



HAL
open science

Phthalates and organophosphate esters in surface water, sediments and zooplankton of the NW Mediterranean Sea: Exploring links with microplastic abundance and accumulation in the marine food web

Natascha Schmidt, Javier Castro-Jiménez, Benjamin Oursel, Richard Sempere

► To cite this version:

Natascha Schmidt, Javier Castro-Jiménez, Benjamin Oursel, Richard Sempere. Phthalates and organophosphate esters in surface water, sediments and zooplankton of the NW Mediterranean Sea: Exploring links with microplastic abundance and accumulation in the marine food web. *Environmental Pollution*, 2020, pp.115970. 10.1016/j.envpol.2020.115970 . hal-02994089v1

HAL Id: hal-02994089

<https://amu.hal.science/hal-02994089v1>

Submitted on 24 Nov 2020 (v1), last revised 22 Feb 2021 (v2)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Phthalates and organophosphate esters in surface water, sediments and zooplankton of the NW Mediterranean Sea: exploring links with microplastic abundance and accumulation in the marine food web.

Natascha Schmidt ^a, Javier Castro-Jiménez ^{a,b,*}, Benjamin Oursel ^a, Richard Sempéré ^{a,*}

^a Aix-Marseille Univ., Toulon Univ., CNRS, IRD, Mediterranean Institute of Oceanography (M I O),
UM 110, Marseille, France

^b IFREMER, Laboratory of Biogeochemistry of Organic Contaminants (LBCO), Rue de l'Île d'Yeu,
BP 21105, 44311, Nantes, Cedex 3, France

* corresponding authors

Text S1: Method details concerning GC-MS analysis of organophosphate esters and phthalates.

GC analyses were conducted with an Agilent 7820A Series GC coupled with an Agilent 5977E MS, operating in selected ion monitoring (SIM) and electron impact (EI, 70 eV) modes. The separation was achieved in a 30 m x 0.25 mm i.d. x 0.25 μm HP-5MS capillary column (Agilent J&W). All target contaminants were quantified by the internal standard (IS) procedure. The injection volume was of 2 μL and the helium carrier gas flow was 1 mL min^{-1} . The temperatures of the MS transfer line and the ion source and the quadrupole were set at 300, 230 and 150 $^{\circ}\text{C}$, respectively. The following conditions were applied: injector temperature: 270 $^{\circ}\text{C}$ (splitless) and the oven was programmed from 90 $^{\circ}\text{C}$ to 132 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C min}^{-1}$, to 166 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$, to 175 at 1 $^{\circ}\text{C min}^{-1}$ (holding time 2 min), to 232 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C min}^{-1}$, and then to 300 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C min}^{-1}$ (holding time 5 min).

Table S1: Summary of GPS position, salinity (0.5 m and bottom), temperature (0.5 m and bottom) and dissolved organic carbon (DOC)* concentrations for each sampling date and sampling station. The depth at which sediment samples were collected is also indicated.

Date	ID	Station	GPS position	Salinity (0.5 m)	Temperature (°C) (0.5 m)	Depth (m)	Salinity (bottom)	Temperature (°C) (bottom)	DOC (µM)
09/05/2017	S1	L'Estaque	43°20.524 N, 5°18.479 E	38.2	14.3	42	38.2	14.1	68
		Frioul	43°16.279 N, 5°18.790 E	38.2	14.6	35	38.2	14.1	66
		Cortiou	43°12.704 N, 5°24.164 E	37.0	14.6	12	38.2	14.3	222
06/07/2017	S2	L'Estaque	43°20.913 N, 5°18.284 E	38.0	19.0	33	38.2	14.4	n.a.
		Frioul	43°16.335 N, 5°18.863 E	38.2	17.8	34	38.2	14.6	70
		Cortiou	43°12.717 N, 5°24.189 E	37.7	17.2	16	38.1	16.0	183
08/09/2017	S3	L'Estaque	43°20.511 N, 5°19.076 E	38.2	15.3	40	38.2	14.5	76
		Frioul	43°16.293 N, 5°18.933 E	38.1	15.7	35	38.2	14.7	84
		Cortiou	43°12.727 N, 5°24.183 E	34.8	15.4	20	38.2	14.5	130
15/11/2017	S4	L'Estaque	43°20.498 N, 5°18.708 E	38.3	14.7	44	38.3	14.2	65
		Frioul	43°16.390 N, 5°18.957 E	38.3	14.7	33	38.4	14.1	62
		Cortiou	43°12.715 N, 5°24.154 E	37.5	14.4	12	38.2	14.5	173
24/01/2018	S5	L'Estaque	43°20.546 N, 5°18.910 E	37.8	13.3	43	38.2	13.0	66
		Frioul	43°16.318 N, 5°18.794 E	38.3	13.3	34	38.2	13.3	69
		Cortiou	43°12.683 N, 5°24.112 E	31.1	13.5	15	38.2	13.4	243
20/03/2018	S6	L'Estaque	43°20.370 N, 5°19.115 E	38.4	13.0	42	38.3	13.0	67
		Frioul	43°16.341 N, 5°18.976 E	38.5	13.1	34	38.3	13.0	73
		Cortiou	43°12.689 N, 5°24.236 E	34.1	13.3	23	38.3	13.2	141

