

# Results from the Swedish National Screening Programme 2009

## Subreport 3: UV-filters

Mikael Remberger, Karl Lilja,  
Lennart Kaj, Tomas Viktor, Eva Brorström-Lundén  
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John Munthe  
Vice President, Research

<p><b>Organization</b> IVL Swedish Environmental Research Institute Ltd.</p>	<p><b>Report Summary</b></p>
<p><b>Address</b> P.O. Box 21060 SE-100 31 Stockholm</p>	<p><b>Project title</b> Results from the Swedish National Screening Programme 2009 Subreport3: UV-filters</p>
<p><b>Telephone</b> +46 (0)8-598 563 00</p>	<p><b>Project sponsor</b> Environmental monitoring, Swedish environmental Protection Agency</p>
<p><b>Author</b> Mikael Remberger, Karl Lilja, Lennart Kaj, Tomas Viktor, Eva Brorström-Lundén</p>	
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<p><b>Summary</b></p> <p>As an assignment from the Swedish Environmental Protection Agency, IVL has performed a screening study concerning UV-filters. Sunscreen lotions are used to protect the skin against sunburn and skin cancer caused by the UV (ultra violet) radiation of sunlight. The active moieties in sunscreens (UV-filters) are usually aromatic compounds which adsorb UV-radiation and release the energy as low energy rays. Surface water collected on bathing places in the summer contained 12 UV-filters out of 13 measured whereas in sediment 10 out of 13 were found. Four of the UV-filters were also found in fish samples. UV-filters were detected in surface water early in the spring (before swimming season) but the concentration and frequency clearly increased during the summer. All measured UV-filters were found in STP effluent water, and all but two in STP sludge. Comparisons of measured concentrations of UV-filters with QSAR derived PNECs and also available experimental ecotoxicity data indicate that several of the included UV-filters pose a potential environmental risk.</p>	
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## Sammanfattning

IVL Svenska Miljöinstitutet har på uppdrag av Naturvårdsverket genomfört en screening av UV-filter i den svenska miljön. Solskyddsprodukter används för att skydda huden mot solbränna och hudcancer orsakad av solens ultravioletta strålning (UV-strålning). De aktiva substanserna i solskyddsprodukter är vanligtvis aromatiska föreningar med förmåga att absorbera UV-strålning och sedan frigöra energin i form av ofarlig lågenergetisk strålning.

UV-filter kan emitteras till miljön via olika källor t ex. punktkällor och diffusa källor. Det övergripande målet med screeningundersökningen var att undersöka förekomsten och bestämma halterna av 13 utvalda UV-filter i olika miljöprover. Resultaten identifierar några olika emissionsvägar och hur stor spridning föreningarna har i den svenska miljön. En provtagningsstrategi i enlighet med detta togs fram. Vidare utvecklades en analysmetod anpassad för frågeställningen.

Genom att solskyddsprodukter appliceras på huden anses de viktigaste emissionsvägarna för UV-filter vara tvättning, duschning och bad. Studien var därför inriktad på att undersöka diffusa källors betydelse i den urbana miljön. För att undersöka emissionen vid friluftsbad insamlades vattenprover från kommunala badplatser vid två tillfällen: före (tidig vår) och under badsäsong. Prover på sediment och fisk insamlades också i anslutning till badplatserna under badsäsongen.

Eftersom UV-filter ingår i många hygien- och kosmetikprodukter och därför når avlopp vid tvätt och dusch togs prover på utgående vatten och slam från några kommunala avloppsreningsverk. Totalt ingick 52 prover i undersökningen fördelade på 24 ytvatten, 8 utgående vatten från reningsverk, 8 reningsverksslam, 7 sediment och 5 fiskprover.

UV-filter påvisades frekvent i ytvatten, både i bakgrundssjöar och i den urbana miljön. Vattenprover från badplatser insamlade under badsäsongen innehöll 12 av 13 undersökta UV-filter och i sedimenten återfanns 10 av 13 föreningar. Fyra av UV-filtren påvisades också i fisk. UV-filter detekterades även före badsäsongen i ytvatten men halten och detektionsfrekvensen ökade markant under sommaren.

UV-filtren påvisades frekvent i utgående avloppsvatten från reningsverk och i rötat slam från reningsprocessen. Alla undersökta föreningar påträffades i utgående vatten och i slam hittades 11 av 13 föreningar.

Koncentrationen varierade mycket mellan de olika UV-filtren. Ytvatten från badplatser under sommaren innehöll generellt liknande halter UV-filter som utgående vatten från reningsverken. De högsta halterna av UV-filter påträffades i vatten från en badplats.

Några av UV-filtren påvisades, om än i låga halter, även i ytvatten, sediment och fisk från tre undersökta bakgrundssjöar.

Sammantaget tyder undersökningen på en utbredd förekomst av UV-filter i den svenska miljön. Viktiga emissionkällor har visat sig vara kommunala reningsverk och användandet av solskyddsprodukter vid bad.

En jämförelse av uppmätta halter av UV-filter med QSAR-framtagna PNEC och befintliga experimentella ekotoxikologiska data visade att flera av de undersökta UV-filtren kan utgöra en potentiell miljörisk.

## Summary

As an assignment from the Swedish Environmental Protection Agency, IVL has performed a screening study concerning UV-filters. Sunscreen lotions are used to protect the skin against sunburn and skin cancer caused by the UV (ultra violet) radiation of sunlight. The active moieties in sunscreens (UV-filters) are usually aromatic compounds which adsorb UV-radiation and release the energy as low energy rays.

The overall objectives of the screening studies were to determine the concentrations of 13 UV-filters in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. A sampling strategy was developed in accordance with these objectives. 52 samples were collected, distributed on 24 surface waters, 8 WWTP-effluents, 8 sludge, 7 sediments and 5 fish. A suitable analytical method for the different samples was developed.

Emissions of UV filters are believed to arise primarily from losses due to washing and bathing. The programme was focused on diffuse sources in an urban environment. In order to investigate the losses of UV-filters during bathing, surface water, sediment and fish samples from bathing places were collected. The sampling was performed in periods outside and during the bathing season.

Due to possible release of the chemicals from personal care products, sewage treatment plants (STPs) were identified as potential sources. Effluent water and sludge from municipal STPs were included in the sampling program.

In general, UV-filters were regularly found in the Swedish water environment, both in background areas and in an urban environment. Surface water collected at bathing places during the summer contained 12 of the 13 investigated UV-filters whereas in sediment 10 out of 13 were found. Four of the UV-filters were also found in fish samples. UV-filters were detected in surface water early in the spring (before swimming season) but the concentration and frequency clearly increased during the summer. All measured UV-filters were found in STP effluent water, and all but two in STP sludge.

There was a great variation in the concentrations among the different UV-filters. Measured concentrations in surface water from bathing places during summer were generally in the same range as in effluent water. The highest measured concentrations of several of the UV-filters were found in surface water samples collected from bathing places.

Some of the UV-filters were also detected in surface water, sediment and fish samples from three background lakes but in lower concentrations. This indicates the widespread occurrence of UV-filters in Swedish surface waters.

Comparisons of measured concentrations of UV-filters with QSAR derived PNECs and also available experimental ecotoxicity data indicate that several of the included UV-filters pose a potential environmental risk.

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## 1 Introduction

As an assignment from the Swedish Environmental Protection Agency, a screening study has been performed by IVL during 2009/2010. This screening includes bis(4-chlorophenyl) sulphone (BCPS), Dechlorane Plus, UV-filters, benzothiazoles, benzenediamines and benzotriazoles. These substances/substance groups are emitted and distributed in the environment via a variety of sources, e.g. different point sources and/or diffusive sources. The overall objectives of the screening studies are to determine the concentrations of the selected substances in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. Table 1 shows the number of the report where individual results are presented.

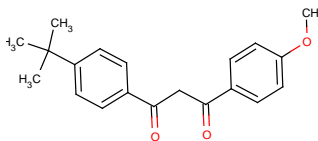
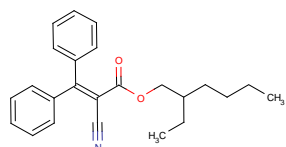
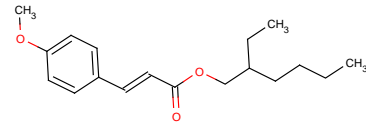
Table 1. Substances / substance groups included in the screening.

Substance / Substance group	Sub-report #
BCPS	1
Dechlorane Plus	2
UV-filters	3
Benzothiazoles, benzenediamines	separate report
Benzotriazoles	separate report

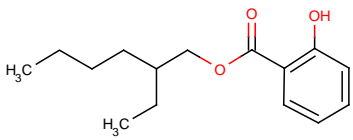
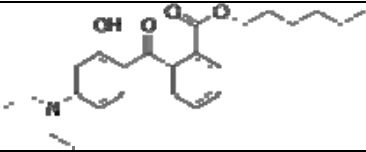
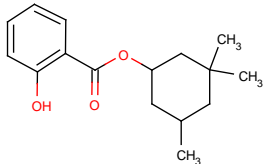
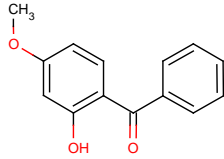
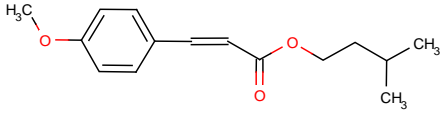
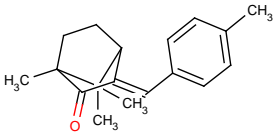
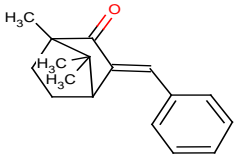
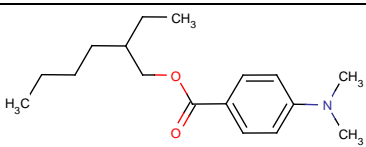
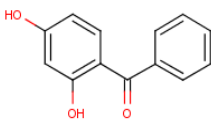
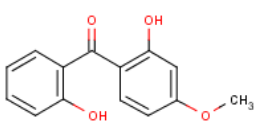
*The screening of benzothiazoles, benzenediamines and benzotriazoles is carried out by IVL and Umeå University in cooperation with the project ChEmiTecs, Organic Chemicals Emitted from Technosphere Articles ([www.chemitecs.se](http://www.chemitecs.se)).*

This subreport considers the screening of UV-filters. Sunscreen lotions are used to protect the skin against sunburn and skin cancer caused by the UV (ultra violet) radiation of sunlight. The active moieties in sunscreens (UV-filters) are usually aromatic compounds which absorb UV-radiation and release the energy as low energy rays. The 13 UV-filters included in this screening are shown together with abbreviations, CAS- numbers and structures in Table 2.

Table 2. UV-filters in this screening

Name	Abbreviation	CAS-no	Structure
Butylmethoxydibenzoylmethane Avobenzone Eusolex 9020	BMDM BMDBM	70356-09-1	
Octocrylene	OC	6197-30-4	
Ethylhexyl methoxycinnamate Eusolex 2292	OMC EHMC	5466-77-3	



Name	Abbreviation	CAS-no	Structure
Ethylhexyl salicylate	EHS	118-60-5	
Diethylamino hydroxybenzoyl hexyl benzoate	DBENZO	302776-68-7	
Homosalate 3,3,5-Trimethyl cyclohexyl salicylate	HMS HS	118-56-9	
Benzophenone-3 2-Hydroxy-4-methoxy- benzophenone Eusolex 4360	BP3	131-57-7	
Isoamyl p-methoxycinnamate	IMC IAMC	71617-10-2	
4-Methyl benzylidene camphor Eusolex 6300	4-MBC	36861-47-9, 38102-62-4	
3-Benzylidene camphor	3-BC	15087-24-8	
Ethylhexyl dimethyl -p-aminobenzoat	EPABA ODPABA	21245-02-3	
2,4-Dihydroxybensophenone	DHB BP1	131-56-6	
2,2'-Dihydroxy-4-metoxybensophenone	DHMB	131-53-3	

Abbreviations according to Rodil *et al.*, 2008; Peck, 2006.

## 2 Chemical properties, and toxicity

### 2.1 Properties

Some chemical properties of the UV-filters included in the screening are summarized in Table 3. UV-filters have generally low water solubility, low vapour pressure, and high log Kow. Common to UV filters are that they absorb UV light in the wavelength range 280-400 nm. To be able to cover the entire UVB (280-320 nm) and UVA (320-400 nm) region sunscreen products often contains several filters.

Table 3. Physical and chemical properties of the included UV-filters.

UV-filter	Log Kow	pKa	Reference
BMDM	4.51	9.74	(Rodil <i>et al.</i> , 2008)
OC	6.88	-	<a href="http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM">http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM</a>
OMC	5.80	-	<a href="http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM">http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM</a>
EHS	5.97	8.13	(Rodil <i>et al.</i> , 2008)
DBENZO	6.54	-	Affected by pH. QSAR in Wernersson 2008
HMS	6.16	8.09	(Rodil <i>et al.</i> , 2008)
BP3	3.79; 3.52	7.56	(Rodil <i>et al.</i> , 2008); Jeon <i>et al.</i> 2006
IMC	4.33	-	<a href="http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM">http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM</a>
4-MBC	5.47	-	(Giokas <i>et al.</i> , 2005)
3-BC	-	-	No data available
EPABA	6.15	2.39	(Rodil <i>et al.</i> , 2008); -N(Me) <sub>2</sub> <sup>+</sup>
DHB	2.96	-	<a href="http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM">http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM</a>
DHMB	3.82	-	<a href="http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM">http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM</a>

The majority of UV-filters are based on benzophenone (BP3, DHB, DHMB, DBENZO) are typical broad-band filters and absorb both in UVA and UVB. Benzophenone filters have high stability to UV-light (BASF, 1995).

