

Occurrence of Organic UV Filters in Surface Waters, Sediments, and Core Sediments in Tokyo Bay, -Organic UV Filters are New POPs?-

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Abstract

Organic UV filters are contained in sunscreen agents, skin creams, body lotions, shampoos, and so forth. Some of them are lipophilic and therefore have a potential for bioaccumulation. A recent report showed that some organic UV filters were detected in fish from Swiss lakes. In this study, we investigated the occurrence of 9 organic UV filters as well as fragrance materials in surface waters, and sediments in rivers in Japan. These results showed they are ubiquitous contaminants in the environment and less biodegradable than fragrance materials. We also investigated their concentrations in sediment cores in Tokyo Bay and revealed that ethylhexyl methoxy cinnamate (EHMC) and benzophenone (BP) were present in the sediment even in 1977. Therefore EHMC and BP, which are most ubiquitous organic UV filters detected in this study, might have a potential for high persistence in the environment.

Ecotoxicity data of organic UV filters are little reported. However, EHMC and BP might have a bioaccumulation and persistence in the environment like Persistent Organic Pollutants (POPs) whose specific properties are Persistent, Bioaccumulative, and Toxic. We need further research.

Introduction

There is growing interest in secondary adverse effects of organic UV filters compounds from personal care products as well as pharmaceuticals. Some of organic UV filters are much more lipophilic compounds than pharmaceuticals. Therefore they have been considered to have a potential for bioaccumulation. Recently, Balmer et al¹ reported that some organic UV filters were present in fish from Swiss lake and supposed that they were bioaccumulative. However, there are few reports for their occurrence, bioaccumulation, and their physical/chemical properties in the environment.

The objective of this study is to evaluate whether some of organic UV filters are ubiquitous and persistent in the environment similar to Persistent Organic Pollutants (POPs). We conducted 2 investigations for this objective. One is to investigate occurrence of 9 organic UV filters in surface waters and sediments in some Japanese rivers in Kanto region. The other is to evaluate their persistence in the environment to measure their concentrations in sediment core in Tokyo Bay.

Materials and Methods

Surface water samples and sediment samples were collected from 43 sampling sites on four large river systems in Kanto region which is situated in a densely populated area (Ara river system, Tone river system, Turumi river, and Tama river system) in October 2006.

Sediment core samples were taken from Tokyo Bay in February 2004. They were collected with acrylic pipe by divers.

Solid-Phase Extraction (SPE) of samples

9 organic UV filters and 16 fragrance materials were analyzed (Table 1 and Figure 2). Fragrance materials are also contained in personal care products and some are lipophilic compounds similar to organic UV filters. Therefore organic UV filters concentrations were compared with fragrance materials concentrations.

Organic UV filters and fragrance materials were measured with a

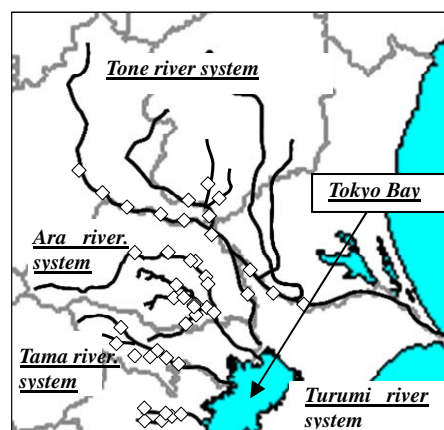


Figure 1 Sampling sites for surface water and sediment in Tone river system, Ara river system, Tama river system, and Turumi river system

multiresidue analytical methods using solid-phase extraction and gas chromatographic mass spectrometry which have been developed in our laboratory.

Filtered surface water samples were extracted using 2 different types of C18 Speed Disk (Bakerbond). Organic UV filters and fragrance materials were eluted with dichloromethane and evaporated under a stream of nitrogen.

Sediment samples, sediment core samples, and suspended particle matters in surface waters were freeze-dried and ultrasonicated successively with dichloromethane and acetone. Surrogate standards were spiked into freeze-dried samples. The solvent was evaporated and diluted with milli-Q water for solid phase extraction. Solid phase extraction was conducted with similar method to that for filtered surface water samples.