n.a. = not available. * DOC data has already been reported in Schmidt et al. (2019).

Schmidt, N., Fauvelle, V., Castro-Jiménez, J., Lajaunie-Salla, K., Pinazo, C., Yohia, C., Sempéré, R., 2019. Occurrence of perfluorinated compounds in the Bay of Marseille (NW Mediterranean Sea) and the Rhône River. *Marine Pollution Bulletin*. <https://doi.org/10.1016/j.marpolbul.2019.110491>

Table S2: Recoveries (in %) of seven PAEs and nine OPEs in sediment (n=3), zooplankton (n=3) and water* (n=5) samples.

	Sediment	n = 3	Zooplankton	n = 3	Water	n = 5
	Recovery	STD	Recovery	STD	Recovery	STD
	(%)	(%)	(%)	(%)	(%)	(%)
DMP	72	1	59	9	80	4
DEP	68	3	58	2	82	3
DiBP	86	2	69	5	74	15
DnBP	103	5	73	5	82	5
BzBP	95	4	68	10	83	4
DEHP	78	3	97	29	73	66
DnOP	103	2	74	6	52	3
TPP	63	7	61	11	108	4
TiBP	87	4	61	6	109	5
TnBP	81	4	75	8	107	6
TCEP	46	6	42	9	131	5
TCPP	57	28	62	5	118	4
TDCP	68	21	44	21	120	4
TPhP	71	1	53	11	111	4
EHDPP	104	2	81	11	61	6
TEHP	99	1	89	12	61	4

*Water sample recoveries have already been reported in Fauvelle et al. (2018).

Fauvelle, V., Castro-Jiménez, J., Schmidt, N., Carlez, B., Panagiotopoulos, C., Sempéré, R., 2018. One-Single Extraction Procedure for the Simultaneous Determination of a Wide Range of Polar and Nonpolar Organic Contaminants in Seawater. *Front. Mar. Sci.* 5, 1–10. <https://doi.org/10.3389/fmars.2018.00295>

Table S3: Concentrations of target compounds found in blanks. For water samples, the mean of 2-3 blanks per extraction batch is reported. Concentrations are given in ng L⁻¹ (water) or ng g⁻¹ (sediment and zooplankton), respectively.

Compound Matrix	Water			Sediment					Zooplankton					
	BLK 1	BLK 2	BLK 3	BLK 1	BLK 2	BLK 3	BLK 4	BLK 5	BLK 1	BLK 2	BLK 3	BLK 4	BLK 5	BLK 6
DMP	1.52	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ	<LOQ	n.d.	n.d.	n.d.	n.d.
DEP	n.d.	2.05	n.d.	1.02	<LOQ	<LOQ	<LOQ	<LOQ	1.18	<LOQ	1.69	1.52	2.01	1.49
DiBP	3.11	24.98	16.53	7.41	5.98	2.35	2.27	1.97	1.75	4.95	2.46	2.41	2.53	5.53
DnBP	1.49	n.d.	n.d.	1.18	0.97	<LOQ	<LOQ	0.97	<LOQ	3.96	<LOQ	1.04	1.04	3.61
BBzP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DEHP	n.d.	n.d.	34.72	4.45	3.42	10.01	3.70	9.77	7.96	4.81	16.87	22.71	7.36	39.21
DnOP	n.d.	n.d.	n.d.	1.64	n.d.	<LOQ	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TiBP	<LOQ	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TnBP	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.d.
TCEP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.49	1.55	1.54	3.30	n.d.	n.d.
TCPP	4.43	4.11	3.78	8.85	7.28	10.97	9.15	8.60	2.02	1.81	2.09	2.01	14.88	20.53
TDCP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.31	1.18	4.53	n.d.	2.55	3.81
TPhP	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
EHDPP	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.d.	n.d.	<LOQ	<LOQ	n.d.
TEHP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected, LOQ = limit of quantification

