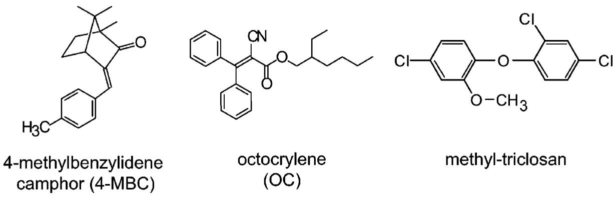
Occurrence of UV Filters 4-Methylbenzylidene Camphor and Octocrylene in Fish from Various Swiss Rivers with Inputs from Wastewater Treatment Plants

HANS-RUDOLF BUSER,[†]
MARIANNE E. BALMER,[*,†]
PETER SCHMID,[‡] AND MARTIN KOHLER[‡]
Agroscope FAW, Swiss Federal Research Station, Plant Protection Chemistry, CH-8820 Wädenswil, Switzerland, and Swiss Federal Laboratories for Materials Testing and Research (Empa), Laboratory of Organic Chemistry, CH-8600 Dübendorf, Switzerland

UV filters are widely used compounds in many personal care products and cosmetics, such as sunscreens. After use, UV filters are washed off from skin and clothes and enter the aquatic environment. Recent studies indicate that some lipophilic UV filters do accumulate in biota and act as endocrine disruptors. In this study, concentrations of 4-MBC (4-methylbenzylidene camphor) and OC (octocrylene), two widely used UV filters, were determined in the muscle tissue of fish (brown trout, *Salmo trutta fario*) from seven small Swiss rivers, all receiving inputs from wastewater treatment plants (WWTPs). Lipid-weight based concentrations of up to 1800 (4-MBC) and 2400 ng g^{-1} (OC) were found. These levels were distinctly higher than those previously observed in white fish (*Coregonus* sp.) and roach (*Rutilus rutilus*) from Swiss lakes with inputs from WWTPs. This suggests a higher availability of these contaminants for fish in rivers than in lakes and identifies WWTPs as a major source for UV filters in the aquatic environment. As compared to lake fish, individual fish from a river showed much greater variation in 4-MBC and OC concentrations, likely as a result of a wider range of exposure in rivers than in lakes. 4-MBC concentrations correlated reasonably well with concentrations of methyl triclosan, a chemical marker for lipophilic WWTP-derived contaminants. The ratio *P*/*Q* of population (*P*) in a watershed to water throughflow (*Q*) is considered to be a measure of the domestic burden from WWTPs. A correlation of methyl triclosan with *P*/*Q* was previously observed with lake fish. However, such a correlation could not be confirmed with river fish. The higher average concentrations of OC as compared to 4-MBC in river fish, and the fact that OC was mostly absent in lake fish, suggests differences in bioaccumulation and availability of these two UV filters.

Introduction

UV filters are ingredients used for sunscreens, skin creams, shampoos, lipsticks, and many other personal care products and cosmetics. Annual production figures for UV filters are estimated to be in the hundreds of tons. After use, they are washed from skin and clothes and enter the aquatic environment either via wastewater treatment plants (WWTPs) or directly from recreational activities (bathing, swimming). UV filters such as 4-MBC (3-(4′-methyl-benzylidene)bornan-2-one; 4-methylbenzylidene camphor) and OC (2-cyano-3,3-diphenyl-2-propenoic acid 2-ethylhexyl ester; octocrylene) are lipophilic (octanol/water partition coefficients, log K_{OW}, 5.1 for 4-MBC and 6.9 for OC) and chemically reasonably stable (for chemical structures, see Figure 1). Octanol/water distribution coefficients in this range do, for chemically stable components, translate into some potential for bioaccumulation.



4-methylbenzylidene camphor (4-MBC)
octocrylene (OC)
methyl-triclosan

FIGURE 1. Chemical structures of UV filters 4-MBC ((*E*)-isomer) and OC and of the chemical marker methyl triclosan.