Analysis

All extracts were analyzed by gas chromatographic mass spectrometry using selected ion monitoring. All

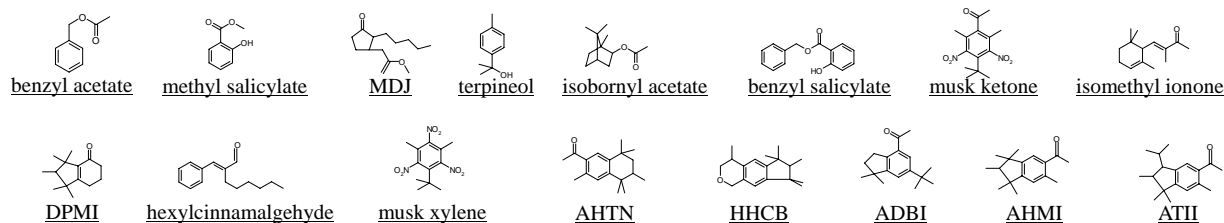
Table 1 Analyzed synthetic fragrance materials, UV filters and their chemical properties

Fragrance materials trade name or abbreviation	Chemical name	log Kow	Vapor pressure (Pa)	Water solubility (mg/l)
benzyl acetate	phenylmethyl ester acetic acid	2.1	21.9	1265
methyl salicylate	2-hydroxy-methyl ester benzoic acid	2.6	0.75	1687
MDJ	3-oxo-2-pentyl-methyl ester cyclopentaneacetic acid	3	0.0549	91.72
terpineol	4-trimethyl-3-cyclohexene-1-methanol	3.3	4.09	335.7
isobornyl acetate	1,7,7-trimethyl-acetate bicyclo[2,2,1]heptan-2-ol	4.3	10	23.23
benzyl salicylate	2-hydroxy-phenylmethyl ester benzoic acid	4.3	0.000449	24.59
musk ketone (MK)	1-[4-(1,1-dimethyl-ethyl)-2,6-dimethyl-3,5-dinitrophenyl]-ethanone	4.3	0.00004	1.9
iso methyl ionone	3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)	4.6	1.3	9
DPMI (cashmeran)	6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone	4.9	5.2	0.17
hexyl cinnamaldehyde	2-(phenylmethylene)octanol	4.9	0.027	2.75
musk xylene (MX)	1-(1,1-dimethylethyl)-3,5-dimethyl-2,4,6-trinitrobenzene	4.9	0.00003	0.49
AHTN (tonalide)	7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene	5.7	0.0608	1.25
HHCB (galaxolide)	1,3,4,6,7,8-hexahydro-4,6,6,7,8-hexamethylcyclopenta- γ -2-benzopyran	5.9	0.0727	1.75
ADBI (celestolide)	4-acetyl-1,1-dimethyl-6- <i>tert</i> -butylindan	6.6	0.02	0.015
AHMI (phantolide)	6-acetyl-1,1,2,3,3,5-hexamethylindan	6.7	0.024	0.027
ATII (traseolide)	5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan	8.1	8.1	85.1

UV filters trade name or abbreviation	Chemical name	log Kow	Vapor pressure (Pa)	Water solubility (mg/l)
benzophenone (BP)	benzophenone	3.2	130	137
benzophenone-3 (BP-3)	2-hydroxy-4-methoxybenzophenone	3.5	unknown	poor *
isoamyl <i>p</i> -methoxycinnamate	isoamyl <i>p</i> -methoxycinnamate	4.3	unknown	poor *
octyl dimethyl PABA (OD-PABA)	octyl dimethyl <i>p</i> -aminobenzoic acid 2-ethylhexyl ester	5.7	unknown	poor *
EHMC	3-(4-methoxyphenyl)-2-propenoic acid 2-ethylhexyl ester	5.8	unknown	poor *
4-MBC	3-(4'-methyl-benzylidene)bornan-2-one	5.9	unknown	poor *
octyl salicylate	2-ethylhexyl 2-hydroxybenzoate	5.97	unknown	poor *
homosalate	3,3,5-trimethylcyclohexyl salicylate	6.2	unknown	poor *
octocrylene	2-cyano-3,3-diphenyl-2-propenoic acid 2-ethylhexyl ester	6.9	unknown	poor *

