Supporting Information

Passive samplers vs sentinel organisms: one-year monitoring of priority and emerging contaminants in coastal waters"

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S1. Information on the sampling area

Cadiz Bay is a semi-enclosed system located in the SW of the Iberian Peninsula (Cadiz, Spain). Seawater from the Atlantic Ocean flows in and out through two entrances (north and south of the bay, respectively). The study area has a Mediterranean climate with an irregular rainfall pattern. During the monitoring (year 2014), rainfall was almost absent from June to September, and the highest rainfall occurred in November (up to 220 L m^{-2}). Temperature and salinity data ranged from 14 ºC to 24 ºC and from 34.9 and 37.4, respectively. The bay has an area of approximately 30 000 ha and it is divided into 2 basins, connected by the narrow Strait of Puntales. It is subjected to a semidiurnal tidal regime. Sampling site ES (= estuary) is the estuary of the Guadalete River, the main river discharging into the bay. This river is 157 km long and flows across the province of Cadiz (SW Spain). It is impacted by run-off from agricultural crops and urban and industrial wastewater discharges from two cities, Jerez de la Frontera (200 000 inhabitants) and El Puerto de Santa Maria (90 000 inhabitants). Sampling site NP (= natural park) is located in Los Toruños, an unpopulated and protected RAMSAR area within the bay that can be potentially affected by wastewater discharges from fish farms and nearby cities such as El Puerto de Santa Maria and Puerto Real (40 000 inhabitants). Sampling site TC1 (= tidal creek 1) and TC2 (= tidal creek 2) are placed in both ends of a tidal marine creek (Sancti Petri creek) that connects the inner part of the bay (TC2) with the Atlantic Ocean (TC1) and is 18 km length. A military naval base and shipyards are located in TC2, whereas TC1 is a beach area highly affected by recreational activities during summer months. Two wastewater treatment plants (WWTPs) from an adjacent town Chiclana de la Frontera (82 000 inhabitants) are currently discharging through small rivers into the Sancti Petri creek. San Fernando (96 000 inhabitants) is another nearby city that was also discharging untreated wastewater in the middle section of this creek but that ended more than one decade ago.

S2. Analysis of target contaminants in silicone rubber strips and clams

Pure standards (> 95%) were purchased for determination of target contaminants. Thus, galaxolide (HHCB) as well as triclosan d3 (TCS-d3), methyl-triclosan ^{13}C12 (MTCS-13C12), mixtures of polycyclic aromatic hydrocarbons (PAHs) (naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene), fluoranthene d10 (FL-d10), chrysene d12 (CHR-d12), phenanthrene d10 (PHE-d10), acenaphthene d10, (ACE-d10), perylene d12 (PER-d12) and

polychlorinated biphenyls (PCB52, PCB138, PCB180 and PCB101) were purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany). Benzophenone 3, octocrylene, nonylphenol technical mixture, musk xylene, musk ketone, triclosan, methyl triclosan, octylphenol, 2-hydroxybenzophenone, homosalate, 2-ethylhexyl salicylate, 2-ethylhexyl-4-methoxycinnamate, 4-methylbenzylidene camphor, triphenylphosphate, tris-isobutylphosphate, triphenylphosphate d15 (TPP-d15) and benzophenone-2,3,4,5,6- d5 (BP-d5) were purchased from Sigma-Aldrich (Madrid, Spain). Celestolide, tonalide, traseolide, phantolide, musk tibetene, musk ambrette, cashmeran and Irgarol were purchased from LGC Standards (Barcelona, Spain). OTNE fragrance was from Bordas Chinchurreta Destilations (Seville, Spain). Tris-n-butylphosphate, 2-ethylhexyldiphenylphosphate, tris-2-ethylhexylphosphate and tris tolyl phosphate isomer m were purchased from Chiron (Norway). Stock solutions of these analytes were prepared in acetone and stored at -20 ºC in tightly closed amber vials. Additionally, solvents such as acetone, n-pentane, methanol and ethyl acetate of HPLC quality were purchased from Sigma Aldrich (Madrid, Spain). PTFE centrifuge filters (0.22 µm pore size) were purchased from National Scientific (Claremont, United States). A derivatizing agent, N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA) from Sigma Aldrich (Madrid, Spain), was used to improve the gas chromatography signal of compounds with polar groups in their structure. Glassware was rinsed with solvents and ultrapure water and baked at 540 ºC before use.

Silicone strips were cleaned with ethyl acetate in a Soxhlet extractor for 72 hours and later immersed in methanol for one day to remove remaining impurities. Silicone strips (100 x 2.5 cm) were prepared from Altesil^{TM} (500 µm thickness) purchased from Altecweb (Altec, United Kingdom). Performance reference compounds (PRCs) selected were: fluoranthene d_{10} (FL-d_{10}), chrysene d_{12} (CHR-d_{12}), phenanthrene d_{10} (PHEN-d_{10}), triclosan d_3 (TCS-d_3), and benzophenone-2,3,4,5,6- d_5 (BP-d_5). Silicone strips were then place in tightly sealed tin cans and stored at -20ºC until use. Cages containing the strips were placed 1 meter below the surface to minimize contamination by atmospheric deposition and photodegradation of target compounds and retrieved after one month. Non-spiked strips were used as laboratory blanks and strips spiked with the PRCs were used as field control to detect possible contamination during the transport, deployment, and retrieval operations. Three unexposed samplers were used to determine the initial amount of PRCs spiked to later calculate sampling rates. Once retrieved, the strips were cleaned gently with water from the sampling site to remove entirely the biofilm that had covered the surface, packed individually in tin cans and stored at -20ºC