Fish are a primary organism to monitor the occurrence of persistent lipophilic contaminants (*1*). Recently, we reported the presence of four of the most common organic UV filters (4-methylbenzylidene camphor, 4-MBC; octocrylene, OC; benzophenone-3, BP-3; and ethylhexyl methoxy cinnamate, EHMC) in fish (white fish, *Coregonus* sp. and roach, *Rutilus rutilus*) from various Swiss lakes (*2*). Currently, however, data on the occurrence of UV filters in environmental and biological samples are still scarce. In light of increasing concern that some UV filters (4-MBC) may act as endocrine disruptors (*3*) and because of the significant amounts of these chemicals being used today, there is a need for a better understanding of the occurrence and environmental fate of UV filters.

In this study, we explored the origin of these contaminants by probing fish (brown trout, *Salmo trutta fario*) from seven Swiss rivers, all receiving inputs from WWTPs. The fish were caught between 0.1 and 0.7 km downstream of WWTPs. In this environment, high concentrations of UV filters are expected, reflecting a worst case situation. The concentrations of UV filters in fish from these locations were then compared to those in fish from lakes, and the relation between concentrations of UV filters and methyl triclosan, a chemical marker for lipophilic WWTP-derived contaminants (*4*), formed from the bactericide triclosan upon wastewater treatment, was investigated. On the basis of these considerations, we tried to shed some more light on the role of WWTPs as sources of UV filters, on the bioaccumulation processes of UV filters in fish, as well as on the differences in the lipid-based tissue concentrations between lake and river-based species.

Experimental Section

Sampling Sites. The sampling sites were on typical smaller rivers in Northern Switzerland that receive inputs from WWTPs. Sampling sites and characteristic properties of these rivers are given in Table 1. Except river #2 (Glatt), with a water throughflow of 1.7 m^3 s^{-1}, water throughflows of all other rivers were below 1 m^3 s^{-1} (0.05−0.95 m^3 s^{-1}). Flow rates reported are estimated Q_{347} water through flow rates at times of drought, representing flow rates exceeded on 347

---

[*] Corresponding author phone: +41 44 783 6222; fax: +41 44 783 6439; e-mail: marianne.balmer@faw.admin.ch.

[†] Swiss Federal Research Station.

[‡] Swiss Federal Laboratories for Materials Testing and Research.

10.1021/es052088s CCC: $33.50
© xxxx American Chemical Society
Published on Web 01/18/2006

TABLE 1. Sampling Sites and Characteristic Properties of Rivers

river	location WWTP	sampling location[a] (km)	population P^b (persons)	river flow $Q_{347}{}^b$ (m^3 s^{-1})	WWTP flow $Q_T{}^b$ (m^3 s^{-1})	wastewater contribution (%)[c]	population/river flow P/Q (persons m^{-3} day)
#1 Lützelmurg	Aadorf	+0.5	14000	0.13	0.087	40	1.25
#2 Glatt	Dübendorf	+0.7	48000	1.67	0.334	17	0.33
#3 Frenke	Niederdorf	+0.7	12000	0.09	0.065	42	1.56
#4 Langete	Rohrbach	+0.5	12000	0.95	0.048	5	0.15
#5 Sissle	Frick	+0.5	9000	0.12	0.040	25	0.87
#6 Surb	Ehrendingen	+0.3	12000	0.15	0.060	29	0.93
#7 Winkelbach	Inwil	+0.1	6600	0.05	0.064	56	1.53

[a] Distance downstream from WWTP discharge. [b] P: population equivalents on the basis of 5 day biological oxygen demand BOD5 (BOD5-based population equivalents were calculated on a basis of 60 g per person and day.); Q_{347}: flow rate of the river in m^3 s^{-1} at times of drought, exceeded at 347 days of the year; Q_T: average dry weather effluent discharge in m^3 s^{-1} (data provided by Swiss Cantons (*5*)). [c] Amount of wastewater as compared to total river flow in %: estimated as $Q_T/(Q_{347} + Q_T)100$.