Benzylidene camphor, (4-MBC, 3-BC) are agents that absorbs in the UVB range. All the camphor sunscreens are supposed to dissipate the photon energy by cis-trans isomerisation (Buser *et al.*, 2005).

The salicylic acid based sunscreen filters (EHS, HMS) absorbs ultraviolet rays with a wavelength from 295 nm to 315 nm (UVB). They do not protect against UVA. It is a relatively weak sunscreen filter. When exposed to sunlight homosalate undergoes some degradation ([www.smartskinicare.com](http://www.smartskinicare.com)).

Cinnamic acid derivatives (OMC, IMC) are chemical sun blocking agents that absorbs ultraviolet radiation in the UVB range. When exposed to sunlight octyl methoxycinnamate (OMC) is converted into a less UV absorbing form, which reduces its effectiveness. This conversion can be partly prevented by certain other UV blockers ([www.smartskinicare.com](http://www.smartskinicare.com)).

Benzoylmethane (BMDM) is a sunscreen with good coverage of the UVA-spectrum and is often combined with UVB-filters in sunscreen products. BMDM has complexing properties and metal ions *e.g.* Fe(III) may therefore induce photochemical degradation. BMDM degrades in the sunlight and loses effectiveness over time.

Ethylhexyl dimethyl-p-aminobenzoate (EPABA) is used as a UVB blocker in sunscreens.

Octacrylene (OC) is a highly stable sunscreen filter and does not degrade in sunlight. It protects other UV blocking agents from UV-induced degradation. It absorbs UVB, short UVA (UVA-2) but not long UVA. It is a relatively weak sunscreen, inadequate when used alone ([www.smartskincare.com](http://www.smartskincare.com)).

## 2.2 Toxicity

During recent years, concern regarding the potential endocrine disrupting properties of UV-filters has been raised. Several studies, both *in vivo* and also using *in vitro* bioassays have found estrogenic, antiestrogenic, androgenic, and anti-androgenic effects of substances used as UV-filters (for a review, see e.g. Díaz-Cruz and Barceló, 2009). The review by Díaz-Cruz and Barceló (2009) covers all UV-filters measured in the present study, except DHMB and DBENZO. All of the UV-filters covered have been found to cause hormonal effects *in vitro*. Further, several elicited multiple hormonal activities, and mixtures have been shown to cause antagonistic, additive and synergistic effects.

For the aquatic environment, most studies have focused on the endocrine effects in fish. Endocrine effects caused by exposure to UV-filters include the induction of vitellogenin (3-BC, 4-MBC, DHB, BP3, and OMC), effects on gonadal histology (3-BC), and also on fecundity (3-BC and BP3) (see e.g. Kuntz and Fent, 2009; Kunz *et al.*, 2006a; Kunz *et al.*, 2006b; Inui *et al.*, 2003; Coronado *et al.*, 2008). Effects on reproduction have also been shown for the mud snail *Potamopyrgus antipodarum* (4-MBC) and the oligochete *Lumbricus variegatus* (3-BC) (Schmitt *et al.*, 2008).

For some UV-filters, there are also ecotoxicity data available for crustaceans, algae and hard corals (Fent *et al.*, 2010b; Rodil *et al.*, 2009; Danovaro *et al.*, 2008). The results from these studies indicate that other effects may be as sensitive as the endocrine effects on fish.

The results of the ecotoxicity studies are presented in more detail, and compared to concentrations measured in this study, in chapter 7.

## 3 Use and emissions

Sunscreen lotions are used to protect the skin against sunburn and skin cancer caused by the UV (ultra violet) radiation of sunlight. UV-filters are also used to protect cosmetic and personal care products from photo chemical degradation. Furthermore, UV-filters especially benzophenone and its derivatives are used in for example plastic products as UV-scavengers (BASF, 1995; Muncke, 2010).

UV-filters are generally used in combinations to improve the photo stability. Photo stable UV-filters with capacity to protect less stable filters are OC and the triazine based sunscreen filter octyl triazone (CAS 16732-73-39). A formulation with good protecting properties is OMC, BP-3 and OC (Gaspar and Maia Campos 2006).

Emissions of UV filters are believed to arise primarily from losses due to washing and bathing. Other sources are the use of cosmetics and personal care products. The allowed maximum concentration of the UV-filters in sunscreen products differs between different countries due to

varying legislation. 600 products containing UV-filters are for sale on the Swedish market. They contain 27 different UV-filters, 26 are aromatic compounds and one is inorganic (TiO<sub>2</sub>).

Data regarding usage in Sweden is summarised in Table 4. Data on use of seven out of 13 UV-filters are confidential in the SPIN-database (Substances i Preparations in Nordic countries. The database is based on data from the Product Registries of Norway, Sweden, Denmark and Finland. The database is financed by the Nordic Council of Ministers, Chemical group). The dominating UV-filters, of those for which data is available, are BP3 and EPABA. The use of these UV-filters has however decreased somewhat between 2007 and 2008.

Table 4. Use of different UV-filters (tonnes) i Sweden (SPIN, 2010)

Compound	CAS	2004	2005	2006	2007	2008	Number of products 2008
BMDM, Avobenzone	70356-09-1	8	10	10	1	4	3
OC	6197-30-4	14	13	9	16	8	12
OMC	5466-77-3	12	10	21	5	2	7
EHS	118-60-5	c	c	c	c	c	c
DBENZO	302776-68-7	c	c	c	c	c	c
HMS	118-56-9	c	c	c	c	c	c
BP3	131-57-7	80	72	110	103	76	50
IMC	71617-10-2	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
4-MBC	36861-47-9	c	c	c	c	c	c
3-BC	15087-24-8	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
EPABA	21245-02-3	34	44	59	76	71	13
DHB	131-56-6	0	0	0	0	0	8
DHMB	131-53-3	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.

Abbreviations see table 2. (c) = confidential. n.r. = no record.

## 4 Previous measurements

Data regarding levels of UV-filters found in sewage treatment plant (STP) effluent, sludge, biota and surface waters, from the literature is summarised in Table 5, Table 6, Table 7, and Table 8 respectively.

Dominating sunscreen filters detected in European STP effluents are BP3, 4-MBC, OMC and OC. The concentrations ranged between <0.01 and 189 ng/l. There was no significant difference in the concentrations between spring and summer (Rodil and Moeder, 2008).

Data on sunscreen filters in STP sludge are scarce. Plagellat *et al.* (2006) reported high concentration of 4-MBC, OMC and OC. The concentrations range between 10 and 18740 ng/g d.w.

Data on UV-filters in sediments are rare. Jeon *et al.* (2006) detected DHMB (500-2140 ng/kg d.w.). Other determined UV-filters were below detection limit (500 ng/kg d.w.).

Dominating sunscreen filters detected in biota from the European environment are BP3, 4-MBC and OMC. The concentrations range was <3 - 810 ng/g l.w. Zenker *et al.* (2008) detected 142 ng EHMC /g (l.w.) in fish collected in river Glatt downstream a STP in Dübendorf and 42 ng/g l.w. in

outflow to Lake Greifen. EHMC could also be detected up-streams the STP in low concentration (4 ng/g l.w.).

Dominating sunscreen filters detected in surface waters collected from European lakes were OC, OMC, 4-MBC and BP3. The concentrations range was below detection limit to 7301 ng/l. High concentrations were detected during the summer in recreational areas but samples collected before the swimming season showed low concentrations or was below detection limit (Rodil & Moeder, 2008; Langford & Thomas, 2008). In an investigation carried out in South Korea, DHB was detected in one out of 25 rivers (47 ng/l) but it was not found in the water samples from lakes. DHMB was not detected in the same rivers and lakes i South Korea (Jeon et al. 2006).

**Table 5.** Levels of UV-filters in STP-effluent found in the literature (ng/l).

Sample	BP3	4-MBC	IMC	OMC	OC	EPABA	EHS	HMS	BMDM	Reference
STP effluent, Leipzig, Germany	19	-	<0.9	<16	<8.5	<0.4	<4	<4	<10	Rodil <i>et al.</i> , 2009
VEAS Oslo, Norway	<-15.5	5.3-17.2	-	164.1-189.3	24.8-31.2	-	-	-	-	Langford & Thomas, 2008
STP effluent May, Leipzig, Germany	42	38	3	23	10	7	-	-	<63	Rodil & Moeder, 2008
STP effluent June Leipzig, Germany	54	38	<1	11	18	2	-	-	<63	Rodil & Moeder, 2008
Switzerland effluent	0.04-5.5	0.2-22	-	0.04-1.2	<0.04-4.3	-	-	-	-	Balmer <i>et al.</i> , 2005
Slovenia, hospital effluent	<133	<190	-	<250	<119	<90	-	<200	-	Cuderman & Heath, 2007
Greece, Shower waste (Pool)	8.2; 9.9	-	-	-	-	5.3; 6.2	-	-	-	Lambropoulou <i>et al.</i> , 2002
STP effluent Switzerland	<0.01-0.7	0.06-2.7	-	<0.01-0.1	<0.01-0.3	-	-	-	-	Balmer <i>et al.</i> , 2005

**Table 6.** Levels of UV-filters in STP sludge found in the literature (ng/g d.w).

	BP3	4-MBC	IMC	OMC	OC	EPABA	EHS	HMS	BMDM	Reference
STP sludge, Switzerland	-	150-4980	-	10-390	320-18740	-	-	-	-	Plagellat <i>et al.</i> 2006

d.w. = dry weight.

**Table 7.** Levels of UV-filters in biota samples found in the literature (ng/g l.w.).

Sample	BP3	4-MBC	IMC	OMC	OC	HMS	Reference
Switzerland, whitefish, roach, perch	<15-123	<18-166	-	<14-72	<5-25	-	Balmer <i>et al.</i> , 2005
Germany fish filet	230; 298	161; 810	-	41; 310	-	720; 3100	Nagtegaal <i>et al.</i> , 1997
Fish	<-2.9	<-3	-	<-5.8	<-4.2	-	Meinerling & Daniels, 2006
Chub ( <i>Leuciscus cephalus</i> )	-	-	-	23-79	-	-	Fent <i>et al.</i> , 2010a
Zebra mussel ( <i>Dreissena polymorpha</i> )	-	-	-	22-150	-	-	Fent <i>et al.</i> , 2010a
Barb ( <i>Barbus barbus</i> )	-	-	-	<5-337	-	-	Fent <i>et al.</i> , 2010a
Gammarus sp.	-	-	-	91-133	-	-	Fent <i>et al.</i> , 2010a
Brown trout ( <i>Salmo trutta</i> )	-	-	-	<5-205	-	-	Fent <i>et al.</i> , 2010a
Eel ( <i>Anguilla anguilla</i> )	-	-	-	30	-	-	Fent <i>et al.</i> , 2010a
Cormorant ( <i>Phalacrocorax</i> sp.)	-	-	-	16-701	-	-	Fent <i>et al.</i> , 2010a

l.w. = lipid weight.

**Table 8.** Levels of UV-filters in surface water found in the literature (ng/l).

Sample	BP3	4-MBC	IMC	OMC	OC	EPABA	EHS	HMS	BMDM	Reference
Recreation area Cospuden, , Germany	40	1140	146	3009	4381	<0.4	748	<4	2431	Rodil <i>et al.</i> , 2009
Ionian sea, Greace	1.8	detected	-	-	-	-	-	-	<24	Giokas <i>et al.</i> , 2004
Swimming pool	4.2	6.9	-	-	-	-	-	-	<	Giokas <i>et al.</i> , 2004
Bathing water 12:00, NW Greace	6.5	13.1	-	7.4	-	-	-	-	<	Giokas <i>et al.</i> , 2005
Bathing water 15:00, NW Greace	8.2	19.7	-	10.7	-	-	-	-	<	Giokas <i>et al.</i> , 2005
Innefjord July, Oslofjord, Norway	27	<1-5	-	159		-	-	-	-	Langford & Thomas, 2008
Huk, Oslofjord, Norway	165.5	9.8	-	44.9	29.9	-	-	-	-	Langford & Thomas, 2008
Kalvöya, Oslofjord, Norway	24	40.7	-	63.1	105.1	-	-	-	-	Langford & Thomas, 2008
Sandvik Beach, Oslofjord, Norway	18.5-240.8	25.4-798.7	-	60.4-389.9	65.3-7301	-	-	-	-	Langford & Thomas, 2008
Sandvik Marina, Oslofjord, Norway	23.6	31.8	-	70.8	90.1	-	-	-	-	Langford & Thomas, 2008
Lake Zurich July/Aug., Switzerland	-	3-22	-	2-26	<2	-	-	-	<20	Poiger <i>et al.</i> , 2004
Lake Zurich April, Switzerland	-	<2-3	-	-	<2	-	-	-	<20	Poiger <i>et al.</i> , 2004
Lake Hyttnersee July/Aug. Switzerland	5-125	2-82	-	4-15	3-27	-	-	-	<20	Poiger <i>et al.</i> , 2004
Lake Hyttnersee April Switzerland	-	2-9	-	5-19	<2	-	-	-	<20	Poiger <i>et al.</i> , 2004
Greifensee August Switzerland	-	430	-	140	85	-	-	-	<20	Poiger <i>et al.</i> , 2004
Lake Cospudener June, Germany	27	25	<2	-	250	2	-	-	<63	Rodil & Moeder, 2008
Lake Bagger June, Germany	55	148	51	33	126	5	-	-	<63	Rodil & Moeder, 2008
River Elstenbecker May, Germany	<11	5	<2	21	<7	3	-	-	<63	Rodil & Moeder, 2008
River Parthe May, Germany	30	15	<2	-	16	<0.2	-	-	<63	Rodil & Moeder, 2008
Switzerland Surface water summer	<2-35	<2-28	-	<2-7	<2	-	-	-	-	Balmer <i>et al.</i> , 2005
Slovenia, river	<-114	<143	-	<-88	34-35	<19, 47	-	345, 165	-	Cuderman & Heath, 2007
Slovenia, Lake	<28-85	<143	-	92	<17-31	<19-34	-	<194	-	Cuderman & Heath, 2007
Greece Epirus coastal water	<3					<3	-	-	-	Lambropoulou <i>et al.</i> , 2002
Rivers South Korea	<5									Jeon <i>et al.</i> 2006
Lakes South Korea	<5									Jeon <i>et al.</i> 2006

## 5 Screening programme

A sampling strategy was developed in order to determine concentrations of UV-filters in different matrices in the Swedish environment. The sampling programme also aimed to identify possible emission sources, uses and pathways. The sampling programme is summarised in Table 9, and details of the samples are given in Table A1 in the Appendix.