until extraction. Before extraction of target contaminants in the laboratory, the silicone strips were washed with ultrapure water and dried with a clean tissue. Extraction of the analytes from the silicone strips were carried out overnight by soaking in pentane in two extraction steps (2 x 150 mL) [1]. Later, both extracts were combined, evaporated to dryness in a Syncore Polyvap (Buchi, Switzerland), re-dissolved in 500 µL of ethyl acetate, and filtered through 0.22 µm PTFE centrifuge filters and derivatized with MTBSTFA by adding 10 µL and leaving the sample 30 min at room temperature. In exceptional cases some gaps occurred throughout the year due to passive sampler loss (10%).Regarding clam samples, they were monthly supplied by a hatchery (Cetarea del Sur, Cadiz Spain) which receive the organisms from the Galician Rias cultures (not available at selected months: February and March (NP and ES), March (TC2) and February and December (TC1)). Their lipid content was calculated gravimetrically after extraction with chloroform-methanol (2:1, v/v) for 10 min, followed by centrifugation and evaporation. The lipid content was expressed as percentage of sample dry weight (lipid mass x 100 / clam dry mass) [2]. Extraction of the analytes from clams was achieved by pressurized liquid extraction (PLE), using an accelerated solvent extractor ASE 200 unit from Dionex (Sunnyvale, CA, USA), with 11 ml stainless-steel cells. The extraction protocol was a modification of previous method developed by our group for marine sediments [3]. Briefly, a cellulose filter was placed on the bottom of the PLE cells, followed by 3 g of silica (activated by heating according to the 3610b EPA method), and 2 g of dried and milled clam sample previously homogenized with 0.5 g of activated silica. Dichloromethane was used as extraction solvent. Three static extraction cycles of 5 min each were used (purge time of 60 s and a flush volume of 60 %), setting temperature and pressure at 100 °C and 1500 psi, respectively. The extracts (30 mL) were then evaporated to dryness using a Syncore Polyvap (Büchi, Switzerland) and re-dissolved in 0.5 ml of ethyl acetate, which was centrifuged at 10000 rpm to remove possible interferences. Extracts were then filtered with a PTFE filter and derivatized with MTBSTFA by adding 10 µL and leaving the sample 30 min at room temperature. The efficiency of the method was check by spiking a pool of freeze dried and milled clam tissues to 50 ng g^{-1} and performing the extraction as described above. Results from these recovery experiments are shown in Table S1.

After extraction from either silicone rubber strips or clams, separation, identification and quantification of analytes were performed using gas chromatography (SCION 456-GC, Bruker) coupled to triple quadrupole mass spectrometry (SCION TQ, Bruker). Capillary gas chromatography analysis was carried out on a BR-5ms column (30 m×0.25 mm i.d. ×0.25 µm

film thickness), keeping the carrier gas flow (helium) at 1 mL min^{-1}, and the transfer line and the injection port temperatures at 280 ºC. The column temperature ramp was as follows: 70 ºC for 3.5 min, increased at 25 ºC min^{-1} to 180 ºC, then at 10 ºC min^{-1} to 300 ºC, and held for 4 min. Injection volume was 1 µL in splitless mode and the solvent delay was set to 4.5 min. The mass detector was operated in multiple reaction monitoring (MRM). Identification of target compounds were based on comparing retention times, two transitions (one for quantification and one for confirmation) and their ion ratio for each analyte to those for commercially available pure standards. Internal standards (acenaphthene d_{10}, triphenylphosphate d_{15}, perylene d_{12} and methyl-triclosan $^{13}C_{12}$) were added at 50 ng g^{-1} [4]. Quantification was performed using the relative response (MS signal corrected by normalizing the area of each analyte with the area of the internal standard, relative response or relative factor were calculated) and calibration curves, constructed in ethyl acetate for each compound, with a six or seven points in the range of 5–500 µg L^{-1}. Further details on GC-MS analysis can be found at reference [3]. All GC-MS/MS data were processed using Bruker MS Workstation 8 and Excel 2016 software.

S3. Calculation of freely dissolved concentrations (C_w)

Sampler-water partition coefficients (K_{sw}) used to estimate aqueous concentrations were either determined previously by our group (for CECs) or taken from existing literature (for selected priority substances) [5, 6] (Table S1). For some UV filters, differences lower than 1.66 log units were found when comparing our log K_{sw} data with those recently published by Verhagen et al. (2019)[7]. These differences translated into variations in the freely dissolved concentrations (C_w) lower than 5% (or 0.07 ng L^{-1}) depending on the K_{sw} values used, except for BP3 and 4MBC (for which differences up to 49%, or 5 ng L^{-1} were foreseen). C_w (ng L^{-1}) were calculated from the measured mass of the analytes in the strips (N_p) using the general uptake equation (Equation 1) from the diffusion model [8].

$$Cw = \frac{\mathrm{Np}}{\mathrm{Ksw\ mp}\ (1 - e^{-\mathrm{Rs\ t}/\mathrm{Ksw\ mp}})} \qquad \text{(Equation 1)}$$

where m_p is the mass of the silicone strip, K_{sw} is the silicone rubber-water partition coefficient, N_p is the measured mass of each analyte, t is the exposure time, and *Rs* is the sampling rate.

Sampling rates are calculated using the PRC fractions (*f*) that are retained as a function of K_{sw} by nonlinear least-squares estimation (Equation 2), due to Rs depends not only the exposure conditions, also of the K_{sw} values of the compounds.

$$f = \frac{N_t}{N_o} = \exp\left(-\frac{Rs\ t}{mp\ Ksw}\right) \quad \text{(Equation 2)}$$

In this study, *log β*, an adjustable parameter estimated estimated using the PRC dissipation data (*f*) by applying the unweighted NLS model [9]. Finally, PRC-based Rs were estimated (Equation 3):

$$Rs = \log \beta - 0.08 \log K_{sw} \quad \text{(Equation 3)}$$

Effects in the K_{sw} values due to changes in the ionic strength and water temperature over the sampling period were expected to be negligible according to Jonker et al. (2015)[10], with predicted deviations <0.06 and <0.25 log units within the range of temperature and salinity occurring in our sampling area [11].

