SUPPORTING INFORMATION

Organophosphate ester (OPE) flame retardants and plasticizers in the open Mediterranean and Black Seas Atmosphere

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SUPPORTING INFORMATION

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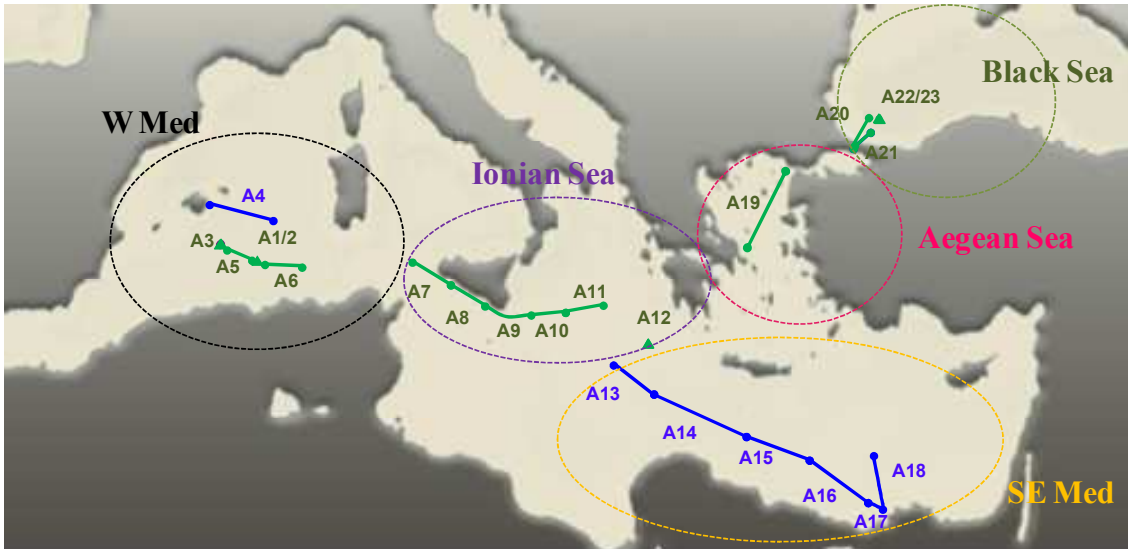
Information regarding sampling, analysis and QA/QC

Figure S1. General overview of the atmospheric aerosol phase samples collected during the two oceanographic campaigns (Green: 2006 cruise; Blue: 2007 cruise) and the studied areas/ sub-basins. Sampling details are presented in Table S1.



Text S1: Air sampling strategy and materials

Two high volume air samplers (MCV, Barcelona, Spain) were installed on the upper deck of the boat (around 6-7 m above the sea level) close to the bow and were operated simultaneously at a flow rate of 40 m^3 h^{-1}. The samplers were automatically stopped when wind was blowing from the poop of the vessel to avoid potential contamination of the samples by the ship exhausts. Additionally, the samplers were manually switch off when the boat was stopped under no wind conditions. Samples were generally collected within twelve hours. The air was drawn through a precombusted Quartz fiber filter (QM-A; Whatman, 8x10 inches) to collect aerosol (TSP) bound compounds and then circulated through a polyurethane foam (PUF) to collect chemicals present in the gas phase. All the

samples were stored in freezers at -20 °C until analysis. All meteorological parameters (wind speeds, water and air temperatures, etc.) were measured routinely during both cruises using the Meteo station on board of RV García del Cid and the systems that records continually the characteristics of surface seawater (salinity, chlorophyll, etc).