Emissions of UV filters are believed to arise primarily from losses due to washing and bathing. Therefore, this screening mainly included measurements in the aquatic environment.

Since no point sources could be identified, the sampling programme was focused on diffuse sources in an urban environment. Surface water, sediment and fish samples from the city of Stockholm were included in the screening.

In order to investigate the losses of UV-filters during swimming, surface water, sediment and fish from bathing places were collected. The sampling was performed during periods outside the bathing season (May, September and December) and during the bathing season (August).

Due to possible release of the chemicals from personal care products, sewage treatment plants (STPs) were identified as potential sources. Sludge and effluent water from municipal STPs in Stockholm and other places were included in the sampling program.

Background levels of the UV-filters in the aquatic environment, were measured in surface water, sediment and fish from three background lakes: Gårdsjön, Sandsjön and Tärnan.

Table 9. Sampling programme.

Site	STPs Effluent	STPs Sludge	Surface water	Sediment	Fish	Total
<b>Background</b>						
Gårdsjön			1	1	1	<b>3</b>
Sandsjön			1	1		<b>2</b>
Tärnan			1			<b>1</b>
<b>Urban area</b>						
Stockholm area	2	2	6	4	3	<b>17</b>
Bathing places			15	1	1	<b>17</b>
Municipal STPs	6	6				<b>12</b>
<b>Total</b>	<b>8</b>	<b>8</b>	<b>24</b>	<b>7</b>	<b>5</b>	<b>52</b>



## 6 Methods

### 6.1 Sampling

**Surface water** samples were collected in 1 L dark glass bottles. When the samples arrived to the laboratory they were acidified and within seven days concentrated on solid phase extraction (SPE) columns see 5.2.2). The SPE-columns were stored in a freezer (-18°C) until chemical analysis.

Surface **sediment** (0-2 cm) samples were collected using a Kajak sampler. The sediment was transferred into pre-muffled (400°C) glass jars and stored in a freezer (-18°C) until chemical analysis.

The **fish** samples from the Stockholm environment were collected using fishing net. From the total catch approximately 10 individuals of Perch (*Perca fluviatilis*) were selected, representing the second-fifth year classes.

Fish from the background Lakes Gårdsjön (Brown Trout; *Salmo trutta*) and Sandsjön (Perch; *Perca fluviatilis*) were collected by means of fishing net.

The fish samples were wrapped in pre-cleaned aluminium foil and stored in a freezer (-18°C) until analysed. Fish muscle was dissected for analysis using solvent washed scalpels. The muscle samples were stored at -18°C in pre-cleaned glass jars.

The staff at the different STPs collected **effluent water** (day samples). The samples were collected in 1 L dark glass bottles. When the samples arrived to the laboratory, they were acidified and within seven days concentrated on SPE-columns (see 5.2.2). The SPE-columns were stored in a freezer (-18°C) until analysis.

**Sludge samples**, from the anaerobic chambers, were taken by the staff at the different STPs. The sludge was transferred into muffled glass jars and stored at 4°C or -18°C until analysed. A glass jar filled with diatomaceous earth (10 % water), which was exposed to the surrounding environment during the sampling, was used as a field blank.

### 6.2 Chemical analysis

#### 6.2.1 Sample preparation

##### 6.2.1.1 Water samples

Acidified surface water and effluents from STPs were filtrated on pre-heated (400°C) glass fibre (GF/C) filters prior to solid phase extraction. Sample volumes varied between 200 and 1000 ml depending on sample type. Filtered samples were spiked with recovery standard and extracted onto C<sub>18</sub> cartridges activated with acetone and HCl (0.05 M). The analytes were subsequently eluted with methanol and a mixture of methanol-dichloromethane. The methanol was removed by extraction with HCl (0.05 M). The GF/C filters were acidified with H<sub>3</sub>PO<sub>4</sub> and extracted with acetone. The

acetone extracts were diluted with acidified ultra-pure water and extracted with a mixture of hexane and MTBE (9:1). The resulting extracts from water and filter were combined.

### **6.2.1.2 Sediment and sludge samples**

The sample size varied depending on sample type (10 g f.w. sediment, 5 g f.w. sludge). The samples were spiked with recovery standard. EDTA and H<sub>3</sub>PO<sub>4</sub> were added before extraction with (a) acetone, (b) methanol-dichloromethane-MTBE mixture. The extractions lasted for one hour each time. The acetone and methanol was washed away by shaking the extract with HCl (0.05 M). The HCl wash was extracted once with MTBE:MTBE (1:1). The extracts were pooled and cleaned-up on "graphitised carbon black" (GCB) columns.

### **6.2.1.3 Fish samples**

Fish samples (muscle, 10 g) were spiked with recovery standard and homogenised in acetonitrile (ACN) according to "QuEChERS" (Anastassiades *et al.*, 2002). The ACN-extracts were safeguarded. Water was added followed by extraction with (a) hexane/MTBE and (b) benzene/MTBE. The final extracts were dried, concentrated and solvent changed to hexane followed by clean-up on an "ethylenediamine-*N*-propyl" (PSA) column

### **6.2.1.4 Derivatization**

The determination of UV-filters was performed in two steps. In the first step the phenolic and neutral UV-filters were acetylated. Acetylation improved the clean-up of the extracts and the chromatographic properties and separation on the GC-column. Acetylation was done with acetic acid anhydride using pyridine/4-*N,N*-dimethylaminopyridene as base.

In the second step the acetylated extracts were methylated followed by determination of BMDM. The methylation was made according to Nagtegaal *et al.* (1997) with minor modifications. The extract was evaporated to dryness and re-dissolved in dry MTBE (dried over molecular sieve 5 Å). Methyl-iodide and NaH was added and the test tube was closed and shaken. The reaction was performed at 85°C for 2 hours in test tubes. The test tubes were cooled and water and hexane was added. After extraction the organic phase was dried, concentrated and transferred to a GC-vial before GC-MS/MS analysis.

## **6.2.2 Instrumental analysis**

The extracts were analysed on a gas chromatograph (GC) coupled to a 7000A Triple Quad MS (Agilent Technologies, Inc. Santa Clara, CA, USA). The instrument was equipped with an auto injector (Agilent 7683B). The injection was in pulsed splitless mode (1 µl) at 240°C. The detector was used in MRM mode with electron ionisation at energy of 70 eV. The fused silica capillary column (VF-5MS 30 m × 0.25 mm i.d. × 0.25 µm film thickness, Varian) was held at 45°C for 1 min., ramped 15°C/min to 200°C, 5°C/min to 300°C, and 15°C/min to 325°C and held at 325°C for 2 min. Helium was used as carrier gas. The analytes were identified by their characteristic retention times and one product ion used for quantification. A second product ion was used as qualifier to increase specificity of the detection (Table 10). Quantification was based on comparison of the peak area to the known peak area of the standard analytes.

The homosalate standard contained two isomers. Both were determined and the sum of the isomers was reported.

Table 10. Precursor and product ions utilized in the MS-MS-quantification.

Analyte	Precursor m/z	Product-1 m/z	CE Volt	Product-2 m/z	CE Volt
Bifenyl	154	153	15	152	30
<i>Iso</i> -amylcinnamate (Recovery standard)	131	103	5	77	30
2-Hydroxydibensfuran acetate (Recovery standard)	184	102	30	128	15
3-Benzylidene camphor	240	225	5	212	5
Ethylhexyl salicylate acetate	138	120	5	92	15
Homosalate acetate-1	138	120	5	92	15
<i>Iso</i> -amyl p-4-methoxycinnamate	178	161	15	132	15
3-(4-Methyl benzylidene) camphor	254	105	40	239	5
Homosalate acetate-2	138	120	5	92	15
Benzylcinnamat (Recovery standard)	192	191	15	189	40
Benzophenone-3 acetate	227	184	30	212	15
2,4-Dihydroxybenzophenon acetate	213	128	40	184	15
Ethylhexyl dimethyl PABA	165	164	15	148	30
Ethylhexyl-4-methoxycinnamate	178	161	15	177	5
2,2'-Dihydroxy-4-metoxybensophenon acetate	227	184	30	128	40
Octocrylene	249	248	5	220	15
DBENZO-acetate	382	280	12.5	298	12.5
BMDM	161	146	5	118	15

Explanations: *m/z* the mass of the ion divided by its charge, CE collision energy. The phenolic UV-filters were acetylated and BMDM methylated (se 5.2.2.1 and 5.2.2.2 for details).

### 6.2.3 Quality control

UV-filters are additives used in personal care products which potentially may cause contamination of samples. Thus, these products were avoided when handling the samples. Furthermore, nitrile plastic gloves were used throughout the analytical work. The use of plastic materials was avoided. Glass equipment and silica gel was heated (400°C) prior to use. Using these precautions, we experienced no problems concerning background levels in the field- and analytical blank samples.

The following quality criteria were used to ensure correct identification and quantification of the target compound: (a) the retention times should match those of the standard compounds within  $\pm 0.05$  min., (b) the intensity ratios of the selected ions should be within  $\pm 15\%$  of the expected / theoretical value and (c) the signal-noise ratios should be greater than 3:1 (Haglund *et al.*, 1993).

Internal standard (recovery standard added to the samples) approach were used for quantification, thus all reported values are recovery-corrected according to the recovery standard. Acceptable recovery rates were  $>50\%$ . Field blanks were exposed to the environments at each sampling station (Keith, 1991). Method blanks and field blanks were included for each sample batch and analysed to assess background interferences and possible contamination of the samples. Concentrations below field blank levels were treated as below limit of detection.

The limit of detection (LOD) was defined as 3 times the blank samples noise but in consideration of the actual sample noise in the target analytes "retention window" in the chromatograms. Possible background levels of analytes were subtracted from measured sample values (Keith 1991; Miller and Miller 1993).

The uncertainty of the chemical analysis is governed by losses during extraction and clean-up, interference from other compounds, trueness of analytical standards, instrumental parameters, and contamination. The uncertainty is expected to be larger for compounds which are analysed the first time than for compounds which previously have been analysed or where similar compounds have been analysed earlier. For the determined UV-filters the analytical uncertainty is estimated to be in the range 20-40%.

## 7 Results and discussion

The results from the measurements of the UV filters are presented in the Appendix where the concentrations of the individual substances are given. Overviews of the detection frequencies, e.g. the fraction of samples where a substance was found in a concentration above the detection limit for the different sample matrices, are given in Table 11.

In general, most of the included UV-filters were regularly found in surface waters and sediments. There were also high detection frequencies in STP effluents and sludge. A number of the UV-filters occurred in all sewage sludge samples. Only four of the 13 compounds occurred in the fish samples.

Table 11 Detection frequency (DF %) for the individual substances in the different sample matrices.

Matrix	Surface water Spring	Surface water Summer	Sediment	Fish	STP Effluent	STP Sludge
Number of samples	7	17	7	5	8	8
	DF %	DF %	DF %	DF %	DF %	DF %
3-BC	0	0	57	0	13	13
EHS	0	24	14	0	13	0
IMC	14	6	43	20	13	63
4-MBC	100	65	29	20	88	100
HMS	14	88	71	0	88	100
BP3	100	100	29	0	100	100
DHB	14	47	71	0	63	75
EPABA	14	76	14	0	25	63
OMC	0	53	43	60	38	100
DHMB	29	59	0	0	25	75
OC	43	94	57	80	63	100
DBENZO	14	59	0	0	63	88
BMDM	0	29	0	0	63	0

Abbreviations see Table 2

Below the concentrations of the UV-filters are discussed for different sample categories.