S4. Quality assurance and quality control (QA/QC)

All analytical data were subject to quality control. This includes analysis of target contaminants in silicone rubber strips and clams before field deployment and performing triplicates for each deployed sample. Relative standard deviations in the concentrations of the compounds detected in the samples were below 15% for silicone strips and 22% for clam samples within each replicate. The results from replicate samples were averaged, and the concentrations in preparation controls and laboratory blanks and non-exposed clams were subtracted (blank signal subtraction, see table S1). Most of the target analytes were not detected in both laboratory blank strips and preparation controls strips. Only OTNE, octocrylene, nonylphenol, galaxolide, EHDP, and EHMC were found at measurable concentrations, although they were always between 1 and 2 orders of magnitude lower than those measured in exposed samples. No differences were found between preparation and field control strips, which indicates that sampler contamination did not result in further contamination during the sampling; these values were used to determine limit of detection for these compounds. The recovery extraction percentages for silicone strips ranged between 64% and 108 % for all the detected compounds, whereas they were between 60% and 105% for clams (see Table S1 for more details on specific analytes). Limits of detection were < 0.093 ng L^{-1} in silicone strips and < 0.17 ng g^{-1} in clams. Matrix suppression was considered for each sample by means of internal standards, being between 2 % and 34 %. Thirty-seven compounds were analyzed in clam samples, 11 compounds less than in silicone strips due to the presence of interferences and/or low recoveries during the extraction (<40 %).

C_w were calculated for 42 out of 48 target compounds detected in silicone strips (6 chemicals were not detected in the samplers), considering both K_{sw} values and sampling rates (Rs) derived from the dissipation of PRCs (Equation 1). After exposure (1 month), the PRC mass percentage retained in the silicone rubber ranged between 10% for more polar compounds (i.e., BP-d_{10}) and more than 65% for fluoranthene-d_{10} and chrysene-d_{12}. The equilibrium time for PRCs was between 8 days for BP-d_{10} and 167 days for the most hydrophobic chemicals. The adjustable parameter β, required for *Rs* calculation (Equation 2), ranged between 12.8 L kg^1 d^{-1} and 28.5 L kg^1 d^{-1}, yielding *Rs* values that varied between 6.4 and 18.5 L d^{-1} during the warmer months and between 3.6 and 8.5 L d^{-1} during the colder months (Table S2). These values are in agreement with data from previous sampling campaigns in the Alna River in Norway [12] and the Belgian coast [13] using the same sampling devices.

Permanova analysis was based on Euclidean distance (water samples and BAFs) or fourth-root transformation (clam samples) for assessing dissimilarity between data, and not dispersion problems were found between data. An experimental design with two factors was considered: 'season' (with four levels, spring, summer, fall and winter) and sites (ES,TC1, TC2 and NP) for the different classes of compounds (PAHs, PCBs, OPRs, fragrances, UV filters, antimicrobials, NP and Irgarol, except for BAFs where individual compounds were taken) were chosen as variables. When significant differences ($\alpha = 0.05$) were identified for each factor, posteriori pair-wise Permanova procedure was conducted to identify differences. Non detectable concentrations were treated as zero. Significant differences ($\alpha < 0.05$) were found only for water samples considering the factor 'season'.

Table S1. Analytical parameters: partition coefficients (octanol-water, log K_{ow} and silicone-water, log K_{sw}), recovery percentage (%) and instrumental limit of detection (LOD), quantification (iLOQ) and background levels in non-exposed clams (C_{clams}).

COMPOUND	log K_{ow}	log K_{sw} (L kg^{-1})	Recovery clams (%)	iLOD (pg)	iLOQ (pg)	C_{clams}±sd (background levels, ng g^{-1})
PAHs						
Naphthalene (NAP)	3.29[a]	3.03[d]	76.8±18	0.08	0.28	3.3±0.31
Acenaphthene (ACE)	3.92[a]	3.62[d]	87±3	0.10	0.33	loq
Acenaphthylene (ACY)	3.94[a]	3.26[d]	89.2±6	0.14	0.46	loq
Anthracene (ANT)	4.5[a]	4.21[d]	84±13	0.24	0.81	1.25±0.28
Fluorene (FLO)	4.02[a]	3.78[d]	96±7	0.18	0.59	loq
Phenanthrene (PHE)	4.46[a]	4.11[d]	91.7±8	0.38	1.28	5.75±1.87
Pyrene (PYR)	4.88[a]	4.69[d]	93±4	0.16	0.53	2.82±1.08
Chrysene (CHR)	5.63[a]	5.26[d]	89.5±11	0.19	0.65	3.8±2.1
Benz(a)anthracene (BaA)	5.63[a]	5.34[d]	75.3±13.5	0.88	2.94	4.1±2.3
Fluoranthene (FLA)	4.9[a]	4.62[d]	88.2±7	0.17	0.58	3.5±2.17
Benzo(b)fluoranthene (BbF)	6.11[a]	5.75[d]	75± 12	0.38	1.25	1.75±0.71
Benzo(k)fluoranthene (BkF)	6.11[a]	5.75[d]	77.3± 9	0.13	0.45	2.1±0.8
Benzo(a)pyrene (BaP)	6.11[a]	5.71[d]	106.2±12	0.68	2.27	1.9±0.64
Benzo (ghi)perylene (BghiP)	6.7[a]	6.03[d]	60±10	0.22	0.72	loq
Indeno(123-cd)pyrene (IcdP)	6.7[a]	6.06[d]	*	3.75	12.50	
PCBs						
PCB52	6[a]	5.82[d]	67±1	0.04	0.12	1.87±0.17
PCB101	6.15[a]	6.29[d]	68±1	0.02	0.08	0.68±0.11
PCB138	7[a]	6.78[d]	77.7±5	0.01	0.03	1.42±0.7
PCB180	7.29[a]	7[d]	86±1.7	0.01	0.03	0.9±0.31
Pesticides (Algaecide)						
Irgarol	3.95[b]	3.60[e]	63±7	0.10	0.33	4.7±0.23
Organophosphorus Flame Retardants (OPFRs)						
Triphenylphosphate (TPP)	4.7[b]	4.94[e]	85±0.7	0.15	0.50	4.5±0.54
Trisisobutylphosphate (TisoBP)	4[b]	4.68[e]	73±16	0.03	0.09	1.25±0.15
Tris-n-butylphosphate (TnBP)	4.6[b]	5[e]	69±12	0.23	0.78	3.54±1.53
Tris(2-ethylhexyl)phosphate (TEHP)	8.9[b]	5.88[e]	93±13	0.05	0.17	loq
2Ethyl hexyl diphenyl phosphate (EHDP)	5.73[b]	5.39[e]	*	1.00	3.33	
Tris tolyl phosphate-Isomer m (TTP)	6.3[b]	5.77[e]	-	0.05	0.18	

