Occurrence and environmental distribution of 5 UV filters during the 1 summer season in different water bodies

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Abstract

Organic UV filters are used worldwide in various personal care products as well as textiles, paints, plastic, food and adhesives. They are main ingredients in sunscreen lotions that are used heavily by beachgoers in the summer season. There is thus an increasing concern regarding the fate of organic UV filters in the

environment and their impact on living organisms. Many of the UV filters in use are hydrophobic and are expected to accumulate in the sediment phase in aquatic systems, but this has yet to be validated in situ. We targeted the UV filters benzophenone 3 (BP3), butyl Methoxydibenzoylmethane (BMDBM), diethylhexyl butamido triazone (DBT), bis-ethylhexyloxyphenol methoxyphenyl triazine (BEMT) and methylene bis-benzotriazolyl tetramethylbutylphenol (MBBT) in a freshwater lake and in a coastal bay in order to understand their distribution during summer 2016. Further, we examined their environmental partitioning by collecting samples from the surface water, the sediment phase and water surface microlayer (SML). We show for the first time the presence of DBT, BEMT and MBBT in environmental matrices (water, SML, and sediment). Notably, these UV filters were detected at low amounts in surface waters with maximum concentrations of 9.9 ng/L for DBT, 18.4 ng/L for BEMT and below detection limits for MBBT, and somewhat higher concentrations in the SML, with maximum concentrations of 43.3 ng/L for DBT, 5625.4 ng/L for BEMT and 45.6 ng/L for MBBT. These filters were detected at even greater concentrations in the sediments, with maximum concentrations of 652.6 ng/g for DBT, 115.0 ng/g for BEMT and 75.2 ng/g for MBBT (dry weight sediment). We also performed controlled laboratory experiments to determine their partitioning behavior and we verified the actual solubility of many of the filters. This will help in determining the environmental fate and finally lead to a better risk assessment of these compounds. Together, these results corroborate the hypothesis that hydrophobic UV filters accumulate in the sediment phase and highlight the importance of discerning whether these UV filters impact the benthic community and their potential for bioaccumulation.

1 Introduction

Over the past fifteen years, public interest in sunscreens has increased because of their potential ecological risk in aquatic environments. Sunscreens use organic UV filters as ingredients in their formulations to protect human skin from sunburns, premature skin aging and skin cancer. Organic UV filters include a heterogeneous group of molecules characterized by conjugated aromatic groups that can absorb UV-A (320–400 nm) and UV-B (280–320 nm) radiation. These UV filters are also added to textiles, plastics, paints, food and adhesives to protect polymers and pigments against photo degradation and to prevent discoloring. In sunscreen lotions, formulations generally combine several filters and ingredients to cover a broad UV spectrum and to improve skin application and water resistance (Osterwalder et al. 2014). More than 50 different UV filters are on the market (Shaath 2010), and their usage varies depending on the regulations of the region.

UV filters enter the aquatic environment directly from recreational activities and indirectly from wastewater treatment plants (WWTPs), see Ramos et al. (2016) and references therein, or leaching from solid waste disposal sites on land. UV filters enter the sewage systems when people shower following bathing or from industrial discharge. Once in the environment, partitioning between water and sediment occurs depending on the lipophilicity of the compound, which is estimated by the octanol-water partition coefficient ($\log k_{ow}$) value. Those compounds with low aqueous solubility tend to accumulate in sediments and

sludge (Ramos et al. 2015). Environmental concentrations of different UV filters are found in numerous reports, with recent reviews summarizing their concentrations in different matrices (Montes-Grajales et al. 2017) including wastewater treatment plants (Ramos et al. 2016), sediments (Tsui et al. 2015) and water bodies (Ramos et al. 2015;Sánchez-Quiles and Tovar-Sánchez 2015).

The possibility that these compounds have negative effects on non-target organisms is one factor that raises concern about the release of UV filters into the environment. This is especially true in areas, like the Mediterranean, that are highly impacted by tourism (Tovar-Sanchez et al. 2019). Further, because UV filters have been detected in various biological materials, such as fish (Balmer et al. 2005; Fent et al. 2010; Tsai et al. 2014; Langford et al. 2015; Gago-Ferrero et al. 2015; Emnet et al. 2015; Sang and Leung 2016), dolphins (Gago-Ferrero et al. 2013; Alonso et al. 2015) and bird eggs (Molins-Delgado et al. 2017), biomagnification is a real concern (Fent et al. 2010; Sang and Leung 2016; Molins-Delgado et al., 2017). Many UV filters are thought to impact non-target organisms via endocrine disruption (Díaz-Cruz and Barceló 2009; Sánchez-Quiles and Tovar-Sánchez 2015). Recently, benzophenone 3 (BP3) was shown to have toxic effects on many living organisms (Downs et al. 2016; Wnuk et al. 2018). As a consequence, this compound was banned in the state of Hawaii, USA ("Office of the governor — news release — Governor David Ige signs bill making Hawaii first in the world to ban certain sunscreens" 2018).

