Occurrence of the Organic UV Filter Compounds BP-3, 4-MBC, EHMC, and OC in Wastewater, Surface Waters, and in Fish from Swiss Lakes

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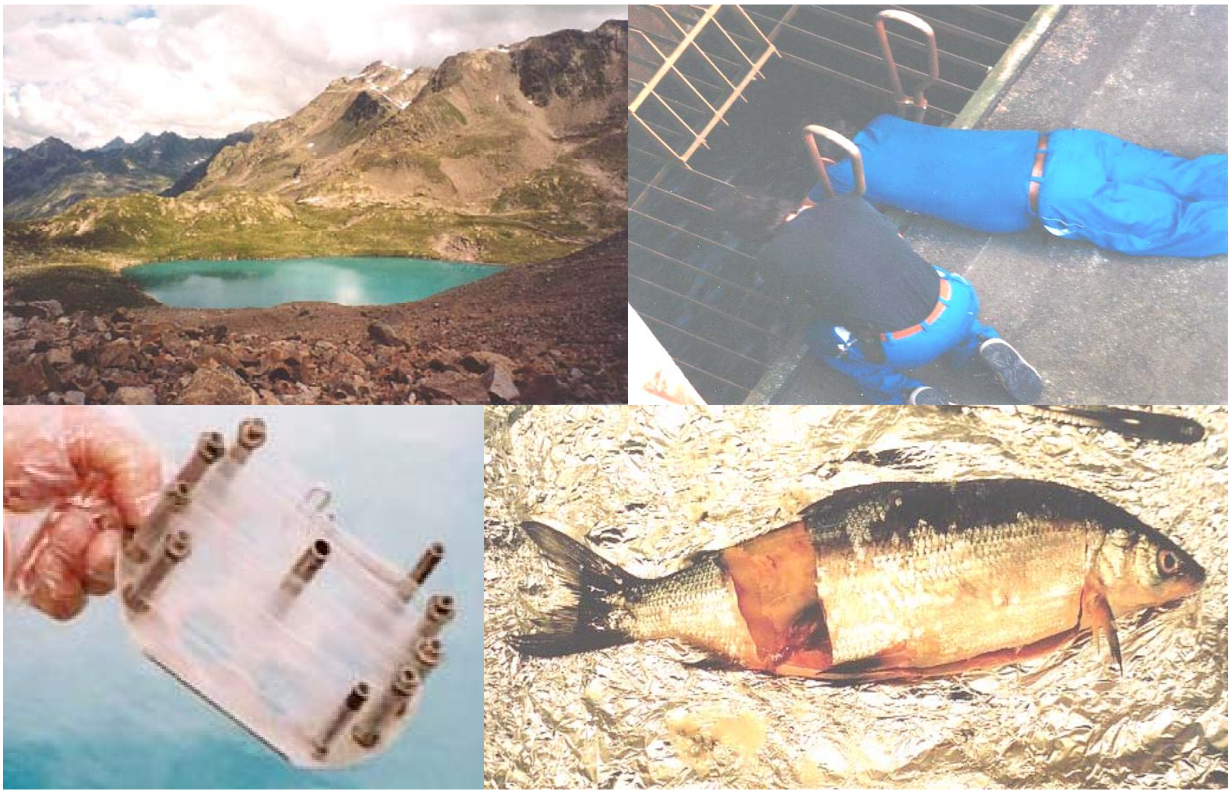

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Summary

Organic UV filters are increasingly used in personal care products such as sunscreen products, cosmetics, beauty creams and skin lotions, lipsticks, hair sprays, hair dyes, shampoos, etc. The compounds enter the aquatic environment from showering, washing, etc. *via* wastewater treatment plants (WWTPs) („*indirect inputs*“), and from recreational activities such as swimming and bathing in lakes and rivers („*direct inputs*“). In this study, the two entry pathways into the aquatic environment were evaluated. The occurrence of four important organic UV filter compounds (benzophenone-3, BP-3; 4-methylbenzylidene camphor, 4-MBC; ethylhexyl methoxy-cinnamate, EHMC; octocrylene, OC) was investigated in samples from wastewater treatment plants (WWTPs) and in surface waters, and in fish from various Swiss lakes.

All four compounds were present in influents of all seven WWTPs investigated with maximum concentration of 19 μg L^{-1} observed for EHMC. The data indicate a seasonal variation with influent loads to WWTPs higher in the warmer season (June 2002) than in the colder one (April 2002), reflecting an increased use of sunscreen products in summer. The loads were in the order EHMC > 4-MBC ~ BP-3 ~ OC. EHMC was also the most prevalent compound listed in two earlier surveys on use and composition of sunscreen products in Switzerland. When these loads in WWTP influents were normalized to the population serviced by the plants, the combined influent loads (sum of four compounds) were up to 16 and 265 g (10’000 persons)$^{-1}$ d^{-1} in April and June 2002, respectively, whereby the June data likely reflected a worst-case situation (weekend with warm weather conditions). Caffeine used as a hydrophilic chemical marker in the study, did not show such a seasonal variation.

The UV filter concentrations in WWTP effluents were considerably lower than in corresponding influents, indicating significant elimination in the WWTPs (4-MBC, 18-82%; BP-3, 68->99%; OC, 88->99%; EHMC, 96.5->99%). The effluents from all WWTPs investigated showed distribution patterns with 4-MBC as the most prevalent compound (maximum concentration, 2.7 μg L^{-1}), followed by BP-3, and lower concentrations of EHMC and OC. The patterns hence were significantly changed from those in the influents because of different elimination of the compounds in WWTPs. When the effluent loads of UV filters were normalized to the population serviced by the WWTPs, the combined loads (sum of four compounds) were up to 19 and 29 g (10’000 persons)$^{-1}$ d^{-1} in April and June, 2002, respectively. Analysis of effluent samples of subsequent days from two of these WWTPs indicated that elimination varied from day to day likely as a result of changed conditions in the plant (water discharge, high-water and storm events, residence time). Data from semi-permeable membrane devices (SPMDs) exposed in the effluent of a further WWTP (Zürich-Werdhölzli), and data from SPMDs exposed in the receiving river (Limmat) up- and downstream this WWTP, supported the above findings from effluent measurements of the other WWTPs.

UV filters were also detected in Swiss midland lakes receiving inputs from WWTPs („*indirect inputs*") and/or recreational activities („*direct inputs*"). All concentrations measured were in the low ng L^{-1} range (<2-35 ng L^{-1}). The concentrations were highest in Hüttnersee, a small lake, used for bathing in summer but with no inputs from WWTPs (up to 35 and 29 ng L^{-1} for BP-3 and 4-MBC, respectively). The compounds were not detected (<2 ng L^{-1}) in Jörisee, a remote mountain lake. The data on the occurrence of UV filters in surface water were supported by data from SPMDs exposed in these lakes. SPMD-derived water concentrations were highest for 4-MBC in Hüttnersee (28 and 40 ng L^{-1}; assuming a sampling volume of 70 L for a 3-week exposure period). The combined concentrations of UV filters in the different lakes in summer 2002 increased in an order Jörisee < Greifensee < Zürichsee < Hüttnersee. This order is different from the order observed for methyl triclosan (Jörisee ~ Hüttnersee < Zürichsee < Greifensee), that was previously used as a chemical marker for WWTP-derived lipophilic contaminants to a lake, and indicates different input pathways of these compounds and thus some importance of *direct inputs* of UV filters during summer.

The input of 4-MBC, the most predominant UV filter in the lakes, was estimated for the situation of Zürichsee, taking earlier estimates from a survey for the *direct inputs*, and the WWTP effluent loads determined in this study for the *indirect inputs* into consideration. The concentrations calculated in this way (steady-state concentration, 40 ng L^{-1}; summer peak concentration, 190 ng L^{-1}) were considerably higher than those actually measured (2-22 ng L^{-1}), suggesting that inputs are overestimated, and/or that elimination processes other than flushing (e. g. photolysis) are effective in the lake. However, the exact nature of these potential removal processes were not yet investigated.

The presence of UV filters in SPMDs, exposed in these lakes and rivers, suggests some potential for bioaccumulation of these compounds in biota. Fish (white fish *Coregonus sp.*, roach *Rutilus rutilu*s, and/or perch *Perca fluviatilis*) from the same lakes (Zürichsee, Greifensee, and Hüttnersee) and from Pfäffikersee and a pre-alpine lake (Thunersee) contained low but detectable concentrations of some UV filters, in particular 4-MBC (up to ~170 ng g^{-1} on a lipid basis). BP-3 concentrations were similar (up to ~120 ng g^{-1}, lipid based), EHMC and OC were only detected in some of the fish (maximal 72 and 25 ng g^{-1}, lipid based, respectively). 4-MBC concentrations were lower than expected from the SPMD data, suggesting less bioaccumulation and/or metabolism of 4-MBC in fish. Again, methyl triclosan was used as a chemical marker for the exposure of fish to lipophilic contaminants from WWTPs.

Zusammenfassung

Organische UV-Filter-Substanzen werden in zunehmenden Masse in verschiedenen Produkten des täglichen Bedarfs eingesetzt; so zum Beispiel in Sonnenschutzmitteln, Kosmetika wie Tagescrèmen, Bodylotions, Lippenstiften, Haarsprays und -farben, Schampoos, etc. Die Substanzen können durch Duschen und Waschen über die Abwasserreinigungsanlagen (ARAs) als *„indirekte Einträge“* oder aber, durch Freizeitaktivitäten wie Schwimmen und Baden in Seen und Flüssen als *„direkte Einträge“* in die Oberflächengewässer gelangen. In dieser Studie wurde die Bedeutung dieser beiden Eintragspfade sowie das Vorkommen von vier wichtigen organischen UV-Filtern in ARAs, Oberflächengewässern und in Fischen aus verschiedenen Schweizer Seen untersucht. Die untersuchten UV-Filter waren Benzophenon-3 (BP-3), 4-Methylbenzyliden-Campher (4-MBC), Ethylhexylmethoxy-Zimtsäure (EHMC) und Octocrylen (OC).

Alle vier Verbindungen wurden in allen sieben untersuchten ARA-Zuläufen nachgewiesen (maximale Konzentration: 19 µg L^{-1} für EHMC). Die Frachten in den Zuläufen zeigten starke saisonale Schwankungen und waren deutlich höher während der wärmeren (Juni 2002) als während der kälteren Jahreszeit (April 2002), was den höheren Verbrauch von Sonnenschutzmitteln im Sommer widerspiegelt. Die Menge der in die ARAs eingetragenen Substanzen nahm in der Reihenfolge EHMC > 4-MBC ~ BP-3 > OC ab. Zwei frühere Studien über Zusammensetzung und Verwendung von Sonnenschutzmitteln in der Schweiz identifizierten ebenfalls EHMC als meist verwendeten UV-Filter. Wenn die Frachten in ARA-Zuläufen bezüglich angeschlossener Personen normalisiert wurden, ergaben sich Mengen von maximal 16 g pro 10'000 Personen und Tag im April beziehungsweise 240 g pro 10'000 Personen und Tag im Juni 2002 (Summe aller vier gemessenen UV-Filter). Die Daten vom Juni 2002 repräsentieren vermutlich eine „Worst-Case“-Situation, da die Messungen nach besonders sonnigen und warmen Wochenenden durchgeführt wurden. Koffein, welches als hydrophiler chemischer Marker verwendet wurde, zeigte keine solche saisonale Schwankung.

Die UV-Filterkonzentrationen in den ARA-Ausläufen waren deutlich geringer als in den entsprechenden Zuläufen, was auf eine signifikante Elimination der Verbindungen in den ARAs hinweist, wobei die Eliminationsraten im Bereich von 18-82% für 4-MBC, 68->99% für BP-3, 88->99% für OC und 97->99% für EHMC lagen. Im gereinigten Abwässern aus allen sechs untersuchten ARAs trat 4-MBC jeweils in der höchsten Konzentration (bis 2.7 µg L^{-1}) auf, gefolgt von BP-3 und deutlich geringeren Konzentrationen von EHMC und OC. Auf Grund der unterschiedlichen Eliminationsraten der UV-Filter, war also das Verteilungsmuster in gereinigten Abwässern deutlich anders als in ungereinigten. Die normalisierte Frachten in den ARA-Ausläufen (Summe aller vier UV-Filter) lagen bei 19 g pro 10'000 Personen und Tag im April beziehungsweise bei 29 g pro 10'000 Personen und Tag im Juni 2002. Messungen der UV-Filterkonzentrationen im gereinigten Abwasser an zwei aufeinanderfolgenden Tagen zeigten, dass die Eliminationsraten der Verbindungen in Abhängigkeit der Betriebs-

bedingungen wie Wasserdurchsatz (Regenereignisse) und Aufenthaltszeit stark schwanken können. Messungen mit Hilfe von semipermeablen Membranen (SPMDs), welche im Auslauf der ARA Werdhölzli, Zürich exponiert wurden, stützten die Messungen von UV-Filtern in den andern Kläranlagenausläufen.

In Seen, welche Einträge von ARAs (*indirekte Einträge*) und/oder durch Freizeitaktivitäten (*direkte Einträge*) erhalten, wurden UV-Filter im tiefen ng L^{-1}-Bereich gemessen (<2-35 ng L^{-1}). Im Hüttnersee, einem kleinen Badesee ohne Kläranlageneinträge, waren die Konzentrationen am höchsten (bis zu 35 ng L^{-1} BP-3 und 29 ng L^{-1} 4-MBC). Im Jörisee, einem abgelegenen Bergsee, wurden die Verbindungen dagegen nicht oder nur in sehr geringen Konzentrationen gemessen (<2 ng L^{-1}). Diese gemessenen Konzentrationen wurden gestützt durch Daten von SPMDs, exponiert in den selben Seen. Die daraus abgeschätzten Konzentrationen waren am höchsten für 4-MBC im Hüttnersee und betrugen 28 bzw. 40 ng L^{-1} (unter Annahme eines beprobten Wasservolumens von rund 70 L während der dreiwöchigen Exposition). Die Konzentrationen der UV-Filter nahmen in der Reihenfolge Jörisee < Greifensee < Zürichsee < Hüttnersee zu. Diese Reihenfolge unterscheidet sich von derjenigen von Methyltriclosan, das als chemischer Marker für die Belastung eines Gewässers mit häuslichen Abwässern verwendet wurde. Dies deutet auf unterschiedliche Eintragspfade von UV-Filtern und Methyltriclosan hin und damit auf die Wichtigkeit von direkten Einträgen von UV-Filtern im Sommer.

Für den Zürichsee wurde der Eintrag von 4-MBC, dem häufigsten UV-Filter in Oberflächengewässern, abgeschätzt. Dazu wurden Daten aus einer früheren Untersuchung zu den *direkten Einträgen* übernommen und die *indirekten Einträge* aus den Messungen in Kläranlagenausläufen hochgerechnet. Daraus berechnete Steady-state-Konzentrationen lagen bei 40 ng L^{-1}, Spitzenkonzentrationen im Sommer bei 190 ng L^{-1} und waren damit deutlich höher als die gemessenen Werte von 2-22 ng L^{-1}. Dies deutet darauf hin, dass die Einträge deutlich überschätzt wurden, und/oder dass 4-MBC abgesehen vom Wasseraustausch (Flushing) auch durch andere Prozesse (z.B. Photolyse) aus Oberflächengewässern eliminiert wird. Welche Eliminationsprozesse dabei von Bedeutung sein könnten, wurde in dieser Studie nicht weiter untersucht.

Das Auftreten der UV-Filter in SPMDs weist auf ein gewisses Bioakkumulationspotential der Verbindungen hin. In Fischen aus den untersuchten Seen (Rotaugen, *Rutilus rutilus* und Egli, *Perca fluviatilis* aus Zürich-, Greifen- und Hüttnersee, sowie Felchen *Coregonus sp.* aus dem Pfäffikersee und dem voralpinen Thunersee) wurden UV-Filter in geringen, aber detektierbaren Konzentrationen nachgewiesen, insbesondere 4-MBC erreichte eine maximale Konzentration von ~170 ng g^{-1} Fischfett. Die Konzentrationen von BP-3 waren ähnlich (maximal ~120 ng g^{-1} Fett), EHMC und OC wurden nur in einzelnen Fischen nachgewiesen (maximal 70 bzw. 30 ng g^{-1} Fett). Die gefundenen 4-MBC Konzentrationen sind tiefer als auf Grund der SPMD-Daten erwartet wurde, was auf eine geringere Bioakkumulation und/oder eine Metabolisierung von 4-MBC in Fischen hindeutet. Wiederum wurde Methyltriclosan als Marker für die Belastung von Fischen mit lipophilen Verbindungen aus häuslichen Abwässern verwendet.