UV Filters						
2Hydroxybenzophenone (2-OHBP)	3.47[b]	3.04[e]	76±6	0.88	2.94	loq
Benzophenone 3 (BP-3)	3.79[b]	3.08[e]	97±9	0.01	0.02	1.02±0.34
Octocrylene (OC)	7.3[b]	4.96[e]	80±14	0.08	0.28	11.8±12.4
Homosalate (HMS)	5.82[b]	4.55[e]	-	0.02	0.08	
2Ethylhexyl salicylate (EHS)	5.77[b]	4.70[e]	-	0.06	0.19	
2-Ethylhexyl-4-methoxycinnamate (EHMC)	5.66[b]	4.77[e]	105±9	0.07	0.22	3.65±2.7
4-Methylbenzylidene camphor (4-MBC)	4.95[b]	3.39[e]	-	1.25	4.17	
Fragrances						
Musk xylene (MX)	4.8[c]	3.31[e]	*	0.38	1.27	
Musk Ketone (MK)	4.3[c]	3.05[e]	108±4.9	0.34	1.14	loq
Musk tibetene (MT)	5.9[a]	4.15[e]	*	3.00	10.00	
Musk ambrette (MA)	5.7[a]	3.91[e]	-	2.50	8.33	
Galaxolide (HHCB)	5.9[c]	3.97[e]	99±8	0.11	0.35	31.7±14.63
Tonalide (AHTN)	5.7[c]	4.01[e]	83±12	0.17	0.57	6.06±1.72
Celestolide (ADBI)	5.9[c]	3.96[e]	78±5	0.21	0.68	loq
Cashmeran	4.9[c]	3.46[e]	60±7	0.58	1.92	loq
Phantolide (AHMI)	5.9[c]	3.78[e]	-	1.15	3.85	
Traseolide (ATII)	6.3[c]	4.36[e]	*	1.36	4.55	
OTNE	5.28[b]	3.63[e]	85±11	0.58	1.92	26.62±15.26
Antibacterials						
Triclosan (TCS)	4.76[a]	3.02[e]	108±3	0.005	0.02	3.64±1.05
Methyl Triclosan (Me-TCS)	5.2[b]	3.62[e]	94±14	0.03	0.11	0.35±0.2
Surfactants						
Nonylphenol mix isomers (NPs)	4.77[a]	3.49[e]	98±13	0.52	1.72	47.2±12.4
Octylphenol (OP)	5.5[b]	3.28[e]	76±13	0.03	0.09	loq

[a] log K_{ow} obtained from Scifinder database.

[b] log K_{ow} obtained from Chemspider database.

[c] log K_{ow} obtained from Posada-Ureta et al., 2012 [14].

[d] log K_{sw} obtained from Smedes et al., 2009 [5].

[e] log K_{sw} obtained from Pintado-Herrera et al., 2016 [6].

* Not quantified due to the presence of unknown interferences

- Low recoveries (<60%), compounds not included in the analytical method

Table S2. A) Performance reference compound (PRC) data by season. (NLS model results: S.E.: estimated error) and B) mean values of the specific sampling rates for each compound per season.

A)

SUMMER		S.E.	**SPRING**		S.E.
log beta	1.37	0.037	log beta	1.45	0.038
beta	23.44	2.002	beta	28.52	2.5
Rs at log K_{sw}=5	9.40	0.80	Rs at log K_{sw}=5	11.4	1
FALL		S.E.	**WINTER**		S.E.
log beta	1.11	0.04	log beta	1.17	0.054
beta	12.88	0.71	beta	14.80	0.861
Rs at log K_{sw}=5	5.20	0.28	Rs at log K_{sw}=5	6	0.34

B)

Compounds	**Rs (spring)**	**Rs (summer)**	**Rs (fall)**	**Rs (winter)**
PAHs				
NAP	16.13	13.42	7.37	8.46
ACE	14.47	12.03	6.61	7.59
ACY	15.46	12.86	7.07	8.11
ANT	12.98	10.79	5.93	6.81
FLO	14.05	11.68	6.42	7.37
PHE	13.22	11.00	6.04	6.94
PYR	11.88	9.88	5.43	6.23
CHR	10.70	8.90	4.89	5.61
BaA	10.54	8.77	4.82	5.53
FLA	12.03	10.01	5.50	6.32
BbF	9.77	8.13	4.47	5.13
BkF	9.79	8.13	4.43	5.13
BaP	9.84	8.19	4.50	5.17
BghiP	9.28	7.72	4.24	4.87
IcdP	9.23	7.68	4.22	4.84
PCBs				
PCB52	9.65	8.02	4.41	5.06
PCB101	8.85	7.36	4.04	4.64
PCB138	8.08	6.72	3.69	4.24
PCB180	7.76	6.46	3.55	4.07

Pesticides (Algaecide)				
Irgarol	14.52	12.08	6.64	7.62
OPFRs				
TPP	11.34	9.44	5.19	5.95
TisoBP	11.90	9.90	5.44	6.25
TnBP	11.22	9.33	5.13	5.89
TEHP	9.54	7.94	4.36	5.01
EHDP	10.44	8.69	4.77	5.48
TTP	9.74	8.10	4.45	5.11
UV-Filters				
2-OHBP	16.10	13.39	7.36	8.45
BP-3	15.98	13.29	7.30	8.39
OC	11.30	9.40	5.17	5.93
HMS	12.19	10.14	5.57	6.40
EHS	11.86	9.86	5.42	6.22
EHMC	11.71	9.74	5.35	6.14
4-MBC	15.09	12.55	6.90	7.92
Fragrances				
MX	15.32	12.74	7.00	8.04
MK	16.07	13.37	7.35	8.43
HHCB	13.56	11.28	6.20	7.12
AHTN	13.46	11.20	6.15	7.07
OTNE	14.44	12.01	6.60	7.58
CELESTOLIDE	13.59	11.30	6.21	7.13
Antibacterials				
TCS	16.28	13.54	7.44	8.54
Me-TCS	14.47	12.03	6.61	7.59
Surfactants				
NP	14.82	12.33	6.77	7.78

Table S3. Target contaminants measured in water samples from Cadiz Bay (SW Spain) at the four different sampling locations (ES, TC1, TC2, and NP) using silicone rubber passive samplers (ng L^{-1}). Values < iLOQ are labeled as nd (not detected). Detection frequency is also shown (%).

