Water-sediment partition and bioaccumulation in fish of selected endocrine disrupting UV filters. Evrotas River case study.

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Introduction and objectives

Personal care products (PCPs) is a generic term that describes a group of chemicals included in many different products widely used in daily life (aftershave, toothpaste, shampoo, cosmetics, etc.), being used in considerable quantities. After use, they may be absorbed by the body and excreted, or washed off after its application [1]. PCPs and their metabolites enter the aquatic environment and reach WWTPs [2]. There, they are partially eliminated and either retained in the sludge or released to the water bodies through the effluents [3]. The last decade, the concern about the potential hazardous risk associated to them and their by-products, that can be more persistent and toxic [4], has been on the rise. Once in the environment and depending on their physicochemical properties, PCPs can adsorb onto the sediments and also be accumulated in the ecosystems' biota. Among PCPs, UV filters is the group attracting more attention by scientists as they are increasingly used in more and more daily-use products worldwide to prevent diseases caused by exposure to UV sunlight.

In the present study we investigated the water-sediment partition and biota bioaccumulation potential of selected organic UV filters in water, sediment and fish samples from Evrotas River (Greece).

Samples

Water (8), fish (4) and sediment (4) samples where collected from the Evrotas river, Grece, in September 2015.

Before storage, water samples were filtered, sediment samples were sieved and lyophilized, and fish samples were homogenized and lyophilized. Then, they were frozen until analysis.

Target compounds

Table 1. *Name, Log K_{ow} and CAS numbers (CAS#) of the UV filters studied. Solubility values in water at 25 ^{o}C.*

Name	BP1	BP2	BP3	4HB	4DHB	DHMB	4MBC	EtPABA	BZT	MeBZT	DMeBZT
CAS#	131-56-6	131-55-5	131-57-7	1137-42-4	131-53-3	131-53-3	36861-47-9	94-09-7	95-14-7	136-85-6	4184-79-6
Solubility (g L^{-1})	0.39	0.98	0.10	0.41	0.60	-	0.02	1.31	20	6	-
Log K_{ow}	3.15	2.78	3.79	2.92	2.19	3.82	4.95	1.86	1.23	1.89	2.06