Table S1. Aerosol phase sampling details

Table S1. Aerosol phase sampling details for the two Mediterranean campaigns							
			Transect coordinates (degrees)				
			Start		End		
Sample	Volume (m^3)	Period	Latitude (N)	Longitude (E)	Latitude (N)	Longitude (E)	Air T (ºC)[a]
A1[b]	330	2 Jul 2006	37.965	5.110	37.965	5.110	24.0
A2[b]	353	3-4 Jul 2006	37.965	5.110	37.965	5.110	n.d.a
A3[b]	300	4 -5 Jul 2006	38.400	3.610	38.430	3.640	n.d.a
A4	441	4-5 Jun 2007	39.061	5.755	39.500	3.200	n.d.a
A5	490	4 Jul 2006	38.140	4.540	38.400	3.610	24.0
A6	379	2 Jun 2006	37.778	6.910	37.850	5.420	n.d.a
A7	305	6 Jun 2006	37.916	11.334	37.288	12.875	18.5
A8	262	6-7 Jun 2006	37.288	12.875	36.707	14.246	19.7
A9	230	7 Jun 2006	36.707	14.246	36.457	16.096	n.d.a
A10	359	7-8 Jun 2006	36.457	16.096	36.530	17.476	18.4
A11	447	8 Jun 2006	36.530	17.476	36.729	18.990	18.9
A12[b]	448	25 Jun 2006	35.722	20.739	35.722	20.739	n.d.a
A13	947	13-14 May 2007	35.081	19.401	34.280	21.020	20.9
A14	950	14-15 May 2007	34.280	21.020	33.111	24.727	34.3
A15	814	15-16 May 2007	33.111	24.727	32.460	27.260	n.d.a
A16	414	16-17 May 2007	32.460	27.260	31.290	30.010	19.7
A17	139	17 May 2007	31.290	30.010	32.585	30.236	20.5
A18	307	19 May 2007	31.441	29.736	32.585	29.436	n.d.a
A19	679	13-14 Jun 2006	38.220	24.830	40.080	26.340	19.9
A20	371	20-Jun-06	41.897	29.609	41.128	29.075	n.d.a
A21	373	16 Jun 2006	41.490	29.710	41.040	29.020	n.d.a
A22[b]	277	19 Jun 2006	41.872	30.073	41.872	30.073	20.3
A23[b]	294	19 Jun 2006	41.885	30.032	41.885	30.032	17.9
[a] Average air temperature during transects adquired from the ship meteo station (n.d.a. =no data available)							
[b] Samples taken at station (Ship not cruising)							

Text S2: Extraction and instrumental method details

Prior to extraction, all samples were spiked with Phenanthrene-d10 and Chrysene-d12 (Sigma-Aldrich) which were used as surrogate standards (50 µl at 1 ng μl^{-1}). QFFs were weighed and Soxhlet extracted with dichloromethane:methanol (2:1, v/v) for 24 h. The extracts were rotary evaporated to 2 ml and purified on a 3% Milli-Q water deactivated alumina column (3 g) with a top layer of anhydrous sodium sulfate. Each column was eluted first with 5 ml of hexane (not containing target OPEs), a second fraction with 12 ml of dichloromethane:hexane (2:1; v:v) and a thrid fraction with 12ml of dichloromethane. The second and thrid fractions selected for OPE analysis were concentrated to 0.5 ml by vacuum rotary evaporation, transferred to a 1.7 ml amber vial, with the corresponding hexane washings, and evaporated to 150 µl under a nitrogen stream. At this step, 300 ng of each internal standards (Tri-n-propyl-d21 phosphate and malathion-d7) were added to the extract.

OPE analysis was conducted by gas chromatography coupled to a mass spectrometer (Thermo Electron, San Jose, CA, USA) and compounds were quantified by the internal standard procedure. The GC was operated in electron impact mode (EI, 70eV). The injector temperature was set at 280 ºC and the splitless mode was used. The separation was achieved in a 30m x 0.25mm i.d. x 0.25µm HP-5MS capillary column (Agilent J&W). The oven temperature was programmed from 90ºC (holding time 1min) to 170ºC at 8ºC/min, to 250ºC at 4ºC/min, then to 300ºC at 10ºC/min (holding time 9min). The injection volume was of 2µl and the helium carrier gas flow was 1 ml min^{-1}. The temperatures of the MS transfer line and the ion source were set at 280 ºC and 230 ºC,

respectively. The detection and quantification of OPEs was performed in the selective ion monitoring (SIM) mode.