Compounds (ng L^{-1})	ES			TC1			TC2			NP		
	Median	Range	Freq (%)	Median	Range	Freq (%)	Median	Range	Freq (%)	Median	Range	Freq (%)
PAHs												
NAP	2.7	nd - 9.17	78	2.3	nd - 10.21	91	2.8	nd - 5.57	80	2.3	0.02 - 6.87	100
ACE	nd	nd - 1.57	22	0.1	nd - 2.95	64	0.4	nd - 1.01	90	0.3	0.17 - 0.88	100
ACY	0.6	nd - 2.59	89	0.5	0.31 - 2.08	100	0.4	0.06 - 0.58	100	0.4	0.12 - 2.18	100
ANT	1.1	nd - 3	78	0.2	nd - 12.41	82	0.2	nd - 0.55	90	0.2	nd - 20.65	90
FLO	5.9	3.5 - 13.04	100	0.8	0.04 - 2.17	100	1.1	0.02 - 4.92	100	1.0	0.18 - 4.64	100
PHE	8.3	2.62 - 15.7	100	1.1	0.51 - 12.2	100	1.9	nd - 6.65	90	2.3	0.25 - 16.16	100
PYR	3.8	1.93 - 6.89	100	1.0	0.44 - 1.58	100	1.8	nd - 2.44	90	1.2	0.39 - 1.54	100
CHR	0.6	0.38 - 1.68	100	0.1	nd - 0.35	91	0.3	nd - 0.75	90	0.3	nd - 0.5	90
BaA	0.2	0.13 - 0.58	100	0.1	0.02 - 1.19	100	0.2	nd - 0.34	90	0.1	0.05 - 0.35	100
FLA	2.0	1.63 - 3.38	100	0.9	0.03 - 2.46	100	1.5	nd - 2.54	90	2.0	nd - 2.52	90
BbF	0.2	0.07 - 0.42	100	0.1	nd - 0.24	91	0.2	nd - 0.61	90	0.2	0.02 - 0.36	100
BkF	0.1	0.02 - 0.15	100	0.1	0.02 - 0.1	100	0.1	nd - 0.36	90	0.1	0.01 - 0.17	100
BaP	nd	nd - 0.27	44	0.1	nd - 0.3	73	0.1	nd - 0.25	70	0.1	nd - 0.27	60
BghiP	nd	nd - 0.07	67	nd	nd - 0.07	73	nd	nd - 0.1	60	nd	nd - 0.12	70
IcdP	nd	nd - 0.08	44	0.1	nd - 0.08	64	nd	nd - 0.09	50	nd	nd - 0.09	60
PCBs												
PCB52	0.1	nd - 0.22	78	nd	nd - 0.04	73	nd	nd - 0.06	80	nd	nd - 0.05	80
PCB101	0.1	0.03 - 0.09	100	nd	nd - 0.02	82	0.1	nd - 0.1	90	0.1	0.01 - 0.08	100
PCB138	0.1	0.04 - 0.13	100	nd	0.01 - 0.04	100	0.1	nd - 0.27	90	0.1	0.01 - 0.11	100
PCB180	nd	nd - 0.03	78	nd	nd - 0.02	55	nd	nd - 0.13	80	nd	nd - 0.02	60
Algaecide												
Irgarol	3.3	0.56 - 25.26	100	1.3	0.09 - 6.85	100	3.5	nd - 14.16	90	1.7	nd - 2.93	90
OPFRs												

TPP	14.1	1.79 - 25.07	100	0.8	0.26 - 3.69	100	1.2	nd - 5.75	90	2.2	0.49 - 14.23	100
TisoBP	4.2	1.01 - 8.56	100	0.2	nd - 0.66	82	0.7	nd - 1.35	70	0.9	nd - 2.1	90
TnBP	2.5	0.26 - 4.73	100	0.1	0.04 - 0.61	100	0.2	nd - 0.54	60	0.5	0.22 - 0.97	100
TEHP	0.1	0.03 - 0.25	100	nd	nd - 0.33	55	nd	nd - 0.2	70	nd	nd - 0.41	80
EHDPP	11.3	2.11 - 15.27	100	1.9	0.66 - 16.23	100	8.4	0.17 - 28.84	100	1.6	0.83 - 15.53	100
TTP	nd	nd - 1.14	44	nd	nd - 0.24	55	nd	nd - 0.12	20	nd	nd - 0.13	20
UV-Filters												
2-OHBP	0.3	nd - 19.75	67	0.1	nd - 11.92	73	0.3	nd - 24.91	80	1.2	nd - 14.23	80
BP-3	49.3	9.47 - 208.17	100	9.3	nd - 119.93	100	9.9	nd - 17.39	90	11.5	1.3 - 45.56	100
OC	78.8	30.6 - 173.09	100	23.1	nd - 265.71	100	9.1	nd - 48.65	80	11.7	nd - 45.18	90
HMS	3.2	0.33 - 15.98	100	0.7	nd - 23.29	82	0.3	nd - 1.25	80	0.3	nd - 2.05	70
EHS	11.5	1.99 - 17.64	100	1.8	nd - 27.16	91	0.9	nd - 1.99	70	0.8	nd - 3.27	80
EHMC	3.0	0.9 - 15.01	100	2.7	0.48 - 8.54	100	1.7	nd - 7.06	90	1.5	nd - 71.76	90
4-MBC	16.6	6.8 - 69.52	100	6.8	nd - 44.8	82	6.6	nd - 37.07	80	7.3	nd - 16.57	90
Fragrances												
MX	30.4	4.51 - 60.14	100	nd	nd - 6.01	45	1.4	nd - 8.6	60	nd	nd - 4	40
MK	52.0	5.24 - 152.68	100	1.2	nd - 18.93	91	2.2	nd - 20.92	80	1.1	nd - 10.35	90
HHCB	430.8	88.41 - 3322.25	100	21.2	7.45 - 144.53	100	28.7	nd - 146.54	90	18.8	7.37 - 49.47	100
AHTN	69.7	11.52 - 205.2	100	1.3	0.4 - 17.22	100	3.9	nd - 17.56	90	2.2	0.73 - 7.46	100
ABDI	1.3	0.32- 4.31	100	nd	nd - 0.2	27	nd	nd - 0.34	20	nd	nd - 0.28	40
OTNE	525.6	55.02 - 1988.39	100	7.0	1.6 - 96.03	100	17.0	nd - 148.1	90	7.5	1.79 - 61.34	100
Antimicrobials												
TCS	68.1	24.21 - 95.02	100	7.9	0.58 - 21.88	100	5.6	nd - 31.33	90	6.6	nd - 16.9	90
Me-TCS	1.5	0.85 - 3.46	100	0.1	0.04 - 0.44	100	0.1	nd - 0.31	80	0.2	0.05 - 0.3	100
Surfactants												
NP	52.3	4 - 175.19	100	3.5	nd - 18.1	73	1.8	nd - 48.9	70	5.0	0.1 - 15.26	100