Analytical methodologies: HPLC-MS/MS

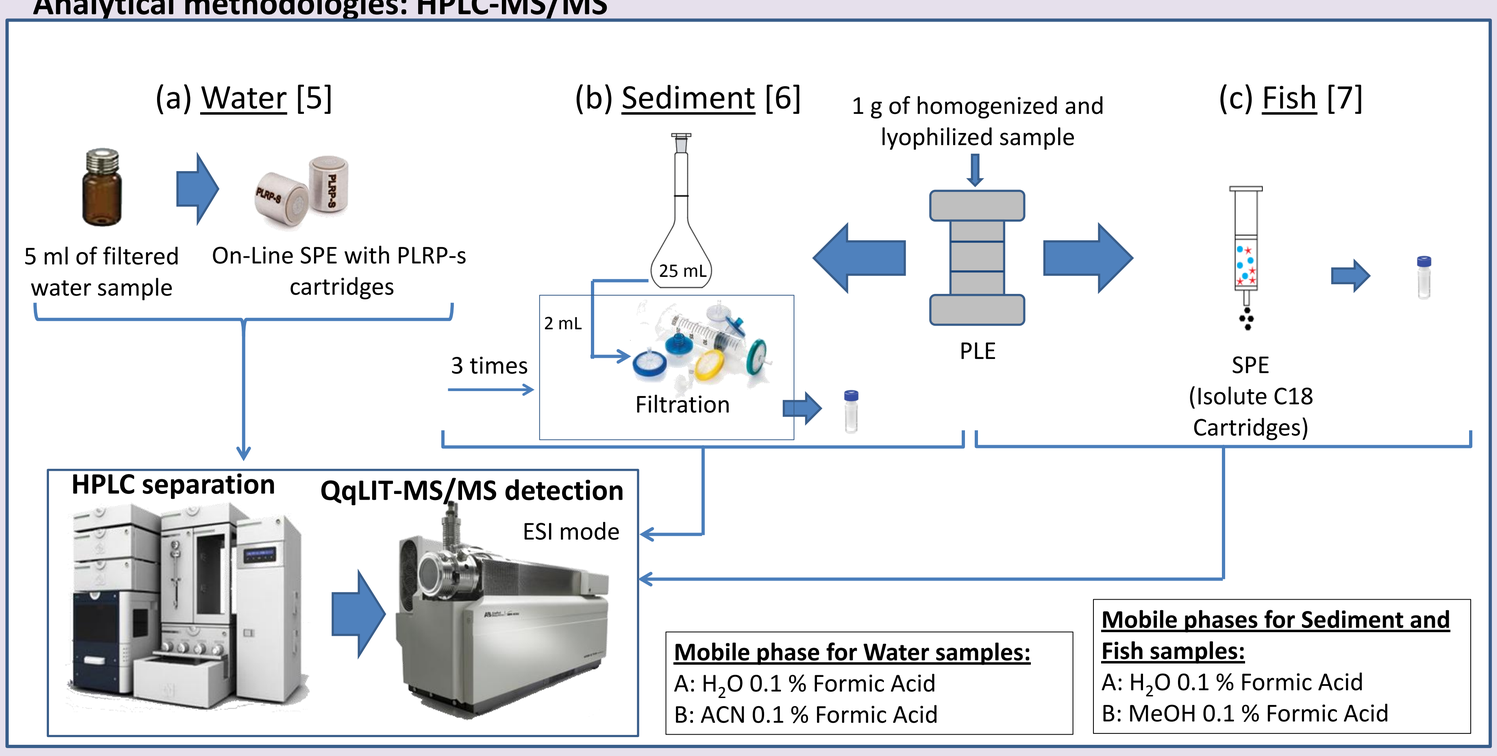

Figure 1. *Scheme of the methodologies applied to determine PCPs in (a) water, (b) sediment and (c) fish. The LODs and LOQs for the three matrices were in the ranges: 0.4-1.2 and 0.5-3.8 ng/L, 0.03-1.2 and 0.1-11.2 ng/g, 0.04-1.3 and 0.1-4.4 ng/g, respectively.*

Results

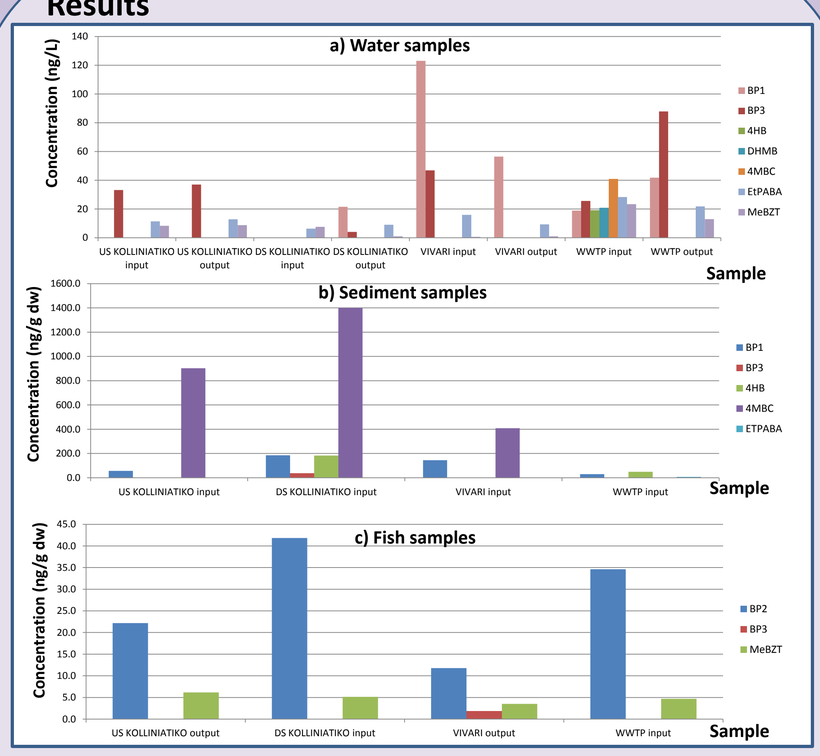

Figure 2. *Concentrations of the target compounds in (a) water, (b) sediment and (c) fish.*

Distribution coefficients (DC)

Table 2. *Sediment–water partition and fish-water bioaccumulation factors.*

Compound	BP1	4HB	EtPABA	MeBZT
log K_{ow}	3.15	2.92	1.86	1.89
Sediment/Water				
Kolliniatikos US (out)	-	-	-	-
Kolliniatikos DS (in)	-	-	-	-
Viologikos DS (WWTP) (in)	4.17E+04	6.69E+04	5.71E+03	-
Vivari (out)	1.23E+05	-	-	-
Mean	**8.23E+04**	**6.69E+04**	**5.71E+03**	**-**
Fish/Water				
Kolliniatikos US (out)	-	-	-	7.06E+02
Kolliniatikos DS (in)	-	-	-	6.75E+02
Viologikos DS (WWTP) (in)	-	-	-	2.01E+02
Vivari (out)	-	-	-	3.75E+03
Mean	**-**	**-**	**-**	**1.33E+03**

- DCs calculated by normalizing the concentrations to Total Organic Carbon (TOC %) for sediments samples and dry weight (dw) for fish samples.
- In many cases, it has not been possible to calculate the DC because of the lack of coincidence of the contaminants between the sediment or fish samples and the water samples.
- Sediment/Water DC values decrease as follows: EtPABA > BP1 ≈ 4HB, which matches with the Log K_{ow} values.
- The mechanism behind the important accumulation of the polar MeBZT in fish is yet uncertain, but its high pKa (8.66) could play a decisive role.

Discussion and conclusions

- Seven compounds out of the eleven investigated were detected in the water samples in the range 0.6-123 ng/L; five compounds in sediment samples in the range 6.3-1400 ng/g (dw); and three compounds in fish samples in the range 1.8-41.8 ng/g (dw).
- DS Kolliniatiko waters are the samples with lower contamination levels, whereas Vivari input and WWTP input present the highest levels. WWTP input present the highest number of contaminants (7).
- Really high concentrations in sediments, especially in DS Kolliniatiko input, with 4MBC as the major contributor.
- DS Kolliniatiko input fish sample is also the most contaminated.
- Concern about the high level of BP2 in fish because of its estrogenic activity.
- The most frequently detected compounds in water samples were EtPABA and MeBZT (100%); in sediment samples it was BP1 (100%); and in fish samples they were BP2 and MeBZT (100%).
- Despite of the low value of Log K_{ow} of MeBZT (1.89), it has been detected in all fish samples.

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