Diethylhexyl butamido triazone (DBT), methylene bis-benzotriazolyl tetramethylbutylphenol (MBBT) and bis-ethylhexyloxyphenol methoxyphenyl

triazine (BEMT) have very high predicted log K_{ow} values (Table 1) and have not been reported in any environmental matrix to date. BP3 and butyl Methoxydibenzoylmethane (BMDBM), have lower log K_{ow} values (Table 1) and are technically easier to detect: butyl methoxydibenzoylmethane (BMDBM), has been detected in various compartments, including seawater and freshwater (Bratkovics and Sapozhnikova 2011; Giokas et al. 2005; Sánchez Rodríguez et al. 2015; Poiger et al. 2004) and in WWTP effluents and influents (Rodil et al. 2009; Tsui et al. 2014) and BP3 has been found in many environmental matrices (ex. (Montes-Grajales et al. 2017; Ramos et al. 2016)). However, for a proper assessment of the environmental fate of these filters, we also need to determine the solubility and the partitioning behavior of these compounds experimentally.

In the current study, we determined the concentration of the widely studied UV filter BP3 and compared the concentration of BP3 with that of less investigated but relatively broadly utilized compounds. We investigated a coastal marine site, the Bay of Banyuls-sur-mer, and a freshwater lake, Villeneuve de la Raho Lake. Both sites experience a high number of sunbathers during the summer months (June to August). In addition to determining the dynamics of the filters during the summer months, we determined in which compartment these UV filters are found. For example, the surface microlayer (SML) has different chemical and biological characteristics than those of the underlying water (Obernosterer et al. 2005) and this air-sea boundary, in which hydrophobic compounds may accumulate and living organisms may be present (Rahlff et al. 2018), can be important in the aquatic environment. Further, given the fairly high log K_{ow} of many UV filters; the expectation is that these compounds will eventually

concentrate into the solid/sediment compartment. However, we do not know how long this partitioning will take and whether UV filters will accumulate in sediments over time. Therefore we also set out to resolve several factors important to better understand the fate of these compounds in aquatic environments.

2 Materials and methods

2.1 Chemicals and solvents

The molecular structures and physicochemical properties of the studied compounds are shown in Table 1. Analytical standards of MBBT, (97 %), BEMT (98 %), DBT (98 %), BMDBM (99 %) and BP3 (98%) were purchased from Sigma-Aldrich (Lyon, France). Analytical or LC-MS grade methanol was purchased from Biosolve (Biosolve Chimie France, Dieuze). Analytical-grade dichloromethane, 1-methyl-2-pyrrolidinone (NMP) and formic acid (98 %) were obtained from Sigma-Aldrich. Pure water was obtained from Elga Purelab Flex System (Veolia LabWater STI, Antony, France). In order to avoid contamination, glassware was cleaned with dichloromethane and dried at 450 °C for 2 hours.

Standard solutions of individual UV filters were prepared in NMP at a concentration of 1 mg/mL. These solutions were kept at -20°C and protected from light. A standard mixture solution was prepared by diluting each individual standard solution with NMP/water (8:2, volume/volume (v/v)) in order to get a concentration range from 1024 to 4 ng/mL. A calibration curve was built both with LC-MS/MS and LC/DAD using these solutions. These standard solutions

were also used for spiking seawater and sediments for recovery studies.

2.2 Sampling sites

All samples were collected from April to October 2016 from two different sites: the main beach in Banyuls-sur-mer (Latitude 42°28'57.5" N, Longitude 3°07'55.4" E), and a nearby artificial lake in Villeneuve-de-la-Raho (Latitude 42°37'46.3" N, Longitude 2°54'18.0" E). Both these sites see highly increased tourism pressure during the summer months. Lake Villeneuve measures more than 200 ha, with 16 ha dedicated to touristic activities including a bathing zone and a 800 m-wide beach. Banyuls-sur-Mer is a small tourist town in the south of France, where the main beach measures 350 meters and is partially enclosed and protected from heavy ocean currents. We sampled the surface water, the water surface microlayer (SML) and the sediment in Villeneuve Lake and Banyuls Bay during the summer season from April to October. We sampled at 5 time points from Villeneuve Lake and at 9 from Banyuls Bay (Table S1). The first time point was before the bathing season for both sites.

2.3 Sampling procedures

All samples were collected using gloves and in order to minimize contamination, the people involved in sampling did not use any UV protection cream. The sampling was always performed in the afternoon where wind conditions were favourable. Water samples were collected in the middle of the bathing zones using an inflatable boat. For Banyuls Bay this was approximately 50 meters from the beach and for lake Villeneuve the sampling was preformed approximately 10 m from the beach. Samples from the water column (approximately 50 cm below

the surface) were collected using a bucket and poured into glass bottles and closed with PTFE caps. The bucket and glass bottles were rinsed several times before final sampling and 3 x 1L were collected at each time point. The SML was collected with a glass plate system (Harvey and Burzell 1972) resulting in 3 x 0.5 L SML samples per time point. The superficial layer (top 5 cm) of sediments from the same zone was collected in glass jars. This was done manually in Lake Villeneuve because the water depth was less than 1 meter, and by snorkeling/freediving in Banyuls bay, where the sediment depths were around 7-8 meters

2.4 Water extraction and LC-MS/MS analysis

Collected water samples were filtered through 47 mm glass microfiber filters with a pore size of 1.6 µm (GF/A Whatman, GE Healthcare, Little Chalfont, UK), using a glass filtration system. All samples were acidified with formic acid (0.1% v/v) and extracted using an automated liquid handler GX-271 ASPEC® (Gilson International, Villiers-le-Bel, France) using Hypersep™ phenyl SPE cartridges 1 g/6 mL (Thermo Fisher Scientific, Illkirch, France). All the eluents were acidified with formic acid (0.1% v/v) to pH 3. Before loading, the cartridges were conditioned with 10 mL of methanol followed by 10 mL of water. Next, an entire 1 L sample was percolated through the cartridge with a constant flow rate (8 mL/min). The cartridge was dried under nitrogen for 10 min (AirLiquide, Toulouse, France). Then, the analytes were extracted with 10 mL of methanol followed by 10 mL of methanol/dichloromethane (1:1, v/v). The extracts were evaporated to dryness under vacuum in an HT-4X system (Genevac, Biopharma Technologies France, Lyon, France) and dissolved in 500 µL of NMP/water (8:2,

v/v) before analysis.