* No detail data

a) Fragrance materials



b) Organic UV filters

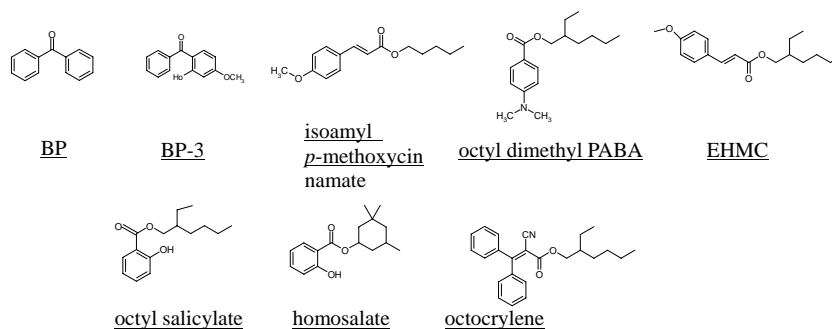


Figure 2 The structure of fragrance materials and organic UV filters in Table

analytes except benzophenone-3 in sediments were recovered acceptably.

Results and Discussion

Occurrence of organic UV filters and fragrance materials in surface waters and sediments in Kanto region

The results of Kanto region surface water and sediment examinations are presented in Table 2. These concentrations are calculated from summation of dissolved fraction and suspended particle matter fraction.

Four organic UV filters and twelve fragrance materials were detected in surface waters. Benzophenone (BP) and ethylhexyl methoxy cinnamate (EHMC) were detected in all surface water samples and their concentrations were very high. 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-2-benzo-pyrane (HHCB) and 7-Acetyl-1,1,3,4,4,6-hexamethyl-tetrahydronaphthalene (AHTN) are considered to be most ubiquitous fragrance materials in the environment. Our research also showed that HHCB and AHTN were detected in all surface water samples. However, BP and EHMC were detected in much higher concentrations than HHCB and AHTN.

Octyl dimethyl PABA (OD-PABA) was also detected in many samples but the concentration was lower than BP and EHMC. 4-methylbenzylidene camphor (4-MBC) was not detected in any sampling points although they were reported to be higher concentration than EHMC and BP in Swiss lakes, wastewater treatment plant influent, and its effluent¹. This may be caused by no permission to use 4-MBC for cosmetic products in Japan.

In sediment samples, 6 organic UV filters and twelve fragrance materials were detected. BP, EHMC, and OD-PABA were detected in all sediment samples. The concentrations of BP and EHMC were much highest among analytes.

These results revealed that 2 organic UV filters (BP and EHMC) were ubiquitous in the surface water and sediment and were present in higher concentrations than fragrance materials. Our other research revealed that organic UV filters were present in wastewater treatment plant influent and effluent in Japan. They continuously flow in rivers through wastewater plant. Therefore their continuous flow is considered to be one reason for their occurrences in the environment. The other reason is estimated that they are less degradable compounds than fragrance materials because they were present in high concentrations in sediments. Unfortunately there are few detail data of biodegradation of organic UV filters. However, they need stability against photodegradation and biodegradation for their usage. To confirm their stability in the environment, we measured their concentrations in sediment core samples in Tokyo Bay where Ara river, Turumi river, and Tama river finally reached.

Table 2 Fragrance materials and organic UV filters concentrations in surface water and sediment in rivers

compounds	surface water (N=43)		sediment (N=43)		
	(av±SD) ng/l	number of detection	(av±SD) µg/kg	number of detection	
benzyl acetate	-	-	0	-	0
terpineol	2.0 ± 3.3	21	1.4 ± 6.5	2	
methyl salicylate	5.3 ± 14.5	30	2.0 ± 0.9	41	
isobornyl acetate	12.2 ± 10.9	43	3.0 ± 1.7	42	
iso methyl ionone	0.6 ± 1.7	9	0.2 ± 0.3	10	
DPMI	-	-	0	-	0
BP	277.7 ± 172.4	43	128.9 ± 104.9	43	
MDJ	2.2 ± 4.0	16	0.1 ± 0.4	2	
ADBI	0.02 ± 0.1	3	0.02 ± 0.1	6	
hexyl cinnamaldehyde	17.4 ± 13.5	41	4.6 ± 5.9	33	
AHMI	-	-	0.02 ± 0.1	2	
octyl salicylate	-	-	0	-	0
ATII	0.05 ± 0.2	2	0.2 ± 0.4	14	
HHCB	9.4 ± 9.4	43	6.6 ± 14.0	43	
AHTN	9.8 ± 9.3	43	5.9 ± 12.4	43	
MX	-	-	0	-	0
homosalate	-	-	0.02 ± 0.1	1	
benzyl salicylate	0.4 ± 1.9	2	-	0	
MK	3.7 ± 8.0	12	0.9 ± 2.0	11	
4-MBC	-	-	0	-	0
BP-3	2.6 ± 4.5	19	0.5 ± 0.8	22	
isoamyl methoxycinnamate	-	-	0.1 ± 0.3	3	
EHMC	380.6 ± 479.5	43	79.0 ± 242.2	43	
OD-PABA	1.8 ± 1.7	30	1.0 ± 0.4	43	
octocrylene	-	-	0	-	0