TABLE 2. Concentrations (ng g^{-1} lipid weight) of UV Filters 4-MBC and OC and of the Chemical Marker Methyl Triclosan (MeTri) in Fish from Various Small Rivers in Switzerland with Inputs from WWTPs

			concentrations (ng g^{-1} lw)			ratios	
river/sample/date	fish weight (g)	lipid (%)	4-MBC	OC	MeTri	4-MBC/MeTri	OC/MeTri
#1 Lützelmurg							
A1-005 May 2003	n.a.	2.4	280	150	660	0.42	0.23
A1-010 May 2003	n.a.	3.4	140	105	410	0.33	0.26
A1-012 Sep 2003	39	1.8	250	540	810	0.31	0.67
A1-014 Sep 2003	62	2.8	190	500	480	0.40	1.02
A1-016 Sep 2003	30	0.62	170	440	410	0.42	1.06
#2 Glatt							
G1-003 Sep 2003	27	3.0	65	150	320	0.21	0.46
G1-005 Sep 2003	30	2.4	350	950	1300	0.27	0.74
G1-006 Sep 2003	31	2.9	590	2400	1300	0.44	1.80
#3 Frenke							
N1-002 Sep 2003	57	1.9	350	1700	1300	0.27	1.30
N1-004 Sep 2003	61	2.5	50	140	200	0.24	0.68
N1-005 Sep 2003	59	3.8	70	40	130	0.54	0.30
#4 Langete							
L1-003 Sep 2003	46	1.5	1800	430	340	5.37	1.30
L1-006 Sep 2003	50	1.7	770	230	340	2.28	0.67
#5 Sissle							
F1-001 Sep 2003	43	1.2	930	990	590	1.60	1.70
#6 Surb							
S1-002 Sep 2003	35	1.7	200	380	680	0.30	0.56
S1-004 Sep 2003	51	1.5	250	450	1100	0.23	0.41
S1-006 Sep 2003	60	2.4	160	370	540	0.30	0.68
#7 Winkelbach							
I1-002 Sep 2003	35	1.9	1100	1400	2100	0.50	0.65
I1-003 Sep 2003	55	2.0	260	710	350	0.75	2.00
Average							
$n = 19$ samples	45	2.2	420	630	700	0.80	0.86
$n = 16$ samples[a]	45	2.3	280	650	760	0.37	0.80

[a] All samples except fish from rivers #4 and #5.

days per year and thus a worst-case situation. The WWTPs located on these rivers serve populations between 6600 and 48 000 persons (on the basis of a 5 day biological oxygen demand BOD5, calculated on a basis of 60 g per person and day) and operate with three to four stages (*5*). This includes mechanical, biological (activated sludge, mostly with nitrification and partially with denitrification), and chemical treatment (with phosphate precipitation by iron salts) and, in most cases, subsequent sand filtration. The treated wastewater flows Q_T discharged by these installations under dry weather conditions ranges from 0.04−0.33 m^3 s^{-1}, corresponding to 0.3−0.8 m^3 per person and day, and represents typical water consumption rates in Switzerland. For each river, an estimate of the percentage of wastewater (based on Q_{347} and Q_T) is given in Table 1. Estimated wastewater contributions in these rivers range between 5 and 56%. All fish from a particular river were collected at distances between 0.1 and 0.7 km downstream of WWTP discharge points, representing a worst-case situation for exposure of fish to WWTP-derived contaminants.

River Fish. Male fish (brown trout, *S. trutta fario*) from seven small rivers were analyzed, as shown in Table 2. One to five fish per river were sampled, and each fish was analyzed individually. All fish were between 1 and 2 years of age (age determination by scale reading) and collected in September 2003, except for river #1, where additional fish from an earlier campaign (May 2003) were analyzed for comparative purposes. The fish from the September campaign were expected to have experienced a typical end of summer and thus worst-case situation with respect to UV filters from an increased use of sunscreens in summer.

Lake Fish. Data from an earlier study in lake fish (white fish, *Coregonus* sp. and roach, *R. rutilus*) are discussed. These fish were analyzed by different methods but yielded comparable data (*2*). As compared to the river fish (brown trout), lake fish (white fish and roach) are on a lower trophic level. Since trout were only available in rivers and white fish and roach were available in lakes, it was not possible to investigate the same fish species in both studies. Thus, some differences between species with respect to, for example, bioaccumulation factors or metabolism cannot be excluded.