LC-MS/MS is more sensitive than LC-DAD (lower limits of detection (LODs)) for the detection of these UV filters. Water samples were analyzed with LC-MS/MS because UV filter concentration was lower in these samples, while sediment samples were analyzed with LC-DAD. Here, chemical analyses were conducted with a Q Exactive Focus Orbitrap System coupled to an Ultimate 3000™ UHPLC system (Thermo Fisher Scientific). Analyses of water samples and standards (5 µL injected) were performed in electrospray positive ionization mode in the 53.4–800 m/z range in profile mode. The parameters were as follow: spray voltage: 3 kV; sheath flow rate: 75; aux gas pressure: 20; capillary temperature: 350°C; heater temperature: 430°C. The analysis was conducted in FullMS data dependent MS2 mode (confirming ions). Resolution was set to 70,000 in Full MS mode, and the AGC (automatic gain control) target was set to $1x10^6$. In MS2, resolution was 35,000, AGC target was set to $1x5e^4$, isolation window was 3 m/z, and normalized collision energy was 35 eV, with an inclusion table. The UHPLC column was a Kinetex Biphenyl 2.6 µm, 150 x 4.6 mm column (Phenomenex). The column temperature was set to 50°C, and the flow rate was 1 mL min^{-1}. The solvent system was a mixture of water (A) with increasing proportions of methanol (B), with both solvents modified with 0.1% formic acid. The gradient was as follows: 20% B 4 min before injection, then from 1 to 7 min, a gradient increase of B up to 100% (curve 2), followed by 100% B for 8 min. The flow was injected into the mass spectrometer starting from 6,5 min after injection. All data were acquired and processed using Trace Finder 3.1 software Trace Finder™ 3.1 software (Thermo Fisher Scientific). Obtained retention times (RT) were the

following: 6,68 min for BP-3; 7,84 min for BM-DBM; 9,26 min for DBT; 13,68 min for BEMT; and 12,79 min for MBBT.

2.5 Sediment extraction and LC-DAD analysis

Collected sediments were frozen at -20°C and then freeze-dried for 24 h. The freeze-dried samples (5 g) were passed through a 1 mm pore sieve and stored at -20°C until extraction. Freeze-dried sieved sediment (1 g) were extracted twice with 5 mL of a mixture of methanol/dichloromethane (1:1, v/v), with 0.1% formic acid and a 10 min sonication. All the supernatants were combined and evaporated under vacuum in an HT-4X system (Genevac, Biopharma Technologies) and dissolved in 1 mL of NMP/water (8:2, v/v) before analysis.

Samples (30 µL injected) were analyzed with an Ultimate 3000™ HPLC system, equipped with a DAD detector (Thermo Fisher Scientific) and a Phenomenex Kinetex Biphenyl 2.6 µm, 150 x 4.6 mm column. The oven temperature was set to 50°C, and the flow rate was 1 mL min^{-1}. The solvent system was a mixture of water (A) with increasing proportions of methanol (B), with both solvents modified with 0.1% formic acid. The gradient was as follows: 10% B 4 min before injection, then from 1 to 15 min, a gradient increase of B up to 100% (curve 2), followed by 100% B for 10 min. The data acquisition software was Chromeleon™ 7.2 (Thermo Fisher Scientific). Standard solutions were injected to generate ten-point calibration curves for the quantification of target compounds. Peak areas were within the linear range of the curve. The obtained retention times (RT) were the following: 9,4 min for BP-3; 11,76 min for BMDBM; 14,9 min for DBT; 20,6 min for BEMT; and 19,5 min for MBBT.

Sediment samples were also analyzed for organic carbon and granulometry. Dried sediments were decarbonized with repeated additions of H_3PO_4 (1M) and HCl (2M) until no effervescence occurred. Decarbonated sediment were dried again at 40 °C at least 24 hours. POC content were then measured using an Elementar Variomax elemental analyzer. Particle size analyses (range: 0.1-3500 µm) was performed using a Malvern3000 laser diffraction particle size analyzer coupled with Hydro EV unit (Wet dispersion).

2.6 Method performance

Water and sediment extraction recovery was determined using spiked samples (100 ng/L for water samples or 100 ng/g dry sediment). Net recovery was calculated by subtracting the analyte concentration observed in unspiked samples from the concentrations in the corresponding spiked samples. The LODs were determined based on the concentrations in a signal-to-noise ratio of 3 and ranged from 1.3 to 5.2 ng/L. The LODs in the sediment samples ranged from 4.6 to 8.6 ng/g. The concentrations were corrected for the contributions from the blanks. Recovery rate and LODs of each compound are shown in Table 2. The values we report in the paper are not corrected for recovery rates.

