL, c-CHL, OXC, heptachlor, t-HE and mirex in most SPMD samples were undetectable.

Concentrations of HCB were 204–856 pg g^{-1} SPMD, and these two values were recorded at stations of M1A and S3, respectively. HCB is not only used as a fungicide but also released into the environment as a by-product of industrial processes and is formed by combustion (van-Birgelen, 1998). Dieldrin was notably higher in concentration at M2 and S stations than M1 stations. PeCB concentrations were highest at M1C among all other stations. The production and use of pentachlorobenzene has ceased over the last decades, but it is still detected in several matrices of the environment. It is very toxic to aquatic organisms and unintentionally released as a by-product of incomplete combustion (Bailey et al., 2009).

The totals included the largest proportion of END-I observed at marina stations. Although endosulfane was banned in many countries

including Turkey, it is still used extensively in South Asia and few other countries. Those high concentrations measured in marina sites, both in Marmara and Mediterranean seas, indicate the historical usage of END-I in the yachts as an insecticide.

3.1.4. Pollutants in BR sorbents and comparison with SPMDs

Butyl rubber (BR) based polymeric macroporous sorbents improved for cleaning up oil spills were installed as potential passive samplers at six stations, and the concentrations of pollutants these sorbents absorbed were compared with the concentrations absorbed by SPMDs.

The total PAH, PCB and OCP concentrations accumulated in BR sorbents to have ranged between 20 and 2083 ng g^{-1}, 638 and 8306 pg g^{-1}, and 2496 and 17,479 pg g^{-1} respectively. Total PAH concentrations in SPMDs at the same six stations were 1.2 to 8 times higher than the concentrations in BRs. Total PCB and OCP concentrations in BRs were similar/higher than that measured in SPMDs, however. The differences in the assimilation of pollutants by SPMD and BR samplers appears to result from the completely different properties of their matrices; SPMDs are filled with a hydrophobic, liquid absorbent, while BR sorbents are hydrophobic polymers with a highly porous structure that retains the molecules. Fig. 2 shows the ratio of PAH concentrations in SPMD and BR samplers to decrease with an increase in the value of the octanol–water partition coefficient, K_{ow}, of the PAH. BR sorbents cannot retain the lower molecular weight PAH compounds effectively but retain greater concentrations of higher molecular weight PAHs than do SPMDs. The log K_{ow} values of detected PAHs range from 3.37 (NAP) to 6.86 (DBahA). The ratio between the concentrations of individual PAHs in SPMD and BR passive samplers (PAH_{SPMD}/PAH_{BR}) converges to 1 at log K_{ow} values of 5–6 indicating that similar concentrations were sampled by both samplers. This ratio diminishes at higher log K_{ow} values. log K_{ow} values of PCB congeners range from 5.5 to 7.0. Such relatively high values result in generally accumulation of higher concentrations of PCBs in BR samplers, the relative retention of PCBs in BR samplers increasing with the number of chlorine atoms in the molecular structure of the PCBs (Table 2). As a result, heptachlorinated PCBs were not observed in most of the stations, but were readily detected in the BR samplers at the same stations. Total OCP concentrations are higher in BR samplers installed to four stations (M1C, M2C, S1 and S2) than that measured in SPMDs. When the individual OCP concentrations were investigated, it is seen that DDT, chlordane and endosulfane related compounds were generally accumulated at higher concentrations in BRs compared to that retained by SPMDs.

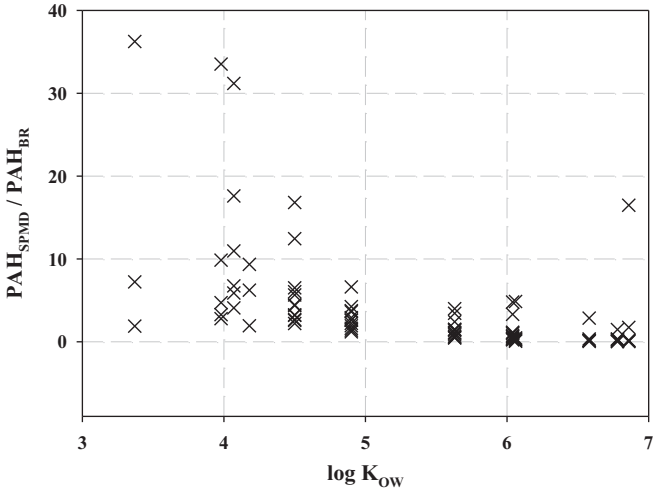

Fig. 2. Change of PAH concentration ratio in SPMDs and BR sorbents with K_{ow} values.