1 Introduction

There is an increasing public interest in pharmaceuticals and ingredients from personal care products (PPCPs), because they may enter the aquatic environment, and reach detectable and potentially harmful concentrations. As such, organic UV filters have come into focus because (i) these compounds are contained and increasingly used not only in sunscreen products but also in many products of daily use, such as cosmetics, skin creams and body lotions, hair sprays, hair dyes, and shampoos, etc. (*1,2*), and (ii) the compounds most often encountered in products are lipophilic and therefore have a potential for bioaccumulation. There is also some concern about UV filters because at least one of the compounds (4-MBC) showed estrogenic activity (*3*). Nevertheless, data on the occurrence of such compounds in the environment and in biota is scarce.

Although life cannot be thought without sunlight, there is growing concern about skin damage by long exposure to the sun‘s ultraviolet rays because it causes premature ageing of skin and leads to skin cancer (*4*). A recent survey indicated that sunscreen products were the first line defense against sun exposure even before clothing and shielding oneself from the sun (*5*). UV filters in sunscreen products and cosmetics protect skin from damage through UV irradiation. There are two basic types of UV filters, inorganic and organic. The inorganic ones (TiO_2, ZnO) work primarily by reflecting, scattering and absorbing UV light, and the organic ones work by absorbing UV light. Generally, both types of UV filters give good protection against UVB (280-315-nm) irradiation, and some offer also protection against UVA (315-400-nm) light, which can penetrate deeper into the skin and which, after longer exposure, can do greater harm. There is an increasing use of sunscreen products, and there is a trend to products with increasing sun protection factor (SPFs). Generally, higher SPFs means higher concentrations of UV filter in the sunscreen products. Often two or more compounds are used to cover the whole range of wavelengths.

There are currently 22 UV filters registered in Switzerland for use in sunscreens although not all of them are equally commercially important. In this study, we investigated the occurrence and behavior of benzophenone-3 (BP-3), 4-methylbenzylidene camphor (4-MBC), ethylhexyl methoxy cinnamate (EHMC), and octocrylene (OC). The chemical names, structures and abbreviations are given in **Table 1** and shown in **Figure 1**. The criteria for this selection were i) frequency of UV filters in products on the market in Switzerland (*6,7*) and ii) the availability of a routine trace analytical procedure such as GC-MS. The important UVA filter butyl methoxy dibenzoylmethane (BM-DBM) was not included in the study because a routine trace-level analytical method was not available (this compound requires derivatization for its detection in the low ng L^{-1} or ng g^{-1} range).

Table 1: *Names, abbreviations and log K_{ow} values of UV filters investigated.*

Abbr.	INCI name [1]	Chemical name	CAS-Nr	log K_{ow}	(source)
BP-3	Benzophenone-3	2-hydroxy-4-methoxy-benzophenone	131-57-7	3.8 3.8	(SRC[2]) (Roche[3])
4-MBC	4-Methylbenzylidene Camphor	3-(4'-methyl-benzylidene)bornan-2-one	36861-47-9	5.9 5.1	(SRC[2]) (Roche, Merck[3])
EHMC	Ethylhexyl Methoxy-Cinnamate [4]	3-(4-methoxyphenyl)-2-propenoic acid 2-ethylhexyl ester	5466-77-3	5.8 6.0-6.3	(SRC[2]) (Roche[3])
OC	Octocrylene	2-ethylhexyl-2-cyano-3,3-diphenylacrylate	6197-30-4	6.9 6.9	(SRC[2]) (Roche, Merck[3])

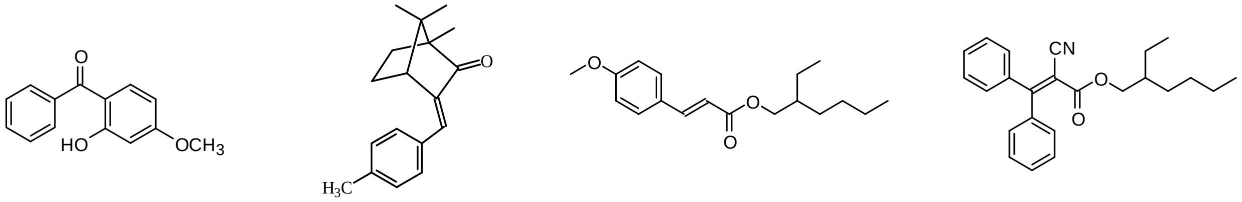
[1] INCI: International Nomenclature of Cosmetic Ingedients

[2] Values calculated with estimation program for log K_{ow} of Syracuse Research Corporation (SRC). Demo program available: http://esc.syrres.com/interkow/kowdemo.htm

[3] Data from Roche (2001) and Merck (2000) safety datasheet, adopted from summary in ref (*8*).

[4] Formerly: Octyl Methoxy-Cinnamate, OMC

All four UV filters are aromatic compounds with further unsaturations in the side-chain. They are colorless or yellow substances with no or little adsorption of visible light but significant UV absorption. The compounds are lipophilic with octanol/water partition coefficients (log K_{OW}) in the range of 3.8 to 7 (see Table 1). Two of the compounds, 4-MBC and EHMC, consist of geometrical (*Z*)- and (*E*)-isomers whereby the commercial products mainly (>99%) consist of the (*E*)-isomers. Upon sunlight exposure, rapid photochemical *E-Z* isomerization occurs, either during use on skin or after release into the environment, and an equilibrium state is attained within minutes (*7,9,10*). The photoequilibration ratios may differ for compound and matrix (solvent).



BP-3 4-MBC EHMC OC

Figure 1: *Structures and abbreviations of the four UV filters investigated (E-isomers shown).*

4-MBC, EHMC and OC are chiral. The enantiomers of these compounds (both, (*E*)- and (*Z*)-isomers in the case of 4-MBC and EHMC) are not expected to show different physico-chemical properties such as UV absorption, and thus not to possess different sunlight protection properties. However, the isomers and enantiomers may differ in biological behavior such as in WWTPs and in surface water. In future, enantioselective analyses of these UV filters may in fact be a means to distinguish between enantioselective biotic and non-enantioselective abiotic degradation pathways.

The amount of UV filters applied to ones skin can be substantial. Assuming a use of 10 g of suncream for a “full body application” (corresponding to about 1 mg per cm^2 skin surface, which is half of the amount generally used for SPF testing (*11*), but seems to be more realistic (*12*)), and an average composition of 5-20% UV filter in a sunscreen product, this amounts to 0.5 to 2 g UV filter compounds per application. All, or at least a significant part, of the applied UV filters eventually enters the aquatic environment through wash- and rub-off. In fact, all investigated UV-filters were previously found in Swiss lakes (*7,13*); EHMC was also detected in wastewater and rivers in England (*14*) and in the river Rhine below Basel (*15*). EHMC, 4-MBC and BP-3 were detected in fish from a German swimming lake (*16*), and EHMC and BP-3 were also detected in human breast milk (*17*). Nevertheless, at the present there is little information on the environmental occurrence, behavior, and fate of these compounds.

There are two principal pathways of UV filter into the aquatic environment discussed in the study: (i) *direct input* from recreational activities such as bathing, swimming with washoff from skin into surface water, and (ii) *indirect inputs* via WWTPs from showering, wash and rub off, and possibly excretion after percutane uptake. The actual use of sunscreens and hence the relative importance of UV filters (compound pattern) may vary with preferences of a regional population and with weather and season.

In this study, initiated by the Swiss Federal Agency for Environment, Forests and Landscape, BUWAL, Berne, we investigated and quantified entry pathways of four major UV filters into the aquatic environment, in particular for the situation of Zürichsee, an important drinking water resource and a lake used for recreational activities. We investigated the occurrence of the compounds in surface water and in samples from wastewater treatment plants (WWTPs). The compounds discharged to WWTPs reflect the consumer habits and thus may offer qualitative and quantitative information on the use of UV filters. WWTP effluents represent one of the principal input pathways of domestic contaminant into the aquatic environment. In this part of the study, caffeine is used as a chemical marker.

In our previous study, the presence of UV filters in SPMDs exposed in surface water suggested some potential for bioaccumulation of these substances (*7*). The occurrence of UV filters in biota, particularly in fish, is of interest for several reasons: i) possible bioconcentration or biomagnification within the food chain (*18*); ii) possible adverse effects on aquatic organisms (e.g. endocrine disrupting activity of 4-MBC (*3*)); and iii) from a food safety aspect (residue situation). In this study, we also evaluated the occurrence of these compounds in fish and in semi-permeable membrane devices (SPMDs) from several Swiss lakes. Methyl triclosan was used as a chemical marker for lipophilic contaminants derived from WWTPs.

2 Selection of Study Sites and Sampling

2.1 Selection and Description of Lakes and Rivers

The lakes selected for the study were Zürichsee, Greifensee, Pfäffikersee, Hüttnersee, Thunersee and, for background measurements, the remote mountain lake, Jörisee (**Table 2, Figure 2** and text below). The lakes were selected to cover inputs from i) waste water treatment plants (WWTPs) and/or ii) recreational activities (swimming/bathing). All lakes, except the mountain lake, are stratified during the warmer season (April - December) with development of an epilimnion and a hypolimnion. In winter (January – March), the lakes are mixed to considerable depth. Surface water was analyzed from Zürichsee, Greifensee, Hüttnersee, and Jörisee, fish from Zürichsee, Greifensee, Pfäffikersee, Hüttnersee and Thunersee, and SPMDs were exposed in Zürichsee, Greifensee, Hüttnersee, and Jörisee, and additionally in the river Limmat, the outflow of Zürichsee.

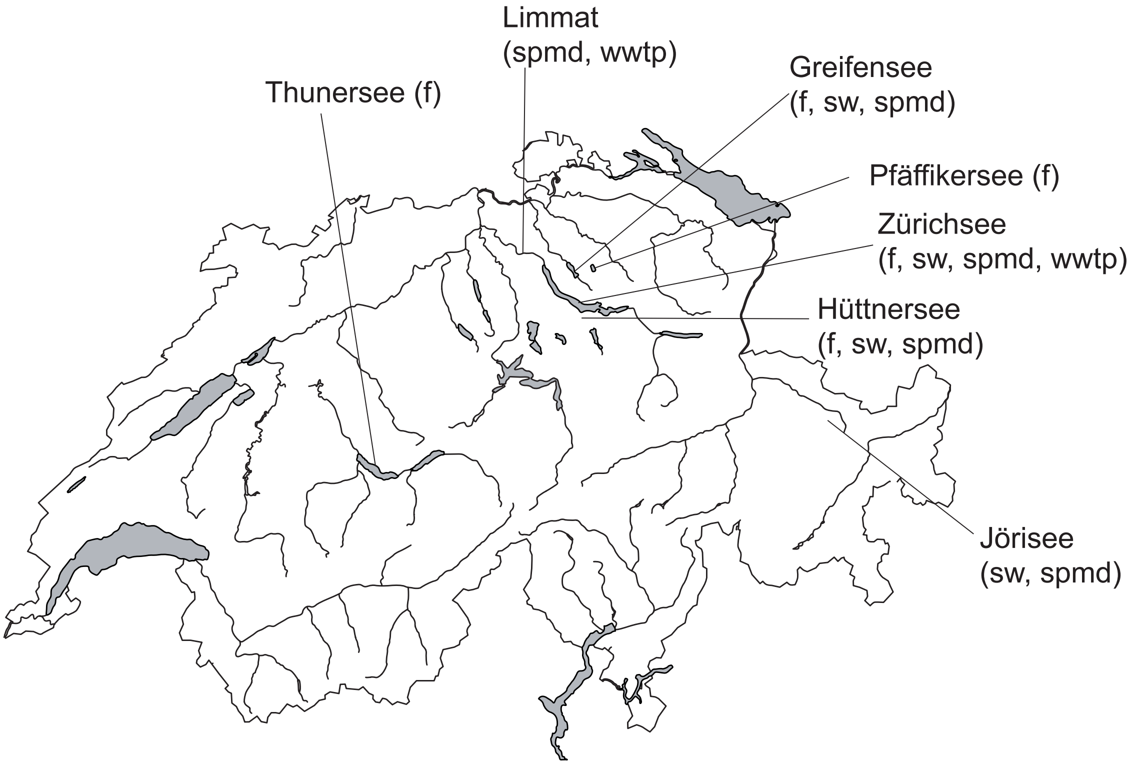


***Figure 2**: Lakes and rivers sampled and types of samples analyzed from the respective sites (f: fish, sw: surface water, spmd: semipermeable membrane devices, wwtp: waste water treatment plant).*

Zürichsee was chosen as the main study site because significant direct and indirect inputs of UV filters are expected. Approximately 330’000 people (P, persons) live in its catchment area and the lake thus receives considerable inputs of anthropogenic compounds. It is the drinking water resource for about 1’000’000 people, and also an important recreational area for a large number of people with, e.g., over 70 public swimming beach sites. Despite the considerable anthropogenic inputs from WWTPs, the lake exhibits good water quality due to the rapid water throughflow (Q, m^3 d^{-1}). The lake represents a typical situation with respect to WWTP-derived contamination level, which can be expressed as the ratio P/Q (0.043 persons m^{-3} d).

Greifensee is situated 10 km east of Zürich and, like Zürichsee, has also considerable recreational activities with several swimming areas. There is a population of 100’000 persons living in its catchment area, and therefore direct and indirect inputs of UV filters are expected. The sizeable population, and the relatively low water throughflow lead to one of the highest P/Q ratios of all larger lakes in Switzerland (P/Q ratio, 0.303 persons m^{-3} d).

Pfäffikersee is a small lake located 20 km north-east of Zürichsee, close to Greifensee with some recreational activities. Its P/Q ratio is 0.173 persons m^{-3} d, and direct and indirect inputs of UV filters are expected.

Thunersee is a pre-alpine lake, situated at 558 m above sea level (asl). Although there is a sizeable population living in its catchment area (94’300), the very large water throughflow leads to generally good water quality (P/Q ratio, 0.010 persons m^{-3} d). The relatively high mean altitude of its catchment area (1790 m), accounts for generally low water temperatures, and hence expectedly, lower direct inputs of UV filters from recreational activities.

Hüttnersee, situated at 658 m asl near Zürichsee, is a small lake with a short water residence time of ~120 d. There is no WWTP located in its catchment area and therefore no indirect inputs of UV filters are expected. However, there is public access to the lake and during summer there are recreational activities. The number of bathers relative to the lake volume and water throughflow is high, so that this lake may represent a worst-case situation with respect to possible contamination with UV filters from direct inputs.

Jörisee (Canton of Graubünden) is a small mountain lake located at an altitude of 2450 m, remote from human activities, receiving inputs only from rain, snow, ice, and dry deposition. It was sampled for background measurements. There are no recreational activities at the lake and no inputs of UV filters are expected.

The river **Limmat** has its source at the outflow of Zürichsee. The river was sampled at its source, and at a Dietikon, approximately 15 km downstream its source, 6.5 km downstream of the WWTP Zürich (370’000 persons serviced). The river Sihl (~30’000 persons in its catchment area) meets the river Limmat about 2 km downstream of its source, there is thus some contribution from the river Sihl at the site in Dietikon (see also **Figure 4**)

Table 2: *Hydraulic parameters and population in the catchment area of the lakes studied.*

Lake	altitude asl [m]	volume V [m^3]	max depth [m]	water residence time τ [c] [d]	water throughflow Q [m^{3}s^{-1}]	flushing rate constant k_w [d] [d^{-1}]	population P [persons]	P/Q [persons m^{-3}d]	samples analyzed [f]
Zürichsee, (lower basin)	406	3.4x10^{9} [b]	136 [b]	440	89 [b]	0.0023	330’000 [a]	0.043	f, sw, spmd
Greifensee	435	1.5x10^{8} [b]	32 [b]	420	4.1 [b]	0.0024	107'000 [e]	0.303	f, sw, spmd
Pfäffikersee	537	5.7x10^{7} [b]	35 [b]	770	0.9 [b]	0.0010	12’900 [e]	0.173	f
Thunersee	558	6.4x10^{9} [a]	217 [a]	690	110 [a]	0.0014	94’300 [a]	0.010	f
Hüttnersee	658	1.1x10^{6} [b]	13 [b]	120	0.1 [b]	0.0083	0	0.000	f, sw, spmd
Jörisee [g]	2450						0	0.000	sw, spmd

Data from [a] (*19*), [b] (*20*), [e] Office for Waste, Water, Energy, and Air, Canton of Zürich, Switzerland (AWEL).

[c] Calculated: τ=V/Q; [d] inverse of water residence time τ.

[f] Samples analyzed from the respective lake: f = fish, sw = surface water, spmd = semi permeable membrane devices.

[g] No hydraulic parameters are available about Jörisee.