### 7.1 Background areas

Several of the UV-filters were found in surface waters from the background lakes, see Figure 1. The surface water from Lake Sandsjön contained eight of the 13 UV-filters, 4-MBC, HMS, BP3, DHB, EPABA, OMC, DHMB and OC. Concentrations of 6.5, 0.24, 2.6, 4.9, 15, 3.0, 0.13, and 8.7 ng/l, respectively, were found. Four of the UV-filters were also detected in the sample from Lake Gårdsjön, HMS, BP3, EPABA and OC. The concentrations in this sample were generally slightly lower, 0.38, 1.4, 0.9 and 4.2 ng/l respectively. In the sample from Lake Tärnan only 4-MBC and BP3 could be found. However, the concentration of 4-MBC, 22 ng/l, was the highest measured concentration in the surface water samples from the background lakes.

The concentrations of 3-BC, EHS, IMC, DBENZO and BMDM were below LOD all three surface water samples from the background lakes.

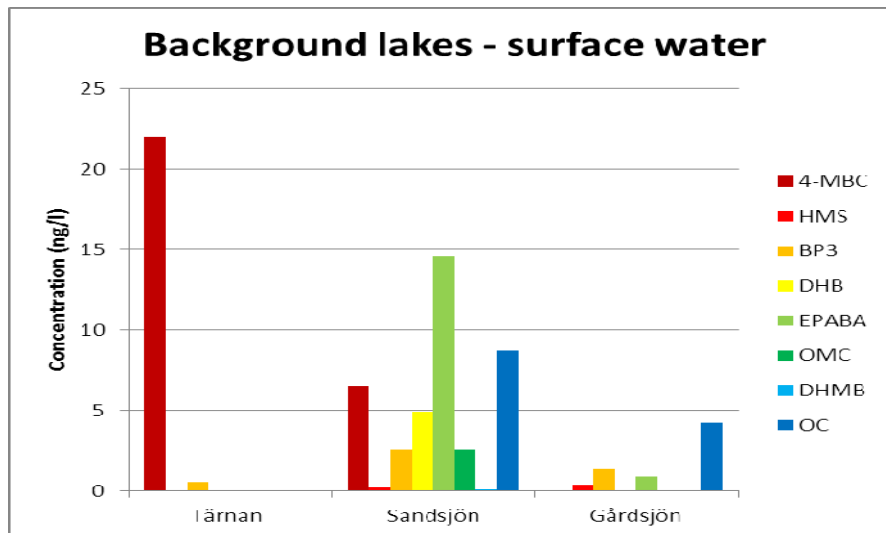


Figure 1. UV-filters in surface water samples from background lakes.

Four of the UV-filters were also found in the sediments from the background lakes. In the sediment sample from Lake Gårdsjön, EHS and 4-MBC were found at concentrations of 2.3 and 6.8 ng/g dw respectively, whereas in the sample from Lake Sandsjön both DHB and EPABA were found at a concentration of 1.2 ng/g dw.

The GC-MS/MS chromatogram of the sediment sample from Lake Sandsjön contained a large peak, corresponding to 450 µg/kg dw, that appeared within the BMDM- window. However, the ion-ratio was not within the quality criteria (se 5.2.4) and the result was therefore rejected.

In the fish sample (brown trout) from Lake Gårdsjön, OC occurred at a concentration of 6.8 ng/g fw. None of the other substances could be found in this sample.

## 7.2 Diffuse sources

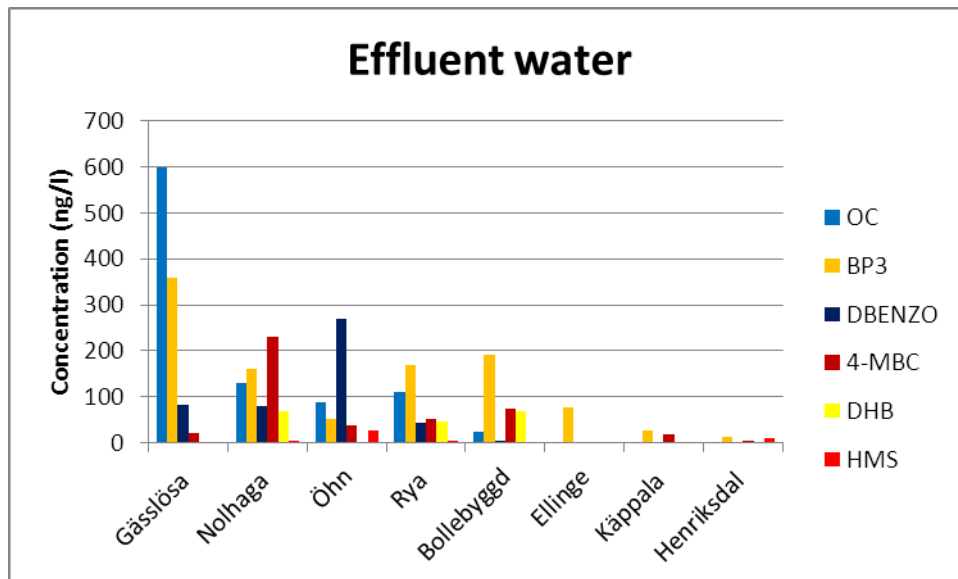
### 7.2.1 Sewage treatment plants (STPs)

The UV-filters were frequently found in both effluent and sludge from the STPs. There was a great variation in the concentrations and distribution pattern among the different samples.

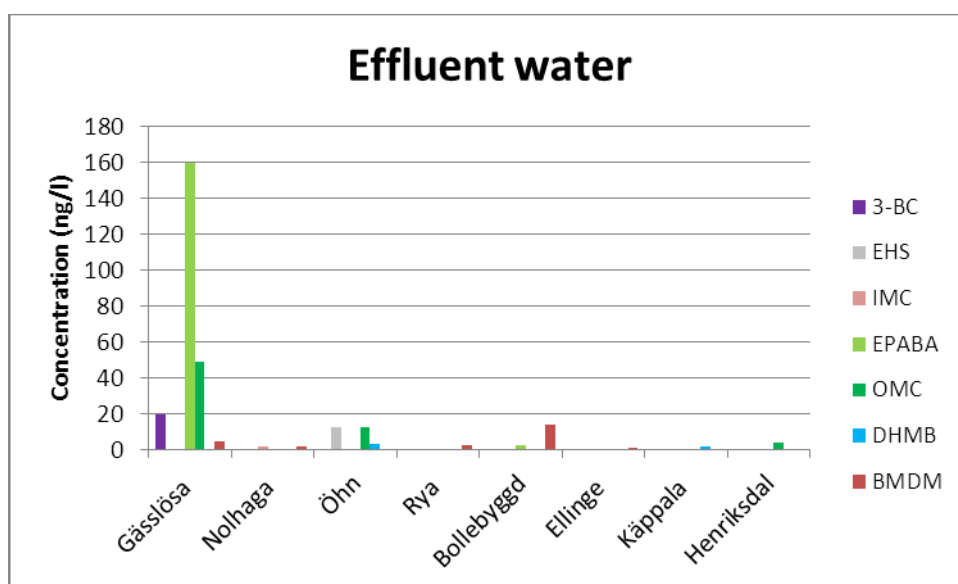
All the UV-filters were found in the effluent water samples, see Figure 2 and Figure 3. BP3 was found in all eight effluent samples, 4-MBC and HMS in seven, OC, DBENZO and DHB in five, OMC in three, EPABA and DHMB in two, and 3-BC, EHS and IMC in one out of eight samples.

OC occurred in the highest concentrations (24-600 ng/l), followed by BP3 (14-360 ng/l), DBENZO (5.5-270 ng/l), 4-MBC (3.0-230 ng/l), EPABA (2.7 and 160), DHB (2.3-68 ng/l), OMC (3.5-49 ng/l), HMS (1.2-26 ng/l), 3-BC (19 ng/l), EHS (12 ng/l) DHMB (1.4 and 3.3 ng/l), and IMC (2.0 ng/l).

The highest total concentration (sum of measured concentrations) was found in the sample from Gässlösa, followed by Nohhaga, Öhn, Rya, Bollebygd, Ellinge, Käppala and Henriksdal.



**Figure 2.** Concentrations of the UV-filters OC, BP3, DBENZO, 4-MBC, DHB and HMS in effluent water from municipal STPs.



**Figure 3.** Concentrations of the UV-filters 3-BC, EHS, IMC, EPABA, OMC, DHMB, and BMDM in effluent water from municipal STPs.

The concentration ranges measured in this investigation were somewhat higher than reported from European STP effluents and the distribution pattern of UV-filters were different (Table 5).. The highest concentration reported in European STP effluents was 189 ng OMC/l.

The dominating UV-filter found in sludge was OC, see Figure 4 and Figure 5. The concentration range was 2 700 – 9 100 ng/g dw. OC constituted 60 – 75% of the summed amount of all UV-

filters found. The median concentration was above 100 ng/g dw also for DBENZO (1 800 – 2 500 ng/g dw; though <5 in Öhn STP), 4-MBC (320 – 1300 ng/g dw), HMS (140-950 ng/g dw) and OMC (31 -410 ng/g dw).

DHB, BP3, EPABA, IMC and DHMB was found in most sludges but in concentrations below 100 ng/g dw. 3-BC was found only in Öhn STP (64 ng/g dw). EHS was not found in sludge (<0.3 ng/g dw).

Data on UV-filters in sludge are scarce, only one report was found (Plagellat et al.2006). In comparison with Plagellat the concentrations found in this investigation as somewhat lower. The concentration pattern of UV-filters also differed.

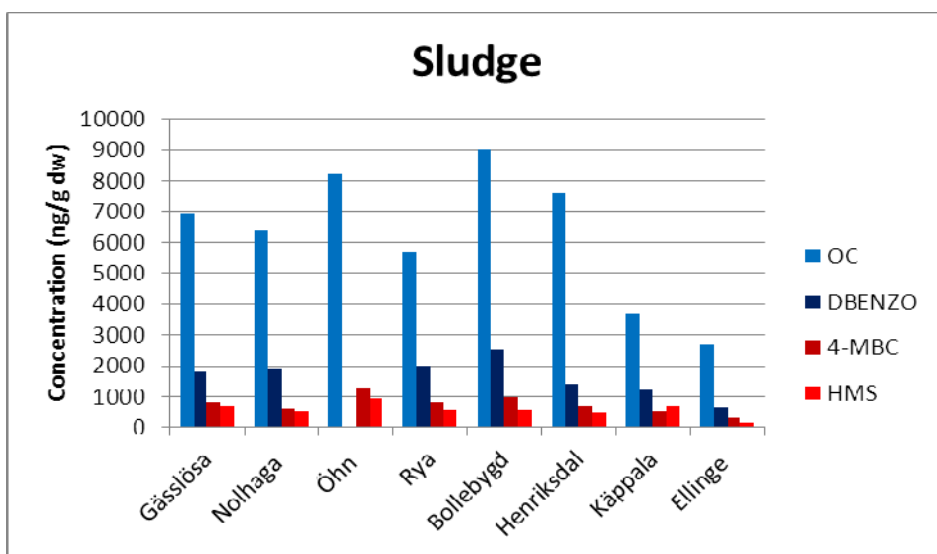


Figure 4. Concentrations of the UV-filters OC, DBENZO, 4-MBC and HMS in sludge from municipal STPs.

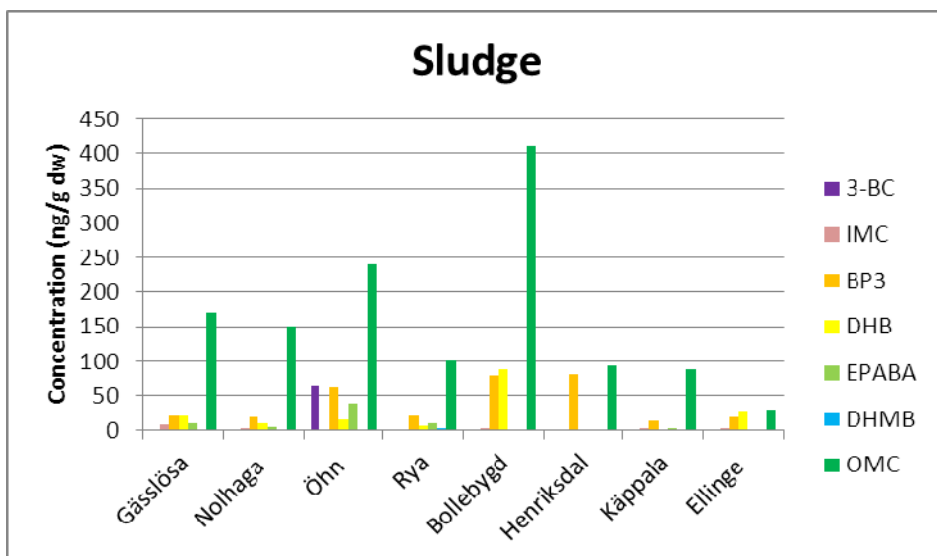


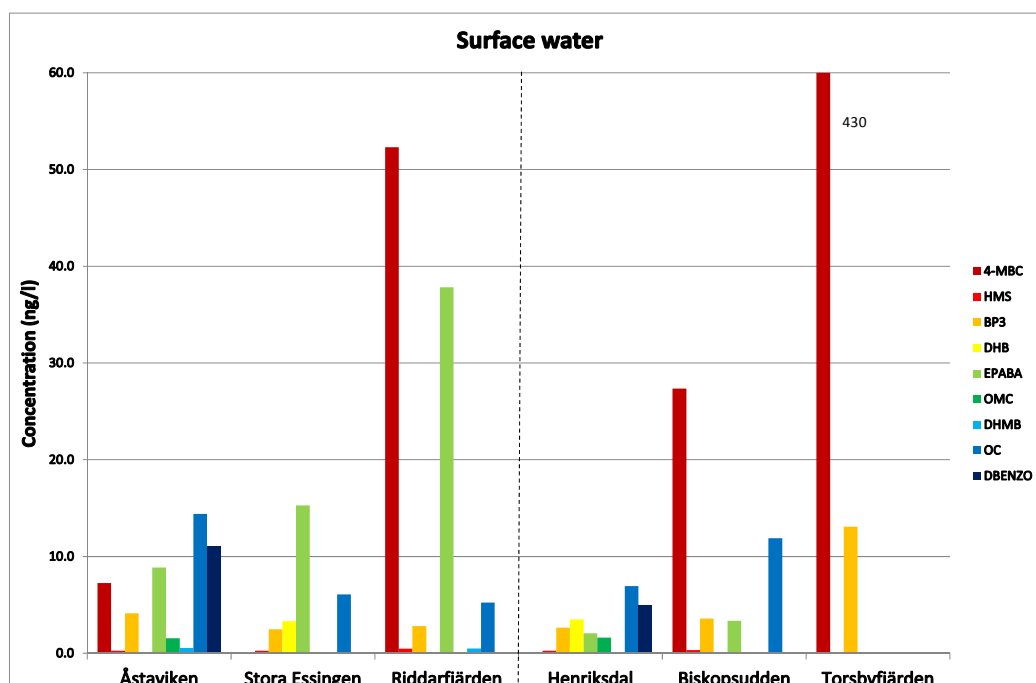
Figure 5. Concentrations of the UV-filters 3-BC, IMC, BP3, DHB, EPABA, DHMB and OMC in sludge from municipal STPs.