Table S4. Target contaminants measured in clam samples (ng g^{-1} dw) from Cadiz Bay (SW Spain) at the four different sampling locations (ES, TC1, TC2, and NP). Values < iLOQ are labeled nd (not detected). Detection frequency is also shown (%).

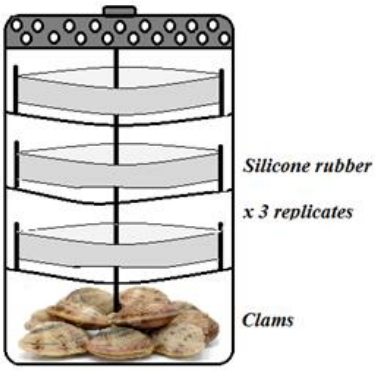
Compounds (ng g^{-1} dw)	ES			TC1			TC2			NP		
	Median	Range	Freq (%)	Median	Range	Freq (%)	Median	Range	Freq (%)	Median	Range	Freq (%)
PAHs												
NAP	1.7	1.57 - 5.51	100	4.1	2.52 - 7.46	100	0.9	nd - 2.8	56	3.1	1.78 - 10.65	100
ANT	1.8	1.16 - 2.78	100	1.3	0.81 - 2.25	100	1.5	nd - 10.75	89	1.1	0.34 - 2.55	100
FLO	nd	nd - 0.58	14		nd	-	0.9	nd - 12.36	44	0.9	nd - 1.39	22
PHE	7.8	5.57 - 10.89	100	7.3	4.7 - 11.75	100	2.4	nd – 8	67	7.7	3.4 - 11.04	100
PYR	6.6	5.77 - 10.52	100	3.6	2.56 - 46.15	100	7.0	2.36 – 87	100	3.6	0.82 - 7.73	100
CHR	4.0	nd - 14.965	86	6.1	1.97 - 13.84	100	nd	nd - 3.38	33	5.1	2.61 - 7.57	100
BaA	1.7	nd - 6.17	86	2.6	0.56 - 4.67	100	3.2	nd - 12.1	89	1.8	0.92 - 3.24	100
FLA	3.8	2.59 - 5.45	100	3.6	1.84 - 12.27	100	2.5	nd – 13	67	3.5	2 - 5.37	100
BbF	0.4	0.07 - 1.12	100	nd	nd	-	0.9	nd - 24.8	56	nd	nd	-
BaP	nd	nd	-	nd	nd	-	nd	nd - 11.8	11	1.8	0.74 - 3.32	100
PCBs												
PCB52	0.1	nd - 0.23	71	0.4	0.20 - 0.53	100	nd	nd – 6	44	0.3	nd - 0.44	78
PCB101	1.0	0.82 - 1.24	100	0.4	0.25 - 0.66	100	0.9	nd - 1.57	89	0.5	nd - 0.68	89
PCB138	1.9	0.23 - 2.35	100	1.1	0.60 - 2.44	100	1.2	nd - 9.1	56	1.3	nd - 2.14	89
PCB180	1.2	nd - 1.49	86	0.4	nd - 0.78	78	0.25	nd - 1.94	56	0.2	nd - 0.52	78
Algaecide												
Irgarol	nd	nd	-	15.4	nd - 106	67	26.70	nd - 81.3	78	nd	nd - 37.1	44
OPFRs												
TPP	17.2	3.38 - 27.59	100	nd	nd	-	nd	nd - 5.5	22	4.9	nd - 8.64	89
TisoBP	1.1	0.52 - 3.28	100	0.5	nd - 1.74	56	nd	nd - 4.67	44	0.7	nd - 1.77	89
TnBP	5.4	2.93 - 7.74	100	4.2	1.59 - 9.16	100	nd	nd - 5.08	44	3.8	nd - 8.9	89
UV filters												

BP-3	1.95	nd - 6.12	71	nd	nd - 5.77	44	1.2	nd - 4.3	89	1.3	nd - 4.51	89
OC	22.7	nd - 52.33	86	20.0	1.20 - 80.57	100	15.6	nd - 159	89	11.2	1.51 -63.34	100
EHMC	18.7	9.99 - 45.80	100	27.1	18 - 79.04	100	5.4	nd - 33.5	78	18.9	2.03 - 79.82	100
Fragrances												
HHCB	32.9	12.95 - 59.19	100	23.4	8.51 - 50.07	100	25.5	nd - 136.95	89	29.7	4.94 - 73.01	100
AHTN	10.7	4.07 - 16.47	100	6.1	1.23 - 16.52	100	0.3	nd - 10.03	67	9.4	1.46 - 16.35	100
OTNE	28.1	9.02-35.96	100	31.1	15.23 - 69.48	100	40.9	9.63 - 93.5	100	38.4	4.86 - 59.40	100
Antimicrobials												
TCS	5.2	3.98 - 11.69	100	nd	nd	-	0.9	nd - 11.82	56	4.5	nd - 10.13	78
Me-TCS	1.3	0.84 - 1.56	100	0.5	0.51 - 0.69	100	nd	nd - 0.84	44	0.50	nd - 0.59	89
Surfactants												
NP	55.1	42.98 - 104.93	100	33.8	nd - 63.97	78	22.3	nd - 157.7	100	48.9	nd - 243.43	100

Table S5. Field bioaccumulation factors (log BAF) estimated for target contaminants in clams deployed at Cadiz Bay (SW Spain). Octanol-water partition coefficients (log K_{ow}) are also shown.