2.7 Sediment/water distribution coefficient experiment

Dry sediment (3 g) was placed into 250 mL Erlenmeyer flasks. A mix of the different UV filters dissolved in acetone was added to the sediment and left overnight in a chemical hood to evaporate the acetone. The final amounts (total) added were 100 ng, 1 µg, and 10 µg of each of the UV filters tested, each in

triplicate. MilliQ water, 100 mL, was then added, and the flasks were incubated in the dark for 24 h at 25°C with constant shaking. The liquid and solid phase were then separated by filtration and extracted, and the UV filters quantified as described above.

3 Results and discussion

3.1 Detection of hydrophobic UV filters in different environmental matrices and experimental solubility measurements.

The UV filters we tested had varying chemical characteristics, with predicted log K_{ow} values from 3.79 to 14.06 (Table 1 and (Ramos et al. 2016)) and many of them were very hydrophobic. Therefore, a method that effectively includes the wide range of chemicals targeted in this study had to be developed for the extraction and concentration from the different environmental matrices tested. For testing the extraction efficiency from water samples, we used spiked seawater and tap water and tested different extraction protocols using different solvents (data not shown). The optimum extraction protocol determined for both the water and sediment samples was a compromise among the different filters. The recovery of BP3, DBT, BEMT and MBBT filters from tap water, seawater and sediment samples ranged from 47 to 80%, but was only 10% for BMDBM extracted from tap water and seawater samples and 2% from sediment (Table 2). Therefore, we must consider these extraction efficiency values when interpreting our data, particularly for BMDBM.

For many filters, the only available data regarding solubility are predicted values. To investigate the water solubility of the five UV filters in greater detail, a private and independent analytical laboratory (Intertek France) measured the water solubility by conducting a water saturation study in pure water and seawater. Solubilities were low ranging from < 4 x 10^4 to 1.3. x 10^8 ng/L. The least water soluble UV filter is MBBT (2500 fold less than BP3), followed by BEMT, DBT and BMDBM (approximatively 500-, 300- and 10-fold less soluble than BP3 respectively; Table 1). Indeed, values for MBBT were not obtained because the saturated water concentration was below the defined limit of detection (LOD) for this study.

This study shows, for the first time, experimental values for the water solubility of BEMT, DBT and MBBT (Table 1). The experimental and predicted values are comparable for BP3 and BMDBM, but for BEMT and DBT, experimental values are much higher. This difference demonstrates the difficulty in predicting the fate of these extremely hydrophobic UV filters in the environment. The hypothesis that such compounds should not be detected in the water column (Ramos et al. 2015) was not supported by the experimental values. Although the solubility of the UV filters was very low in filtered seawater, one can expect that a portion of these compounds might also absorb onto planktonic microorganisms and suspended matter. Indeed, we filtered the water before we passed the water through SPE columns, so we did not measure any UV filter absorbed to particles bigger than 1.6 µm. Therefore, our values represent dissolved UV filter and filters absorbed to very small particles. For example, polycyclic aromatic hydrocarbons (PAHs) have been detected in water (water

accommodated fraction), although they are also virtually insoluble in water (Forth et al. 2017). In the water column, PAHs are predominantly associated with the solid-phase particulate matter that eventually settles in marine sediments (Hassan et al. 2018; Wang et al. 2001). This is most likely also the case for many of the hydrophobic UV filters.

3.2 Temporal dynamics of UV filter concentrations in Lake Villeneuve and Banyuls Bay

3.2.1 Surface water

In many samples from surface waters, we could not detect any of the UV filters in quantities above LOD. For clarification, the graphs in Figure 1 depict the sampling points where all three replicates from one timepoint contained the specific UV filter above the LOD, while figure 2 depict maximum values for any one sample (not triplicates). Generally, we could not detect any of the filters in surface waters in the early summer season. The highest concentrations in the lake were found for BMDBM and BEMT in July and August with average concentrations of 14.5 and 7.2 ng/L, respectively, whereas MBBT and DBT concentrations were below LOD. In Banyuls Bay, only BEMT was found at peak concentrations of approximately 12 ng/L, (Figure 1), DBT could be detected above the LOD in some samples with a maximum value of 9.88 ng/L (Figure 2) and we could only determine a concentration above LOD for BP in one sample, namely August 8th with 1.52 ng/L. However, BMDBM, and MBBT were not detected.

Concerning the surface water, many studies detail different concentrations of UV filters, but of the five UV filters in this study, most data are available for the two least hydrophobic compounds, BP3 and to a small extent, BMDBM (see review article (Sánchez-Quiles and Tovar-Sánchez 2015)). The highest concentration of BP3 in the Villeneuve Lake surface water was found in September and was close to 3 ng/L (Figure 1a and Figure 2a). BP3 has previously been detected in lakes with maximum values of 125 ng/L (Poiger et al. 2004), 35 ng/L (Balmer et al. 2005) and 40 ng/L (Rodil et al. 2009); thus, the maximum values we report here are not exceedingly high. BP3 concentrations in Banyuls Bay, which did not surpass LOD (Figure 1D and 2A), were also low compared with concentrations found in previous studies. For example, concentrations of BP3 in (filtered) seawater samples from recreational areas were as high as 241.9 ng/L in Mallorca (Tovar-Sanchez et al. 2013) and an extreme value of 1,390,000 ng/L has been reported in the US Virgin Islands (Downs et al. 2016). These varying values can be partly explained because BP3 is more commonly used in the US due to the limited number of filters that are allowed, and the use of BP3 is perhaps more limited in Europe due to regulations (European Union 2009).