## 7.2.2 Urban environment

The sampling program in the urban environment included surface water, sediment and fish. The samples were collected in September in central Stockholm (Årstaviken, Stora Essingen and Riddarfjärden) and in a gradient through the 6 inner Stockholm archipelago (outside the effluent point of the Henriksdal STP, Biskopsudden and Torsbyfjärden). Further, samples were taken at bathing places during spring and summer, see 4.1.

In Figure 6 the concentrations found in surface water from central Stockholm and from the gradient are presented. All UV-filters except 3-BC, EHS, IMC and BMDM, occurred in these samples. The concentration of 4-MBC in the sample from Torsbyfjärden (430 ng/l) was the highest concentration detected. All other values were below 60 ng/l and most below 10 ng/l. Along the gradient the numbers of detected UV-filters decreased, while the detected measured concentrations increased.



**Figure 6.** Concentrations of UV-filters in surface water sampled in central Stockholm (Årstaviken, Stora Essingen and Riddarfjärden) and in a gradient through the inner Stockholm archipelago (Henriksdal, Biskopsudden and Torsbyfjärden).

In surface waters from bathing places sampled in the summer OC and DBENZO dominated with maximum concentrations of 1200 and 960 ng/l respectively. In the corresponding spring samples these substances were only occasionally detected and at a maximum of 4.3 and 12 ng/l (Figure 7, Table 12). The same general tendency but at concentrations less than 100 ng/l was seen for HMS, BP3, DHB, EPABA, OMC, DHMB, EHS and BMDM (Figure 8, Table 12).

4-MBC was frequently found but with no seasonal difference. IMC was found only twice at low concentrations and 3-BC not at all (Figure 9, Table 12).

Thus OC occurred in the highest concentrations, followed by DBENZO, EHS, HMS, EPABA, 4-MBC, BP3, OMC, DHB, BMDM, DHMB and IMC. The highest total concentration (sum of the UV-filters) was found during the summer in Magelungen followed by Rönningesjön.

The same UV-filters were detected in European lakes but at significantly higher concentrations. OC was also in the European lakes the dominating UV-filter. DEBENZO was detected regularly in the Swedish lakes but was unfortunately not determined in the European lakes (Table 8).

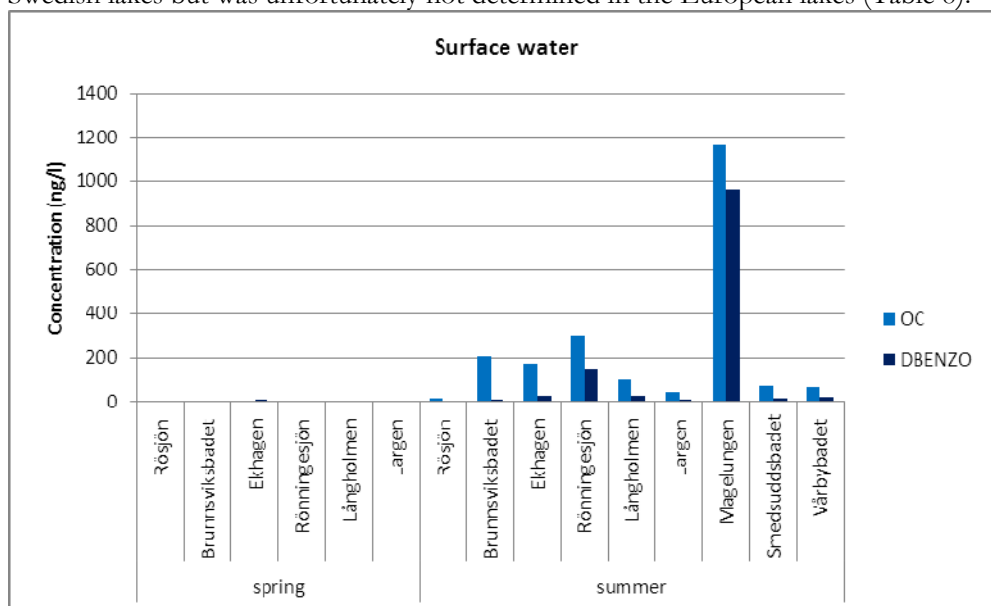


Figure 7. Concentrations of the UV-filters OC and DBENZO in surface water sampled at bathing places during spring and summer.

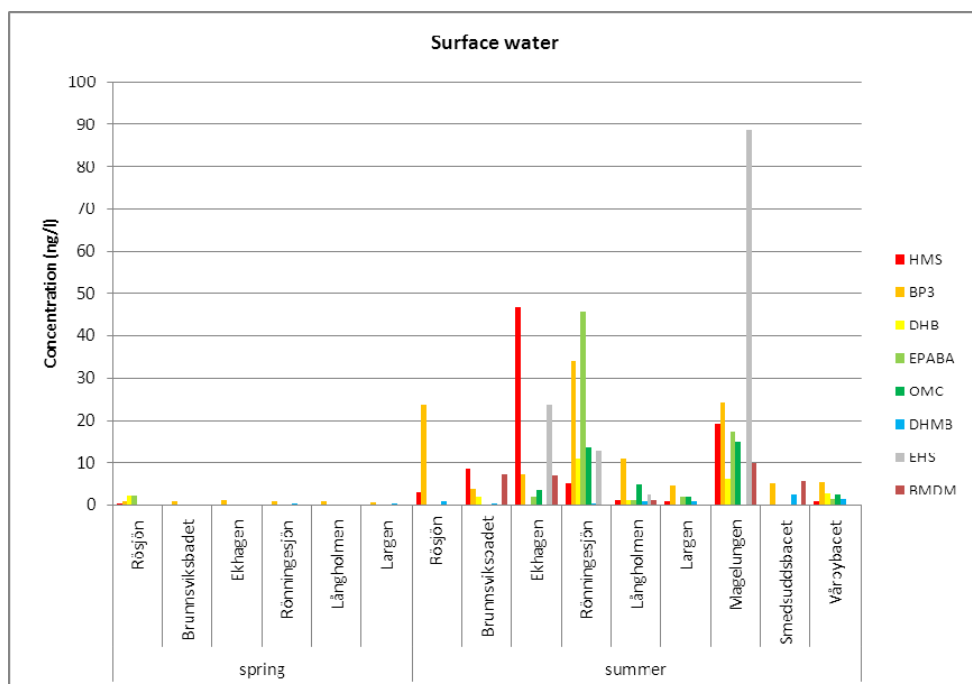


Figure 8. Concentrations of the UV-filters HMS, BP3, DHB, EPABA, OMC, DHMB, EHS and BMDM in surface water sampled at bathing places during spring and summer.

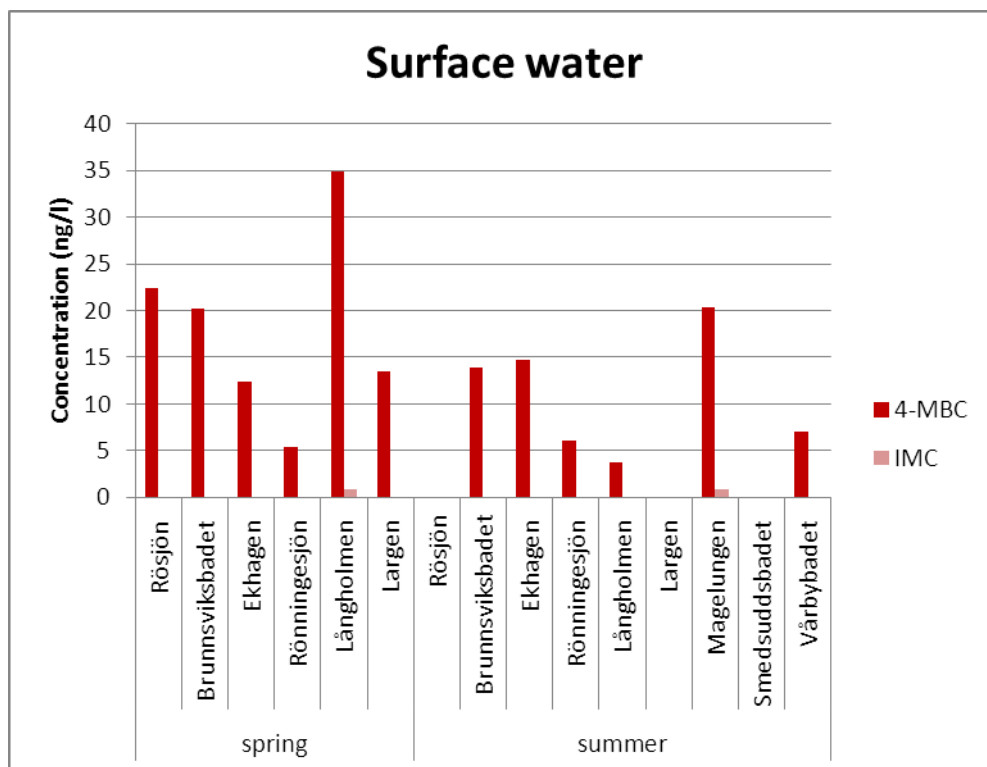
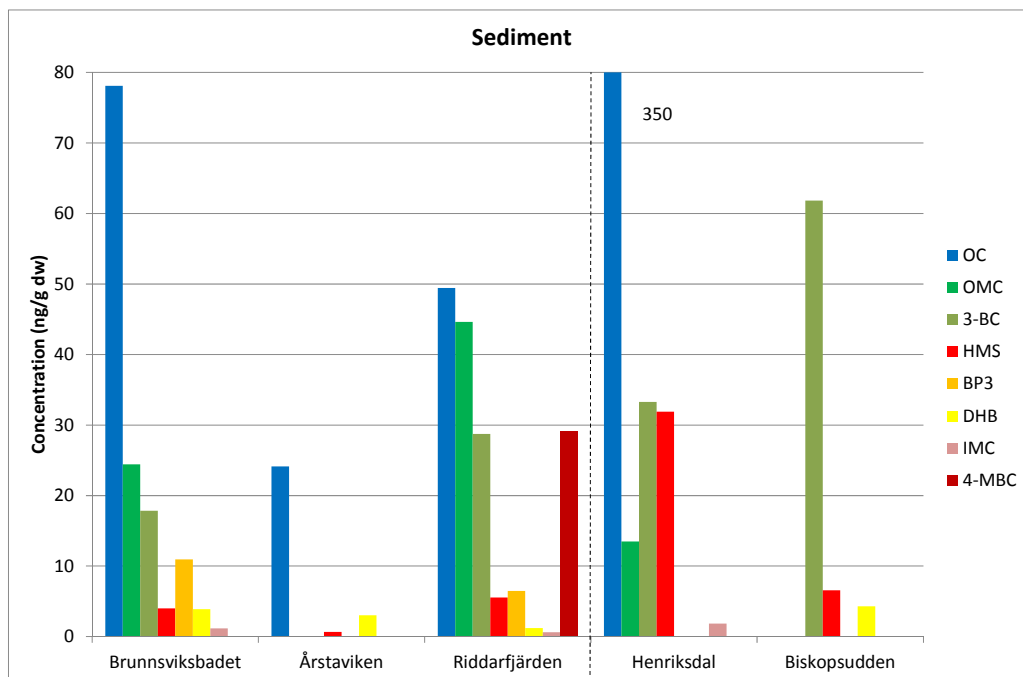


Figure 9. Concentrations of the UV-filters 4-MBC and IMC in surface water sampled at bathing places during spring and summer.

Table 12. Concentrations and detection frequencies of UV-filters in surface water sampled at bathing places during spring and summer.