Analytical Methods. Fish filets were separated from the skin with a knife, and the skin was scraped to collect the lipids under the skin. Between 10 and 25 g of filet and scraped tissue was suspended in 100 mL of ultrapure water and pureed with a hand blender. The fine suspension was transferred quantitatively into a 2 L separation funnel and fortified with 10 ng of $^{15}N_3$-musk xylene (prepared according to ref *6*) and extracted (shaking 1 min each time) with a mixture of dipotassium oxalate (2 mL, 35%), ethanol (100 mL), diethyl ether (50 mL), and *n*-pentane (70 mL) (*7*). The lipid content was determined gravimetrically. Following extraction, lipids were removed by gel permeation chromatography (Biobeads S-X3, 30 × 2.5 cm column, elution with 5 mL min^{-1} of a 1:1 mixture of cyclohexane/ethyl acetate, sample collection time from 18 to 38 min). Solvents were evaporated to 1 mL. Isooctane (2 mL) and hexane (5 mL) were added, and the volume was reduced again to 2 mL. Further cleanup was performed on silica gel columns (5 g + 1 g of Na_2SO_4 on top of the column). After conditioning (5 mL) and sample loading, the silica gel column was eluted with 35 mL of hexane (fraction #1), then with 40 mL of a 1:1 mixture of hexane/dichloromethane (fraction #2) and 40 mL of dichloromethane (fraction #3). UV filters were contained in fractions #2 and #3. For the determination of UV filters, 10% each of fractions #2 and #3 were recombined, and the volume was reduced to 100 μL.

Samples were analyzed by gas chromatography−mass spectrometry (GC−MS) using a VG Tribrid magnetic sector mass spectrometer (Mass Lab Group, Manchester, UK) with electron-impact ionization (EI) at an electron energy of 55 eV. Data were acquired in full-scan (*m*/*z* 35−435, 1.16 s/scan) or selected-ion-monitoring (SIM) mode (details are given in ref *2*). In SIM mode, the following ions were used to monitor UV filters (quantification and confirmation ions, respectively): *m*/*z* 254.17 and 239.14 (4-MBC), 249.08 and 361.20 (OC), 303.97 and 301.97 (methyl triclosan), and 285.06 ($^{15}N_3$-musk xylene). The amounts of analyte were determined from peak area ratios relative to the internal standard ($^{15}N_3$-musk xylene). The concentrations of 4-MBC were reported as the sum of (*Z*)- and (*E*)-4-MBC. Detection limits varied between samples depending upon lipid content but were in the order of 5−20 ng g^{-1} (lipid weight, lw) for 4-MBC and OC and 2−10 ng g^{-1} (lw) for methyl triclosan. Special care was taken to keep blank levels low. Typical method blank levels were 6−10 ng per sample for 4-MBC and <2 ng per sample for methyl triclosan. Data are reported as lipid-weight-based concentrations (lw).

Results and Discussion

4-MBC Present in River Fish and Lake Fish. 4-MBC was detected in all river fish at concentrations ranging from 50 to 1800 ng g^{-1} lw (average, 420 ng g^{-1}), as reported in Table 2. These levels were mostly higher than those previously observed in lake fish, ranging from below 20 to 170 ng g^{-1} lw (average 86 ng g^{-1}). The mostly higher 4-MBC concentrations in river fish were not unexpected because of the large contributions of wastewater to these rivers. There is little difference between the levels in fish from the May and September campaigns carried out in river #1.