The peak value of BMDBM in the Villeneuve Lake surface water was approximately 14.5 ng/L, whereas BMDBM was not detected in Banyuls Bay. Regarding BMDBM concentrations in lakes, there are only a few studies that can be used for comparison, and they report varying concentrations, from below detection level (Poiger et al. 2004) to a very high concentration of over 2000 ng/L (Rodil et al. 2009). For the coastal marine environment, BMDBM was detected in relatively high concentrations in beaches in Gran Canaria, with a

median value of 59.4 ng/L (Sánchez Rodríguez et al. 2015), and the maximum concentration of 321 ng/L was found in coastal water samples from South Carolina (Bratkovics and Sapozhnikova 2011).

Notably, we found BEMT at significant concentrations in the lake and Banyuls Bay surface waters, with maximum concentrations of 13.8 and 18 ng/L, respectively, see figure 2a. Further, DBT was detected at the height of summer, albeit at concentrations very close to the calculated LOD. To our knowledge, this is the first report of detection of this UV filter in the water phase in the environment. This finding is notable considering the extremely low predicted and experimentally determined water solubility values of this compound. Indeed, this compound should be practically insoluble in the water phase (Table 1). However, we propose that, similar to PAHs, hydrophobic UV filters are in the water-accommodated fraction presumably associated with suspended particles.

3.2.2 SML

The concentrations of some of the UV filters in the SML in Villeneuve Lake showed a clear trend during the summer months, with a peak in July-August (Figure 1B). Furthermore, the SML contained higher concentrations of the UV filters than the surface water (note the difference in scale between Figure 1 A and B and Figure 2 A and B). The peak average concentrations of BEMT and BMDBM were 4281 and 531 ng/L, respectively. However, the variability was very high at these sampling points. Additionally, July and August samplings in the lake were both performed when many swimmers were present, and we observed an “oily layer” on the water during these peak sampling times. We know of no

other reports on the SML in lakes.

The SML in Banyuls Bay contained consistently over 10 ng/L of BEMT, with a peak average concentration on June 28 at 101.2 ng/L (Figure 1e). The concentrations of the other UV filters were below detection level for most of the samples. The concentrations of BP3 remained below LOD, which is very low compared with previous values in Mallorca which exceeded 100 ng/L in many cases (Tovar-Sanchez et al. 2013). The variations reported between sites and over the season can be explained by variations in the environmental conditions and because the SML can only be established when the wind speed is below 5 m/s (Romano and Garabetian, 1996).

3.2.3 Sediment

The dynamics of UV filters in the sediment were very different from those we observed for the surface water and SML. Notably, we detected several of the UV filters in significant amounts in April, before the bathing season. In particular, in Lake Villeneuve BEMT, MBBT and DBT were found at average concentrations of 48.2, 47.8 and 22 ng/g (dw) sediment, respectively. Further, DBT and BEMT concentrations in Lake Villeneuve sediments increased during the summer season, and the highest detected average values were 628.8 and 87 ng/g (dw), respectively, at the end of September. MBBT, BP-3 and DBM concentrations were more or less stable and slightly decreased at the last sample point in October (Figure 1c).

The results regarding the concentrations of UV filters in the Banyuls Bay

sediment were unexpected because the concentrations of many of the UV filters were actually higher in the beginning of May than those at the last time points (Figure 1f). This was the case for all UV filters except BEMT. BP3 was the only UV filter to follow a dynamic during the summer season with a maximum average peak of 49.4 ng/L in July, and this value is relatively high compared with that of other studies. Baron et al. (2013) found low concentrations of BP3 (max 2.96 ng/g) in estuary samples, and Tsui et al. (2015) found a maximum concentration of 39.8 ng/g. Indeed, the low concentrations of BP3 found in sediments from highly industrialized areas (Peng et al. 2017) suggest BP3 partitions less into the sediment phase or is degraded. One reason for these differences could be that the source of UV filters to sediments in Banyuls Bay is direct, through the swimmers at the beach, whereas the marine sediments from China described by Tsui et al. (2015) are affected by industrial and municipal discharge sources. BMDBM is also reported previously in marine sediments at concentrations up to 64.4 ng/g (Tsui et al. 2015), but we were only able to detect BMDBM above our LOD in two samples from lake sediment, presumably due to the low recovery rate of this molecule in the extraction process. It is also worth noting that the sediments from both sites contained a relatively low percentage of organic carbon (Table S2). The median organic carbon percentage of Banyuls Bay sediments was 0.032 % and 0.011 % for sediments from Lake Villeneuve, and samples from both these contained more than 95% sand (particles > 63 μm).

There are only a few studies that have examined the concentrations of UV filters in the sediments of lakes. One comparative study found both BP3 and BMDBM in several German lakes also at several time points during the year (Kaiser et al.

2012). These authors detected BP3 at a maximum concentration of 3.6 ng/g and BMDBM at 62.2 ng/g, which are within the same order of magnitude of concentrations we found in Villeneuve Lake for BP3. However, they observed more of a seasonal dynamic with a sharp increase in the peak summer season, whereas our results showed a more steady concentration of these compounds in the summer season (Figure 1c). This same study Kaiser et al. (2012) found octocrylene (OC) concentrations up to 652 ng/g in some lake sediments, and we found maximum detectable concentrations for DBT, BEMT and MBBT (629, 88 and 57 ng/g, respectively). Furthermore, we found a higher concentration of the UV filters in the sediment in the lake than that in the bay sediment (Figure 1c), except for BP3.