UV-filter	Spring		Summer	
	Conc. (ng/l)	Det. freq.	Conc. (ng/l)	Det. Freq.
BMDM	< 1	0/6	1.0-9.9	5/9
OC	1.3 - 4.3	3/6	16-1200	9/9
OMC	< 1 (< 2)	0/6	1.9 - 15	6/9
EHS	< 3 (< 6)	0/6	2.6 - 89	4/9
DBENZO	12	1/6	8.3 - 960	8/9
HMS	0.35	1/6	0.82 - 19	8/9
BP3	0.55 – 1.3	6/6	3.9 - 34	9/9
IMC	0.84	1/6	0.84	1/9
4-MBC	5.4 - 35	6/6	3.8 - 15	6/9
3-BC	< 8 (< 16)	0/6	< 8 (< 16)	0/9
EPABA	2.1	1/6	1.2 - 46	6/9
DHB	2.0	1/6	1.2 - 11	6/9
DHMB	0.20 - 0.34	2/6	0.40 - 2.3	7/9

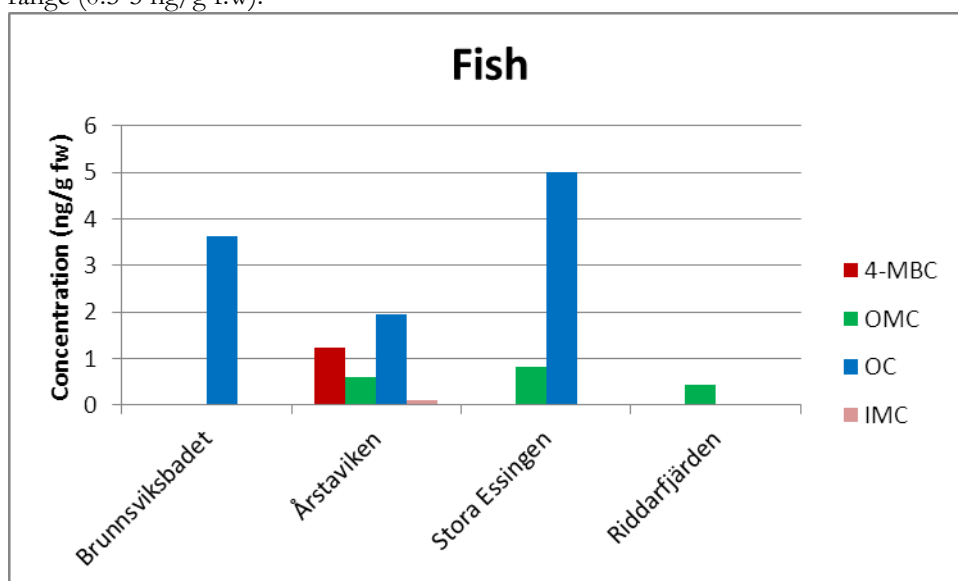
All UV-filters except EHS, EPABA, DHMB, DBENZO and BMDM, were found in the sediments from Stockholm, see Figure 10. In the sample from Riddarfjärden, eight of the UV-filters were found, in the sample from the bathing place Brunnsviksbadet seven, in the sample taken outside the effluent point of Henriksdal STP six, in the sample from Årstaviken and in the sample from Biskopsudden three of the UV-filters were found.



**Figure 10.** Concentrations of UV-filters in sediment sampled at a bathing place (Brunnsviksbadet), in central Stockholm (Årstaviken and Riddarfjärden) and in a gradient through the inner Stockholm archipelago (Henriksdal and Biskopsudden).

Reported data on UV-filters in sediments are rare. Jeon et al., (2006) reported DHMB in sediments (500-2140 ng/kg d.w.) but other determined UV-filters were below detection limit (500 ng/kg d.w.).

The concentrations of UV-filters found in fish muscle are presented in Figure 11. Four of the substances (OC, OMC, 4-MBE, IMC) were detected and the concentrations were all in the same range (0.5-5 ng/g f.w.).



**Figure 11.** Concentrations of UV-filters in fish (perch) sampled at a bathing place (Brunnsviksbadet) and in central Stockholm.

The concentrations reported regarding fish collected from lakes in Europe were from less than LOD to 3100 ng/g l.w. The dominating compounds were HMS, 4-MBC and OMC (Table 7).

## 8 Comparison with toxicity data

Due to the limited amount of ecotoxicity data available, measured concentrations were compared to Predicted No Effect Concentrations (PNEC) derived by Quantitative Structure Relationship (QSAR), calculations presented by Wernersson (2008), see Table 13. The PNECs for sediment has however been recalculated to be expressed on a dry weight basis and assuming an organic carbon content of 5%. Further, for UV-filters with a  $\log K_{ow} > 5$  an additional assessment factor of 10 was applied in order to also include the direct uptake from sediment as an exposure pathway. Measured environmental concentrations (MEC) were also compared to the limited experimental ecotoxicity data available (the ecotoxicity data is compiled in Table A3 in the Appendix).

A MEC/PNEC ratio above 1 indicates a potential environmental risk. Ratios above 1 were found for OC, OMC, DBENZO, HMS, 4-MBC and 3-BC. For the STP effluent samples, comparisons have been made without introducing a dilution factor. Below, comparisons to QSAR derived PNECs and available ecotoxicity data is presented in more detail.

For OC, the QSAR derived PNEC was exceeded in five surface water samples, all taken from bathing places during summer. The PNEC was exceeded in one sediment sample which was taken outside the effluent point of the Henriksdal STP. For effluents, the concentration of OC was in the same range as the PNEC in one sample but exceeded it in an additional three samples. OC was however not detected in the effluent sample from Henriksdal STP.

Only one ecotoxicity study regarding OC has been found in the scientific literature; Danovaro *et al.* (2008) studied the effect of UV-filters on coral bleaching. A concentration of 0.033 mg/l caused a 3% release of zooxanthellae, and a significant shift in pigments, but no visible bleaching could be seen.

For OMC, the QSAR derived PNEC for sediment was exceeded in the sediment samples from Riddarfjärden and Brunnsviksbadet. The validity of this PNEC is supported by the available experimental ecotoxicity data. No experimental benthic ecotoxicity studies on OMC has been found, but the ecotoxicity has been studied towards the pelagic species *Daphnia magna* (EC50 of 0.29 mg/l), *Oryzias latipes* (LOEC estrogenic activity of 9.87 mg/l) and *Scenedesmus vacuolatus* (EC50 of 0.19 mg/l), by Fent *et al.* (2010b), Inui *et al.* (2003) and Rodil *et al.* (2009), respectively. From this data, the algae appear to be the most sensitive species. Applying an assessment factor of 1000 to the EC50 value in accordance with the EU-TGD (ECB, 2003) results in surface water PNEC of 190 ng/l. This is slightly lower compared to the QSAR derived surface water PNEC. OMC has also been shown to cause coral bleaching and release of zooxanthellae after exposure to 0.033 and 0.05 mg/l (Danovaro *et al.*, 2008). Thus, the available experimental ecotoxicity data also indicate a potential environmental risk of OMC.

**Table 13.** Comparison of measured concentrations with PNECs derived from QSAR estimates.

UV-filter	MEC			PNEC		MEC/PNEC		
	STP effluent (ng/l)	Surface water (ng/l)	Sediment (ng/g dw)	Water <sup>a</sup> (ng/l)	Sediment <sup>b</sup> (ng/g dw)	STP effluent	Surface water	Sediment
BMDM	0.75-14	1.0-9.9	-	3000	250	0.00025-0.0047	0.00033-0.0033	-
OC	24-600	1.3-1200	24-350	89	180	0.27- <b>6.7</b>	0.014- <b>13</b>	0.13- <b>1.9</b>
OMC	3.5-49	1.6-15	13-45	300	18	0.012-0.16	0.0053-0.050	0.72- <b>2.5</b>
EHS	12	2.6-89	2.3	1400	60	0.0086	0.0019-0.064	0.038
DBENZO	5.5-270	5-960	<	400	64	0.014-0.68	0.013- <b>2.4</b>	-
HMS	1.5-26	0.24-47	0.6-32	400	22	0.0038-0.065	0.00060-0.12	0.027- <b>1.5</b>
BP3	14-360	0.6-34	6.5-11	5700	370	0.0025-0.063	0.00011-0.0060	0.018-0.030
IMC	2	0.84	0.63-1.8	1300	120	0.0015	0.00065	0.0053-0.015
4-MBC	3-230	3.8-430	6.8 and 29	50	3	0.06- <b>4.6</b>	0.076- <b>8.6</b>	<b>2.3-9.7</b>
3-BC	19	<	18-62	300	11	0.063	-	<b>1.6-5.6</b>
EPABA	2.7-160	0.9-46	1.2	1200	15	0.0023-0.13	0.00075-0.038	0.08
DHB	2.3-68	1.2-11	1.2-4.3	22000	2100	0.00010-0.0031	0.000055-0.00050	0.00057-0.0020
DHMB	1.4-3.3	0.13-2.3	<	33000	2100	0.000042-0.00010	0.0000039-0.000070	-

<sup>a</sup>PNEC from QSAR and an assessment factor of 10. Data from Wernersson (2008) except for DHB and DHMB for which the values were derived with the same methodology using EpiSuite v.4.00 (US EPA, 2010).

<sup>b</sup>PNEC sediment derived from PNEC water using equilibrium partitioning by Wernersson (2008) according to the EU-TGD (ECB, 2003), but in this report recalculated to dry weight and assuming an organic carbon content for sediment of 5%. For DHB and DHMB the same methodology was applied using Koc values derived by EpiSuite v.4.00 (MCI method) (US EPA, 2010).

The QSAR derived PNEC water for DBENZO was exceeded in the sample taken from the bathing place Magelungen during summer. No experimental ecotoxicity data for this UV-filter have been found in the scientific literature.

For HMS the QSAR derived PNEC in sediment was exceeded in the sample taken outside the effluent point of the Henriksdal STP. Also for this UV-filter, experimental ecotoxicity data is lacking.

Concentrations of 4-MBC exceeded the QSAR derived PNECs in effluent water, surface water and sediment samples. For the surface water sample from Riddarfjärden a concentration equal to the PNEC was found, whereas for the sample from Torsbyfjärden in the inner Stockholm archipelago a concentration almost ten times above the PNEC was measured (430 ng/l).

Pelagic ecotoxicity of 4-MBC has been studied by Fent *et al.* (2010b), Kunz *et al.* (2006b), Inui *et al.* (2003) and Danovaro *et al.* (2008). Fent *et al.* (2010b) studied the toxicity towards the crustacean *D.*

*magna*, and report an acute EC50 (immobilisation) of 0.56 mg/l, and a chronic LOEC (reproduction) of 0.05 mg/l. Kunz *et al.* (2006b) found 4-MBC to affect growth of fathead minnow (*Pimephales promelas*) resulting in a sub-chronic NOEC of 0.1 mg/l, whereas Inui *et al.* (2003) found estrogenic activity after exposure of Medaka (*O. latipes*) to 9.9 mg/l for seven days. Further, Danovaro *et al.* (2008) showed that exposure of the coral species *Acropora* sp. and *Acropora pulchra* to 0.033 mg/l and 0.05 mg/l, caused bleaching and a 10% and 95% release of zooxanthellae, respectively. Thus, fish appear to be less sensitive compared to both *D. magna* and the coral species. Applying an assessment factor of 1000 to the acute crustacean EC50 value in accordance with the EU-TGD (ECB, 2003) results in a PNEC of 560 ng/l. This is in the same range as the concentration found in the sample from Torsbyfjärden, thus ten times higher compared to the QSAR derived PNEC.

Concentrations of 4-MBC also exceeded the QSAR derived PNEC in the sediment samples from Riddarfjärden (29 g/g dw) and Lake Gårdsjön (6.8 ng/g dw). Effects of 4-MBC towards sediment dwelling organisms have been studied by Schmitt *et al.* (2008). 4-MBC was shown to affect the reproduction (number of unshelled embryos) of the mud snail *Potamopyrgus antipodarum* after chronic exposure. The No Effect Concentration (NOEC) was 260 ng/g dw, the EC10 25.4 ng/g dw and the EC50 1170 ng/g dw. According to the EU-TGD (ECB, 2003) an assessment factor of 100 can be applied to the NOEC or EC10 value if benthic toxicity data only is available for one species. The EC10 and NOEC would thus result in PNECs of 0.245 and 2.6 ng/g dw respectively. It should be noted that a wide confidence interval is reported for the EC10, this value is thus uncertain. However, measured concentrations in sediment from Lake Gårdsjön and Riddarfjärden exceed both PNECs derived. Thus, for benthic organisms the available experimental ecotoxicity data also indicate a potential environmental risk of 4-MBC.

Concentrations of 3-BC exceed the QSAR derived PNEC for sediment in the samples from Brunnsviksbadet, Riddarfjärden, Henriksdal and Biskopsudden. As for 4-MBC, available experimental ecotoxicity data also indicate a potential environmental risk of 3-BC with regard to benthic organisms. Schmitt *et al.* (2008) also studied benthic toxicity of 3-BC. For *P. antipodarum* a NOEC for mortality of 1720 ng/g dw was found. For the oligochaete *Lumbriculus variegatus* a NOEC for weight and reproduction of 1490 ng/g dw was found, but extrapolated EC10-values for weight and reproduction of 950 ng/g dw and 19.2 ng/g dw respectively, are also reported. According to the EU-TGD (ECB, 2003) an assessment factor of 50 can be applied to the lowest NOEC or EC10 value if benthic toxicity data is available for two species. The toxicity values derived for *L. variegatus* thus result in PNEC values of 30 ng/g dw and 0.38 ng/g dw. Again, it should be noted that a wide confidence interval is reported for the EC10, this value is thus uncertain. The concentrations found, 18-62 ng/g dw, all exceed the lower PNEC, and are in the same range or exceed also the higher PNEC.