For rivers #1, #4, and #6, the 4-MBC concentrations of individual fish from the same river were within factor of 2−3. In fish from rivers #2, #3, and #7, however, wider concentration ranges of 4-MBC exceeding a factor of 4 were encountered. As an example, two fish from river #2 showed reasonably high concentrations of 4-MBC (350 and 590 ng g^{-1} lw), while a third fish had a much lower concentration (65 ng g^{-1} lw). The 4-MBC concentration in the latter fish, however, was still within the range of fish from lake Greifensee, the origin of river #2 (*2*). These data demonstrate that there is much greater variation in 4-MBC concentrations in river fish than in lake fish and suggests that individual fish may have experienced different exposure despite the fact that all fish were of similar age and collected at the same site. As shown next, this was also observed for the concentrations of methyl triclosan in river fish. On the basis of these data, we conclude that there is a much greater variation in actual exposure toward UV filters and methyl triclosan of fish in a river than in a lake. Whether this is due to migration of the fish (between cleaner and more contaminated waters) or by other factors is not clear yet.

OC Present in River Fish but Mostly Absent in Lake Fish. All river fish showed the presence of OC at concentrations ranging from 40 to 2400 ng g^{-1} lw (average, 630 ng g^{-1}) as reported in Table 2. Comparing the samples taken in May and September in river #1, there is an indication for a seasonal dependence of OC concentrations, probably reflecting the increased use of sunscreens during summer. Lipid-weight-based tissue concentrations of OC were 3−5 times higher in fish samples from the September sampling campaign (440−540 ng g^{-1} lw) as compared to the May campaign (105 and 150 ng g^{-1} lw). In most, although not all, river fish, the concentrations of OC were higher than those of 4-MBC (14 out of 19 samples). This is different from the situation with lake fish, where OC was not present except in fish from one lake (Hüttnersee, 25 ng g^{-1} lw, see ref *2*) and suggests a generally lower availability of OC in lakes. Possible explanations for such an observation include substance-specific transport, sorption, and degradation processes as well as biological factors such as different uptake rates and metabolic processes for the two compounds.

Methyl Triclosan as a Chemical Marker for WWTP-Derived Lipophilic Contaminants. Methyl triclosan is discharged by wastewater treatment plants (WWTPs), originating from microbial transformation of triclosan, a widely used disinfectant in personal care products, textiles, and plastics. Because of its ubiquitous presence, methyl triclosan was proposed as a chemical marker for lipophilic contaminants from WWTPs (*4*). As shown in Table 2, methyl triclosan was present in all river fish samples, indicating that these fish were indeed exposed to wastewater. Methyl triclosan concentrations in river fish ranged from 130 to 2100 ng g^{-1} lw and were mostly higher than those previously observed in lake fish (range, 4−370 ng g^{-1}, see ref *4*). This is not unexpected considering the fact that the river fish were caught just below the discharge points of WWTPs. The concentrations also seem reasonable when compared to those reported for river fish in another study on breams (*Abramis brama*) from German rivers when compared on a wet weight basis (up to 39 ng g^{-1} in our study, up to 26 ng g^{-1} in ref *8*). As for the UV filters, significant variations in methyl triclosan concentrations of fish from the same river are observed.

Correlation of 4-MBC and OC with Methyl Triclosan. Concentration ranges and average concentrations for 4-MBC, OC, and methyl triclosan in river and lake fish are summarized in Table 3. Usually, although not in every single case, UV filter concentrations in river fish increased with methyl triclosan concentrations. In Figure 2, we plot lipid-based concentrations of 4-MBC and OC in fish versus those of methyl triclosan. The plots suggests some correlation for