3.3 Environmental distribution of UV filters

Previous studies assume that hydrophobic UV filters will partition into the sediment phase. Nevertheless, environmental concentrations of MBBT, BEMT and DBT in the different compartments (sediment, water phase and SML) have not been reported. To further explore the distribution of these compounds in the environment, we defined "environmental distribution coefficients (*env* K_d)" for sediment/water and SML/water. For this calculation, we used the median value over the entire season for each UV filter from both the lake and Banyuls Bay (Table 3).

We also experimentally determined the distribution sediment/water ratio by performing controlled laboratory experiments for 24 h. The distribution ratio between water and solid phase is determined by: $K_d = C_s/C_w$, where C_s is the

concentration (ng/kg) in the solid phase and C_w is the concentration in the water phase (ng/L). Thus, we could easily and directly compare the K_d among the different UV filters. Furthermore, the sorption isotherms were determined after fitting the data to the Freundlich model in which plotting the log C_s to log C_w should give a linear response, which was the case in our study (Figure S2). The Freundlich model equation is $C_s = K_f \times C_w^{\,n}$, where K_f characterizes the absorption capacity of the solid and n measures the intensity of the absorption (or the nonlinearity). Indeed, we observed some nonlinearity of the sorption kinetics of the UV filters; the lowest concentration (100 ng added or 1 µg/L) gave a higher K_d than that of 10 and 100 µg/L (Table 3). Thus, the UV filters adsorbed to the sediment in a higher proportion at low concentrations.

Clearly, the experimental K_d values varied greatly among the different UV filters (Table 3); thus, although many of the UV filters partitioned into the sediment phase, the filters partitioned at different ratios or alternatively at different rates. BEMT strongly distributed into the sediment phase, with the highest K_d value of over 3000, although MBBT and DBT also produced high values, whereas BP3, with the experimental K_d of approximately 10, was expected to distribute into the sediment at a comparatively low rate. We determined a K_d for BMDBM of 777, which is substantially different from a previous report (Li et al. 2016) with values from approximately 11 to 45.8 depending on the sediment. These differences could also be due to differences in experimental design; for example, Li and colleagues used only an 8-hour contact time and did not actually measure the amount sorbed to the sediment (Li et al. 2016).

We could not determine the "environmental Kd (*env* K_d)" values for many of the filters because they were not present above the methodological LOD in the surface water. For the UV filters that we could determine the sediment/water "*env Kd*", we see that the "*env Kd*" values were in the same order of magnitude as the experimental ones. Further, from the SML Kd, we can see that many of the filters are present at higher concentrations in the SML compared to the surface water.

Once the UV filters are adsorbed to the sediments, and if no degradation or dilution processes occur, the UV filters can potentially accumulate over time. Data regarding the degradation of UV filters in sediments are scarce. Volpe et al. (2017) found that EH-DPAB degraded after approximately 60 days in aerobic microcosms with marine sediments but found even slower degradation of 4-MBC, with a half-life of over a year. Compared to Volpe et al. (2017), Liu et al. (2013) found shorter half-lives of 4-MBC in their experiments, but in a different environment, namely aquifer sediments. Of the UV filters we examined, BP3 degrades in aquifer sediments (Liu et al. 2013) within 5-6 days. Li and colleagues followed the potential degradation of BMDBM in sediment microcosms, but whether BMDBM was degraded or adsorbed to the sediment to a greater extent with time was unclear (Li et al. 2016).

We would expect that in an open environment, hydrodynamic processes would result in a dilution of the UV filters. Thus, an accumulation from year to year or even throughout the season would not be likely in Banyuls Bay. However, we observed a considerably higher concentration of DBT and MBBT in the April

samples (beginning of the season) than that at the end of the season in Banyuls Bay. This means that, surprisingly, UV filters may accumulate from the previous season. This accumulation most likely occurred because tides in the Mediterranean are not significant and because the bay is relatively closed. In future research, the concentrations of UV filters over several years in both Banyuls Bay and the lake should be monitored to determine whether UV filters accumulate in the sediments with time.

4 Conclusions

This study showed for the first time the presence of DBT, BEMT and MBBT in environmental matrixes (water, SML and sediment), which is interesting because these compounds, with high predicted log K_{ow} values, are presumed insoluble in water. Indeed, substantial concentrations of these compounds were measured during peak tourist time in the surface water and SML in Villeneuve Lake. However, we hypothesize that lipophilic UV filters are adsorbed to suspended particulate matter and might not be fully solubilized in the water phase. We show, both by sampling efforts in the environment and laboratory experiments, that a large proportion of the hydrophobic UV filters predictably partitioned into the sediment phase. Further, although some of these compounds, such as BP3, degrade relatively quickly in sediment systems, many of the hydrophobic UV filters are most likely not easily biodegraded once sequestered in the sediment phase, although this has yet to be confirmed. Thus, future ecotoxicological evaluation of lipophilic UV filters should be performed on benthic marine species as it has already been done in freshwater systems (Kaiser et al. 2012).

Overall, our work improves comprehension of the partitioning of three highly water insoluble UV filters (BEMT, MBBT and DBT). The fact that BP3 and other UV filters are found at various trophic levels in the literature suggests that some of these compounds can biomagnify. Further tests are required for a better understanding of their bioaccumulation and the potential toxicological risks to marine organisms, starting with the zoobenthos. Importantly, we must investigate whether the uptake of very lipophilic UV filters by benthic organisms (bioaccumulation) occurs for a full understanding of the potential risk of these compounds to ecosystems.