Reproductive effects on fathead minnow caused by 3-BC has also been studied (Kunz *et al.*, 2006a; 2006b; Kunz and Fent, 2009). The lowest effect concentrations were found by Kunz *et al.* (2006a). A NOEC for vitellogenin induction and also reduced fecundity (no spawns, eggs/female, eggs/spawn) of 0.033 mg/l was found. Further, the NOEC for effects on gonadal histology was 0.0005 mg/l. Kunz *et al.* (2006b) found an effect on growth with a NOEC of 0.1 mg/l. Applying an assessment factor of 10 to the lowest NOEC would result in a PNEC of 50 ng/l. This is lower compared to the QSAR derived PNEC indicating that it may not be protective. 3-BC was however not found in surface water, and the concentration found in one STP effluent sample was below 50 ng/l.

There are also aquatic ecotoxicity data available for some of the UV-filters for which measured concentrations did not exceed the QSAR derived PNECs. These are BP3, IMC, EPABA and DHB.

For BP3 ecotoxicity studies on fish, crustaceans, algae and corals are available. Coronado *et al.* (2008) found that 0.62 mg/l caused induction of vitellogenin and reduced total hatch for medaka. At 0.016 mg/l also percent daily hatch was affected. An acute EC50 of 1.9 mg/l for *D. magna* was reported by Fent *et al.* (2010b), and Rodil *et al.* (2009) present an EC50 of 0.36 mg/l for *S. vacuolatus*. Also BP3 was shown to cause coral bleaching and release of zooxanthellae after exposure to 0.033 and 0.05 mg/l by Danovaro *et al.* (2008). The lowest value, 0.016 mg/l, is approximately 45 times lower compared to the highest concentration found (STP effluent) and 1500 times lower compared to the highest concentration in surface water.

For IMC and EPABA only acute ecotoxicity data for algae (EC50 values of 0.76 and 0.17 mg/l respectively) has been found (Rodil *et al.*, 2009). Applying an assessment factor of 1000 to these values would result in PNECs of 760 and 170 ng/l. This is lower compared to the PNECs derived from QSAR estimates. However, measured concentrations are below these values; only the highest measured concentration of EPABA in STP effluent water is in the same range as the PNEC.

For DHB only toxicity studies on fish have been found. Vitellogenin induction caused by exposure to DHB has been studied by Kunz *et al.* (2006b) and Kunz and Fent (2009). Kunz and Fent (2009) found a NOEC of 1.2 mg/l for fathead minnow. This is almost 18000 times higher compared to the highest measured concentration in water (effluent).



## 9 Summary and conclusions

In general, UV-filters were regularly found in the Swedish water environment, both in background areas and in the urban environment. Surface water contained 12 out of 13 measured UV-filters whereas in sediment 10 out of 13 were found. Four of the UV-filters (4-MBC, OMC, OC and IMC) were also found in fish samples.

There were also high detection frequencies of the UV-filters in STP effluents and sludge. All measured UV-filters were found in STP effluent water, and also, with the exception of EHS and BMDM, in STP sludge.

There was a great variation in the concentrations among the different UV-filters. Measured concentrations in surface water from bathing places during summer were generally in the same range as in effluent water. Further, the highest measured concentrations of several of the UV-filters (OC, EHS, DBENZO, HMS and 4-MBC) were found in surface water samples. Some of the UV-filters were also detected in water samples from background lakes but in lower concentrations. This indicates the widespread occurrence of UV-filters in Swedish surface waters.

For most of the UV-filters detection frequencies and/or concentrations clearly increased in surface water sampled during the summer. This, and also the fact that surface water contained concentrations in the same range as effluent water, indicates the importance of direct emissions during bathing to the occurrence of UV-filters in the environment. Usage during bathing is also a plausible explanation to the measured concentrations in samples taken from the background lakes.

Previous measurements found in the literature is summarised in chapter 4. The data is limited and it is thus not possible to draw any far-reaching conclusions based on comparisons. In general, the concentrations of UV-filters found in effluent and sludge in this screening was in the same order of magnitude as reported in other investigations in Europe. Also the concentrations in surface water and biota found in this study were in the same range as previously reported in fish from Switzerland and Germany.

Comparisons of measured concentrations of UV-filters with QSAR derived PNECs and also available experimental ecotoxicity data indicate that several of the included UV-filters pose a potential environmental risk. Risk ratios above one for effluent water were found for OC and 4-MBC, for surface water for OC, DBENZO and 4-MBC, and for sediment for OC, OMC, HMS, 4-MBC and 3-BC.

Based on results from the present screening the following can thus be concluded:

- UV-filters are widely spread and they can be found both in background areas and in the urban environment.
- Concentrations found in surface water are in the same range as in effluent water and detection frequencies and/or concentrations generally increase during summer. This indicates the importance of direct emissions during bathing to the occurrence of UV-filters in the environment.
- Several of the included UV-filters pose a potential risk to the Swedish environment.

## 10 Acknowledgements

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## Appendix

**Table A1.** Information on samples.

Sample ID	Type	Site	Matrix	Comment	Sampling date	Coordinates (RT90)
8217	Background	Gårdsjön, Stenungsund	Surface water		2009-12-18	
7674	Background	Gårdsjön, Stenungsund	Sediment		09-12-18	
8388	Background	Gårdsjön, Stenungsund	Biota	Brown trout		
7953	Background	Sandsjön	Surface water		2009-09-11	
7954	Background	Sandsjön	Sediment		2009-09-11	
7871	Background	Tärnan Österåker	Surface water		2009-05-30	6608704; 164490
7959	Urban	Årstaviken Stockholm	Surface water		2009-09-16	
7960	Urban	Årstaviken Stockholm	Sediment		2009-09-16	
7969	Urban	Årstaviken Stockholm	Biota		2009-09-16	
7967	Urban	Riddarfjärden Stockholm	Surface water		2009-09-16	
7968	Urban	Riddarfjärden Stockholm	Sediment		2009-09-16	
7972	Urban	Riddarfjärden Stockholm	Biota	Perch	2009-09-16	
7961	Urban	Stora Essingen Stockholm	Surface water		2009-09-16	
7971	Urban	Stora Essingen Stockholm	Biota	Perch	2009-09-16	
7963	Urban	Henriksdal Stockholm	Surface water	Gradient	2009-09-16	
7965	Urban	Biskopsudden Stockholm	Surface water	Gradient	2009-09-16	
7985	Urban	Torsbyfjärden Stockholm	Surface water	Gradient	2009-09-17	
7964	Urban	Henriksdal Stockholm	Sediment	Gradient	2009-09-16	
7966	Urban	Biskopsudden Stockholm	Sediment	Gradient	2009-09-16	
8004	STP	Gässlösa Borås	Effluent		2009-09-29 - 2009-09-30	
8005	STP	Gässlösa Borås	Sludge		2009-09-30	
8006	STP	Öhn Umeå	Effluent		2009-09-30 - 2009-10-01	
8007	STP	Öhn Umeå	Sludge		2009-10-01	
8008	STP	Bollebygd Västra Götaland	Effluent		2009-09-29 - 2009-09-30	
8009	STP	Bollebygd Västra Götaland	Sludge		2009-09-30	
8118	STP	Nolhaga Alingsås	Effluent		2009-11-11	
8119	STP	Nolhaga Alingsås	Sludge		2009-11-12	

Sample ID	Type	Site	Matrix	Comment	Sampling date	Coordinates (RT90)
8164	STP	Käppala Lidingö	Effluent		2009-11-19	
8165	STP	Käppala Lidingö	Sludge		2009-11-19	
8211	STP	Ryaverken Göteborg	Effluent		ink 09-12-17	
8212	STP	Ryaverken Göteborg	Sludge		ink 09-12-17	
8676	STP	Henriksdal Stockholm	Effluent		2010-08-24	
8234	STP	Henriksdal Stockholm	Sludge		2010-01-21	
8269	STP	Ellinge Eslöv	Effluent		2010-01-27	
8270	STP	Ellinge Eslöv	Sludge		2010-01-27	
7853	Bathing place	Rösjön Täby	Surface water	Spring	2009-05-25	6592939;1624237
7883	Bathing place	Rösjön Täby	Surface water	Summer	2009-08-18	
7867	Bathing place	Brunnsviksbadet Stockholm	Surface water	Spring	2009-05-26	6584511; 1627570
7875	Bathing place	Brunnsviksbadet Stockholm	Surface water	Summer	2009-08-10	6584511; 1627570
7987	Bathing place	Brunnsviksbadet Stockholm	Sediment		2009-09-17	
8401	Bathing place	Brunnsviksbadet Stockholm	Biota	Perch	2009-09-17	
7868	Bathing place	Ekhagen/Sjöstugan Stockholm	Surface water	Spring	2009-05-26	6585730; 1628696
7874	Bathing place	Ekhagen/Sjöstugan Stockholm	Surface water	Summer	2009-08-10	6585730; 1628696
7869	Bathing place	Rönningesjön Täby	Surface water	Spring	2009-05-29	6596359; 1630485
7873	Bathing place	Rönningesjön Täby	Surface water	Summer	2009-08-07	6596359; 1630485
7870	Bathing place	Långholmen Stockholm	Surface water	Spring	2009-05-29	6580011; 1626329
7877	Bathing place	Långholmen Stockholm	Surface water	Summer	2009-08-10	6580011; 1626329
7872	Bathing place	Largen Österåker	Surface water	Spring	2009-05-30	6611456; 1653826
7880	Bathing place	Largen Österåker	Surface water	Summer	2009-08-11	
7876	Bathing place	Magelungen Stockholm	Surface water	Summer	2009-08-10	6570616, 1630071
7878	Bathing place	Smedsuddsbadet Stockholm	Surface water	Summer	2009-08-11	6580352; 1626126
7879	Bathing place	Vårbybadet Stockholm	Surface water	Summer	2009-08-10	

**Table A2.** Measured concentrations

ID	Type	Site	Matrix	Comment	Unit	BMDB	EHS	HMS-1	HMS-2	ΣHMS	3-BC	4-MBC	BP3	DHB	DHMB	EPABA	DBENZO	IMC	OMC	OC
8217	Backgr.	Gårdsjön	Surface w		ng/l	<1	<3	<6	0.38	0.38	<8	<8	1.4	<1	<0.1	0.9	<6	<0.5	<1	4.2
7674	Backgr.	Gårdsjön	Sed.		ng/g dw	<4	2.3	<0.1	<0.5	<0.5	<0.1	6.8	<5	<1	<1	<1	<1	<0.2	<10	<2
8388	Backgr.	Gårdsjön	Biota	Brown Trout	ng/g fw	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.05	<1	<0.2	<0.2	<1	<0.5	<0.05	<2	6.8
7953	Backgr.	Sandsjön	Surface w		ng/l	<1	<3	<6	0.24	0.24	<8	6.5	2.6	4.9	0.13	15	<6	<0.5	3	8.7
7954	Backgr.	Sandsjön	Sed.		ng/g dw	-	<0.1	<0.1	<0.5	<0.5	<0.1	<0.2	<5	1.2	<1	1.2	<1	<0.2	<10	<2
7871	Backgr.	Tärnan	Surface w		ng/l	<1	<3	<6	<0.2	<0.2	<8	22	0.6	<1	<0.1	<1	<6	<0.5	<1	<3
7959	Urban	Årstaviken	Surface w		ng/l	<1	<3	<6	0.28	0.28	<8	7.3	4.1	<1	0.54	8.8	11	<0.5	1.6	14
7960	Urban	Årstaviken	Sed.		ng/g dw	<5	<0.1	<0.1	0.6	0.6	<0.1	<0.2	<5	3.0	<1	<1	<1	<0.2	<10	24
7969	Urban	Årstaviken	Biota		ng/g fw	<1	<0.1	<0.1	<0.1	<0.1	<0.1	1.2	<1	<0.2	<0.2	<1	<0.5	0.12	0.6	1.9
7967	Urban	Riddarfjärden	Surface w		ng/l	<1	<3	<6	0.47	0.47	<8	52	2.8	<1	0.50	38	<6	<0.5	<1	5.2
7968	Urban	Riddarfjärden	Sed.		ng/g dw	<2	<0.1	0.27	5.3	5.6	29	29	6.5	1.2	<1	<1	<1	0.63	45	49
7972	Urban	Riddarfjärden	Biota	Perch	ng/g fw	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.05	<1	<0.2	<0.2	<1	<0.5	<0.05	0.4	<0.3
7961	Urban	St. Essingen	Surface w		ng/l	<1	<3	<6	0.26	0.26	<8	<8	2.5	3.3	<0.1	15	<6	<0.5	<1	6.1
7971	Urban	St. Essingen	Biota	Perch	ng/g fw	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.05	<1	<0.2	<0.2	<1	<0.5	<0.05	0.8	5.0
7963	Urban	Henriksdal	Surface w	Gradient	ng/l	<1	<3	<6	0.27	0.27	<8	<8	2.6	3.5	<0.1	2.1	5.0	<0.5	1.6	6.9
7965	Urban	Biskopsudden	Surface w	Gradient	ng/l	<1	<3	<6	0.32	0.32	<8	27	3.6	<1	<0.1	3.4	<6	<0.5	<1	12
7985	Urban	Torsbyfjärden	Surface w	Gradient	ng/l	<1	<3	<6	<0.2	<6	<8	430	13	<1	<0.1	<1	<6	<0.5	<1	<6
7964	Urban	Henriksdal	Sed.	Gradient	ng/g dw	<3	<0.1	12	20	32	33	<0.2	<5	<1	<1	<1	<1	1.8	13	350
7966	Urban	Biskopsudden	Sed.	Gradient	ng/g dw	<1	<0.1	2.9	3.7	6.6	62	<0.1	<5	4.3	<1	<1	<1	<0.2	<10	<2
8004	STP	Gässlösa	Eff.		ng/l	4.5	<6	<12	2.5	2.5	19	20	360	<2	<0.1	160	84	<1	49	600
8005	STP	Gässlösa	Sludge		ng/g dw	<5	<0.3	190	510	700	<0.3	810	21	20	0.7	11	1800	7.9	170	6900
8006	STP	Öhn	Eff.		ng/l	<2	12	24	1.4	25	<16	37	51	<2	3.3	<2	270	<1	12	88
8007	STP	Öhn	Sludge		ng/g dw	<4	<0.3	220	720	950	64	1300	62	15	0.8	39	<5	<0.7	240	8200
8008	STP	Bollebygd	Eff.		ng/l	14	<6	<12	1.5	1.5	<16	75	190	68	<0.2	2.7	5.5	<1	<2	24
8009	STP	Bollebygd	Sludge		ng/g dw	<30	<0.3	140	440	580	<0.3	970	79	89	<3	<3	2500	2.7	410	9100
8118	STP	Nolhaga	Eff.		ng/l	2.0	<6	<12	4.8	4.8	<16	230	160	67	<0.2	<2	81	2.0	<2	130
8119	STP	Nolhaga	Sludge		ng/g dw	<10	<0.3	120	390	510	<0.3	640	18	9.8	0.9	5.9	1900	2.6	150	6400
8164	STP	Käppala	Eff.		ng/l	<2	<6	<12	1.2	1.2	<16	18	28	2.3	1.4	<2	<12	<1	<2	<6
8165	STP	Käppala	Sludge		ng/g dw	<3	<0.3	210	490	690	<0.3	510	14	<3	0.5	3.5	1200	3.9	89	3700
8211	STP	Rya	Eff.		ng/l	2.1	<6	<12	3.8	3.8	<16	51	170	47	<0.2	<2	43	<1	<2	107
8212	STP	Rya	Sludge		ng/g dw	<5	<0.3	130	470	590	<0.3	830	20	6.2	2.8	9.9	2000	<0.7	100	5700