Compound	Field derived log BAF			log K_{ow}
	Min	Mean	Max	
PAHs				
NAP	2.29	3.19	5.26	3.29
ANT	2.10	3.62	4.58	4.50
FLO	2.21	3.05	4.05	4.02
PHE	2.12	3.27	4.00	4.46
PYR	2.73	3.60	4.64	4.88
CHR	3.63	4.28	5.84	5.63
BaA	3.52	4.20	5.34	5.63
FLA	2.86	3.40	4.47	4.90
BbF	2.62	3.59	5.19	6.11
BaP	3.66	4.17	4.90	6.11
PCBs				
PCB 52	3.14	4.01	5.18	6.00
PCB 101	3.60	4.23	5.02	6.15
PCB 138	3.75	4.41	5.39	7.00
PCB 180	3.13	4.29	4.82	7.29
OPFRs				
TPP	2.25	3.33	4.79	4.70
TisoBP	2.09	2.92	3.82	4.00
TnBP	2.82	3.97	4.69	4.60
UV Filters				
BP-3	1.33	2.17	4.23	3.79
OC	1.52	2.90	4.89	7.30
EHMC	2.40	3.96	4.72	5.66
Fragrances				
HHCB	1.10	2.68	4.00	5.90
AHTN	1.03	3.00	4.28	5.70
OTNE	1.15	3.12	3.98	5.28
Others emerging compouds				
Irgarol	3.26	4.31	5.69	3.95
TCS	1.64	2.64	3.98	4.76
Me-TCS	2.47	3.41	4.11	5.20
NP	2.39	3.56	4.84	4.77

A



B

Figure S1. A) Scheme of a sampling cage containing 3 silicone rubber strips placed in holders (upper part) and 25-30 clam individuals (*Ruditapes philippinarum*) (lower part). B) Silicone rubber strip in a holder before and after deployment.

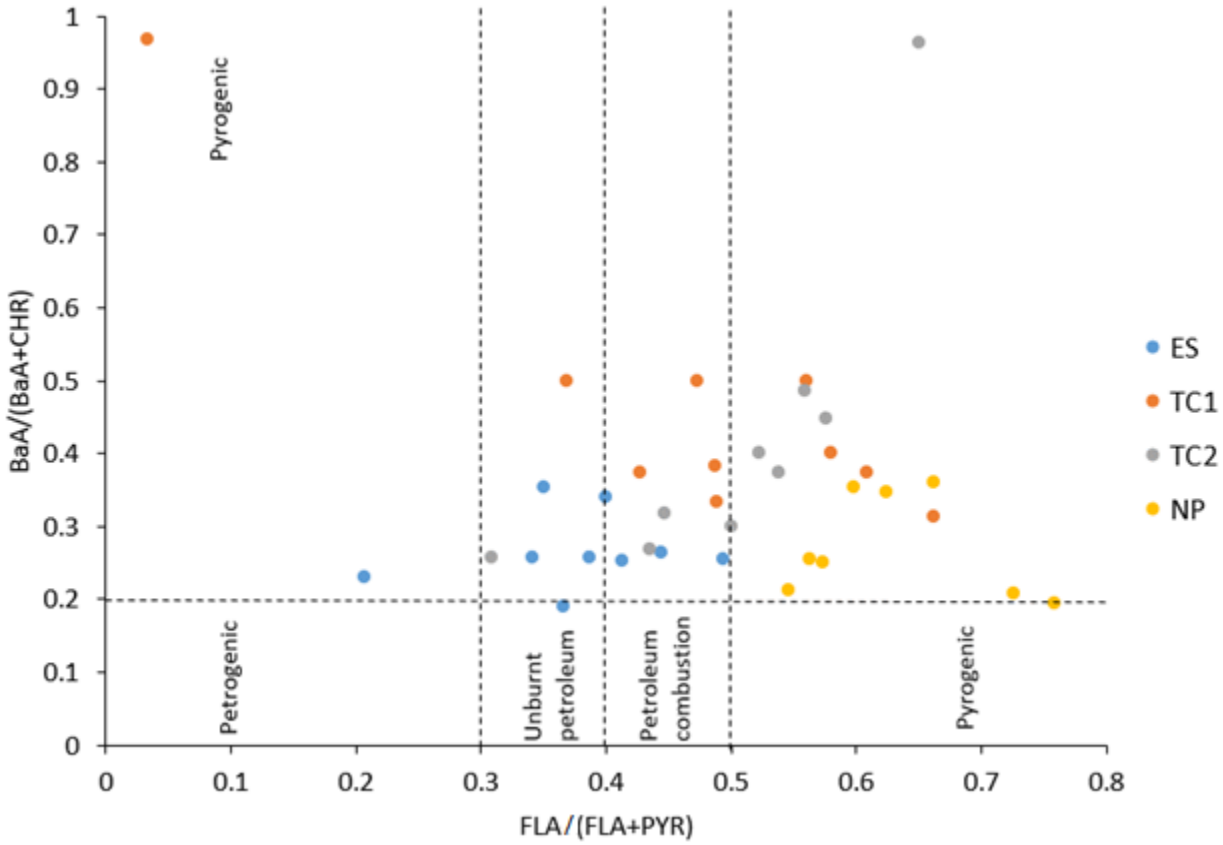


Figure S2. PAH ratios of concentrations measured with SR passive samplers in Cadiz Bay (SW Spain).