Concentrations of organic UV filters in sediment core samples in Tokyo Bay

Organic UV filters concentrations in sediment core samples from 1977 to 1997 were measured. Figure 3 showed BP, EHMC, HHCB, and AHTN concentrations in sediment core samples.

Among organic UV filters, BP and EHMC were detected in all core samples and OD-PABA was detected in only 2 core samples. EHMC concentration in 1977 was found to be much higher than that in 1999 and decreasing remarkably however sun screen cosmetics consumption volume in Japan is increasing according to national survey data from 1985. On the other hand, BP concentration is gradually increasing from 1977. Tamada et al² reported that PCB concentrations in same sediment core samples during this period was approximately 100 ng/g-dry sediment. Therefore, BP and EHMC concentrations in sediment core samples were as high as PCB concentrations. On the contrary, HHCB and AHTN were detected in all sediment core samples, but lower concentrations than BP and EHMC.

There are few data for BP or EHMC productions in Japan. BP and EHMC might be biodegradable compounds. But they were detected in high concentrations in sediment core samples even in 1977. This result may indicate that BP and EHMC are persistent in the environment.

Conclusion

This research could never conclude whether BP and EHMC are persistent organic pollutants or not. POPs are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. This research could reveal some of their properties in the environment. Further researches are needed.

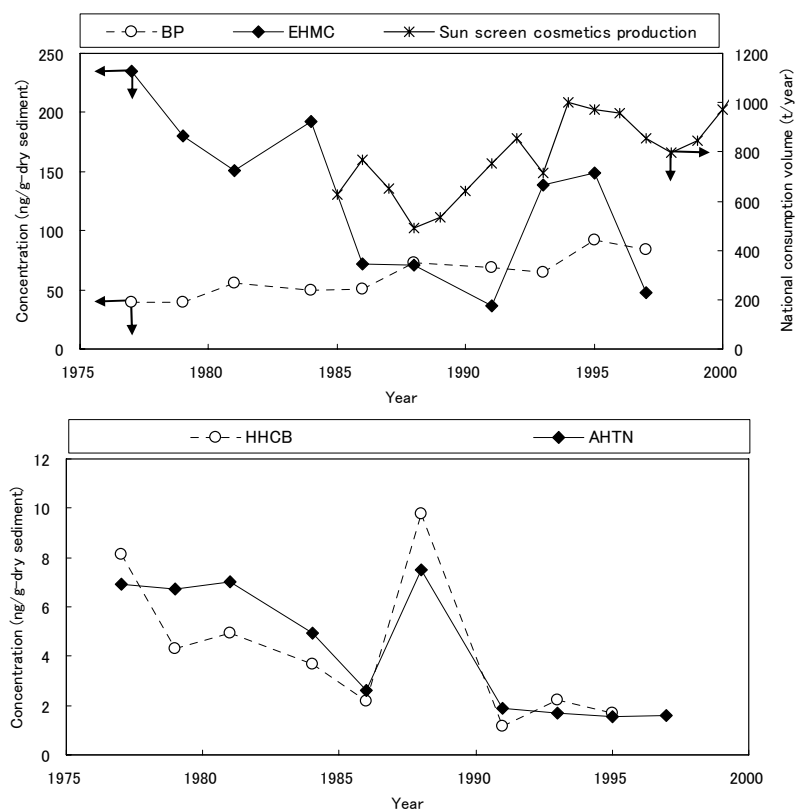


Figure 3 Historical trend of organic UV filters concentrations in Tokyo Bay sediment

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