Table S4: PAE concentrations (in ng g⁻¹ dw) in zooplankton samples (sized >1000 µm; 500-1000 µm; 150-500 µm) collected on six sampling days (S1-S6) in the Bay of Marseille (L'Estaque, Frioul and Cortiou station).

	L'Estaque						Frioul						Cortiou					
	S1	S2	S3	S4	S5	S6	S1	S2	S3	S4	S5	S6	S1	S2	S3	S4	S5	S6
<i>Zooplankton</i> > 1000 µm																		
DMP	-	-	642	39	-	29	-	-	27	56	-	30	-	-	32	501	12	41
DEP	-	-	19	11	-	8.9	-	-	16	16	-	19	-	-	32	19	21	14
DnBP	-	-	305	386	-	67	-	-	349	178	-	47	-	-	93	527	1601	218
DiBP	-	-	120	118	-	41	-	-	90	92	-	127	-	-	56	224	64	172
BzBP	-	-	35	75	-	91	-	-	n.d.	37	-	184	-	-	98	n.d.	166	125
DEHP	-	-	3553	3803	-	1090	-	-	4062	1885	-	1057	-	-	8285	7838	3721	20573
DnOP	-	-	180	n.d.	-	n.d.	-	-	n.d.	149	-	113	-	-	398	544	197	1048
Σ PAEs	-	-	4 854	4 432	-	1 327	-	-	4 544	2 413	-	1 577	-	-	8 994	9 653	5 782	22 191
<i>500-1000</i> µm																		
DMP	n.d.	-	456	5.9	n.d.	17	n.d.	150	n.d.	16	2.8	n.d.	9.1	2.1	n.d.	6.1	-	9.6
DEP	21	-	14	13	33	9.8	24	23	12	14	26	17	25	16	25	20	-	12
DnBP	258	-	113	42	n.r.	177	159	150	38	80	n.r.	189	217	151	69	50	-	69
DiBP	88	-	25	10	n.r.	50	62	48	8.2	42	n.r.	56	82	38	26	26	-	26
BzBP	204	-	25	n.d.	n.d.	203	175	67	n.d.	n.d.	n.d.	158	72	33	78	57	-	109
DEHP	309	-	2192	658	1434	865	601	3846	778	811	2703	545	8040	5681	4019	12247	-	15642
DnOP	66	-	168	12	62	88	79	252	27	20	132	74	353	138	134	1003	-	767
Σ PAEs	946	-	2 993	741	1 529	1 410	1 100	4 536	863	983	2 864	1 039	8 798	6 059	4 351	13 409	-	16 635
<i>150-500</i> µm																		
DMP	3.1	7.1	197	21	n.d.	n.d.	n.d.	117	n.d.	14	5.7	n.d.	9.0	24	6.2	43	n.d.	19
DEP	17	29	7.0	20	23	47	162	38	14	19	11	39	27	17	9.9	26	17	108
DnBP	163	288	104	133	66	64	537	815	197	60	194	103	27	74	40	51	206	98
DiBP	68	110	31	40	55	36	65	224	75	9.4	47	19	60	44	45	34	230	138
BzBP	49	340	35	74	95	173	54	88	n.d.	n.d.	40	127	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DEHP	2521	1257	2930	2737	1245	1991	869	6341	3506	1653	2126	951	33568	14346	5032	30736	1397	43228
DnOP	87	96	125	235	73	152	21	570	1361	27	133	7.6	1203	901	182	2166	182	3377
Σ PAEs	2 908	2 127	3 429	3 260	1 557	2 463	1 708	8 193	5 153	1 782	2 557	1 247	34 894	15 406	5 315	33 056	2 032	46 968

n.d. = not detected; n.r. = not reported due to contamination through rubber boot fragments that washed from the boat into the sampling net; “-“ indicates that not enough biomass was available for extraction.