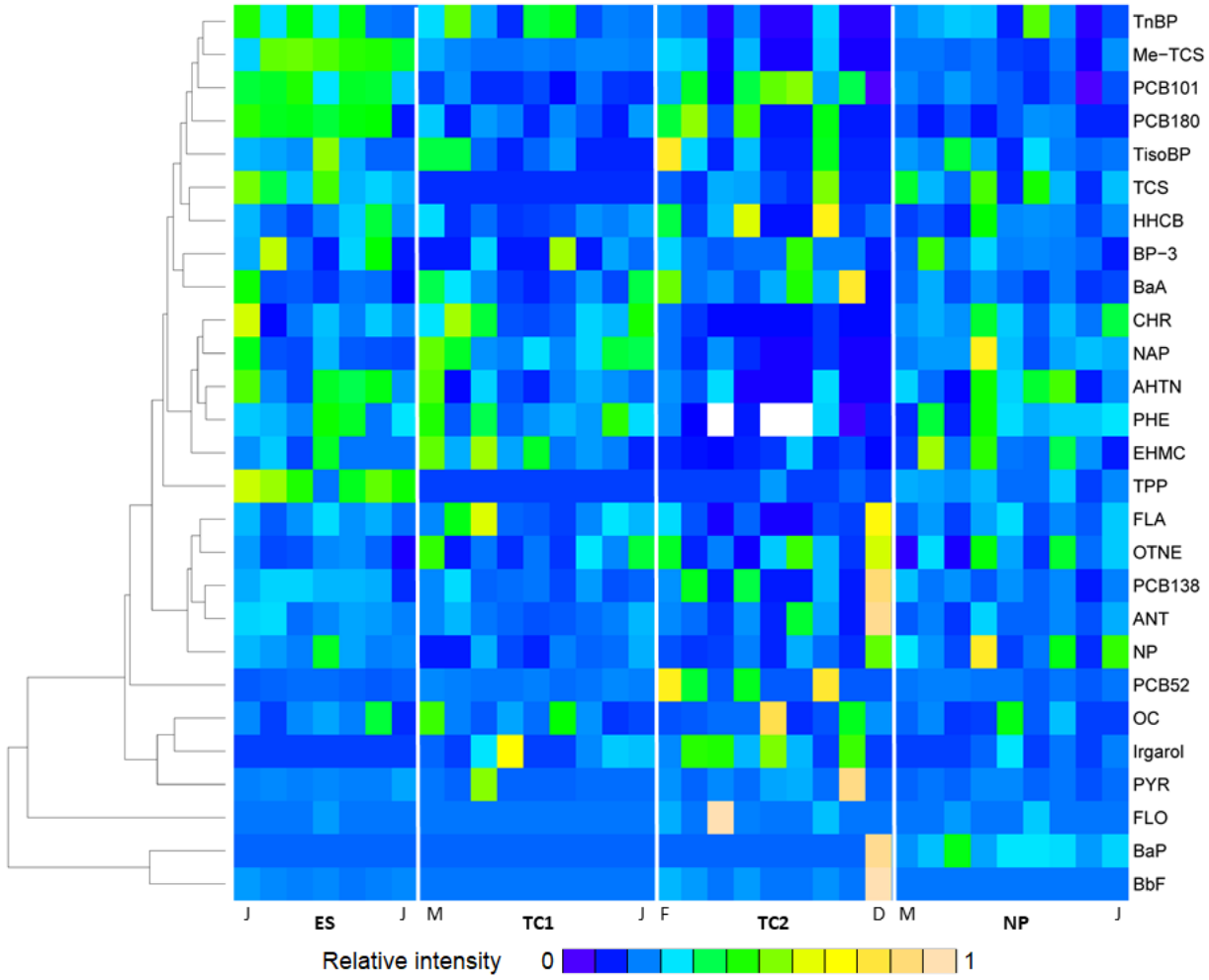


Figure S3. Hierarchical cluster analysis (HCA) showing the distribution patterns of the concentrations in clams of target contaminants at sampling sites ES, TC1, TC2, and NP in Cadiz Bay between February 2014 and January 2015.

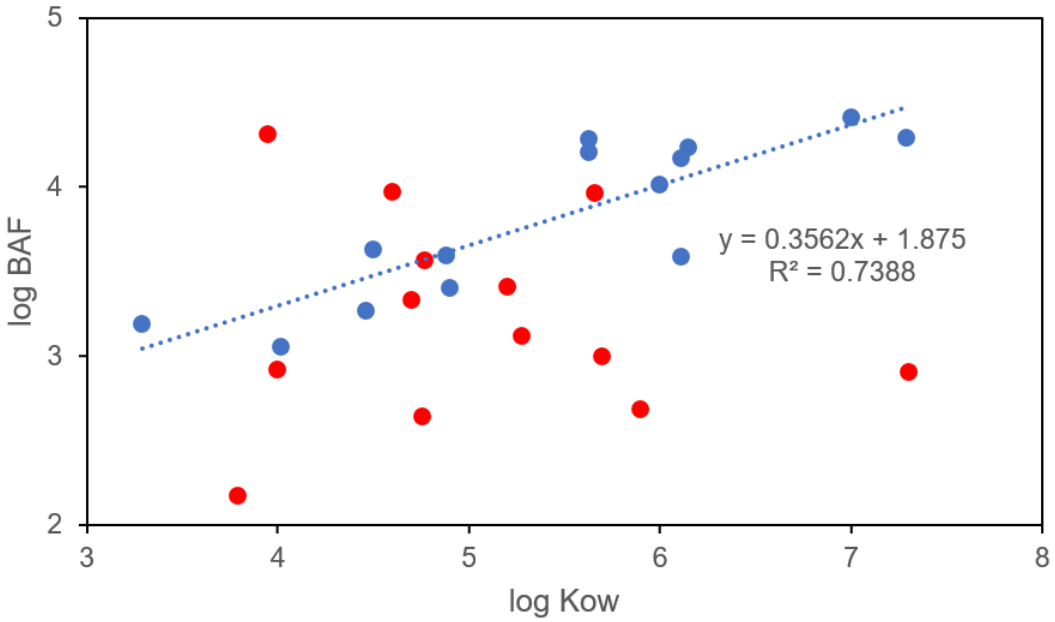


Figure S4. Average log BAF vs log Kow for target compounds. A positive correlation (R^2 = 0.7388) was found for PAHs and PCBs (blue dots), whereas it was non-existent for other contaminants (red dots).

Table (enclosed as Excel file):

Table S6. Seasonal concentrations (mean values) from Cadiz Bay (SW Spain) at the four different sites.

A) Seasonal concentrations of the target contaminants measured in water samples.

B) Seasonal concentrations of the target contaminants measured in clam samples.

C) Seasonal concentrations of the field log BAF of the target contaminants estimated.

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