Surface water samples were taken in July/August 2002 from Greifensee, Zürichsee, Hüttnersee and, for background measurements, from Jörisee. Samples were generally taken at 1 to 2.5 m depth. From Zürichsee, additional samples from the hypolimnion (20 m depth) were analyzed. Samples from Zürichsee and Greifensee were taken above the deepest point using a 10-L Niskin bottle; samples from Hüttnersee and Jörisee were grab samples taken by boat in the middle of the lake and from the shore, respectively. All water samples were filled on-site into methanol-rinsed, 1-L glass bottles, protected from light and refrigerated at 4°C upon arrival at the laboratory.

2.2 Selection and Sampling of WWTPs

Wastewater samples were obtained from 6 municipal wastewater treatment plants (WWTPs) located in the region of Zürich (see **Figure 3** and **Table 3**), discharging treated effluent into Zürichsee. These installations serve populations of about 10’000 to 25’000 persons and are modern, 3- or 4-stage installations that include mechanical, biological, and chemical treatment, and in most cases subsequent sand filtration. Influent samples from these WWTPs were taken after the primary sedimentation basins, and treated effluent samples were taken after sand filtration. All samples were flow-proportionally collected during 24 hours.

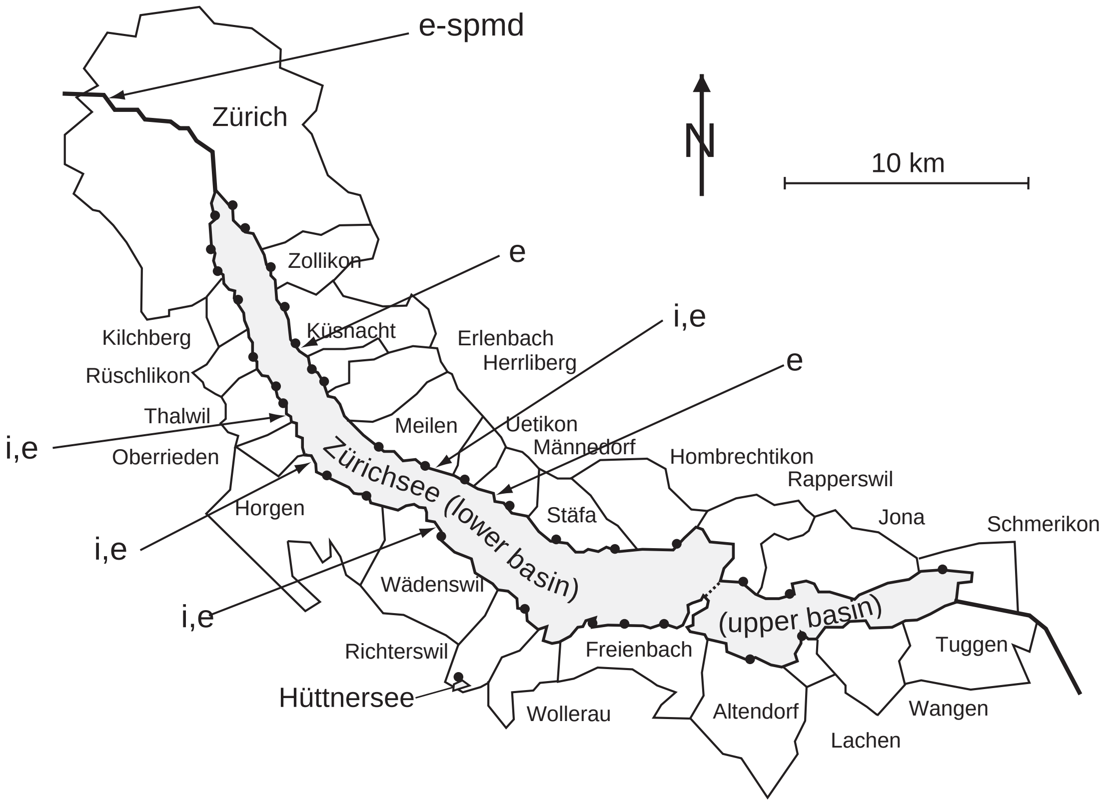


Figure 3: *Zürichsee and Hüttnersee with public swimming areas (circles) and WWTPs sampled, indicated by arrows (i: influent, e: effluent of WWTP sampled; e-spmd: SPMD exposed in effluent).*

Wastewater samples analyzed were from two sampling campaigns carried out in April and June, 2002, respectively (**Table 3**). In April 2002, samples were taken during a longer period of cool weather with maximum air temperatures of 17°C and expectedly little outdoor activities and use of sunscreen products. In contrast, the samples in June 2002 were taken during a warm and sunny period with afternoon temperatures up to 31°C and more outdoor activities and thus presumably higher use of sunscreen products. The first sampling campaign thus reflects a more usual situation, and the latter likely represents a situation with high usage of sunscreens and hence rather a "worst-case" situation for inputs to WWTP. In addition, the effluent of a further WWTP (Werdhölzli, Zürich) was sampled using SPMDs in April/May and in August/September 2002, respectively (**Table 3**).

Table 3: *Overview WWTP sampling.*

WWTP	population serviced [persons]	sampling date	water throughput [m^3d^{-1}]	samples analyzed[a]
Horgen	20'560	Apr 15, 2002, Monday	11'900	i, e
Meilen	22'000	Apr 15, 2002, Monday	10'318	i, e
		Jun 24, 2002, Monday	12'000	i, e
Thalwil	19'548	Jun 24, 2002, Monday	17'229	i, e
Wädenswil	19'000	Jun 24,2002, Monday	15'122	i, e
Küsnacht	16'475	Apr 23, 2002, Tuesday	6'574	e
		Apr 24, 2002, Wednesday	30'105	e
Männedorf	9'044	Apr 23, 2002, Tuesday	4'340	e
		Apr 24, 2002, Wednesday	14'243	e
Zürich, Werdhölzli	370'000	Apr 30 - May 21, 2002	242'000	e(spmd)
		Aug 14 - Sep 4, 2002	207'000	e(spmd)

[a] Samples analyzed: i = influent, e = effluent, e(spmd) = SPMD sampling of effluent

2.3 Selection and Sampling of Fish

Fish from Zürichsee, Greifensee, Pfäffikersee, Thunersee, and Hüttnersee were analyzed. The selection of fish species (white fish, roach or perch) varied with the lakes, as a consequence of their availability. White fish (*Coregonus sp.*, German name: Felchen) is a very common plankton feeding fish and was analyzed from Pfäffikersee and Thunersee. Roach (*Rutilus rutilus*, German name: Rotauge, local name: Schwalen) is a common fish in most lakes, it is a plankton and bottom feeding species. Roach was analyzed from Zürichsee, Greifensee, and Hüttnersee. Perch (*Perca fluviatilis*, German names: Barsch, Egli) is a partly predatory species, commonly present in all lakes, but subject to strong natural population fluctuations, and therefore sometimes of limited availability. Perch was only analyzed from Hüttnersee. No fish was available for background measurements from the remote mountain lake, Jörisee, and fish from the relatively clean pre-alpine Thunersee was used for that purpose.

All fish were obtained from local fishermen who were instructed to wear gloves and to handle the fish with great care to prevent contamination. The fish were separated from the remaining catch and immediately packed into clean polyethylene bags on boat. Within one day, each specimen was seized, weighed, wrapped in aluminium foil, packed in heat sealed polyethylene bags, labeled and stored at –20°C. Further details of the fish specimens analyzed (species, location, date of catch, weight, fat content) are given in Table 14 (paragraph 4.7).

2.4 SPMD Sampling

Semipermeable membrane devices (SPMDs) are passive samplers, consisting of thin layflat polyethylene tubes, containing triolein. SPMDs are used to measure time-weighted average water concentrations of dissolved lipophilic compounds (log $K_{OW} > 3$) (*21*). The mechanism of uptake by the SPMD mimics accumulation through membranes into the lipids of organisms such as fish. Thus, the compounds accumulated by SPMDs may also be accumulated in organisms.

SPMDs were exposed for ~3 weeks in Zürichsee (outflow), Greifensee (outflow), Hüttnersee (middle of the lake), the river Limmat, and, for background measurements, in the remote mountain lake, Jörisee (~6-week exposure, near the shore). SPMDs were deployed in lakes at a depth of about 1 m. In Zürichsee and in the river Limmat, the SPMDs were exposed in April/May 2002 to study a spring situation with expectedly lower loads of UV filters, and in August/September 2002 to study a summer situation with higher loads (peak bathing season). In Greifensee and Hüttnersee, SPMDs were exposed in July/August 2002 to measure summer situations only. During the summer campaign, most exposures were done in duplicate (2 SPMDs per site, see **Table 4**). In Jörisee, two SPMDs were deployed during summer (July/September 2002). Two SPMD were kept as a storage blank and analyzed for control purposes.

Table 4: *SPMD Exposures in lakes, river Limmat, and WWTP effluent (2002).*

location	date of exposure	duration [d]	No of SPMDs	average water temperature [°C]
Zürichsee (outflow at Zürich)	Apr 30 – May 21	21	1	12
	Aug 14 – Sep 04	21	2	21
Limmat (at Dietikon, 6 km below outflow of WWTP)	Apr 30 – May 21	21	1	12
	Aug 15 – Sep 04	20	1	21
WWTP Werdhölzli Zürich, effluent	Apr 30 – May 21	21	1	16
	Aug 14 – Sep 04	21	1	21
Greifensee (outflow)	Jul 17 – Aug 07	21	2	22
Hüttnersee (mid lake)	Jul 08 – Jul 26	18	2	21
Jörisee (near shore)	Jul 30 – Sep 09	41	2	10

In the river Limmat, the SPMDs were exposed at the same time at the outflow of Zürichsee, and at Dietikon, upstream and downstream the WWTP Zürich (Werdhölzli). Comparison of the concentrations in these SPMDs would then reflect inputs from WWTP Werdhölzli. In addition, SPMDs were also exposed directly in the WWTP effluent (**Figure 4**)

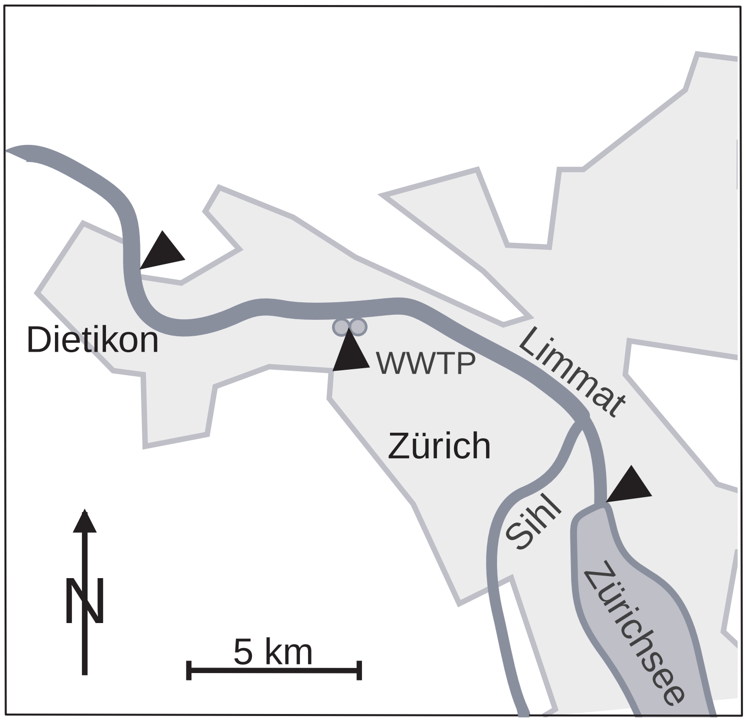


Figure 4: *SPMDs were exposed concurrently in the outflow of Zürichsee (river Limmat), in the effluent of WWTP Werdhölzli, Zürich and in the river Limmat at Dietikon, about 6.5 km below the WWTP in spring and summer 2002. Sampling sites are indicated by arrows.*

The sampling efficiency of SPMDs for a particular compound depends on its physico-chemical properties, and is controlled by the sampler design and environmental variables such as temperature and hydrodynamics of the water body. In this study, it was assumed that integrative sampling was terminated before most analytes reached equilibrium concentration in the membrane and that uptake was linear with time (see refs (*22-24*)). Thus, the concentration of a compound in the SPMD (C_{SPMD}, ng $SPMD^{-1}$) is a function of its average dissolved concentration in water (C_{water}, ng L^{-1}), the sampling rate (R_S, L d^{-1} $SPMD^{-1}$), and the time of exposure (t, d) according to equation 1 (adapted from refs (*21,24*)):

$$C_{SPMD} = C_{water} \times R_S \times t \qquad (1)$$

whereby the sampling rate R_S itself is a function of parameters such as temperature, phase transfer (kinetics), etc. Reported sampling rates for lipophilic compounds other than the UV filters are in the range of 2-9 L d^{-1} $SPMD^{-1}$ (*22,23*). According to refs (*21,23,25*), biofouling may reduce the sampling rate (10% by moderate biofouling, up to 50% by heavy biofouling). The sampling rate is generally increasing with the octanol/water partition coefficient K_{OW}.

Expectedly it is thus higher for 4-MBC, EHMC and OC (log $K_{OW} > 5$), and somewhat lower for BP-3 (log $K_{OW} = 3.8$) (*22,23*). The sampling rate for BP-3 may also be lower because of the partial dissociation of the compound at the pH of the lake. However, for this study, we assumed relatively low sampling rates of 3-4 L d^{-1}, because in most lakes some biofouling was observed, and the sampling rate was assumed to be the same for all four UV filters and for methyl triclosan, the lipophilic marker used with these samples. The volumes sampled by the SPMDs during the 18 to 21-day exposures in Zürichsee, Greifensee, Hüttnersee and the river Limmat were thus assumed to be ~70 L, and ~100 L for the 41-day exposure in Jörisee (longer exposure and less biofouling, but lower water temperature). The fraction sorbed onto particulate organic carbon f_{POC} in lake water is estimated to be negligible for BP-3 and 4-MBC (~0.1% and ~2%, respectively), about 20% for EHMC and may be considerable (~60%) for OC (estimates based on a POC (particulate organic carbon) of 0.5 mg L^{-1}, a typical concentration in the epilimnion of Zürichsee during summer; f_{POC} calculated according to ref (*26*) and as described in ref (*7*).)

3 Experimental

3.1 Chemicals, Reagents, and Reference Compounds Used in the Study

The sources and purities of the compounds were as follows: ethylhexyl methoxy-cinnamate (EHMC; EUSOLEX 2292, purity, >99.5%); 4-methylbenzylidene camphor (4-MBC; EUSOLEX 6300, > 99.5%); Benzophenone-3 (BP3; EUSOLEX 4360, > 99%); octocrylene (OC; EUSOLEX OCR, ≥98%); courtesy of Merck, Darmstadt, Germany (for chemical names see **Table 1**). Different ^{13}C-labelled compounds were used as internal standards: $^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl (PCB#77), $^{13}C_3$-caffeine, and $^{13}C_6$-metolachlor, all from Cambridge Isotope Laboratories, Cambridge, MA.

The chemicals, reagents and solvents were: anhydrous Na_2SO_4, p.a. from Merck, Darmstadt, Germany, heated for 14 hours at 540°C; dichloromethane and cyclohexane, "ultra residue analyzed", J.T. Baker, from Stehelin, Basel; silicagel, 230-400 mesh "for column chromatography" from Merck, dried at 140°C for 14 h, then deactivated with 5% water; n-hexane, "for gas chromatography", Merck; ethyl acetate and cyclopentane, "for residue analysis" from Fluka, Buchs Switzerland.

Precautions were taken to prevent contamination from personnel, equipment and glass ware. Prior to use all glassware were cleaned twice with the solvent used in the different procedures, and gloves were worn throughout all steps of sample processing. Procedural blanks were routinely done.

3.2 Solid-Phase Extraction and Cleanup of Surface Water and WWTP Samples

Extraction of UV filters from wastewater and surface water samples was effected by solid-phase extraction (SPE) using reusable glass columns containing approximately 10 mL of a macroporous polystyrene absorbent (Bio-Beads SM-2, 20-50 mesh, Bio-Rad Laboratories, Hercules, CA). Prior to use, the columns were washed with dichloromethane, methanol, and water (fossil groundwater, Aqui, Zürich). In order to prevent cross contamination, separate columns were used for WWTP samples (influent and effluent) and surface water.