ID	Type	Site	Matrix	Comment	Unit	BMDB	EHS	HMS-1	HMS-2	ΣHMS	3-BC	4-MBC	BP3	DHB	DHMB	EPABA	DBENZO	IMC	OMC	OC
8676	STP	Henriksdal	Eff.		ng/l	<6	<1	5.0	5.2	10	<10	3.0	14	2.3	<0.2	<2	<6	<1	3.5	<3
8234	STP	Henriksdal	Sludge		ng/g dw	<10	<0.3	180	280	460	<0.3	720	82	<3	<3	<3	1400	<0.7	93	7600
8269	STP	Ellinge	Eff.		ng/l	0.75	<3	<6	<0.2	<6	<8	<8	77	<1	<0.1	<1	<6	<0.5	<1	<3
8270	STP	Ellinge	Sludge		ng/g dw	<15	<0.3	41	100	140	<0.3	320	19	28	1.5	<3	650	2.8	31	2700
7853	Bath. pl.	Rösjön	Surface w	Spring	ng/l	<1	<3	<6	0.35	0.35	<8	22	1.0	2.0	<0.1	2.1	<6	<0.5	<1	1.3
7883	Bath. pl.	Rösjön	Surface w	Summer	ng/l	<2	<3	<6	3.2	3.2	<8	<8	24	<1	0.87	<1	<6	<0.5	<1	16
7867	Bath. pl.	Brunnsviks	Surface w	Spring	ng/l	<1	<3	<6	<0.2	<6	<8	20	0.8	<1	<0.1	<1	<6	<0.5	<1	2.5
7875	Bath. pl.	Brunnsviks	Surface w	Summer	ng/l	7.2	<6	<12	8.8	8.8	<16	14	3.9	1.8	0.41	<2	9.5	<1	<2	210
7987	Bath. pl.	Brunnsviks	Sediment		ng/g dw	<10	<0.1	1.4	2.6	4.0	18	<0.2	11	3.9	<1	<1	<1	1.2	24	78
8401	Bath. pl.	Brunnsviks	Biota	Perch	ng/g fw	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.05	<1	<0.2	<0.2	<1	<0.5	<0.05	<23	3.6
7868	Bath. pl.	Ekhagen	Surface w	Spring	ng/l	<1	<3	<6	<0.2	<6	<8	12	1.3	<1	<0.1	<1	12	<0.5	<1	4.3
7874	Bath. pl.	Ekhagen	Surface w	Summer	ng/l	6.9	24	45	1.3	46	<16	15	7.2	<2	<0.2	2	27	<1	3.7	170
7869	Bath. pl.	Rönningesjön	Surface w	Spring	ng/l	<1	<3	<6	<0.2	<6	<8	5.4	1.0	<1	0.30	<1	<6	<0.5	<1	<3
7873	Bath. pl.	Rönningesjön	Surface w	Summer	ng/l	<2	13	<12	5.3	5.3	<16	6.1	34	11	0.40	46	150	<1	14	300
7870	Bath. pl.	Långholmen	Surface w	Spring	ng/l	<1	<3	<6	<0.2	<6	<8	35	0.8	<1	<0.1	<1	<6	0.8	<1	<3
7877	Bath. pl.	Långholmen	Surface w	Summer	ng/l	1.0	2.6	<12	1.2	1.2	<16	3.8	11	1.2	0.96	1.2	26	<1	5	100
7872	Bath. pl.	Largen	Surface w	Spring	ng/l	<1	<6	<12	<0.4	<12	<16	14	0.6	<1	0.34	<2	<6	<1	<2	<3
7880	Bath. pl.	Largen	Surface w	Summer	ng/l	<2	<6	<12	0.82	0.82	<16	<8	4.7	<2	0.98	1.8	8.3	<1	1.9	43
7876	Bath. pl.	Magelungen	Surface w	Summer	ng/l	9.9	89	<12	19	19	<16	20	24	6.1	<0.2	18	960	0.84	15	1200
7878	Bath. pl.	Smedsudds	Surface w	Summer	ng/l	5.7	<6	<12	<0.4	<12	<16	<16	5.3	<2	2.3	<2	16	<1	<2	70
7879	Bath. pl.	Vårbybadet	Surface w	Summer	ng/l	<2	<6	<12	1.0	1.0	<16	7.0	5.5	2.9	1.3	1.3	20	<1	2.5	63



**Table A3.** Available *in vivo* ecotoxicity data for the studied UV-filters.

UV-filter	matrix	Species	Duration	Endpoint		Value	Unit	Reference
3-BC	Water	<i>Pimephales promelas</i>	14 d	VTG	LOEC	400	µg/l	Kunz and Fent (2009)
3-BC	Water	<i>Pimephales promelas</i>	21 d	gonadal histology	NOEC	0.5	µg/l	Kunz <i>et al.</i> (2006a)
3-BC	Water	<i>Pimephales promelas</i>	21 d	VTG and fecundity (no spawns, eggs/female, eggs/spawn)	NOEC	33	µg/l	Kunz <i>et al.</i> (2006a)
3-BC	Water	<i>Pimephales promelas</i>	14 d	VTG	LOEC	435	µg/l	Kunz <i>et al.</i> (2006b)
3-BC	Water	<i>Pimephales promelas</i>	14 d	Growth	NOEC	100	µg/l	Kunz <i>et al.</i> (2006b)
3-BC	Sediment	<i>Lumbriculus variegatus</i>	28 d	weight and reproduction	NOEC	1.49	mg/kg dw	Schmitt <i>et al.</i> (2008)
3-BC	Sediment	<i>Lumbriculus variegatus</i>	28 d	weight	EC10	0.95 (0.11-5.50)	mg/kg dw	Schmitt <i>et al.</i> (2008)
3-BC	Sediment	<i>Lumbriculus variegatus</i>	28 d	reproduction	EC10	0.0192 (0.00240-0.252)	mg/kg dw	Schmitt <i>et al.</i> (2008)
3-BC	Sediment	<i>Potamopyrgus antipodarum</i>	56 d	mortality	NOEC	1.72	mg/kg dw	Schmitt <i>et al.</i> (2008)
4-MBC	Water	<i>Acropora sp.</i>	56 d	release of zooxanthellae	10%	0.033	mg/l	Danovaro <i>et al.</i> (2008)
4-MBC	Water	<i>Acropora pulchra</i>	56 d	release of zooxanthellae	95%	0.05	mg/l	Danovaro <i>et al.</i> (2008)
4-MBC	Water	<i>Daphnia magna</i>	48 h	immobilisation	EC50	0.56	mg/l	Fent <i>et al.</i> (2010b)
4-MBC	Water	<i>Daphnia magna</i>	21 d	reproduction	LOEC	0.05	mg/l	Fent <i>et al.</i> (2010b)
4-MBC	Water	<i>Oryzias latipes</i>	7 d	Estrogenic activity	LOEC	9.9	mg/l	Inui <i>et al.</i> (2003)
4-MBC	Water	<i>Pimephales promelas</i>	14 d	Growth	NOEC	0.1	mg/l	Kunz <i>et al.</i> (2006b)
4-MBC	Sediment	<i>Potamopyrgus antipodarum</i>	56 d	unshelled embryos	NOEC	0.26	mg/kg dw	Schmitt <i>et al.</i> (2008)
4-MBC	Sediment	<i>Potamopyrgus antipodarum</i>		unshelled embryos	EC10	0.0254 (0.00254-0.348)	mg/kg dw	Schmitt <i>et al.</i> (2008)
4-MBC	Sediment	<i>Potamopyrgus antipodarum</i>	56 d	unshelled embryos	EC50	1.17 (0.39-3.51)	mg/kg dw	Schmitt <i>et al.</i> (2008)
DHB	Water	<i>Pimephales promelas</i>	14 d	VTG	NOEC	1.2	mg/l	Kunz and Fent (2009)
DHB	Water	<i>Pimephales promelas</i>	14 d	VTG	LOEC	4.9	mg/l	Kunz <i>et al.</i> (2006b)
BP3	Water	<i>Oncorhynchus mykiss</i>	14 d	VTG	LOEC	0.75	mg/l	Coronado <i>et al.</i> (2008)
BP3	Water	<i>Oryzias latipes</i>	21 d	VTG, % total hatch	LOEC	0.62	mg/l	Coronado <i>et al.</i> (2008)
BP3	Water	<i>Oryzias latipes</i>	21 d	% daily hatch	LOEC	0.016	mg/l	Coronado <i>et al.</i> (2008)
BP3	Water	<i>Acropora sp.</i>		release of zooxanthellae	83%	0.033	mg/l	Danovaro <i>et al.</i> (2008)
BP3	Water	<i>Acropora pulchra</i>		release of zooxanthellae	84%	0.05	mg/l	Danovaro <i>et al.</i> (2008)

UV-filter	matrix	Species	Duration	Endpoint		Value	Unit	Reference
BP3	Water	<i>Daphnia magna</i>	48 h	immobilisation	EC50	1.9	mg/l	Fent <i>et al.</i> (2010b)
BP3	Water	<i>Scenedesmus vacuolatus</i>	24 h	cell density	EC50	0.36±0.012	mg/l	Rodil <i>et al.</i> (2009)
EPABA	Water	<i>Scenedesmus vacuolatus</i>	24 h	cell density	EC50	0.17±0.022	mg/l	Rodil <i>et al.</i> (2009)
IMC	Water	<i>Scenedesmus vacuolatus</i>	24 h	cell density	EC50	0.76±0.098	mg/l	Rodil <i>et al.</i> (2009)
OC	Water	<i>Acropora sp.</i>		release of zooxanthellae	3%	0.033	mg/l	Danovaro <i>et al.</i> (2008)
OMC	Water	<i>Acropora sp.</i>		release of zooxanthellae	86%	0.033	mg/l	Danovaro <i>et al.</i> (2008)
OMC	Water	<i>Acropora pulchra</i>		release of zooxanthellae	90%	0.05	mg/l	Danovaro <i>et al.</i> (2008)
OMC	Water	<i>Daphnia magna</i>	48 h	immobilisation	EC50	0.29	mg/l	Fent <i>et al.</i> (2010b)
OMC	Water	<i>Oryzias latipes</i>	7 d	Estrogenic activity	LOEC	9.87	mg/l	Inui <i>et al.</i> (2003)
OMC	Water	<i>Scenedesmus vacuolatus</i>	24 h	cell density	EC50	0.19±0.012	mg/l	Rodil <i>et al.</i> (2009)