Chemicals

Tris-(2-chloroethyl)phosphate (TCEP), Tris[2-chloro-1-(chloromethyl)ethyl]phosphate (TDCP), Tris- (1-chloro-2-propyl)phosphate (TCPPs, mix of isomers), Tri-iso-buthyl phosphate (TiBP), Tri-n-buthyl phosphate (TnBP), Triphenyl phosphate (TPhP), 2-Ethylhexyl diphenyl phosphate (EHDPP), Tri(2-ethylhexyl) phosphate (TEHP) and Tricresyl phosphate (TCrP, mix of isomers) and the surrogate Phenanthrene-d10 and Chrysene-d12 were obtained from Sigma-Aldrich. The internal standards Tri-n-propyl-d21 phosphate and malathion-d7 were form C/D/N Isotopes Inc, Canada. All solvents used were GC pesticide residue analysis grade and were pruchasd in Sigma-Aldrich.

Text S3: Quality assurance /Quality control details

Pre-cleaning of material

QFF were individually wrapped in (n-hexane cleaned) aluminum foil, baked at 450 ºC for 8 h and then stored at -18 ^{o}C in a sealed plastic bag until used.

Blanks

Aerosol field blanks, consisting on cleaned QFFs, were collected. The materials were transported to the sampling area, mounted in the sampler, dismounted and transported back to the ship laboratory and then processed together with the samples. Procedural

blanks (sampling) consisting on clean filters (packed in the lab and untouched until analysis) were employed in order to evaluate the potential contamination of samples due to handling during the cruises. Procedural blanks (analysis) consisting on only extracting solvent (Soxhlet extracted and cleaned-up as for the samples) were also processed for each batch of fourteen samples.

Table S2. OPE blank levels (ng) in the aerosol samples (mean ± SD, N=6)

TCEP	0.7 ± 1.6
TDCP	n.d.
TCPP-1	8.4 ± 9.7
TCPP-2	1.7 ± 42
TCPP-3	n.d.
TiBP	4.8 ± 7.0
TnBP	2.5 ± 6.2
TPhP	2.5 ± 3.1
EHDPP	1.3 ± 3.3
TEHP	n.d.
TCrP-1	n.d.
TCrP-2	n.d.
TCrP-3	n.d.
TCrP-4	n.d.
n.d. = not detected	

Table S3. Instrumental limits of detections (LODs)

	[ng]	[pg m^{-3}] [b]
TCEP	0.5	1.1
TDCP	0.3	0.6
TCPP-1	0.1	0.2
TCPP-2	0.3	0.6
TCPP-3	0.5	1.1
TiBP	0.05	0.1
TnBP	0.05	0.1
TPhP	0.05	0.1
EHDPP	0.05	0.1
TEHP	0.05	0.1
TCrP-1	0.1	0.2
TCrP-2	0.1	0.2
TCrP-3	0.1	0.2
TCrP-4	0.5	1.1
[a]LODs calculated as S/N > 3		
[b]Average sampling volume of campaign = 470 m^3		

Information regarding atmospheric levels, occurrence and spatial distribution

Table S4. Atmospheric aerosol concentrations of OPEs (pg m^{-3}, median, mean and range) in the different Mediterranean sub-basins and in the SW Black Sea.