WWTP influent samples were centrifuged at 10'000 rpm during 20-30 min using a Sorvall Instruments RC5C ultracentrifuge (Kendro Laboratory Products AG, Zürich) prior to extraction; WWTP effluent and surface water samples were extracted directly. For this purpose, volumes of 200 mL (WWTP samples) and 1 L (surface water) were fortified with 130 ng (effluent) or 1300 ng (influent) of $^{13}C_3$-caffeine or 50 ng of $^{13}C_6$-metolachlor as internal standard, respectively, and passed through the SPE columns at about 10 mL/min. The analytes were recovered from the SPE absorbent with 5 mL methanol and then with 10 mL dichloromethane. The combined extracts were vigorously shaken, and the phases were allowed to separate. The dichloromethane phase was transferred into a glass vial. Two additional portions of dichloromethane (10 mL for WWTP samples, 5 mL for surface water) were passed through the column and partitioned with the aqueous/methanolic phase. The combined dichloromethane extracts were reduced in volume (~0.5 mL) with a gentle stream of air at room temperature.

The silica gel cleanup was carried out using Pasteur pipettes with a glass wool plug, filled with 700-800 mg silica gel and topped with 10 mm of Na_2SO_4. After a pre-wash with 5 mL of eluent, the concentrated sample extracts were applied and the analytes eluted with 10 mL of ethyl acetate/methanol 95:5 (WWTP samples) or ethyl acetate (surface water samples) into a 20-mL vial. The eluates were then carefully concentrated with a gentle nitrogen stream. After transferring the samples into 2-mL vials using ethyl acetate and re-concentration to 100-1000 µL, aliquots of 1-2 µL were used for GC-MS analysis. Fossil ground water was processed as procedural blank and fortified at concentrations of 20, 50, and 100 ng L^{-1} of each UV filter for the determination of recoveries.

3.3 SPMD Analysis

The membranes used were standard SPMDs from Exposmeter AB (Tavelsjö, Sweden) consisting of thin layflat tubes made from semipermeable polyethylene membranes (90 cm x 2.5 cm), containing 1.0 mL triolein. The membranes were mounted in a spread configuration on fixtures in perforated stainless steel containers for exposure in surface waters or WWTP effluents.

After exposure, the membranes were carefully cleaned with a small nylon tooth brush and fossil groundwater, air dried at room temperature and stored in airtight cans at –20 °C until dialyzed. The membranes were dialyzed three times with 50 mL of cyclopentane/dichloromethane 95:5 for at least 8 hours each time; 8 ng of $^{13}C_{12}$-PCB#77 were added to the first portion of extractant as internal standard. The combined dialyzates were reduced in volume at room temperature, and the residues were re-dissolved in 2.0 mL cyclohexane/dichloromethane 65:35, of which 1 mL was further processed by GPC (see below). For quality control, two non-exposed SPMD membranes were dialyzed as a procedural blank, and dialyzates from further non-exposed SPMDs were fortified with 50, 100, and 200 ng of each UV-filter for recovery determinations. Blank and recovery samples were processed in the same way as the exposed SPMDs.

3.4 Extraction of Fish Samples

Initially, fish were analyzed at the Cantonal Food Inspectorate KAL, St. Gallen (courtesy: C. Droz and K. Romanin) using 5 g of the edible portion of filet. After removal of scales and most of the skin, the filets of a fish were homogenized using a laboratory blender (Büchi, Flawil, Switzerland). 5.0 g of the homogenized fish filets were then mixed with 10 g Hydromatrix (Chem-Tube Hydromatrix, Varian, Steinhausen, Switzerland), a diatomaceous earth, used as extraction enhancer, and the blend was subjected to ASE (accelerated solvent extraction; Dionex, Zurich) with cyclohexane/dichloromethane 1:1 at room temperature and a pressure of 1500 psi, during 9 min (3 cycles; total solvent volume, ~40 mL). The lipid extract was fortified with the internal standard (8 ng of $^{13}C_{12}$-PCB#77), dried with Na_2SO_4, decanted, and reduced in volume over night with a gentle stream of air at room temperature. The dried lipid extract was re-dissolved in 2.0 mL cyclohexane/dichloromethane 65:35. An aliquot of 0.5 mL was transferred to a conical flask and reduced to constant weight for determination of fat content. An aliquot of 1 mL (i.e. half of the extracted fat) was subjected to GPC and silica clean up (see below). For determination of recoveries, samples form a fish were analyzed prior to and after fortification with 200 ng of each UV filter. Procedural blanks were carried out with each series of fish samples. Because the lipid content of the edible portion of some fish was very low (<1%), and because relatively small sample weights (5 g) were processed, only small amounts of fat were isolated for analysis of these fish and, consequently, the detection limits were higher when the concentrations were calculated on a lipid basis.

The analyses were then repeated with some fish using larger sample aliquots (20 g) and the tissue was taken from just under the skin with expectedly more lipids. In these analyses, 20 g of fish tissue was mixed with 50 g Na_2SO_4 in a ceramic mortar. The blend was filled into a glass column (about 3 cm x 35 cm) and the lipids were extracted using a total of 210 mL cyclohexane/dichloromethane (1:1) in 4 portions with a total extraction time of 4 hours. The combined extracts were carefully reduced in volume to 10 mL at room temperature with a gentle stream of air. 1.0 mL of the total extract (i.e. 10%, corresponding to 2.0 g fish filet) was transferred into a vial and reduced to constant weight for determination of fat content. The remaining extract, or an aliquot corresponding to a maximum of 200 mg lipids, was fortified with 8 ng of $^{13}C_{12}$-PCB#77 as internal standard and subjected to GPC and the silica cleanup (see below). These extracts contained considerably more lipid material and the relative contribution of blank contamination was reduced compared to the ASE-procedure. The analysis thus lead to considerably improved detection limits and more reliable results. Similar procedures for extraction of lipids from animal tissues are described in the literature (e.g. refs (*27,28*)).

3.5 GPC and Silica Cleanup of SPMD Extracts and Fish Lipids

Gel permeation chromatography (GPC) of SPMD extracts and fish lipids was carried out using a high performance liquid chromatography pump, operating at a flow rate of 3.0 mL min^{-1} with cyclohexane/dichloromethane 65:35 as mobile phase at the Cantonal Food Inspectorate, St. Gallen, Switzerland (courtesy: C. Droz and K. Romanin). As stationary phase, 20 g Biobeads S-X3 200-400 mesh, a porous styrene divinylbenzene for size exclusion chromatography (BioRad Laboratories, Hercules, CA), packed into a Biocart medium pressure column (1.5 cm i.d.) yielding a final length of 40-41 cm, were used. The time window for collection of the eluate containing the UV filters was determined with appropriate standard solutions, and was from 14.5 to 27 min. The collected fraction (about 37 mL) was carefully reduced in volume to ~1.5 mL over night using a gentle draft of air. The GPC eluates were then further reduced in volume to 200 µL with a gentle stream of nitrogen, and those from the fish samples were subjected to further cleanup on silica gel to remove interfering compounds such as fatty acids, as described for the water samples but using n-hexane/ethyl acetate 9:1 for elution. Finally, the eluates were concentrated to a volume of 50 µL, and an aliquot of 1-2 µL was used for GC-MS analysis.

3.6 GC-MS Analysis of UV Filters

GC-MS analysis was performed on a VG Tribrid magnetic sector mass spectrometer (Mass Lab Group, Manchester, UK) under electron-impact ionization (EI, 55 eV, 200 °C) and full-scan (m/z 35-435) or selected-ion-monitoring (SIM) conditions. The mass spectrometer was operated with a mass resolution $M/\Delta M = 500$. The gas chromatographic separation was carried out using a 25-m BGB-5 fused silica column (0.32 mm i.d.; BGB Analytik Adliswil, Switzerland) and split/splitless injection (SSL) with an injector temperature of 280°C and 60 sec splitless time. The column was temperature programmed as follows: 70°C, 2 min isothermal, 20°C min^{-1} to 160°C, then at 8°C min^{-1} to 280°C, followed by an isothermal hold of 10 min at this temperature to elute high boiling, otherwise interfering compounds such as sterols. Data acquisition was started at 160°C and retention times were measured from this point (**Table 5**). Aliquots of 1-2 µL were injected (total sample volumes, 100-1000 µL for WWTP and surface water samples, 50 µL for the fish and SPMD samples). The (*Z*)- and (*E*)-isomers of 4-MBC and EHMC were resolved by GC (elution of (*Z*)- prior to (*E*)-isomers).

Table 5: *Ions monitored (SIM) and retention times in GC-MS analysis.*

compound	quantification ion (m/z)		confirmation ion (m/z)		retention time [min]	
BP-3	228.08	$M^{+\bullet}$	227.08	$(M-H)^+$	7.5	
4-MBC	254.17	$M^{+\bullet}$	239.14	$(M-CH_3)^+$	7.4 (*Z*)-	7.8 (*E*)-isomer
EHMC	178.06	$(M-C_8H_{16})^{+\bullet}$	290.19	$M^{+\bullet}$	8.9 (*Z*)-	10.4 (*E*)-isomer
OC	249.08	$(M-C_8H_{16})^{+\bullet}$	361.20	$M^{+\bullet}$	13.9	
methyl triclosan	303.97	$M^{+\bullet} + 2$	301.97	$M^{+\bullet}$	8.8	
internal standards [a]						
$^{13}C_{12}$-PCB#77	303.97	$M^{+\bullet} + 2$			9.5	
$^{13}C_6$-metolachlor	244.12	$(M-C_2H_5O)^{+\bullet}$			7.3	
$^{13}C_3$-caffeine	197.09	$M^{+\bullet}$			5.7	

[a] Internal standards: $^{13}C_{12}$-PCB#77 was used for quantification of UV filters in fish and SPMD samples, $^{13}C_6$-metolachlor in surface water samples, $^{13}C_3$-caffeine in wastewater samples.

The ions monitored in SIM are listed in **Table 5**. The amounts of analyte were determined from peak area ratios relative to the internal standard ($^{13}C_{12}$-PCB#77 for SPMDs and fish, $^{13}C_6$-metolachlor for surface water, $^{13}C_3$-caffeine for WWTP samples), and in reference to suitable standard solutions prepared with known amounts (0-200 ng) of the analytes.

Two of the UV filters, EHMC and 4-MBC, undergo *E-Z* (cis-trans) isomerization of the styrene or alkene double bonds under the influence of light (*10*). As with other styrene and stilbene compounds this isomerization, in dilute solution, is rapid and reversible and leads to a mixture of isomers, whereby the *Z/E* ratios differ for compound, UV spectrum of the light source, and possibly for matrix (solvent, co-solutes) (*10,29*). The UV filters EHMC and 4-MBC are produced as pure or practically pure (*E*)-isomers and correspondingly, analysis of freshly prepared standard solutions, yielded only one peak for each of the compounds. However, after light exposure, additional peaks are observed, corresponding to the (*Z*)-isomers of 4-MBC and EHMC. E.g., the *Z*/(*Z*+*E*) ratios in water for 4-MBC were ~0.45 and for EHMC ~0.7. In ethyl acetate, the ratios for 4-MBC were ~0.2 and for EHMC ~0.5. Almost all field samples showed the presence of both isomers, although sometimes in varying ratios. Because light exposure and hence photochemical isomerization also occurred to some extent during sample preparation, cleanup, and analysis, the *Z*/*E* ratios determined in the final extracts are not necessarily indicative for the ratios in the natural samples. Therefore, the concentrations of (*Z*)- and (*E*)-4-MBC, and those of (*Z*)- and (*E*)-EHMC were summed and reported as totals for 4-MBC and EHMC, assuming the same detector response for respective (*E*)- and (*Z*)-isomers.

3.7 Blanks, Recoveries, and Limits of Detection

In **surface water and WWTP samples**, all four UV filters were recovered acceptably, with recoveries in the range of 78-94% relative to the internal standards. The concentrations reported are not corrected for recoveries. The limits of detection (LOD) were 2 ng L^{-1} for surface water, and 10 ng L^{-1} for wastewater. Procedural blanks using fossil ground water repeatedly showed the presence of small amounts of BP-3 (8 ng L^{-1}) and EHMC (6 ng L^{-1}) and the concentrations for these UV filters were corrected accordingly.

In **SPMDs**, recoveries of BP-3, 4-MBC, EHMC and OC were in the range of 40-100%. Data from duplicate exposures showed reasonable agreement (±10-25% at concentrations > 500 ng $SPMD^{-1}$). The SPMD storage blank showed the presence of small amounts of EHMC (~20 ng $SPMD^{-1}$) and the concentrations were corrected accordingly. LODs were 10, 5, 10, and 2 ng $SPMD^{-1}$ for BP-3, 4-MBC, EHMC and OC, respectively.

In **fish**, recoveries of BP-3, 4-MBC, EHMC and OC were in the range of 59-116%, respectively. Data are reported in ng g^{-1} fish filet and as lipid based concentrations in ng g^{-1} lipid. Procedural blanks showed repeatedly the presence of small amounts of UV filters from solvent, apparatus, and/or reagents (EHMC, up to 25 ng per sample, corresponding to 2-3 ng g^{-1} filet). For 5-g fish samples extracted by ASE, the LODs for fish with a lipid content >0.5% were 30-120 ng g^{-1} for BP-3, 20-100 ng g^{-1} for 4-MBC, 50-380 ng g^{-1} for EHMC, and 10-60ng g^{-1} for OC (concentrations on a lipid basis). For the 20-g fish samples (column extraction) LODs were lower: 13-60 ng g^{-1} for BP-3, 6-13 ng g^{-1} for 4-MBC, 15-62 ng g^{-1} for EHMC, and 3-11 ng g^{-1} for OC on a lipid basis (because LODs depend on the lipid content, only ranges can be given). Reported concentrations were not corrected for recoveries.

4 Results and Discussion

4.1 General Considerations

4.1.1 Principal Entry Pathways of UV filters into the Aquatic Environment

In this study, two principal input pathways for UV filters from sunscreen products and other personal care products into the aquatic environment were considered: i) *direct inputs* into surface waters from recreational activities (release from skin during bathing and swimming), and ii) *indirect inputs* into surface water *via* wastewater treatment plants (WWTPs), e.g. from sunscreens washed off during showering or from renal excretion after oral uptake (i.e. after application of lipsticks) or uptake through the skin (**Figure 5**). The relative contribution of the two pathways is presently difficult to estimate. The former pathway involves just a part of the population (those swimming in natural waters), but is direct, whereas the latter pathway involves a larger number of people in the catchment area (all those using sunscreens and other personal care products containing UV filters), but is less direct and occurs mainly after some elimination in WWTPs. First estimates for the direct inputs into Zürichsee and Hüttnersee were reported in ref (*7*). These estimates were based on a survey among visitors of public swimming areas and on average product composition of sunscreens available on a proprietary basis. However, data for indirect inputs *via* WWTPs so far are not available. The inputs of UV filters from sunscreen products are expected to vary with seasons and weather (higher in summer with warmer, sunnier weather) whereas those from other personal care products (shampoos, cosmetics) may be less affected. Seasonal variations are also not expected for other anthropogenic compounds such as caffeine and methyl triclosan used as chemical markers for domestic pollution.

4.1.2 Chemical Markers

Assuming that inputs of a compound into a lake are entirely from WWTPs (*indirect inputs*) and that flushing is the only relevant process, by which the compound is removed from the lake, the concentrations in water (C_{water}) are expected to be proportional to the population in the catchment area (P, persons) and inversely proportional to the water throughflow of a lake (Q, m^3 d^{-1}), hence to correlate with P/Q according to equation 2:

$$C_{water} = f \times P/Q \qquad (2)$$

where f is a proportionality factor determined by the actual amount of compound used (g $person^{-1}$ d^{-1}) and its fraction transferred to a lake. Such a linear relationship between C_{water} and P/Q was previously observed for caffeine, a chemical marker for contamination of surface water with domestic wastewater (*30*).

Methyl triclosan was suggested as a chemical marker for lipophilic WWTP-derived contaminants in fish and SPMDs. A linear correlation was observed between its lipid based concentration in fish C_{fish} and P/Q of a lake (*31*)

$$C_{fish} = C_{water} \times BCF_L = f \times P/Q \times BCF_L \qquad (3)$$

where BCF_L (L kg^{-1}) is the lipid based bioconcentration factor of a compound, defined as C_{fish}/C_{water}.

However, the situation is further complicated for UV filters, because direct inputs to the lakes cannot be neglected. Thus, the concentrations would be higher than those expected from the P/Q ratio of a lake. An evaluation and comparison of UV filter concentrations to concentrations of chemical markers in water and/or fish may thus give indications of the relative magnitude (or importance) of the different entry pathways of UV filters to those lakes.