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Conflict of interest statement

We need to disclose that this work has been financially supported by the Pierre Fabre Laboratories, but this does not influence the results. The company was not involved in the work plan and they wanted to have independent data on the occurrence and concentration of some filters that have never been quantified in the natural environment.

Figure Captions

Fig. 1 Dynamics of selected UV filters in Villeneuve Lake and Banyuls Bay surface water (a and d), surface microlayer (b and e) and sediment (c and f). The UV filters are BMDBM (open inverse triangles), BP3 (triangles), MBBT (diamonds),

BEMT (circles) and DBT (squares). Note that charts b and c have a log scale on the y-axis, but a, d, e and f do not. All points are the average of triplicate sampling points, and the standard error bars are shown

Fig. 2 Box and whiskers plot of all values in the water phase (a), SML phase (b) and the sediment (c) for the two different sites. The median is shown by the bold line, the hinges are the 25th and 75th percentiles and the whiskers are roughly the 95% confidence intervals; the other points shown are outliers. Note, the axis in panel C is cut

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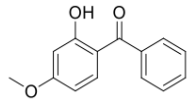
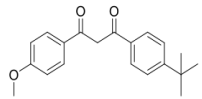
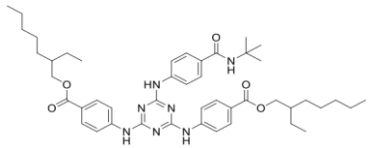
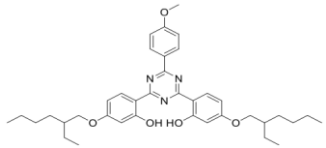
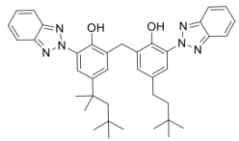
Table 1: UV filters information

Abbr.	Chemical names	CAS	Molecular weight (g/mol)	Log K_{OW}	Molecular structure	Water solubility (ng/L)		
						Experimental[b]		Predicted (tap water)[a]
						tap water	sea water	
BP3	Benzophenone 3	131-57-7	228.2	3.79		1.3E+08	8.7E+07	6.9E+07
BMDBM	Butyl methoxydibenzoylmethane	70356-09-1	310.4	4.51		1.9E+07	4.7E+07	1.5E+06
DBT	Diethylhexyl butamido triazone	154702-15-5	765.9	14.06		2E+05	< 2E+05[c]	1.3E-05
BEMT	bis-ethylhexyloxyphenol methoxyphenyl triazine	187393-00-6	627.8	9.29		3E+05	< 6E+04[c]	1.5E-10
MBBT	methylene bis-benzotriazolyl tetramethyl butylphenol	103597-45-1	658.8	12.5		< 4E+04[c]	< 1E+05[c]	4.5E-04

[a] Predicted by EPI Suite™ (Ramos et al., 2016)

[b] Values obtained by Intertek France

[c] The water solubility was less than the quantification limit of the method used by Intertek

Table 2. Recoveries and method limits of detection of analysis of BP3, BMDBM, DBT, BEMT and MBBT in seawater and sediment samples.

	Water samples		Sediment samples	
Compound	Recovery (%)	LOD (ng/L)	Recovery (%)	LOD (ng/g)
BP3	67	1.3	47	4.6
BMDBM	10	2.3	2	6.8
DBT	71	2.3	75	8.6
BEMT	80	2.3	60	7.5
MBBT	47	5.2	80	3.9

Table 3. Distribution coefficients (L/kg) of UV filters determined experimentally and calculated from environmental samples

	Exp.[a]			Lake		Banyuls bay	
	K_d	K_f	R^2	K_d sed[b]	K_d SML[c]	K_d sed[b]	K_d SML[c]
BMDBM	777±150	463	0.9777	N.D.	9.14	N.D.	N.D.
BP3	10±0.8	19.6	0.985	3765	1.23	N.D.	N.D.
MBBT	2212±453	1492	0.9921	N.D.	N.D.	N.D.	N.D.
BEMT	3506±641	3129	0.9837	9939	6.81	3756	2.76
DBT	2829±467	1848	0.9870	N.D.	N.D.	7678	1.26

a= K_d determined experimentally from an average of triplicate tubes and 2 different concentrations (n=6), b= K_d determined from median concentrations in sediments and median concentrations in the water column with a minimum of 3 samples over LOD, c= K_d determined from median concentrations in the SML and median concentrations in the water column with a minimum of 3 samples over LOD, N.D.=not detected