	Western Mediterranean [n=6]			Ionian Sea-Sicily [n=6]			South-East Mediterranean [n=6]			Aegean Sea	Black Sea [n=4]		
Compound	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range	(n=1)	Median	Mean	Range
TCEP	220.3	328.2	(69.7 - 853.9)	159.6	366.5	(102.8 - 841.0)	229.9	242.0	(119.5 - 478.9)	86.5	492.4	868.5	(308.0 - 2417.3)
TDCP	75.2	80.2	(n.d. - 115.1)	156.6	230.6	(n.d. - 459.6)	51.8	116.5	(n.d. - 298.5)	n.d	85.9	80.4	(n.d. - 96.9)
∑TCPPs[a]	844.5	849.6	(126.4 - 1797.8)	959.8	1113.7	(301.2 - 2338.8)	926.0	1003.6	(560.1 - 1903.0)	499.7	819.8	1158.7	(538.8 - 2722.4)
TiBP	240.0	247.3	(4.2 - 532.1)	80.5	118.2	(60.0 - 329.9)	377.3	375.8	(95.6 - 643.6)	58.5	150.2	139.4	(66.5 - 190.7)
TnBP	309.7	295.4	(56.5 - 498.2)	265.4	263.0	(77.5 - 508.4)	309.0	343.1	(226.1 - 598.6)	189.9	310.5	298.1	(202.4 - 369.0)
TPhP	20.9	22.2	(2.7 - 44.0)	22.0	24.3	(n.d. - 42.8)	35.6	40.5	(20.4 - 79.5)	6.9	34.7	27.5	(2.7 - 40.1)
EHDPP	539.8	539.8	(n.d. - 834.0)	433.2	433.2	(n.d. - 762.5)	276.4	294.2	(n.d. - 435.4)	n.d.	183.5	183.5	(n.d - 310.0)
TEHP	160.3	167.0	(85.1 - 268.4)	194.9	189.5	(55.8 - 307.4)	88.4	100.3	(56.7 - 176.4)	95.4	174.8	144.1	(36.3 - 190.7)
∑TCrPs[b]	47.7	47.7	(n.d. - 58.3)	77.2	78.1	(n.d. - 99.0)	38.1	58.9	(n.d. - 128.3)	22.7	70.2	70.2	(n.d. - 72.9)
$\sum_{14}$OPEs	**1728.0**	**2145.6**	**(413.5 - 4672.5)**	**2172.8**	**2365.8**	**(812.9 - 5107.1)**	**2087.7**	**2437.8**	**(1620.2 - 4247.1)**	**959.6**	**2006.9**	**2823.4**	**(1717.0 - 6165.5)**

[a] sum of three TCPP isomers; [b] sum of four TCrP isomers ; n.d.= not detected (values <LODs)

Table S5. Atmospheric aerosol concentrations of OPEs (pg m^{-3}) in all samples across de Mediterranean and in the SW Black Sea

Compound	*Western Mediterranean*						*Ionian Sea / sicily*						*South-East Mediterranean*						*Aegean Sea*	*Black Sea*			
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14	A15	A16	A17	A18	A19	A20	A21	A22	A23
TCEP	180.8	853.9	210.4	424.1	69.7	230.2	186.1	825.1	102.8	110.8	133.2	841.0	122.6	119.5	224.7	478.9	270.9	235.1	86.5	611.8	308.0	2417.3	373.0
TDCP	75.2	115.1	n.d.	n.d.	50.4	n.d.	459.6	156.6	n.d.	75.5	n.d.	n.d.	40.4	44.0	51.8	n.d.	147.8	298.5	n.d.	58.3	85.9	n.d.	96.9
∑TCPPs[a]	1003.7	1797.8	685.3	1258.2	126.4	226.2	1593.2	966.3	529.7	953.3	301.2	2338.8	636.1	972.7	879.3	1903.0	1070.6	560.1	499.7	627.1	538.8	2722.4	1012.5
TiBP	232.4	333.4	133.9	532.1	4.2	247.7	85.0	92.5	60.0	76.0	65.9	329.9	95.6	171.4	406.7	589.2	643.6	348.0	58.5	156.7	190.7	159.3	66.5
TnBP	179.1	498.2	212.0	419.0	56.5	407.4	321.0	340.0	77.5	209.8	121.0	508.4	314.4	303.6	226.1	598.6	327.1	288.8	189.9	317.3	369.0	336.7	202.4
TPhP	36.0	20.6	2.7	44.0	21.2	8.9	10.5	12.2	42.8	n.d.	31.9	n.d.	20.4	47.5	27.8	24.2	79.5	43.5	6.9	37.7	33.4	40.1	2.7
EHDPP	n.d.	834.0	n.d.	245.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	103.9	762.5	320.2	188.6	232.7	435.4	n.d.	n.d.	n.d.	n.d.	87.4	310.0	n.d.
TEHP	177.8	219.6	268.4	142.9	85.1	108.2	288.8	307.4	95.0	162.2	55.8	227.6	70.6	91.3	121.4	176.4	56.7	85.5	95.4	190.7	36.3	179.7	187.4
∑TCrPs[b]	n.d.	n.d.	58.3	n.d.	n.d.	37.1	n.d.	n.d.	77.2	58.1	n.d.	99.0	n.d.	31.3	34.8	41.3	128.3	n.d.	22.7	n.d.	67.5	n.d.	72.9
$\sum_{14}$ OPE	**1885.0**	**4672.5**	**1571.1**	**3065.9**	**413.5**	**1265.8**	**2944.2**	**2700.1**	**985.0**	**1645.5**	**812.9**	**5107.1**	**1620.2**	**1970.0**	**2205.4**	**4247.1**	**2724.5**	**1859.5**	**959.6**	**1999.6**	**1717.0**	**6165.5**	**2014.2**