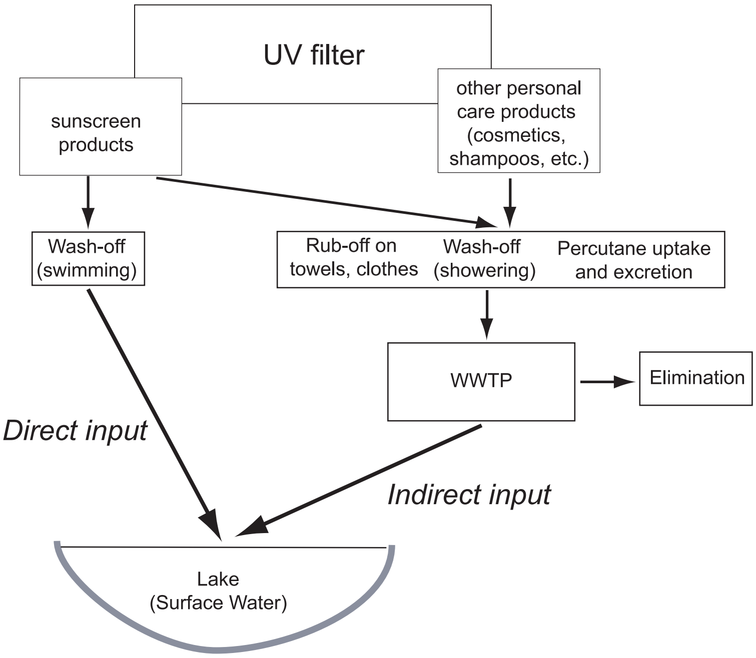


***Figure 5**: Two principal entry pathways, direct and indirect, of UV filters to surface waters (lakes).*

4.2 Use and Direct Inputs of UV Filters to Surface Waters

Direct inputs of UV filters were previously estimated for Zürichsee and Hüttnersee (*7*). Because there are no sales statistics for sunscreen products in Switzerland, the estimates were based on a survey on sunscreen usage among visitors at two public swimming areas at Zürichsee and an extrapolation based on a market survey, average product compositions (listed in **Table 6**), and official visitor statistics (source: Sportamt der Stadt Zürich). The numbers of visits during the bathing season in summer 1998 were estimated at 1’440’000 and 6’200 for Zürichsee and Hüttnersee, respectively. According to this survey, 87% of all respondents used sunscreens products, whereby half of them indicated to apply sunscreens more than once during a visit, and to more or less the whole body. Furthermore, it was assumed, that one "full body application" would correspond to 10 g sunscreen or a total of about 1 g UV filter, and that 50% of the applied UV filters were washed off during bathing. Direct inputs, estimated in this way, were 224 kg EHMC, 152 kg OC, 145 kg 4-MBC, and 77 kg BP-3 for Zürichsee for 1998, and between ~1 kg (EHMC) and 0.3 kg (BP-3) for Hüttnersee.

These estimates indicate that UV filter burden to lakes strongly depends on season and that direct inputs of UV filters are considerable. According to official statistics, the number of visitors in 2002 was similar (97%) to that in 1998. Therefore, direct inputs, as calculated for 1998, were adopted for this study, although they may overestimate actual inputs for the following reasons: i) The percentage of persons using sunscreen products is astonishingly high. Possibly the rate of return from interviewees using sunscreen products was higher than from those not using sunscreens. ii) The assumed wash-off rate of 50% is possibly biased high, because in laboratory tests less than 30% of water resistant UV filters were washed off (*32*). iii) Not all visitors at the swimming areas actually go into the water. The loads as calculated in this previous study, therefore, likely represent worst-case situations.

In a recent market survey in Switzerland (by Hauri and co-workers in 2002), 47 sunscreen products were analyzed for their UV filter content (*6*). An average UV filter content per product was calculated from the concentration measured in these products (**Table 6**). In contrast to the average composition estimated in the above survey (Poiger and co-workers in 1998 (*7*)), these values are not weighted by the use frequency of sunscreen products, and do not include consumers preferences for brands or SFPs. Nevertheless, the average composition of sunscreens, estimated from the two surveys, are in good agreement. Both surveys suggested EHMC as the UV filter used in the highest quantities, followed by OC and 4-MBC. BP-3 was ranked sixth and seventh, respectively. Further important UV filters were BM-DBM (butyl methoxy-dibenzoylmethane), PBSA (phenyl-benzimidazole sulfonic acid), OS (octyl salicilate) and OT (octyl triazone), which are not listed in Table 6, because they are not investigated in this study. The average contents of BP-3, 4-MBC, EHMC, and OC in sunscreens were between 0.8% and 2.4% when using the data from ref (*7*), and between 0.3-4.3% when using the data from ref (*6*).

***Table 6:** Estimated average contents of UV filters in sunscreen products and derived amounts used per application.*

UV filter	average content in sunscreen products [%]		amount per "full body application" [mg]	
	survey Poiger (*7*)	survey Hauri (*6*)	survey Poiger (*7*)	survey Hauri (*6*)
BP-3	0.8	0.3	80	30
4-MBC	1.5	1.6	150	160
EHMC	2.4	4.3	240	430
OC	1.6	1.5	160	150

In **Table 6** we also list the average quantities of UV filters applied per person, assuming an application amount of 1 mg sunscreen product cm^{-2} and a treated body surface of 1 m^2 ("full body application"). When using the data of ref (*7*), one „full body application" (10 g), on average, would correspond to 80-240 mg per UV filter (data from ref (*6*), 30-430 mg). The patterns of relative average quantities of the four UV filters in sunscreens are shown in **Figure 6**.

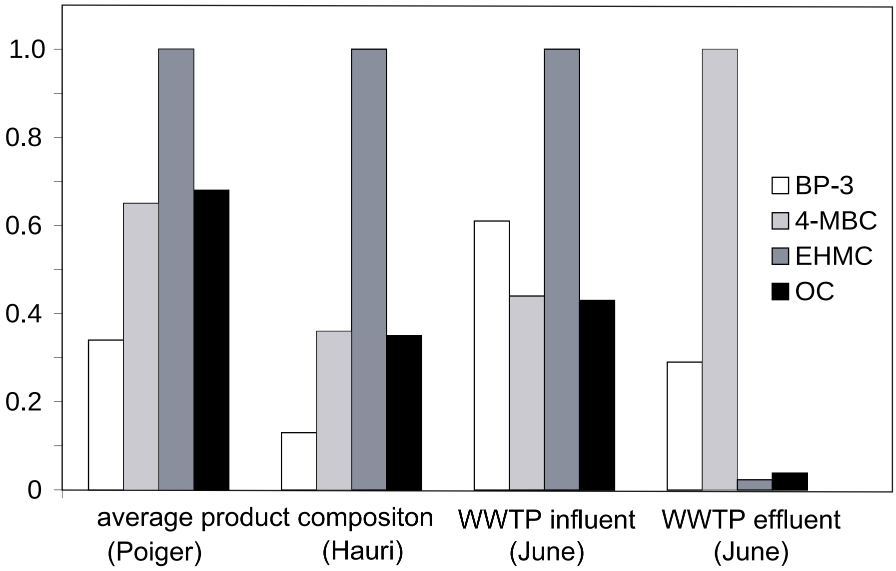


Figure 6: *The patterns of relative average quantities of the four UV filters in sunscreen products as calculated from the surveys carried out by Poiger et al. in 1998 and by Hauri et al. in 2002 (6,7), using two different methodolgies and the patterns of loads in WWTP influents and effluents. Note: only the four UV filters investigated in this study were considered. The data are normalized to the most prevalent UV filter. WWTP data are based on average loads of WWTPs Meilen, Horgen, and Wädenswil on June 24, 2002 to represent summer situation.*

4.3 Indirect Inputs of UV Filters to Surface Waters

4.3.1 Occurrence of UV Filters in WWTP Influents

In **Table 7**, we report concentrations and loads of BP-3, 4-MBC, EHMC, and OC in influents and effluents of four WWTPs sampled in April and June, 2002. UV filters were observed in wastewater from all installations and on all occasions, with a maximum influent concentration of ~19 μg/L (EHMC). Influent concentrations and corresponding loads (g d^{-1}) were higher in June than in April 2002, indicating seasonal variability, likely from a higher use of sunscreen products in summer. When the influent loads of the UV filters were normalized for the different populations serviced by the WWTPs, the loads in April 2002 (two installations) were 0.6-6.6 g (10'000 persons)$^{-1}$ d^{-1} per compound and 9-16 g (10'000 persons)$^{-1}$ d^{-1} for the sum of the four UV filters (**Table 7**). In June 2002 (three installations), the corresponding normalized influent loads were 9-119 and 87-265 g (10'000 persons)$^{-1}$ d^{-1}, respectively. It should be noted, that these loads only include the dissolved fractions of UV filters (samples were taken after primary sedimentation and were centrifuged). Assuming a typical POC (particulate organic carbon) concentration of 30 mg/L in the influent, the fraction sorbed on particulate matter is estimated to be <5% for BP-3, ~60% for 4-MBC (log K_{OW} = 5.1), and >90% for EHMC and OC (log K_{OW} = 6.0 and 6.9, respectively). Hence, the actual loads of 4-MBC, EHMC and OC to WWTPs are expectedly higher.

Table 7: *Influent and effluent concentrations [ng L^{-1}] and corresponding total loads per day [g d^{-1}] and loads normalized to population [g (10'000 persons)$^{-1}$ d^{-1}] of UV filters from WWTPs in the region of Zürichsee (2002). Also reported are data for caffeine from ref (30).*

WWTP (population)	troughput	compound	influent			effluent			elimination
sampling date	[m^3 d^{-1}]		[ng L^{-1}]	[g d^{-1}]	[g (10'000 persons)$^{-1}$ d^{-1}]	[ng L^{-1}]	[g d^{-1}]	[g (10'000 persons)$^{-1}$ d^{-1}]	[%]
Horgen (20'560)	11'900	BP-3	900	10.7	5.2	290	3.4	1.7	68
Apr 15 Mo		4-MBC	640	7.6	3.0	200	2.4	1.2	69
		EHMC	1140	13.6	6.6	40	0.5	0.2	97
		OC	170	2.0	1.0	20	0.2	0.1	88
		sum UV filter		34	16		6.5	3.2	
		caffeine	18809	223.8	110	502	6.0	2.9	97
Meilen (22'000)	10'318	BP-3	720	7.4	3.4	53	0.6	0.3	93
Apr 15 Mo		4-MBC	560	5.8	2.6	310	3.2	1.5	44
		EHMC	480	5.0	2.3	13	0.1	0.06	97
		OC	133	1.4	0.6	6	0.1	0.03	96
		sum UV filter		20	8.9		4.0	2.5	
		caffeine	50000	516	230	9480	97.8	44.5	81
Jun 24 Mo	12'000	BP-3	7700	92.4	42.0	570	6.8	3.1	93
		4-MBC	6500	78.0	35.5	2280	27.4	12.5	65
		EHMC	18800	226	102.5	25	0.3	0.1	>99
		OC	11700	140	63.8	60	0.7	0.3	>99
		sum UV filter		536	244		35.2	16.0	
		caffeine	30000	360	163	1240	14.9	6.8	96
Thalwil (19'548)	17'229	BP-3	7800	134.4	68.8	320	5.5	2.8	96
Jun 24 Mo		4-MBC	5500	94.8	48.5	980	16.9	8.6	82
		EHMC	13500	233.5	119.4	22	0.4	0.2	>99
		OC	3200	55.4	28.3	10	0.2	0.1	>99
		sum UV filter		518	265		23.0	11.7	
		caffeine	33000	567	291	118	2.0	1.0	>99
Wädenswil (19'000)	15'122	BP-3	2680	40.5	21.3	690	10.4	5.5	74
Jun 24 Mo		4-MBC	3280	49.6	26.1	2700	40.8	21.5	18
		EHMC	3950	59.7	31.4	72	1.1	0.6	98
		OC	1070	16.2	8.5	123	1.9	1.0	89
		sum UV filter		166	87		54.2	28.6	
		caffeine	26000	393	210	2360	35.7	18.8	91

For further WWTPs see Table 8, for normalized effluent loads see also Table 9.

In WWTP influents, the most prevalent compound was EHMC, lower, but still sizeable, amounts of the other UV filters were observed. The pattern of relative quantities of the 4 compounds (EHMC > BP-3 ~ 4-MBC ~ OC) observed in these WWTP influents were similar to the patterns of average contents in suncreens ((*6,7*) see above and **Figure 6**). The relative quantity of BP-3 was higher than expected from average sunscreen compositions, possibly due to its use in other products than sunscreens, e.g. as product stabilizer in shampoo or plastics, and/or due to underestimation of the loads of the other UV filter compounds (sorption to POC, see above). There is hardly information available about UV filter contents and use of the numerous personal care products on the market, although they may not be neglected (*33*).

The normalized inputs (sum of 4 UV filters) on average were more than 10 times, those of individual UV filters (EHMC, OC) up to 50-100 times higher in June than in April 2002. Caffeine, used as a chemical marker in the study, did not show such a pronounced seasonal variation (ratio between lowest and highest load, 2.6; concentrations adopted from ref (*30*)). The loads of UV filters in summer likely arise from increased use of sunscreen products, whereas other personal care products are expectedly used more continuously throughout the year.

4.3.2 Occurrence of UV filters in WWTP Effluents. Evidence for Elimination in WWTPs

Effluent concentrations in the WWTPs were consistently lower than influent concentrations (see **Table 7**) indicating some elimination of UV filters in the WWTPs. Because influents and effluents were sampled on the same day, corresponding samples may not originate exactly from the same package of wastewater. Furthermore, influent loads to WWTPs likely are underestimated because of some adsorption of the lipophilic compounds onto particulate matter which is removed in the primary sedimentation basins (see 4.3.1). Therefore, overall elimination could be higher than calculated in Table 7.

Elimination seems to vary between compounds, between installations, and may even vary from day to day within the same WWTP. Elimination E, calculated as the ratio

$$E\ (\%) = 100\ (L_{in} - L_{out})/L_{in} \qquad (4)$$

where L_{in} is the load of a UV filter compound in the influent after primary sedimentation, and L_{out} is its load in the effluent, was lowest for 4-MBC (18-82%) which appears to be the most persistent of these UV filters in WWTPs. Higher eliminations were observed for BP-3 (68-96%) and OC (88->99%), and highest for EHMC (97->99%, see **Table 7**). Elimination for caffeine varied considerably (81.0-99.6%). Among the two 2-ethylhexyl esters, EHMC and OC, the latter appears to be more persistent which is in agreement with reported data from biodegradation experiments, where EHMC was found to be “readily” but OC only “slightly” biodegradable (Roche safety data sheets, adopted from summary in ref (*8*)). Nevertheless, OC is removed considerably in WWTPs, most likely due to sorption on activated sludge (log K_{OW} (OC) = 6.9). 4-MBC, the compound showing least elimination in our study, in fact is reported as “not readily” biodegradable (*8,34*) and expectedly 4-MBC (log K_{OW} = 5.1) sorbes less to activated sludge than OC or EHMC.

Only little is published about the behaviour of UV filters in WWTPs so far. In two WWTPs in the UK (both with trickling filters and activated sludge treatment) effluent concentrations of EHMC were about 300 and 100 ng L^{-1}; the elimination was 91 and 98% (*14*). These concentrations are higher than those detected in our study, whereas elimination is somewhat lower. In raw wastewater from an urban WWTP in France a BP-3 concentration of ~1'600 ng L^{-1} was found (*35*), which is in the range of the concentrations measured in summer in our study. Both studies citied do not provide information about sampling date (season), water throughput or loads.

Table 8: *Effluent concentrations and corresponding loads of UV filter compounds and caffeine of two WWTPs sampled on subsequent days in April 2002 with low and high wastewater discharge.*

WWTP (population)	sampling date	troughput [m^3 d^{-1}]	compound	effluent [ng L^{-1}]	effluent [g d^{-1}]	effluent [g (10'000 persons)$^{-1}$ d^{-1}]
Küsnacht (16'475)	April 23 Tu	6'574	BP-3	62	0.4	0.25
			4-MBC	520	3.4	2.1
			EHMC	16	0.1	0.1
			OC	5	0.03	0.02
			sum UV filter		3.9	2.5
			caffeine [a]	41	0.3	0.2
	April 24 We	30'105	BP-3	69	2.1	1.3
			4-MBC	400	12.0	7.3
			EHMC	5	0.2	0.1
			OC	8	0.2	0.1
			sum UV filter		14.5	8.8
			caffeine [a]	28	0.9	0.5
Männedorf (9'044)	April 23 Tu	4'340	BP-3	140	0.6	0.7
			4-MBC	580	2.5	2.8
			EHMC	21	0.1	0.1
			OC	52	0.2	0.2
			sum UV filter		3.4	3.8
			caffeine [a]	56	0.2	0.3
	April 24 We	14'243	BP-3	240	3.4	3.8
			4-MBC	640	9.1	10.1
			EHMC	75	1.1	1.2
			OC	270	3.9	4.3
			sum UV filter		17.5	19.4
			caffeine [a]	92	1.3	1.4

[a] Caffeine concentrations adopted from ref. (*30*).