Table S5: OPE concentrations (in ng g⁻¹ dw) in zooplankton samples (sized >1000 μm; 500-1000 μm; 150-500 μm) collected on six sampling days (S1-S6) in the Bay of Marseille (L'Estaque, Frioul and Cortiou station).

	L'Estaque						Frioul						Cortiou					
	S1	S2	S3	S4	S5	S6	S1	S2	S3	S4	S5	S6	S1	S2	S3	S4	S5	S6
<i>Zooplankton</i> <i>> 1000 μm</i>																		
TPP	-	-	n.d.	n.d.	-	n.d.	-	-	n.d.	n.d.	-	n.d.	-	-	n.d.	n.d.	n.d.	n.d.
TiBP	-	-	183	301	-	85	-	-	766	218	-	68	-	-	188	155	79	309
TnBP	-	-	8.3	4.6	-	n.d.	-	-	32	8.4	-	4.4	-	-	21	25	9.8	74
TCEP	-	-	88	92	-	44	-	-	217	145	-	92	-	-	162	123	197	107
TCPP	-	-	367	477	-	128	-	-	-	287	-	-	-	-	548	646	261	1487
TDCP	-	-	217	221	-	129	-	-	n.d.	n.d.	-	80	-	-	707	n.d.	1606	2267
TPhP	-	-	15	16	-	n.d.	-	-	19	18	-	5.3	-	-	38	12	16	64
EHDPP	-	-	114	83	-	6.6	-	-	148	162	-	50	-	-	124	139	69	149
TEHP	-	-	92	n.d.	-	n.d.	-	-	n.d.	n.d.	-	n.d.	-	-	80	94	n.d.	175
Σ OPEs	-	-	1 084	1 195	-	393	-	-	1 182	838	-	300	-	-	1 868	1 194	2 238	4 632
<i>500-1000 μm</i>																		
TPP	n.d.	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.
TiBP	49	-	286	51	261	112	55	140	64	74	144	76	97	81	54	87	-	131
TnBP	50	-	4.7	3.5	25	n.d.	5.3	13	21	4.0	12	n.d.	9.2	4.7	23	15	-	53
TCEP	209	-	95	132	507	160	167	171	162	141	299	186	121	149	100	126	-	120
TCPP	-	-	180	67	497	-	-	352	137	131	302	-	459	416	207	386	-	764
TDCP	1269	-	566	57	n.d.	1024	2200	517	500	-	53	1099	1175	n.d.	403	786	-	484
TPhP	n.d.	-	12	7.3	16	n.d.	n.d.	48	22	12	18	n.d.	19	25	16	23	-	21
EHDPP	42	-	74	82	55	21	37	314	104	215	72	40	149	171	100	160	-	188
TEHP	n.d.	-	9.5	6.5	7.8	39	n.d.	n.d.	67	n.d.	n.d.	n.d.	87	n.d.	80	113	-	120
Σ OPEs	1 619	-	1 227	406	1 369	1 356	2 464	1 555	1 077	577	900	1 401	2 116	847	983	1 696	-	1 881
<i>150-500 μm</i>																		
TPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TiBP	70	88	169	263	359	152	53	276	929	79	53	251	121	193	48	128	103	120
TnBP	42	14	5.0	8.6	27	n.d.	14	19	79	40	5.6	n.d.	11	68	13	66	68	38
TCEP	171	206	158	99	205	235	206	583	207	129	72	219	228	162	121	130	177	218
TCPP	-	269	240	229	716	-	-	933	-	210	111	-	1532	906	483	970	-	644
TDCP	1558	2610	40	643	-	891	-	985	-	523	460	583	192	2038	591	1030	-	931
TPhP	3.8	69	20	16	n.d.	n.d.	n.d.	70	n.d.	21	5.9	n.d.	29	31	15	27	n.d.	38
EHDPP	68	310	89	227	53	48	-	572	-	697	66	79	405	178	98	311	53	398
TEHP	n.d.	n.d.	n.d.	21	n.d.	146	-	121	n.d.	77	9.6	91	271	288	103	229	n.d.	365
Σ OPEs	1 913	3 566	721	1 507	1 360	1 472	273	3 559	1 215	1 776	783	1 223	2 789	3 864	1 472	2 891	401	2 752

n.d. = not detected; “-” indicates that not enough biomass was available for extraction or that TCPP and/or TDCP could not be quantified due to matrix effects.