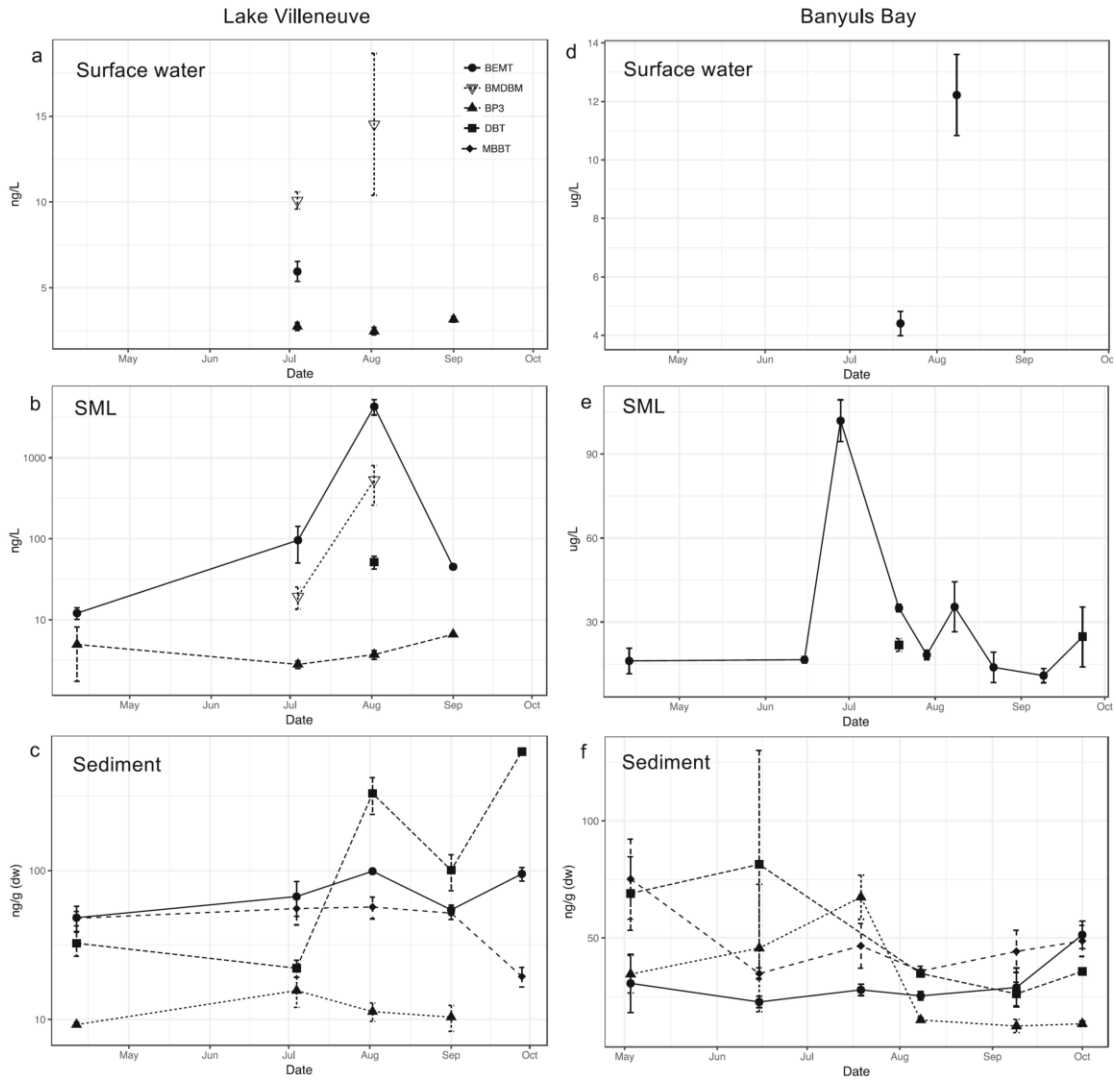


Fig. 1 Dynamics of selected UV filters in Villeneuve Lake and Banyuls Bay surface water (a, d), surface microlayer (b, e), and sediment (c, f). The UV filters are BMDBM (open inverse triangles), BP3 (triangles), MBBT (diamonds), BEMT (circles), and DBT (squares). Note that charts b and c have a log scale on the y axis, but a, d, e, and f do not. All points are the average of triplicate sampling points, and the standard error bars are shown

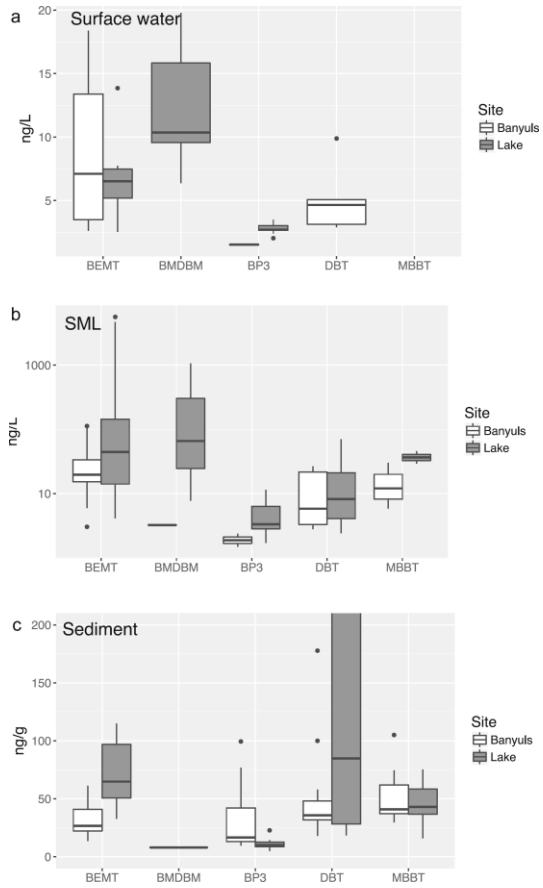


Fig. 2 Box and whiskers plot of all values in the water phase (a), SML phase (b), and the sediment (c) for the two different sites. The median is shown by the bold line, the hinges are the 25th and 75th percentiles, and the whiskers are roughly the 95% confidence intervals; the other points shown are outliers. Note that the axis in c is cut