In **Table 8**, we list the effluent concentrations and loads from two further installations (Küsnacht and Männedorf), measured on subsequent days in April 2002. For these two installations, the water discharges were moderate on the first day (April 23, 2002, Tuesday) with 400 and 480 L person^{-1} d^{-1}, respectively. However, due to heavy rain events (28 mm in 24-hours) on the following day (April 24, 2002, Wednesday), wastewater discharges were much higher (1800 and 1600 L person^{-1} d^{-1}). Despite the substantial dilution of wastewater with rain water on the second day, the concentrations of UV filters in the effluents did not decrease but in fact were the same or even increased. Hence, the corresponding effluent loads (totals of four compounds) increased 3.7- and 5-fold, and a similar behavior was observed for caffeine, likely as a result of reduced residence time and consequently less elimination in the plants. The data indicate that effluent loads are variable and depend on actual conditions in the WWTPs (wastewater discharge, residence time). Furthermore, during heavy rain events the amount of wastwater may exceed the capacity of the WWTP, so that untreated wastewater (stormwater overflow) may enter the rivers and lakes, and lead to additional loads.

Table 9 summarizes the normalized effluent loads for all installations. The effluent loads (total of all four compounds) when normalized for the populations, were 1.9-19.4 g (10'000 persons)$^{-1}$ d^{-1} in April, and 9-28.6 g (10'000 persons)$^{-1}$ d^{-1} in June, 2002 with gross averages ~3 times higher in June than in April 2002. In WWTP effluents, 4-MBC was clearly most prevalent (up to 21.5 g (10'000 persons)$^{-1}$ d^{-1}) among the four UV filters, followed by BP-3 (up to 5.5 g (10'000 persons)$^{-1}$ d^{-1}). While EHMC was the most abundant UV filter in the influents, the effluent loads for EHMC were low on all occasions (maximum, 1.2 g (10000 persons^{-1}) d^{-1}). The effluent loads of OC were similarly low (~1 g (10'000 persons)$^{-1}$ d^{-1}) except when water discharges were very high (Männedorf, April 24, 2002, 4.3 g (10'000 persons)$^{-1}$ d^{-1}). The pattern of the average relative quantities of the four UV filters as observed in WWTP effluents is shown in **Figure 6**. Overall, the effluent concentrations and loads of UV filters showed less seasonal variation than the influent concentrations and loads.

***Table 9:** Normalized effluent loads [g (10'000 persons)$^{-1}$ d^{-1}] of UV filter compounds and caffeine from WWTPs (2002); data from Table 7 and 8.*

WWTP	sampling date	BP-3	4-MBC	EHMC	OC	sum UV filter	caffeine
Horgen	Apr 15 Mo	1.7	1.2	0.2	0.1	3.2	2.9
Meilen	Apr 15 Mo	0.3	1.5	0.05	0.05	1.9	44.5
Küsnacht	Apr 23 Tu	0.25	2.1	0.1	0.02	2.5	0.2
	Apr 24 We	1.3	7.3	0.1	0.1	8.8	0.5
Männedorf	Apr 23 Tu	0.7	2.8	0.1	0.2	3.8	0.3
	Apr 24 Tu	3.8	10.1	1.2	4.3	19.4	1.4
Average April	(all occasions)	1.3	4.2	0.3	0.8	6.6	
	(low water discharge) [a]	0.7	1.9	0.1	0.1	2.9	
Meilen	Jun 24 Mo	3.1	12.5	0.1	0.3	16.0	6.8
Thalwil	Jun 24 Mo	2.8	8.6	0.2	0.1	11.7	1.0
Wädenswil	Jun 24 Mo	5.5	21.5	0.6	1.0	28.6	18.8
Average June		3.8	14.2	0.3	0.5	18.8	

[a] Values from April 15 and April 23 used for average calculation only.

4.3.3 UV Filter Loads in Effluent of the WWTP Zürich, Derived from SPMDs

Further data are available from SPMDs exposed on two occasions (in April/May and in August/September 2002) in the effluent of WWTP Zürich (Werdhölzli) at the same time as the SPMDs in Zürichsee and in the river Limmat were exposed. The summed concentrations of the four UV filters in the WWTP effluents were 21'000 and 32'000 ng SPMD^{-1} in spring and summer, respectively (see **Table 12**). As in the direct effluent measurements from the other WWTPs, the most prevalent UV filters in spring and summer was 4-MBC with a maximum concentration in August 2002 of ~20'000 ng SPMD^{-1}, followed by OC (maximum ~11'000 ng SPMD^{-1}). The concentrations of EHMC and BP-3 were considerably lower (50-900 ng SPMD^{-1}).

In the following, an estimation for the effluent load is made from SPMD data for 4-MBC. Assuming total sampling volumes of ~70 L (see 2.4) by the SPMDs, the concentration of 4-MBC in the effluents is estimated at 220 and 290 ng L^{-1} in spring and summer 2002, respectively. Taking the average wastewater discharges of 2.8 and 2.4 m^{3} s^{-1} during the respective sampling periods into account, the actual effluent loads calculated are then ~54 and 59 g d^{-1}, and the normalized effluent loads are then 1.5 and 1.6 g (10'000 persons)$^{-1}$ d^{-1} in spring and summer 2002, respectively. These data are in the range of the spring data of other WWTPs (1.2-2.8 g (10'000 persons)$^{-1}$ d^{-1} (see **Table 9**) where direct effluent measurements were made (excluding data from high-water events) but they are significantly lower (~10 times) than those summer data. The SPMD data, however, reflect averages over 3-week periods, in July/August 2002 during a longer period of rather rainy weather, whereas the direct effluent measurements reflected 24-h data, likely from „worst-case“ situations (Mondays after hot weekends in June 2002).

Another estimate for the effluent loads from this WWTP can be made from the data of the SPMDs exposed in the river Limmat, above (outflow of Zürichsee) and below (at Dietikon) the WWTP (**Table 12**). Assuming sampling volumes of ~70 L for the river exposed SPMDs, the concentrations of 4-MBC of 250 and 560 ng SPMD^{-1} in spring 2002 correspond to concentrations of ~3.6 and ~8 ng L^{-1} in water, and thus to river loads of 43 and 95 g d^{-1} above and below the WWTP, respectively (average waterflow, 138 m^{3} s^{-1}). The concentrations of 770 and 1'250 ng SPMD^{-1} in summer 2002 correspond to concentrations of ~11 and ~18 ng L^{-1}, and thus to river loads of 120 and 194 g d^{-1} above and below the WWTP, respectively (average waterflow, 125 m^{3} s^{-1} (*36*)). These loads indicate contributions of 52 and 74 g d^{-1} of 4-MBC from the WWTP and the river Sihl to the river Limmat in spring and summer 2002, respectively. When these contributions are normalized for the population (~400'000 persons, including catchment area of river Sihl), the normalized wastewater effluent loads were about 1.3 and 1.9 g (10'000 persons)$^{-1}$ d^{-1}, respectively. This is in good agreement with the SPMD-derived effluent loads (54 and 59 g d^{-1} or 1.5 and 1.6 g (10'000 persons)$^{-1}$ d^{-1}, respectively). **Figure 7** shows the corresponding mass balance for 4-MBC inputs to the river Limmat from WWTP Werdhölzli.

All SPMD-derived concentrations for EHMC and BP-3 indicated low loads (<0.1 g (10'000 persons)$^{-1}$ d^{-1}) which is in agreement with the data from direct wastewater effluent measurements. OC showed larger effluent loads than expected from direct effluents, what may be explained by the possibly higher sampling rate of OC compared to the other UV filter compounds (see 2.4). Again, these SPMD derived effluent concentrations of UV filters show reasonable agreement with data from direct wastewater effluent measurements of other WWTPs, except the peak effluent loads measured during the warm weather period in June 2002.

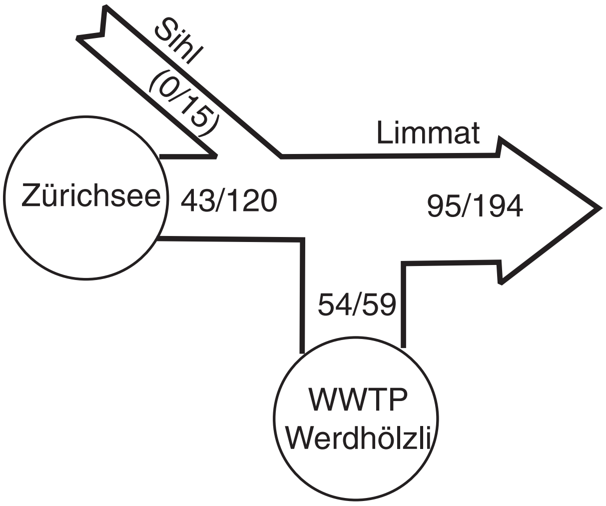


Figure 7: *4-MBC loads in g d^{-1} in spring/summer 2002 calculated from SPMDs exposed concurrently in the outflow of Zürichsee, in the effluent of WWTP Zürich (Werdhölzli), and in river Limmat at Dietikon. Values for the tributary river Sihl are calculated to balance the loads above and below WWTP.*

4.3.4 Additional Measurements in WWTPs in 2003

Supplementary data from a recent sampling campaign, where influent and effluent measurements of four WWTPs were carried out in August and September 2003, are reported in **Table 10**. Two WWTPs, Thalwil and Männedorf, are in the catchment area of Zürichsee, the WWTPs Kloten-Opfikon and Wetzikon discharge to the river Glatt and to the river Aa (tributary of Greifensee), respectively.

The normalized influent loads of UV filters, calculated from measurements in September 2003, were similar to those from April 2002 (or somewhat higher for EHMC and OC): 2-8 g (10’000 persons)$^{-1}$ d^{-1} of BP-3, 4-8 g (10’000 persons)$^{-1}$ d^{-1} of 4-MBC, 9-30 g (10’000 persons)$^{-1}$ d^{-1} of EHMC, and 4-17 g (10’000 persons)$^{-1}$ d^{-1} of OC were found. The influent loads to WWTP Wetzikon were similar to those of the other WWTPs in spring, although they were measured in summer. August 12 was in a rather warm and sunny period with afternoon temperatures of >30°C, in September the temperatures were considerably lower: below 10°C on the sampling day and 16°C (maximum) the day before sampling. The data from WWTP Wetzikon supports the assumption, that the high influent loads measured in other plants in June 2002 represented worst-case situations.

For the WWTPs Thalwil and Männedorf, effluent loads of 0.04-0.5 (BP-3), 0.5-0.8 (4-MBC), 0.05-0.2 (EHMC), 0.06-0.2 (OC) g (10’000 persons)$^{-1}$ d^{-1} were calculated. These values are in a similar range as those measured in April 2002 (considering data from low/normal water throughput). The WWTPs Kloten-Opfikon and Wetzikon are modern plants with high water capacity and long residence times. Correspondingly there is a tendency of higher elimination and lower effluent loads in these two plants, but they seem not to be representative for the catchment area of Zürichsee.

Table 10: *Influent and effluent concentrations [ng L^{-1}], loads [g d^{-1}], and normalized loads [g (10’000 persons)$^{-1}$ d^{-1}] from WWTPs sampled in 2003.*

WWTP (population)	Q [m^3 d^{-1}]	UV filter	influent [ng L^{-1}]	influent [g d^{-1}]	influent [g (10'000 pers)$^{-1}$ d^{-1}]	effluent [ng L^{-1}]	effluent [g d^{-1}]	effluent [g (10'000 pers)$^{-1}$ d^{-1}]	elimination %
September 16, 2003									
Thalwil	4036	BP-3	1079	4.4	2.2	22	0.09	0.04	98
(19'780)		4-MBC	1918	7.7	3.9	388	1.57	0.79	80
		EHMC	4310	17.4	8.8	99	0.40	0.20	98
		OC	2127	8.6	4.3	27	0.11	0.06	99
Männedorf	2610	BP-3	2292	6.0	6.3	194	0.51	0.53	92
(9'500)		4-MBC	3007	7.8	8.3	164	0.43	0.45	95
		EHMC	9599	25.1	26.4	18	0.05	0.05	>99
		OC	6093	15.9	16.7	88	0.23	0.24	99
Kloten-Opfikon	13’630	BP-3	1729	23.6	7.9	nd	<0.05	<0.02	>99
(29’769 [a])		4-MBC	1604	21.9	7.3	61	0.83	0.28	96
		EHMC	6799	92.7	31.1	20	0.27	0.09	>99
		OC	2100	28.6	9.6	nd	<0.05	<0.02	>99
August 12, 2003 [b]									
Wetzikon	12’456	BP-3	1567	9.6	4.8	14	0.09	0.04	99
(19'600)		4-MBC	2157	13.4	6.7	63	0.39	0.20	97
		EHMC	4913	30.6	15.3	14	0.09	0.04	>99
		OC	2736	17.0	8.5	nd	<0.05	<0.02	>99

[a] Wastewater from the airport Zürich (Unique), corresponding to about 20’000 additional inhabitants, is also discharged to the WWTP Kloten-Opfikon, but was not considered to contribute significantly to UV filter laods.
[b] In the case of Wetzikon, the data were calculated from twelve 2-hour flow proportional samples.
nd: not detected, concentrations in the effluent were below limit of detection (<10 ng L^{-1}).

4.4 Comparison of Indirect and Direct Inputs of UV filters to Zürichsee

In the following, *indirect inputs* (WWTP-derived) are compared to *direct inputs* (from recreational activities) for the situation of Zürichsee. *Direct inputs* were adopted as estimated by Poiger and co-workers (*7*), as discussed in 4.2. The *indirect inputs* were extrapolated from data measured in WWTP effluents (average data from Table 9) using the following assumptions: larger inputs were considered in the summer season (92 d from June through August, e.g. for 4-MBC load, 14 g (10’000 persons)$^{-1}$ d^{-1}) and lower inputs in the colder season (273 d from September to May, e.g. 4-MBC load, 4 g (10’000 persons)$^{-1}$ d^{-1}). The inputs from WWTPs to Zürichsee estimated in this way for 4-MBC and BP-3 were 78 and 21 kg year^{-1}, respectively, and thus in a similar range as the direct inputs (145 and 77 kg/season, **Table 11**). In contrast, the inputs of EHMC and OC from WWTPs were significantly lower than direct inputs, because of good elimination of these two compounds in the WWTPs. Note: both, *direct* and *indirect inputs* are worst-case scenarios.

Table 11: *Estimated indirect inputs of UV filters from WWTPs compared to estimated direct inputs for Zürichsee.*

	BP-3	4-MBC	EHMC	OC	sum UV filter
Average normalized inputs from WWTPs [g (10’000 persons)$^{-1}$ d^{-1}]					
warmer season (Jun – Aug, 92 d)	4	14	0.3	0.5	
colder season (Sep – May, 273 d)	1	4	0.3	0.8	
Indirect inputs from WWTPs for Zürichsee (330’000 persons) [g d^{-1}]					
warmer season (Jun – Aug, 92 d)	130	460	10	16	
colder season (Sep – May, 273 d)	33	130	10	26	
Annual indirect input to Zürichsee [kg y^{-1}]	21	78	4	9	112
Annual direct input to Zürichsee (survey 1998) [kg y^{-1}] [a]	77	145	224	152	598

[a] Data from ref (7).

4.5 Occurrence of UV filters in Surface Waters

4.5.1 Concentrations in Lake Water from Direct Measurements Using Solid-Phase Extraction

The concentrations of BP-3, 4-MBC, EHMC, and OC measured in the various lakes are reported in **Table 12**. Generally, very low concentrations were observed, if the compounds were detected at all. The most prevalent compounds were BP-3 and 4-MBC. The highest concentration of any of the four compounds was observed in Hüttnersee (BP-3, 35 ng L^{-1}), and BP-3 was also detected in samples from Zürichsee (10-20 ng L^{-1}) and Greifensee (30 ng L^{-1}). 4-MBC was detected in Hüttnersee (maximum, 29 ng L^{-1}), Zürichsee (2-11 ng L^{-1}), and Greifensee (12 ng L^{-1}). EHMC was detected only at marginal concentrations in Hüttnersee (2-5 ng L^{-1}) and Zürichsee (up to 7 ng L^{-1}). OC was detected only in two of the samples at low concentrations (~3 and 5 ng L^{-1}). None of the compounds were detected in concentrations significantly above blank level in the remote mountain lake, Jörisee.

In Zürichsee, where samples from different depths were analyzed, the concentrations generally were higher in the epilimnion (depths, 1 and 2.5 m) than in the hypolimnion (depth, 20 m). This is in agreement with the presumption, that inputs of UV filters occur predominantly into the surface layer, as expected for inputs from WWTPs and recreational activities.