Table 2
The change of PCB concentrations (pg g^{-1}) in SPMD and BR sorbents with number of chlorine atoms in the structure.

Stations-BR						
Cl-number	M1C	M2A	M2C	S1	S3	S-CS
3	149	639	409	2555	903	384
4	97	404	335	1783	808	173
5	134	495	422	1894	1252	187
6	171	476	317	1626	1165	152
7	88	121	72	435	331	40
SPMD						
3	57	487	370	973	637	475
4	66	282	222	506	455	222
5	22	236	127	286	479	243
6	35	150	25	240	588	60
7	nd[a]	nd	nd	64	94	nd

[a] nd: not detected.

3.2. Estimation of hydrophobic pollutant concentrations in the ambient waters

Two existing theoretical approaches have been used to measure the concentrations of hydrophobic pollutants in the ambient waters (Booij and Smedes, 2010; Huckins et al., 2006). Both suppose the concentrations within the SPMDs to be at or near to equilibrium with the corresponding concentrations in the ambient waters, previous work (Karacık et al., 2013) suggesting that with a sampling time of 30 days, this is true. The rate of entry of pollutants into the SPMDs is therefore equal to the rate of dissipation of the isotopic performance reference compounds (PRCs) into the ambient water. The rates varied beween 0.8 and 6.8 L d^{-1}. It is apparent that the turbidity and the rate of flow of the ambient water indeed had a great effect on the dissipation rates. The highest rates of dissipation were observed at ÇS stations where the Çanakale Straits are little more than a km wide and the upper waters flow rapidly from the Black Sea (Oğuz and Sur, 1989). Similarly the lowest dissipation rates were recorded at stations in bays or in marinas where the flow of water is obviously low. Generally, rates of dissipation of the order of 1 L day^{-1} though smaller than previous workers found at turbulent locations with rapid currents (Augulyte and Bergqvist, 2007; Djedjibegovic et al., 2010; McCarthy, 2008; Wang et al., 2009) are similar to dissipation rates observed at less turbulent stations conditions (Harman et al., 2009; Verweij et al., 2004). The reduction of sampling rates may also result from the formation of a muddy layer (fouling) on SPMDs, especially in shallow areas affected by the re-suspension of sediments.

Considering dissipation rates of PRCs at equilibrium state, Huckins et al. (2006) immediately showed that C_W, the concentration of a specified chemical in the ambient water at a sampling station was given by

$$C_{W,SPMD} = \frac{N}{V_S K_{sw}\left(1-e^{-\frac{R_S t}{V_S K_{sw}}}\right)} \quad (2)$$

where N is the measured concentration of the chemical in the SPMD after t days of passive sampling, R_S, the measured rate of sampling, V_S is the volume of the SPMD and K_{sw} is the partition factor between the SPMD and the ambient water. K_{sw} values were calculated by Eq. (3) using K_{ow} values of the compounds (Huckins et al., 2006).

$$\log K_{sw} = a_0 + 2.321 \log K_{ow} - 0.1618 (\log K_{ow})^2 \quad (3)$$

where a_0 is −2.61 for PAHs, PCBs and 4,4′-DDE and −3.20 for polar pesticides.In order to ensure that this straightforward physical model described the observations of passive sampling Huckins et al. (2006), suggested that the model can only be applied to PRCs when their apparent equilibrium retainment in the sampler exceeded 20% and was less than 80%. Accordingly, it was only necessary to consider the observed

SPMD concentrations and sampling rates of fluoranthene and anthracene in the application of Eq. (2).

Booij and Smedes (2010), were reluctant to discard SPMD data obtained at or near to equilibrium when the PRCs experienced retainments below 20% or exceeding 80%. Accordingly, they suggested the use of Eq. (4) rather than Eq. (2).

$$C_W = \frac{N}{K_{SW}\, m \left(1 - e^{-\frac{B\, t}{K_{SW}\, M^{0.47} m}}\right)}. \quad (4)$$

In this equation M is the molecular weight of the PRC, m is the mass of the SPMD, B is an arbitrary constant and the other symbols are identical with those in Eq. (2). The value of B is determined from the best fit of $B/M^{0.47}$ m to R_S/V_S.