[a] sum of three TCPP isomers; [b] sum of four TCrP isomers ; n.d.= not detected (values <LODs)

Figure S2. Relative predominance of OPE in the studied basins. Error bars represent the standard deviation (%).

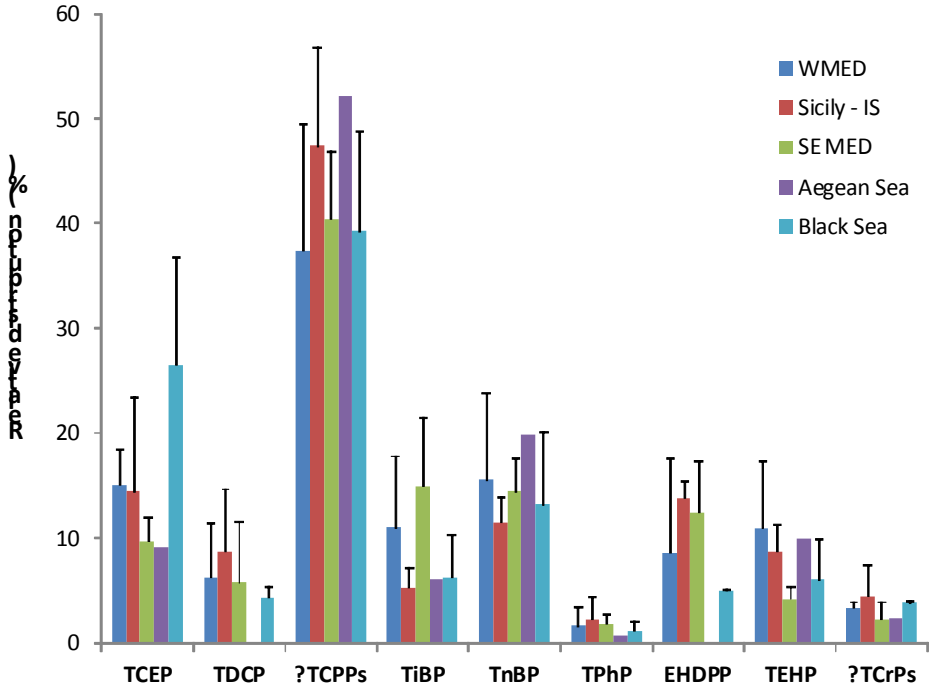


Figure S3. Spatial distribution of selected OPEs and $\sum_{14}$OPEs

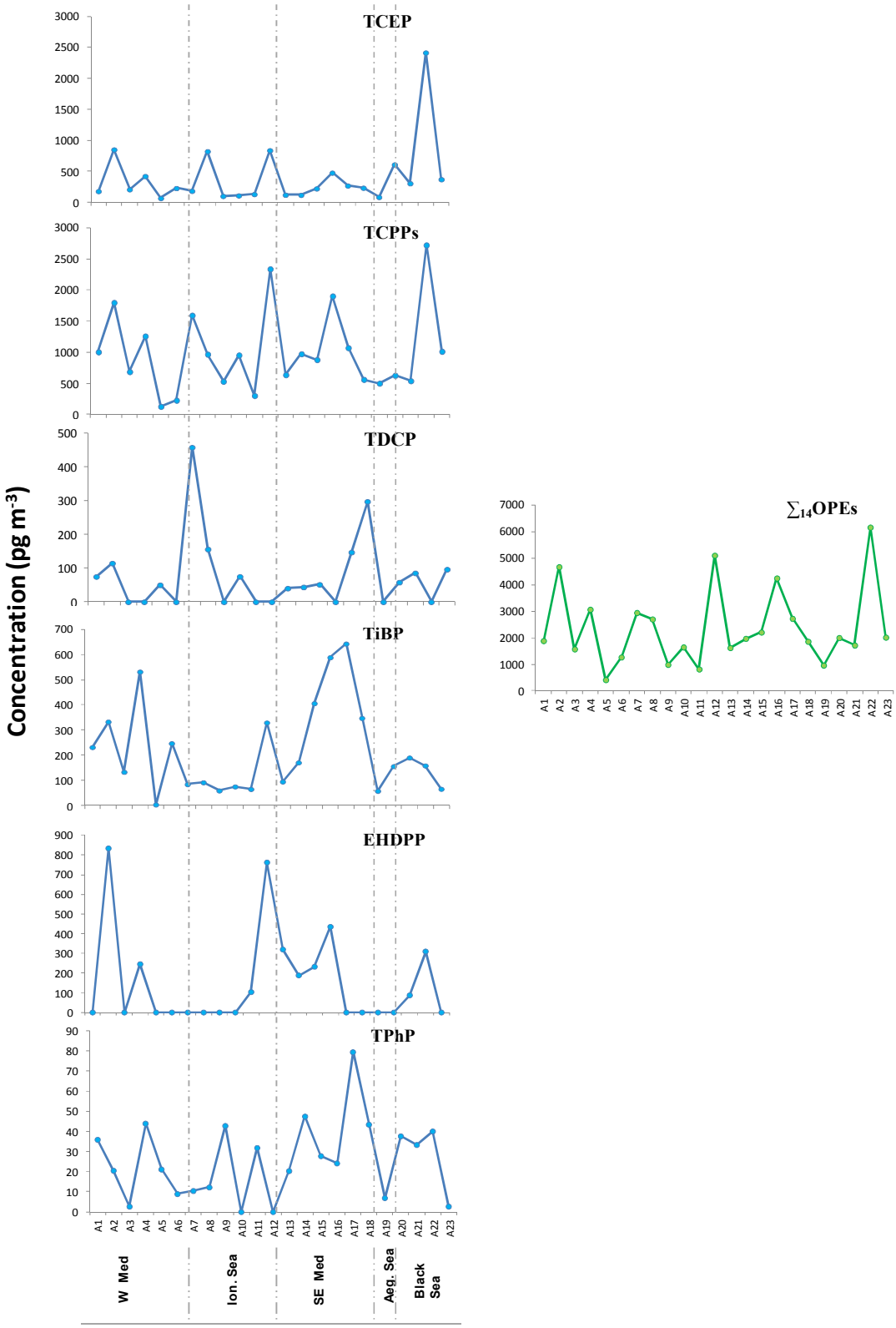
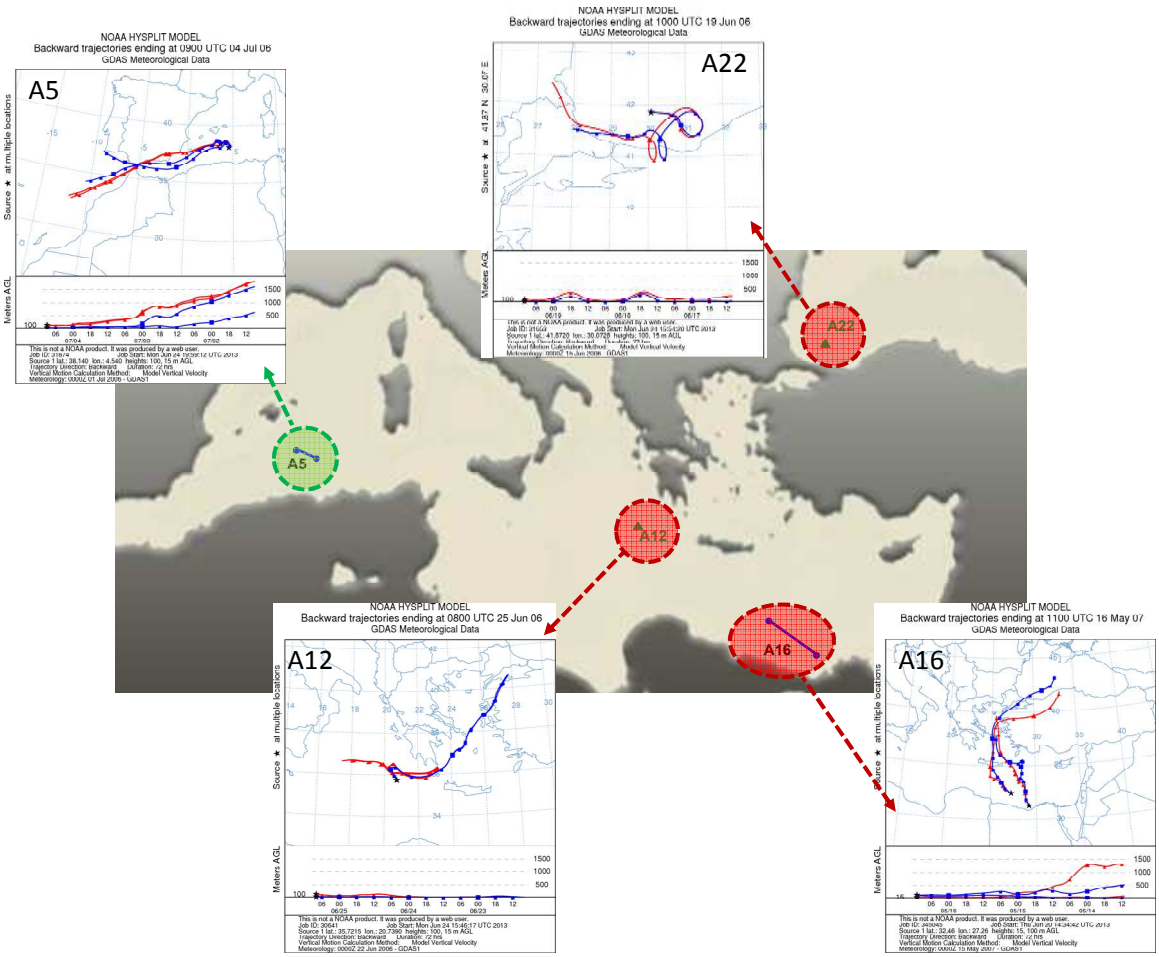