The concentrations of UV filters measured in 2002 were similar to those measured in 1998 (*7*), except that higher peak concentrations for BP-3 and 4-MBC were observed in 1998 (Hüttnersee, 125 and 82 ng L^{-1}, respectively) than in 2002. A possible explanation of the lower peak concentrations in 2002 is that sampling was done during a period of cooler weather in 2002, whereas in July/August 1998 sampling was done during sunnier and warmer weather with expectedly more recreational activities.

Table 12: *Concentrations[a] [ng L^{-1}] of UV filter compounds in water samples from Swiss lakes (Summer 2002)*

Lake	Date	Depth [m]	BP-3	4-MBC	EHMC	OC
Jörisee	Jul 30	1	nd	nd	nd	nd
	Sep 09	1	nd	nd	nd	nd
Zürichsee	Aug 07	2.5	20	8	6	~3
		20	11	4	~2	nd
	Sep 04	1	14	11	7	nd
		2.5	10	6	nd	nd
		20	10	2	nd	nd
Greifensee	Aug 28	2.5	20	12	nd	nd
	Jul 22	1	30	10	nd	5
Hüttnersee	Jul 08	1	23	29	5	nd
	Jul 26	1	35	8	~2	nd
Concentrations estimated from SPMDs [b]						
Jörisee	Jul 30 – Sep 09		<0.2	<0.2	<0.2	<0.1
Zürichsee	Aug 14 – Sep 04		2; 1	10; 12	<1	7; 10
Greifensee	Jul 17 – Aug 07		2; 1	6; 6	<1	0.6; 2
Hüttnersee	Jul 08 – Jul 26		3; 2	28; 40	<1; 3	2; 5
Concentrations detected in summer 1998 [c]						
Zürichsee			<2-4	3-22	<2-26	<2
Hüttnersee			5-125	9-82	4-15	3-27

[a] The concentrations are not corrected for recoveries. EHMC values are corrected for blank contribution.

[b] Concentrations estimated from SPMDs exposed in summer 2002, see 4.5.2.

[c] Concentration ranges detected in samples from 1998 (July - August), reported in ref (*7*).

nd: not detected above detection limit (<2 ngL^{-1}).

In other studies UV filters were detected in surface waters: in May through August 1997 in the river Rhein below Basel maximum EHMC concentrations of 28 ng L^{-1} were measured (unpublished study, data reported in (*15*)). SPMD-derived concentrations of EHMC were about 2-5 ng L^{-1} in two rivers (Aire and Calder) in densely populated areas in the UK (*14*). In a German swimming lake none of BP-3, 4-MBC, or EHMC were detected in summer 1991 and 1993 above the detection limit of 4 ng L^{-1}, with exception of one sample (~4 ng L^{-1} of 4-MBC) (*16*). To our knowledge no further measured environmental concentrations of any of these UV filters are available.

4.5.2 Data from SPMDs Exposed in Lakes and a River

In contrast to conventional water sampling, SPMDs provide integrative results for the entire sampling period, including episodic events (e.g. higher inputs on a sunny weekend) and may, therefore, be more representative. In **Table 13** we report the concentrations of UV filters measured in the SPMDs exposed during spring and summer 2002 in lakes and the river Limmat. The SPMDs from Jörisee showed the lowest concentrations (combined concentrations, <30 ng SPMD^{-1}) and those from Hüttnersee showed the highest concentrations of UV filters (combined concentrations, ~3000 ng SPMD^{-1}), in between were the concentrations of Greifensee (~600 ng SPMD^{-1}), Zürichsee (~1500 ng SPMD^{-1}), and river Limmat (~2000 ng SPMD^{-1}, all concentrations in summer). The concentrations thus increased in the order

Jörisee < Greifensee < Zürichsee < Limmat < Hüttnersee

This order is different from that observed for methyl triclosan in the same SPMDs. Methyl triclosan was previously used as a chemical marker for the WWTP-derived burden of lipophilic contaminants and thus increased with P/Q (persons per water throughflow) in the order Jörisee ~ Hüttnersee < Zürichsee < Greifensee (see 4.1.2 for more details). The different order of the concentrations of UV filters and methyl triclosan in surface waters, clearly indicates different input pathways, i.e. the relative importance of *direct inputs* of UV filters. Hüttnersee receives no inputs from WWTPs. Consequently the methyl triclosan concentration was low. Nevertheless, UV filter (particularly 4-MBC) concentrations were highest in Hüttnersee, and the presence of these compounds is expected to be entirely due to recreational activities. Although, WWTP-derived loads are expectedly higher in Greifensee, 4-MBC concentrations in summer were higher in Zürichsee than in Greifensee (720 and 820 compared to 430 and 435 ng SPMD^{-1}). This suggests, that Zürichsee is used more intensely for recreational activities, and thus receives more direct UV filter inputs. The importance of such *direct inputs* (beside *indirect inputs* from WWTPs) was also discussed in paragraph 4.4. Concentrations of 4-MBC and methyl triclosan in SPMDs from various lakes vs. P/Q are shown in **Figure 8**.

The most abundant UV filter in all surface water exposed SPMDs was 4-MBC with concentrations of ~2’800 ng SPMD^{-1} (Hüttnersee). The concentrations of OC (maximum of ~700 ng SPMD^{-1} in Zürichsee), EHMC (maximum of ~300 ng SPMD^{-1} in the river Limmat) and BP-3 (maximum of ~200 ng SPMD^{-1} in Hüttnersee) were lower. The concentrations in the SPMDs deployed in Greifensee and Zürichsee were similar to those measured in SPMDs from these lakes in 1998 (*7*).

Generally the concentrations of UV filters in the SPMDs exposed in Zürichsee and the river Limmat during summer were higher than in those exposed during spring. This increase was most evident for 4-MBC and OC, and was less pronounced for BP-3 and even not evident for EHMC. These data suggest significantly higher concentrations of some UV filters in the lake during summer as a result of direct inputs from recreational activities and increased WWTP emissions to the lake. The data also suggest that EHMC likely is more rapidly degraded in surface waters, particularly during summer (photolysis). Degradation of EHMC in surface waters (rivers) was also reported in ref (*14*).

Table 13: *UV filter and methyl triclosan concentrations in SPMDs [ng SPMD^{-1}] exposed in 2002^{a}.*

location	date of exposure	BP-3	4-MBC	EHMC	OC	methyl triclosan
Jörisee	Jul 30 – Sep 09	nd; nd	nd; nq	nd, nd	nd; nq	nd; nd
Greifensee	Jul 17 – Aug 07	120; 80	435; 430	nd; nq	40; 120	56; 85
Hüttnersee	Jul 08 – Jul 26	200; 120	1950; 2790	nq; 200	150; 320	nd, nd
Zürichsee	Apr 30 – May 21	nq	250	160	24	25
	Aug 14 – Sep 04	110; 50	720; 820	nq; nd	510; 700	32; 28
Limmat at Dietikon	Apr 30 – May 21	nq	560	290	130	87
	Aug 15 – Sep 04	50	1250	320	435	137
WWTP Werdhölzli	Apr 30 – May 21	900	15700	380	3480	2850
Zürich, effluent	Aug 14 – Sep 04	405	20100	nq	11000	4000
Concentrations in SPMDs exposed in summer 1998 [b]						
Greifensee	Aug 05 – Aug 26	na	430	140	85	33
Zürichsee	Aug 05 – Aug 26	na	950	360	380	16

[a] Data were corrected for blank contributions

[b] Data reported in refs (*7,37*) .

nd: not detected above LOD; nq: not quantified if below 2 x LOD; na: not analyzed

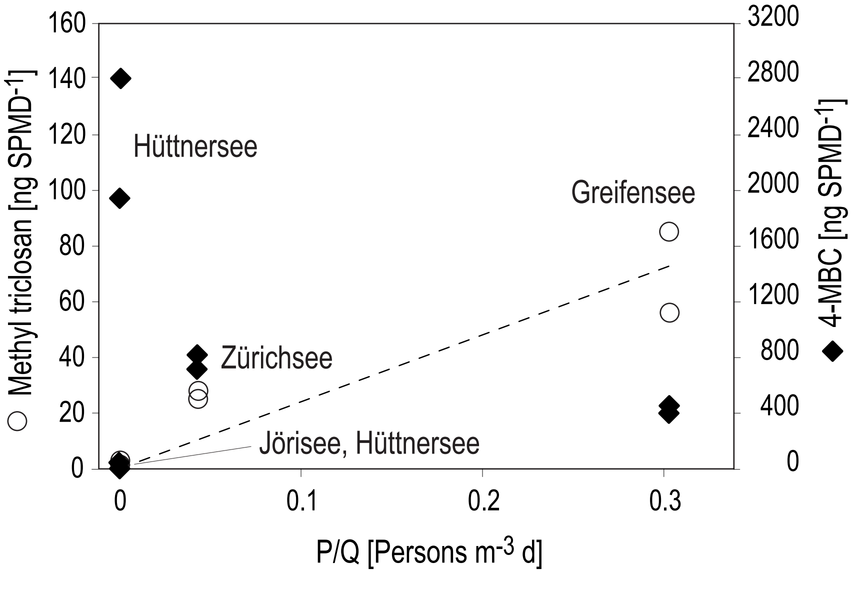


***Figure 8**: Concentrations of methyl triclosan (○, left scale) and 4-MBC (♦, right scale) in SPMDs exposed in various lakes in summer 2002* vs *respective wastewater load (expressed as P/Q). In contrast to 4-MBC inputs, methyl triclosan inputs are increasing with P/Q as indicated by the dashed line.*

Lake water concentrations estimated from SPMD data are in the same range as detected in water by direct measurement (see **Table 12**). The maximum concentrations derived from

SPMDs in Hüttnersee were 28 and 40 ng L^{-1} for 4-MBC (July 2002), as compared to 29 ng L^{-1} from direct measurement. The SPMD-derived concentrations in Zürichsee and Greifensee were lower (maximum, 10-12 ng L^{-1}) and those in Jörisee at or below the detection limits (<0.2 ng L^{-1}). The SPMD-derived concentrations were highest for 4-MBC, followed by OC, and lowest for BP-3 and EHMC. The SPMD-derived concentrations for BP-3 are lower than those expected from direct measurements (solid-phase extraction), possibly due to the lower sampling rate of BP-3 compared to the other UV filters (see also 2.4).

4.6 Calculated Concentrations of 4-MBC in Zürichsee

In the following we attempt to predict the concentrations of 4-MBC in Zürichsee from WWTP inputs and direct inputs from recreational activities. The concentrations were calculated using MASASlight, a computer program for “Modeling Anthropogenic Substances in Aquatic Systems” (*38,39*). The fate of compounds is described by a set of differential equations. Beside morphological and hydraulic parameters, such as lake volume and flushing, various elimination processes and variable input data were considered. Lakes were treated as a well mixed one-box system during circulation (winter, from December 27 to April 9 (*40*)) and as a two-box system with a well mixed epilimnion (5 m depth, water exchange flow between the two boxes ~5.7 m^3 s^{-1} (*40*)) and a well mixed hypolimnion during stratification (April 10 to December 26). Average flushing rate constants k_w for various periods were calculated from actual flow rates of river Limmat in 2002 (*36*) and were as follows: 0.0264 d^{-1} from April 10 – May 31, 0.0285 d^{-1} from June 1 - August 31, 0.0317 d^{-1} from September 1 – December 26, and 0.00172 d^{-1} from December 27 - April 9. During stratification k_w-values considered epilimnion volume only (lake effluent at surface), whereas for the mixed period the entire lake volume was considered. With regard to the entire lake and the whole year 2002, the mean flushing rate constant was 0.0023 d^{-1}. Other lake parameters were used as given in **Table 2**.

As a first step, concentrations resulting from the estimated inputs of 4-MBC into the lake and flushing as the only elimination process were calculated. A two-phase input was assumed: a lower input during 273 days of the year and a higher input during summer (92 days, Jun 1 – Aug 31). Inputs deduced from WWTP effluent data lead to estimated 4-MBC inputs of 130 g d^{-1} (low input) and 460 g d^{-1} (high input), respectively (see **Table 11**). Additionally an average direct input from recreational activities of 1’600 g d^{-1} during summer (92 days, June – August) was assumed, corresponding to totally 145 kg MBC during the entire season, as reported in ref (*7*). These inputs would lead to a peak concentration of ~190 ng L^{-1} in summer and to a steady-state concentration (same concentration at the end of the mixing period as at the beginning of stratification) of ~40 ng L^{-1} (“scenario 1”). The calculated time course of the concentration in the epilimnion clearly mirrors the seasonal variation of inputs, while concentrations in hypolimnion are almost time independent (see **Figure 9**).

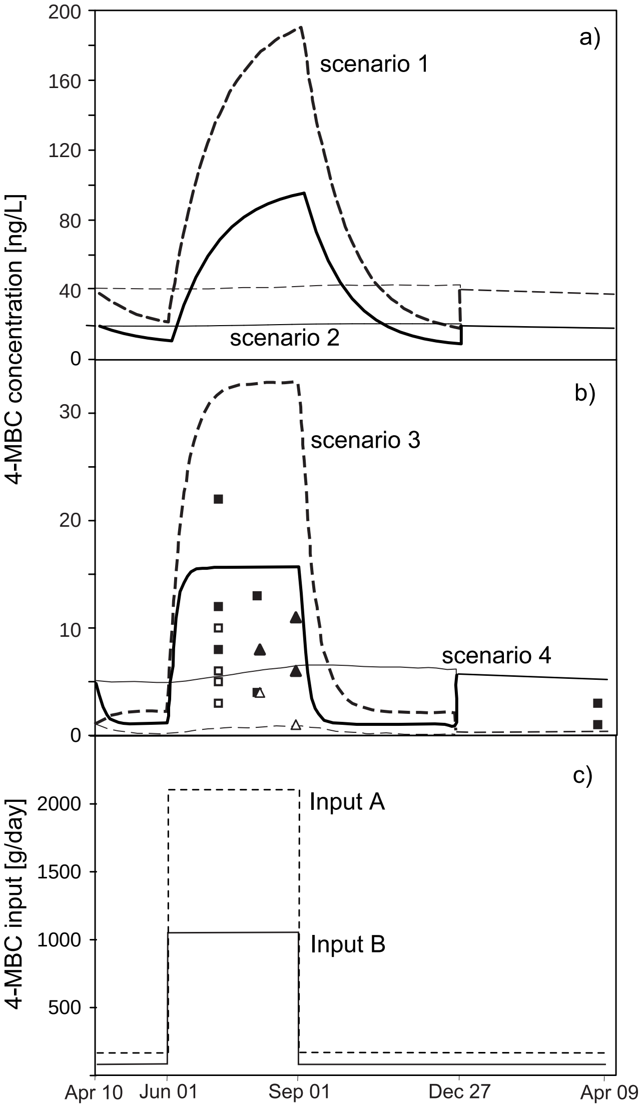


***Figure 9**: Calculated time courses of 4-MBC concentrations in Zürichsee under various assumptions: a) Concentrations based on worst-case inputs (dashed lines, scenario1, input A) and one half input (input B, scenario 2), with no degradation other than flushing. b) Concentrations based on input B including sedimentation and an additional degradation process with k_{deg}=0.05 d^{-1} (dashed line, scenario 3) or sedimentation and an elimination process in the epilimninon only (e.g. photolysis) with k_{epi}=0.15 d^{-1} (scenario 4). Thicker lines represent the epilimnion, thin lines hypolimnion concentrations. 4-MBC concentrations measured in 1998 (□ hypoliminion, ■ epilimnion) and in 2002 (Δ hypolimion, ▲ epilimnion). c) Inputs as described in the text (worst-case, input A used for scenairo 1) and half inputs (B, used for scenarios 2-4).*

Both, direct and indirect inputs assumed for “scenario 1” are worst-case assumptions and therefore likely overestimate the actual situation (see section 4.2). “Scenario 2” was then calculated by assuming only one half of indirect inputs from WWTPs and one half of direct inputs, as compared to “scenario 1”. This resulted in a peak concentration of ~95 ng L^{-1} and a steady-state concentration of 20 ng L^{-1}, still higher than those actually measured in water samples (about a factor 10-20). In both scenarios so far, no elimination processes except flushing were considered. In the following, additional elimination processes were introduced.

Including sedimentation did not result in substantially lower concentrations. Sedimentation rate constants k_{sed} were estimated according to refs (*26,41*) based on log K_{OW} = 5.1, a particulate organic carbon concentration (POC) of 0.5 mg L^{-1} in the epilimnion and 0.25 mg L^{-1} in the hypolimnion and mixed lake (*42*), and a settling velocity v_s = 2.5 m d^{-1} (*40*). The resulting sedimentation rate constants k_{sed} were 0.00051 d^{-1} in the hypolimnion and in the mixed lake, and it was k_{sed} = 0.0084 d^{-1} in epilimnion, and hence, less than half of the respective flushing rate constants k_w. Therefore two further types of elimination processes were introduced: I) an elimination process independent of time and depth, k_{deg}, as simplified model for e.g. chemical degradation or biodegradation, and II) a process, occurring only in the epilimnion of the lake (such as photolysis). Degradation rate constants were chosen such that steady state and/or peak concentrations were similar to the measured ones.