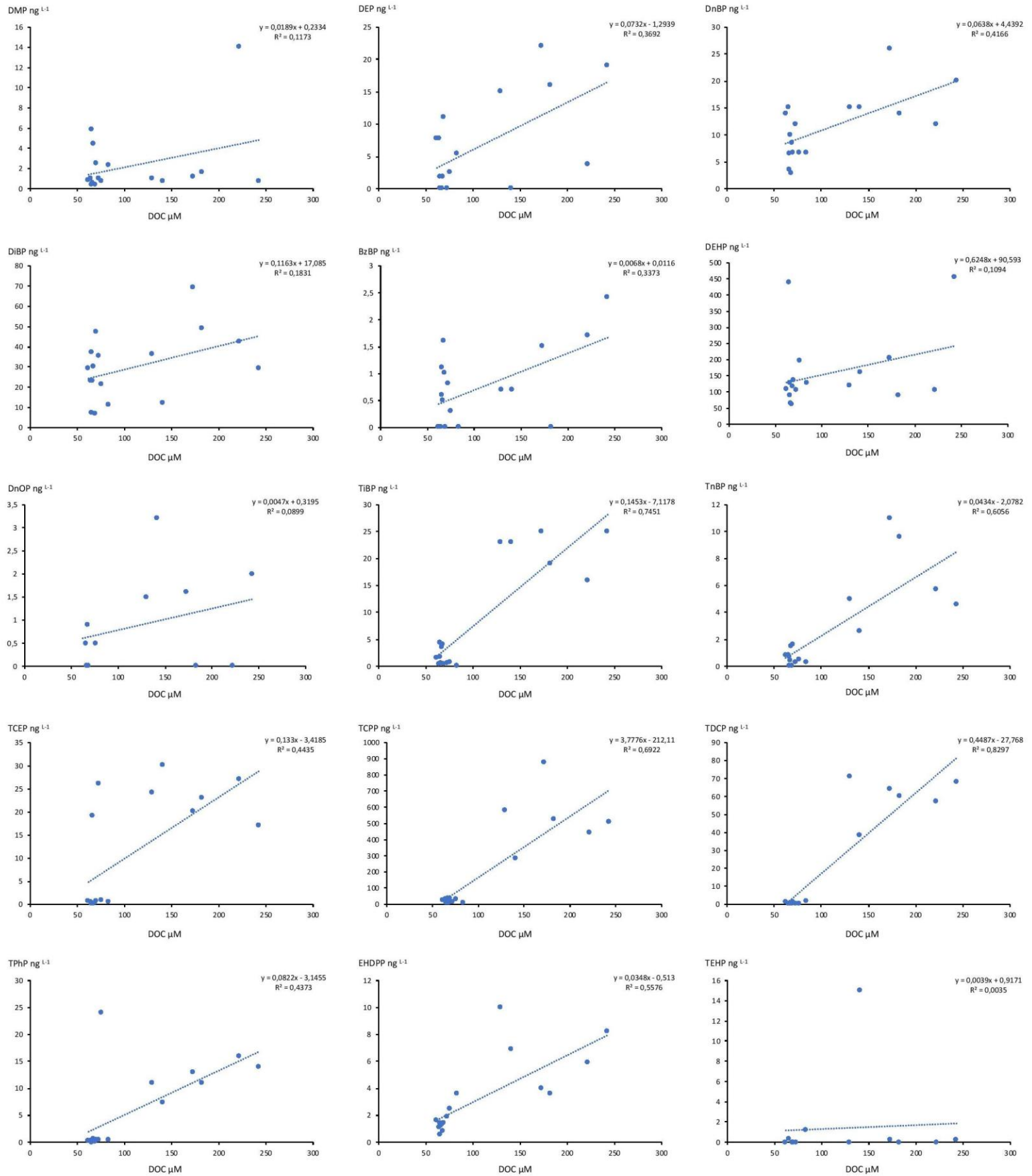


Figure S1: Scatterplots investigating the relationship between dissolved organic carbon (DOC) and individual PAE and OPE concentrations.