Figure S4. Location of samples presenting the highest and the lowest ∑OPE aerosol phase concentrations and corresponding air mass back trajectories



Information regarding deposition fluxes to the Mediterranean Sea

Table S6. Dry deposition fluxes (median, mean and range) of OPEs (ng m^{-2} d^{-1}) in the different Mediterranean sub-basins and in the SW Black Sea.

	Western Mediterranean [n=6]			Ionian Sea-Sicily [n=6]			South-East Mediterranean [n=6]			Aegean Sea	Black Sea [n=4]		
Compound	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range	(n=1)	Median	Mean	Range
TCEP	38.1	56.7	(12.1 - 147.5)	27.6	63.3	(17.8 - 145.3)	39.7	41.8	(20.7 - 82.8)	14.9	85.1	160.3	(53.2 - 417.7)
TDCP	13.0	13.9	(8.7 - 19.9)	27.1	39.8	(13.0 - 79.4)	8.9	20.1	(7.0 - 51.6)	n.c	14.8	13.9	(10.1- 16.7)
∑TCPPs[a]	145.9	145.8	(21.8 - 310.7)	165.8	192.5	(52.0 - 404.1)	160.0	173.4	(96.8 - 328.8)	86.3	141.7	211.7	(93.1 - 470.4)
TiBP	41.5	42.7	(0.7 - 92.0)	13.9	20.4	(10.4 - 57.0)	65.2	64.9	(16.5 - 111.2)	10.1	27.3	24.8	(11.5 - 33.0)
TnBP	53.5	51.0	(9.8 - 86.1)	45.9	45.4	(13.4 -87.9)	53.4	59.3	(39.1 - 103.4)	32.8	56.5	52.9	(35.0 - 63.8)
TPhP	3.6	3.8	(0.5 - 7.6)	3.8	4.2	(1.8 - 7.4)	6.2	7.0	(3.5 - 13.7)	1.2	6.1	4.9	(0.5 - 6.9)
EHDPP	93.3	93.3	(42.5 - 144.1)	74.9	74.9	(18.0 - 131.8)	47.8	50.8	(32.6 - 75.2)	n.c	34.3	34.3	(15.1 - 53.6)
TEHP	27.7	28.9	(14.7 - 46.4)	33.7	32.7	(9.6 - 53.1)	15.3	17.3	(9.8 - 30.5)	16.5	31.7	25.7	(6.3 - 33.0)
∑TCrPs[b]	8.2	8.2	(6.4 - 10.1)	13.3	13.5	(10.0 - 17.1)	6.6	10.2	(5.4 - 22.2)	3.9	12.1	12.1	(11.7 - 12.6)
$\sum_{14}$OPEs	**298.6**	**370.8**	**(71.5 - 807.4)**	**375.5**	**408.8**	**(140.5 - 882.5)**	**360.8**	**421.3**	**(280.0 - 733.9)**	**165.8**	**346.8**	**513.9**	**(296.7 - 1065.4)**