A depth-independent elimination rate constant (type I) of k_{deg} = 0.05 d^{-1} (about 20 k_w) led to a peak concentration in the range of the measured concentrations (33 ng L^{-1}) and very low steady state concentrations (<1 ng L^{-1}, “scenario 3”). In “scenario 4” a type II elimination rate constant k_{epi}, occurring only in the epilimnion was assumed. To provide concentrations similar to that measured, a k_{epi} = 0.15 d^{-1} was necessary. These rough calculations indicate, that i) inputs likely are over estimated (worst case assumptions) and ii) presumably elimination processes (additional to flushing and sedimentation) matter, although 4-MBC is known to be chemically stable and not readily biodegradable ((*34*) and data from WWTPs). However, the nature of these elimination processes (possibly photochemical) was not yet further studied.

4.7 Occurrence of UV Filters in Fish.

UV filters were determined in fish from various lakes using two different methods for sample preparation (see 3.4). Analysis of fish using 5-g samples and the ASE procedure indicated for all fish low concentrations (maximum, 10 ng g^{-1} fish filet) of UV filters, only marginally above those of method blanks (up to 4 ng g^{-1}). When the data were corrected for blank contributions, the concentrations were 5 ng g^{-1} fish filet or lower. The concentrations of methyl triclosan, the chemical marker, in these fish ranged from <0.05 (roach, Hüttnersee) to 2.7 ng g^{-1} fish (white fish, Pfäffikersee) with negligible blank contributions (<0.04 ng g^{-1}).

Due to the low lipid contents in some of the fish samples (<0.5%) and the small samples (5 g) the total amounts of UV filters in the final extracts were hardly exceeding the relatively high blank levels. Therefore calculation of UV filter concentrations seemed not to be appropriate. Nevertheless, the lipid based concentrations of all four UV filters in fish with >0.5 % lipids were <400 ng g^{-1} (lipid basis). When the concentrations of methyl triclosan were calculated on a lipid basis, fish from the same lake had similar concentrations, indicating that the concentrations of this lipophilic marker were measured reliably, not affected by the low amounts of extracted lipids.

***Table 14:** Concentrations (and LOD) of UV filter compounds and methyl triclosan in fish*

Sample	Date	Species	Weight	Fat	Extraction method [a]	Concentrations (LOD) [ng g^{-1} lipid] [b]				
			[g]	[%]		BP-3	4-MBC	EHMC	OC	methyl triclosan
Thunersee										
Th-F02	22.01.02	white fish	170	8.6	ASE	nq (15)	nq (18)	72 (49)	nd (7)	5 (1)
Th-F03	22.01.02	white fish	170	1.1	ASE	nq (120)	nq (140)	nd (380)	nd (59)	6 (4)
Pfäffikersee										
Pf-F01	01.09.02	white fish	651	2.8	ASE	nd (46)	nq (56)	nq (150)	nd (23)	43 (2)
Pf-F02	01.09.02	white fish	561	4.8	ASE	nq (27)	nq (33)	nq (88)	nd (14)	56 (1)
Zürichsee										
Zu-S185	05.06.02	roach	214	0.6	CE	112 (36)	80 (10)	64 (37)	nd (7)	84 (1)
Zu-S198	05.06.02	roach	133	0.9	CE	92 (25)	73 (7)	nq (26)	nd (5)	78 (1)
Greifensee										
Gr-S301	09.08.02	roach	162	1.2	CE	89 (20)	94 (5)	nq (21)	nd (4)	233 (1)
Gr-S304	09.08.02	roach	146	2.8	CE	118 (13)	60 (4)	nq (14)	nd (3)	201 (1)
Hüttnersee										
Hu-E01	May 02	perch	84	0.4	CE	123 (53)	166 (14)	nq (56)	25 (10)	nd (1)
Hu-S12	08.09.02	roach	412	1.0	CE	66 (24)	44 (6)	nq (25)	nd (5)	4 (1)
Procedural blanks [c] [ng $sample^{-1}$]										
Method Blank ASE					ASE	6.5	8	21	<0.8	<0.2
Method Blank CE					CE	<4.1	<1.1	4.3	<0.8	0.1

[a] Extraction procedure used for the respective sample (ASE = Accelerated Solvent Extraction, 5-g samples; CE = Column Extraction, 20-g samples). CE provided more reliable results (lower detection limits). Therefore for Zürichsee, Greifensee, and Hüttnersee only results from CE-samples are reported. For Thunersee and Pfäffikersee only values for ASE samples were available.

[b] Concentrations of UV filter compounds and methyl triclosan in fish and respective limits of detection (LOD) in parenthesis. LOD is determined from procedural blank and calculated for each sample by taking into account sample size and lipid content. All concentrations are corrected for blank contribution and reported as not detected (nd) if < LOD and as not quantified if > LOD but < 2 LOD.

[c] Note: concentrations in procedural blanks are given in ng per sample!

The analyses of fish from Hüttnersee, Zürichsee, and Greifensee (2 fish each) were then repeated, using column extraction and larger (20-g) samples and tissue with expectedly higher lipid contents. The lipid-based concentrations for methyl triclosan were in the same range as in fish from the first series. The blank levels for this series were lower and corresponded to 4.3 ng per total sample (EHMC) or less (BP-3, 4-MBC, OC). The concentrations of all UV filters in these fish were low (up to 3 ng g^{-1} fish) when corrected for blank contributions. The compounds most frequently detected were 4-MBC and BP-3 (in 6 fish), followed by EHMC (in 2 fish). OC was not detected except in one fish from Hüttnersee. When the concentrations were calculated on a lipid basis, they were up to 166 ng g^{-1} for 4-MBC, up to 123 ng g^{-1} for BP-3, up to 64 ng g^{-1} for EHMC, and <25 ng g^{-1} for OC (**Table 14**). The limits of detection (LOD) were determined by blank contribution, not by the analytical procedure itself. Blank levels were determined per entire sample and therefore blank contribution varied between individual fish samples when calculated as ng per g lipid due to variable lipid contents. LODs are also reported in **Table 14**.

The data indicated that UV filters are detectable in some fish. However, the concentrations were low and only marginally above blank levels, and they did not exceed 100-170 ng g^{-1} on a lipid basis. The data reported in ref (*16*) for roach from a small recreational lake in Germany were in a similar range (BP-3, 230 ng g^{-1}; 4-MBC, 160 ng g^{-1}; EHMC, 40 ng g^{-1}, all lipid based); the concentrations in perch were somewhat higher (BP-3, 300 ng g^{-1}; 4-MBC, 880 ng g^{-1}; EHMC, 310 ng g^{-1}, all lipid based).

4.8 Bioconcentration of 4-MBC and Comparison with Methyl Triclosan in Fish and SPMDs

The uptake mechanisms of lipophilic contaminants by fish are i) passive uptake through water exposed surfaces, mainly gills (*bioconcentration*), and ii) uptake by consumption of food (*biomagnification*). According to various authors (*43-45*), for most contaminants bioconcentration is predominant in lakes, except for highly lipophilic compounds, of which a major fraction is sorbed onto particulate matter. The two compounds that will be discussed in this paragraph, 4-MBC and methyl triclosan, are thus expected to be bioconcentrated rather than biomagnified. Their lipophilic properties and presence in SPMDs (paragraph 4.5) point to a significant bioaccumulation potential.

Methyl triclosan was used as chemical marker for lipophilic persistent WWTP-derived contaminants in fish (see ref (*31*) and paragraph 4.1.2). Its concentrations in fish increased with P/Q ratio of the lakes. Fish from Hüttnersee and Thunersee (P/Q = 0.00 and 0.01 persons m^{-3} d, respectively) showed the lowest methyl triclosan concentrations (<1-4 ng g^{-1}, lipid based), and fish from Greifensee, the lake with the highest domestic burden (P/Q = 0.303 persons m^{-3} d), showed the highest concentrations (200 and 230 ng g^{-1}). Fish from Zürichsee (P/Q = 0.043 persons m^{-3} d) was in-between (78 and 84 ng g^{-1}). Fish from Pfäffikersee showed somewhat lower concentrations (43 and 56 ng g^{-1}) than expected from its P/Q ratio of 0.174 persons m^{-3} d. A linear relationship of P/Q and methyl triclosan in fish was previously described for fish from these lakes (*31*).

The lipophilic properties of 4-MBC, the most frequently detected UV filter in fish, are very similar to those of methyl triclosan (log K_{OW} = 5.1 compared to log K_{OW} = 5.0, ref (*46*)). The comparison of their occurrence in fish and SPMDs may therefore provide additional indications on bioaccumulation of 4-MBC. A comparison of 4-MBC and methyl triclosan in fish is shown in **Figure 10.**

In paragraph 4.5 and **Table 13** we reported the concentrations of 4-MBC and methyl triclosan in SPMDs exposed in the lakes. SPMDs mimic a worst case situation in terms of concentration of lipophilic compounds in aquatic organisms (fish), as there is only passive uptake, but no metabolism. Assuming, that bioconcentration is the dominant uptake process for 4-MBC and methyl triclosan, and that both compounds are not metabolized in fish, the concentration of each compound in fish would expectedly be proportional to its concentration in SPMDs (from the same lake), provided, that fish and SPMDs were exposed to the same concentrations.

Under consideration of equations 1 (concentration in SPMD is proportional to the concentration in water) and 3 (concentration in fish is proportional to the concentration in water), the following relationship would be valid for the concentration C of a compound *i* in water samples, exposed SPMDs, and fish from a lake:

$$C_{i,\text{ water}} \propto C_{i,\text{ SPMD}} \propto C_{i,\text{ fish}} \qquad (5)$$

Consequently, the ratios of 4-MBC concentrations to methyl triclosan concentrations (R = $[C_{4\text{-MBC}}]/[C_{\text{me-triclosan}}]$) in SPMDs ($R_{\text{SPMD}}$) and in fish ($R_{\text{fish}}$) are expected to be similar for a lake. These ratios calculated from the concentrations in **Tables 13** and **14** are listed in **Table 15**.

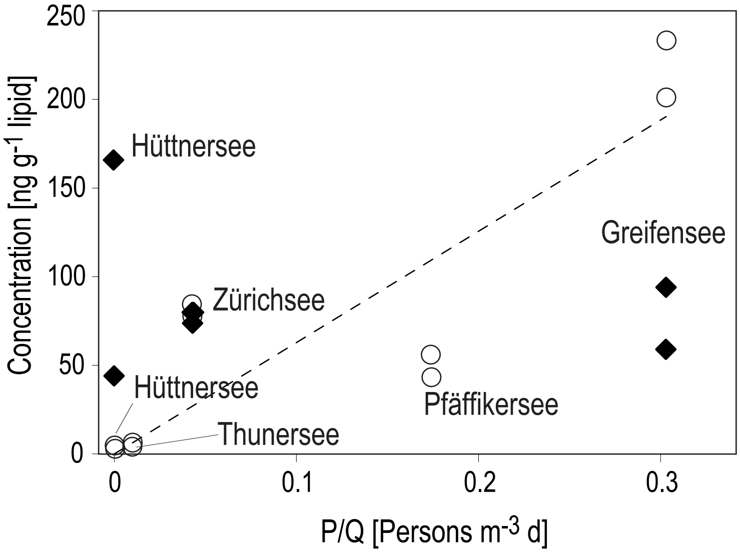


***Figure 10**: Concentrations of methyl triclosan (○) and 4-MBC (♦) in fish (lipid basis) from various lakes vs the respective wastewater load (expressed as P/Q). In contrast to 4-MBC, methyl triclosan concentrations are increasing with P/Q as indicated by the dashed line, suggesting different sources and/or different fate (e.g. metabolism) of the two compounds.*

***Table 15:** Ratios of 4-MBC to methyl triclosan concentrations in SPMDs (R_{SPMD}) and fish (R_{fish})*

	R_{SPMD} ([4-MBC]/[me-triclosan])		R_{fish} ([4-MBC]/[me-triclosan])	
	May	August	min	max
Zürichsee	10	23; 29	0.94	0.95
Greifensee		7.8; 5.1	0.3	0.4
Hüttnersee [a]		>1900	11	> 166
Limmat	6.4	9.1		
WWTP	5.5	5.0		

[a] For Hüttnersee R_{SPMD} and R_{fish} was not defined for all samples, because of methyl triclosan concentrations below LOD.

In all SPMDs deployed in the lakes, the river Limmat, and in the effluent of WWTP Werdhölzli, the concentrations of 4-MBC clearly exceeded those of methyl triclosan ($R_{SPMD} > 1$). R_{SPMD} was ~5-8 for Greifensee, 10-30 for Zürichsee, 6-9 for Limmat, and ~5 for the WWTP effluent. For SPMDs from Hüttnersee the ratio could not be properly calculated, because methyl triclosan concentrations were below the detection limit; the highest 4-MBC concentrations, however, were measured in this lake (>1900 ng SPMD^{-1}). The ratios derived from 4-MBC and methyl triclosan in fish were significantly smaller than those observed in the SPMDs from the same lake ($R_{fish} << R_{SPMD}$), the concentrations of 4-MBC in fish were thus lower than expected from the SPMD data.

Although the exposure conditions of SPMDs and fish were not exactly the same with respect to time (3-weeks exposures of SPMDs during summer or spring versus life-long exposures for fish) and location (SPMD, fixed at one location in surface water of the lake; fish, migrating between surface water and deeper regions of a lake), it is still reasonable to compare the fish and SPMD data for the following reasons: First, it is generally assumed that equilibrium concentrations of compounds with a moderate lipophilicity in fish is attained reasonably fast (within days to weeks (*45*)) which would suggest that the duration of an exposure would not be too important. Second, all fish for which a comparison was made were collected during the warmer season (May through September) when inputs of UV filters were largest, and during the time when we also exposed most of the SPMDs. Third, the data from the SPMDs exposed in Zürichsee in April/May also showed a much higher ratio than in fish. At this time the lake was not fully stratified and the SPMD data thus indicates that the relative concentrations under a mixed lake situation in spring cannot be completely different from a summer situation. The lower concentrations of 4-MBC relative to methyl triclosan in fish suggest that 4-MBC is less bioaccumulated than expected form the SPMD data, likely as a result of some metabolism in fish and/or less uptake of the compound from water. However, to our knowledge, these issues were not studied so far.

5 Outlook

In this study we reported on the presence of four important organic UV filters (BP-3, 4-MBC, EHMC and OC) in influent- and effluent-samples from WWTPs. Comparison of estimated input loads of UV filters to Zürichsee showed that both, *indirect inputs* via WWTPs and *direct inputs* from swimming and bathing in the lake are important. In agreement with a previous study, the UV filter concentrations in surface waters (various Swiss lakes and river Limmat), were in the low nanogram per liter range and thus (as shown for 4-MBC) lower than expected from input estimates, indicating some elimination of the compounds in surface waters. Comparison of concentrations of 4-MBC and methyl triclosan (a chemical marker for lipophilic WWTP-derived contaminants) in semipermeable membrane devices (SPMDs) supported the importance of direct inputs. In fish some of the UV filters were present in detectable amounts, in particular 4-MBC. However, the concentrations were lower than expected from SPMD data, suggesting less uptake and/or some metabolism of 4-MBC in fish.

Despite these insights, there are still numerous open questions concerning the fate and behavior of UV filter compounds in WWTPs and in the environment, particularly the occurrence and importance of various elimination mechanisms and removal processes from lake water besides flushing and sedimentation. It is not known so far, whether there are any relevant metabolites. Studies on uptake and metabolism of the compounds in aquatic organisms, particularly fish are not available in the open literature. Additionally, the presence of these compounds in other fish species (i.e. predatory species, such as perch), and possible biomagnification within the foodchain should be investigated in more detail.

One of the UV filter, 4-MBC, proves to be of special interest for several reasons: i) it is one of the most frequently used organic UV filters, ii) it is the most persistent of the investigated UV filters, and, therefore most prevalent in WWTP effluents, surface waters and fish, and iii) reliable analytical procedures for the various compartments were established within this study (i.e. no blank problems). Further studies should, therefore, focus on 4-MBC. The compound is chiral, the technical product consists of a racemic mixture of the two enantiomers. In contrast to the *E*/*Z* isomer ratio, entantiomer ratios are not affected by abiotic processes. The ratios of the enantiomers in/on various matrices such as skin, surface water, wastewater, or fish would be of major interest, because of their expectedly different environmental and biological behavior such as biodegradation, metabolism or effects.

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