Fig. 3a, b and c show the total concentrations in the ambient waters at each station of PAHs, PCBs and OCPs respectively. The individual concentrations of pollutants calculated by two methods are given in supplementary files (Table S1a,b,c and Table S2a,b,c). As one expected Eqs. (2) and (4) both revealed similar concentrations of pollutants in the ambient waters. Thus the total PAH concentrations, C_W, ranged between 0.8 (at station M1A) and 168 (at station S3) ng L^{-1} derived from Eq. (2) but between 0.9 and 184 ng L^{-1} derived from Eq. (2). NAP, PHEN, FA, PYR and FL were observed to make the greatest contributions to the PAH concentrations in the ambient waters. The total PCB concentrations in the station waters, also similar whether derived from Eq. (2) or Eq. (4), were very small at SB stations but rose to their maximum values of 186 pg L^{-1} at the shipyard station S2 but also 150 pg L^{-1} in station S-CS, indicating that the major concentrations of PCBs may not have originated directly from shipbuilding activity. Most non-ortho and mono-ortho PCBs could not be detected, indicator PCBs dominated the low concentrations observed even in the ambient waters. Somewhat larger total OCP concentrations were observed in the ambient waters. These ranged, again, both from Eq. (2) and from Eq. (4), from 98 (at station M1C) to 848 pg L^{-1} (at the shipyard station, S2).

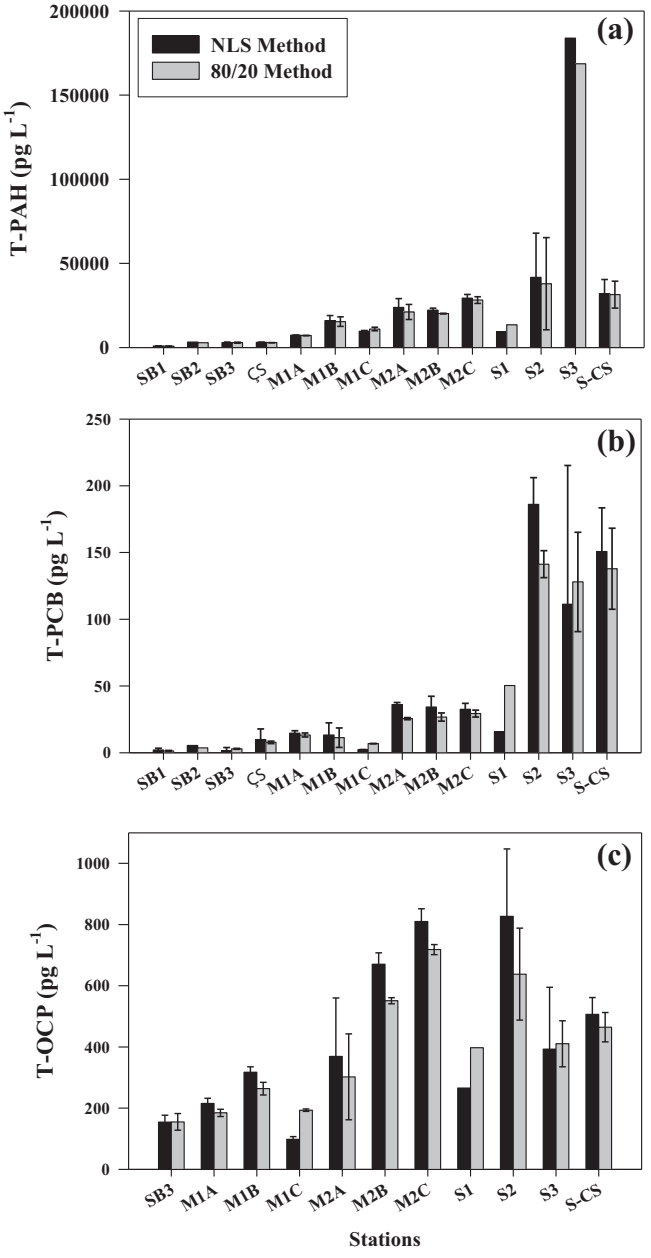

Fig. 3. SPMD-derived water concentrations by using two calculation methods (NLS; Non-linear Least Square and 80/20) in the sampling stations.