[a] sum of three TCPP isomers; [b] sum of four TCrP isomers, n.c = not calcualted (aerosol cocentrations ≤LOD)

Table S7. Dry deposition fluxes of OPEs (ng m^{-2} d^{-1}) in all samples across de Mediterranean and in the SW Black Sea

Compound	*Western Mediterranean*						*Ionian Sea / sicily*						*South-East Mediterranean*						*Aegean Sea*	*Black Sea*			
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14	A15	A16	A17	A18	A19	A20	A21	A22	A23
TCEP	31.2	147.5	36.4	73.3	12.1	39.8	32.2	142.6	17.8	19.1	23.0	145.3	21.2	20.7	38.8	82.8	46.8	40.6	14.9	105.7	53.2	417.7	64.5
TDCP	13.0	19.9	n.c	n.c	8.7	n.c	79.4	27.1	n.c	13.0	n.c	n.c	7.0	7.6	8.9	n.c	25.5	51.6	n.c	10.1	14.8	n.c	16.7
∑TCPPs[a]	173.4	310.7	118.4	217.4	21.8	39.1	275.3	167.0	91.5	164.7	52.0	404.1	109.9	168.1	152.0	328.8	185.0	96.8	86.3	108.4	93.1	470.4	175.0
TiBP	40.2	57.6	23.1	92.0	0.7	42.8	14.7	16.0	10.4	13.1	11.4	57.0	16.5	29.6	70.3	101.8	111.2	60.1	10.1	27.1	33.0	27.5	11.5
TnBP	31.0	86.1	36.6	72.4	9.8	70.4	55.5	58.8	13.4	36.2	20.9	87.9	54.3	52.5	39.1	103.4	56.5	49.9	32.8	54.8	63.8	58.2	35.0
TPhP	6.2	3.6	0.5	7.6	3.7	1.5	1.8	2.1	7.4	n.c	5.5	n.c	3.5	8.2	4.8	4.2	13.7	7.5	1.2	6.5	5.8	6.9	0.5
EHDPP	n.c	144.1	n.c	42.5	n.c	n.c	n.c	n.c	n.c	n.c	18.0	131.8	55.3	32.6	40.2	75.2	n.c	n.c	n.c	n.c	15.1	53.6	n.c
TEHP	30.7	37.9	46.4	24.7	14.7	18.7	49.9	53.1	16.4	28.0	9.6	39.3	12.2	15.8	21.0	30.5	9.8	14.8	16.5	33.0	6.3	31.1	32.4
∑TCrPs[b]	n.c	n.c	10.1	n.c	n.c	6.4	n.c	n.c	13.3	10.0	n.c	17.1	n.c	5.4	6.0	7.1	22.2	n.c	3.9	n.c	11.7	n.c	12.6
$\sum_{14}$ OPE	**325.7**	**807.4**	**271.5**	**529.8**	**71.5**	**218.7**	**508.8**	**466.6**	**170.2**	**284.3**	**140.5**	**882.5**	**280.0**	**340.4**	**381.1**	**733.9**	**470.8**	**321.3**	**165.8**	**345.5**	**296.7**	**1065.4**	**348.1**

[a] sum of three TCPP isomers; [b] sum of four TCrP isomers, n.c = not calcualted (aerosol cocentrations ≤LOD)