3.3. A numerical approach for estimation of boat-related pollution in marinas

Marina basins contain organic and inorganic pollutants such as PAHs, PCBs, OCPs and toxic metals originated from docked yachts/boats and marina operations. The paints and leached pollutants from the hulls, sanitary wastes and discharged petroleum products are the main sources of those pollutants (US EPA, 2001). In this study, PAH and POP (PCBs and OCPs) loads in a marina basin were calculated by using a simple numerical model. There are limited studies in the literature, estimating the pollutant concentrations numerically. For example, Marsik and Johnson (2010) estimated traffic pollutant levels using the mass balance relationship between the traffic-related pollutant concentrations and Dinerman et al. (2011) conducted a sampling campaign in order to quantify fuel derived pollutants related to boating activity in the Sea of Galilee, its marinas and its main contributing streams.

In this numerical model, it is assumed that the yachts and boats release PAHs and POPs in time. On the other hand, pollutants have their own specific decay rates in the marine environment. The half-lives of PAH and POP compounds were assumed to be only the function of time, regardless of the amount of the contaminants.

Firstly, to construct the numerical model, M1 was selected as a "model calibration marina". M1, which has been in service for eleven years, has a sea capacity and dry-dock service for approximately 600 and 100 yachts, respectively. The marina offers port, technical and pollution control services, such as: Boat hull pressure washing and cleaning; dry-dock services; lift and launching; travel lift; repair and maintenance services; engine and machine repair and maintenance services; electric works; woodworks; metal works; rig, sail and canvas works etc. For pollution control, the marina has sea water circulation pumps, waste water collection and treatment plants, solid waste collection stations, bilge water and waste engine oil collection services.

A reference site in the outer waters of M1 was selected to determine the background water concentration of pollutants. The annual sea/land capacities and occupancy rates for the marina were obtained. Generally, 8 to 14 m yachts in length have been using the marina and the average yacht length was found as 12 m. In the numerical model, K_{POP} and K_{PAH} are the coefficients representing the amount of pollutants released from an average length of a 12 m yacht annually, given in Eqs. (5) and (6):

$$C_{PAH}(t) = K_{PAH} N(t) \quad (5)$$

$$C_{POP}(t) = K_{POP} N(t) \quad (6)$$

where, C_{PAH} and C_{POP} are the concentration of pollutants as a function of time, $N(t)$ the is total number of yachts at the marina on annual basis. Using the measurements from the reference site and the annual data for M1, the coefficients K_{POP} and K_{PAH} can be calculated.

The half-lives of PAH and POP compounds are represented by k_{PAH} and k_{POP} functions which are obtained by using Lagrange Interpolation Polynomials (Chapra and Canale, 1998). The half-lives of PAHs and POPs were assumed as three and ten years respectively, which can be expressed in the quadratic form for the "model calibration marina". Quadratic form can properly simulate the reduction of the pollutants considering the service time of the marina in years and those functions were calculated from Eqs. (7) and (8):

$$k_{PAH}(t) = 0.0104t^2 - 0.1896t + 0.9938 \tag{7}$$

$$k_{POP}(t) = 0.0009t^2 - 0.0569t + 0.9938. \tag{8}$$

The present (2013) pollutant concentrations in M1 is the sum of the background concentration (C_b) and marina based pollution in 10 service years, expressed in Eq. (9):

$$C_{Marina}(2013) = C_b + \sum_{t=1}^{10} C_{Marina}(t). \tag{9}$$

The amount of the pollutants in the marinas accumulates in years because of the boat-related activities. On the other hand, the released pollutant levels decrease due to the natural decay of those specified pollutants, depending on the half-lives of the compounds. Therefore, the present POP and PAH concentrations can be written as follows:

$$C_{PAH}\ (2013) = C_{b,\ PAH} + K_{PAH}\sum_{t=1}^{10} N(t)\ k_{PAH}(t) \tag{10}$$

$$C_{POP}\ (2013) = C_{b,\ POP} + K_{POP}\sum_{t=1}^{10} N(t)\ k_{POP}(t) \tag{11}$$

where, t is the year, C_{PAH} (2013) and C_{POP} (2013) are the present concentrations of PAH and POP compounds in the marina, $C_{b,PAH}$ and $C_{b,POP}$ are the background concentrations at the reference site, $N(t)$ is the total number of yachts at the marina on annual basis. Using the present concentrations, the coefficients K_{POP} and K_{PAH} are calculated by re-arranging Eqs. (10) and (11). The re-arranged forms of the equations are given by Eqs. (12) and (13).

$$K_{PAH} = \frac{C_{PAH}(2013) - C_{b,\ PAH}}{\sum_{t=1}^{10} N(t)\ k_{PAH}(t)} \tag{12}$$

$$K_{POP} = \frac{C_{POP}(2013) - C_{b,\ POP}}{\sum_{t=1}^{10} N(t)\ k_{POP}(t).} \tag{13}$$

The numerical model was developed by using the Microsoft Excel spreadsheets. Initially, K_{POP} and K_{PAH} were calculated from the SPMD-derived water data by using Eqs. (12) and (13) for M1 and found as 0.019 and 3.290, respectively. Then, those coefficients were used to estimate the pollutant concentrations resulting from the yachts and boats at the two independent parts of the second marina (M2A and M2B), by using Eqs. (10) and (11).

The second marina has been in service for twenty seven years and has two independent parts. The sea and land capacities of the first part are approximately 500 and 200 yachts, respectively. The second part has higher capacities with approximately 750 and 225 yachts for sea and dry-dock services. The second marina offers similar services with the model calibration marina and the average length of yachts in the second marina is at the same range as M1.

The second marina (M2) has been operating since 1987. Considering the total service time, the reduction of POPs with time can properly be simulated with the quadratic form given in Eq. (8). However, since the half-life of PAHs is assumed as three years, the fifth order polynomial—instead of a third or fourth order form—well represents the decay of the PAH compounds for 26 years of service time. Therefore, using Lagrange Interpolation Polynomials, $k_{PAH}(t)$ function is expressed as Eq. (14):

$$k_{PAH}(t) = -2.760\text{E}{-}7t^5 + 2.733\text{E}{-}5t^4 - 1.071\text{E}{-}3t^3 + 2.118\text{E}{-}2t^2 - 0.219t + 0.999. \tag{14}$$

Using the mass balance relationship between the boat-related pollutant concentrations for the second marina, Eqs. (15) and (16) were used to calculate C_{POP} (2013) and C_{PAH} (2013) for the two independent parts of the second marina.

$$C_{PAH}\ (2013) = C_{b,\ PAH} + K_{PAH}\sum_{t=1}^{26} N(t)\ k_{PAH}(t) \tag{15}$$

$$C_{POP}\ (2013) = C_{b,\ POP} + K_{POP}\sum_{t=1}^{26} N(t)\ k_{POP}(t). \tag{16}$$

The reference site measurements for the second marina were $C_{b,PAH} = 12{,}000$ pg L^{-1} and $C_{b,POP} = 443$ pg L^{-1}. K_{POP} and K_{PAH} were taken as 0.019 and 3.290 respectively from the model calibration marina calculations. The results of the numerical model for predicting the boat-related organic pollution and the measured concentrations (by use of SPMDs) in M1, M2A and M2B were found to be quite consistent (Table 3).

4. Conclusion

The organic contaminant profile patterns in passive samplers showed that shipyards have a great potential for the organic pollutants in coastal areas. BR sorbents showed a very good performance for sampling of PAHs, PCBs as well as OCPs from the sampling sites. Comparisons between the BR sorbents and SPMDs showed that both samplers produce similar results for the chemicals which have K_{ow} values of around 6. Interestingly, at higher K_{ow} values, BR sorbents were able to sample certain PAHs which were not detected in SPMDs, probably due to the higher hydrophobic character of the sorbents. Since PRCs were not spiked in butyl rubber sorbents, the data from BRs could not be used for estimation of seawater pollutant concentrations. However, the promising results from this study related to the accumulation of organic compounds by BRs, indicate the need for further research to use those sorbents with PRC spiking. Lipid-containing SPMDs have been shown to be useful tools for estimation of organic contaminants in water and the two existing theoretical approaches used for the calculations of sampling rates by using PRCs gave similar results. Comparison of SPMD-derived data and model results suggests that the results produced by the model are close to those obtained from the SPMD-data. Therefore, the implemented model is assumed to be both a verified

Table 3
Measured and numerically calculated pollutant concentration (ng g^{-1}) values in marinas.

Marina	SPMD-derived T-PAH	Calculated T-PAH	SPMD-derived T-POP	Calculated T-POP
M1	11,000 ± 3652	11,268	285 ± 105	232
M2A	25,815 ± 3551	21,799	854 ± 70	602
M2B	23,833 ± 3733	21,018	481 ± 137	577

implementation of the assumptions and a valid representation of the system. In the numerical model, the coefficients which are representing the amount of pollutants released from an average length of a 12 m yacht were defined, therefore it can be a useful tool to assess the boat-related pollutants in a marina that serves a similar length of yachts and also for management purposes. For the future work, the present model can be extended to be used in shipyards and shipbreaking yards.

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