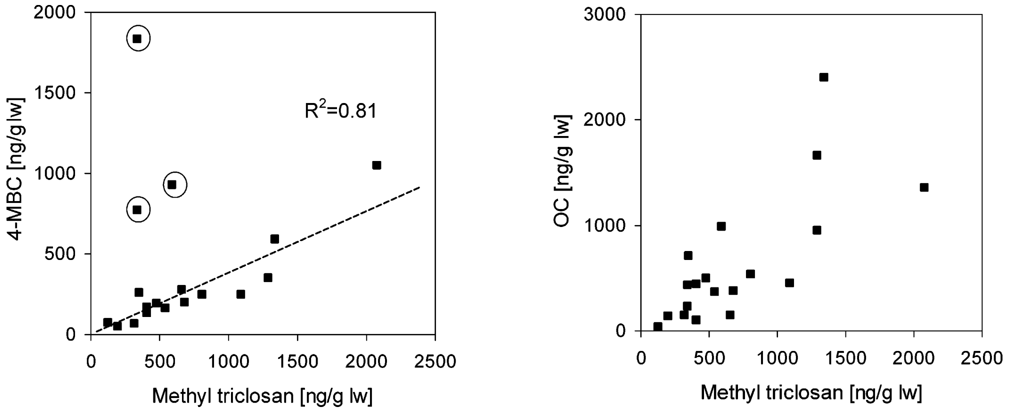


FIGURE 2. Concentrations (ng g^{-1} lw) of UV filters 4-MBC (left panel) and OC (right panel) vs methyl triclosan in brown trout from small rivers. For concentrations of 4-MBC and methyl triclosan, a reasonable correlation ($R^2 = 0.81$, dashed line) was found, when data from rivers #4 and #5 (indicated by circles) with extraordinary high 4-MBC concentrations were excluded. For concentrations of OC and methyl triclosan, a positive trend but no significant correlation ($R^2 = 0.54$) was observed.

TABLE 3. Concentration Ranges and Average Concentrations (ng g^{-1} lipid weight) of UV Filters 4-MBC and OC as Well as Chemical Marker Methyl Triclosan (MeTri) in River Fish (Brown Trout) as Compared to Swiss Lake Fish (White Fish and Roach)

species	4-MBC range (av) (ng g^{-1} lw)	OC range (av) (ng g^{-1} lw)	MeTri range (ng g^{-1} lw)
river fish	50−1800 (420)	40−2400 (630)	130−2100
lake fish	<20−170 (86)	n.d.[a]	4−370

[a] The concentrations of OC in lake fish were below the limit of detection (varying between samples with lipid content, 3 < LOD < 60) in all but one sample (Hüttenersee, 25 ng g^{-1} lw).

4-MBC with methyl triclosan but less so for OC. As shown in Table 2, the actual concentration ratios of 4-MBC versus methyl triclosan in fish from five rivers (#1−3, #6, and #7) were within a reasonably narrow range (0.21−0.75, mean/standard deviation: 0.37 ± 0.14) and similar to the ratios of fish from lake Greifensee (0.3 and 0.4), a lake receiving inputs of UV filters mainly from WWTPs (*2*). However, fish from rivers #4 and #5 showed unusual high 4-MBC to methyl triclosan ratios (1.6 −5.4), suggesting a different exposure situations for these fish. These data points represent the three outliers in Figure 2 (left panel). Such high ratios suggest far greater exposure to 4-MBC than from treated wastewater alone. In principle, this could result from discharges of untreated wastewater during heavy rain and storm events, when the capacities of WWTPs are exceeded (overflows), resulting in higher emissions of UV filters (reduced elimination) and lower emissions of methyl triclosan (lower conversion from triclosan). Up to now, a specific explanation for these increased 4-MBC/methyl triclosan ratios could not be found. Higher 4-MBC to methyl triclosan ratios were also observed in some lake fish (0.9−1.0 in roach from lake Zürichsee, see ref *2*) and, in that case, attributed to additional (direct) inputs of 4-MBC to this lake from recreational activities.

***P*/*Q* Concept and Methyl Triclosan as a Chemical Marker in River Fish.** Provided that there is a similar usage by a population, and similar emission characteristics of WWTPs, the concentration of a persistent lipophilic contaminant in an aquatic system (C_{water}) and eventually in fish (C_{fish}) is expected to be proportional to the population (*P*, number of persons in the watershed) and inversely proportional to the water throughflow of the aquatic system (*Q*, m^3 day$^-$1, see refs *4* and *9*).

$$C_{\mathrm{fish}} = \mathrm{BCF_L}\, C_{\mathrm{water}} = \mathrm{BCF_L}\, f\, P/Q \tag{1}$$

As shown in eq 1, the concentration of a lipophilic contaminant in fish C_{fish} (lw) may be estimated based on the *P*/*Q* ratio, the compound-specific, lipid based bioconcentration factor $\mathrm{BCF_L}$, and a proportionality factor *f*, assuming steady-state concentrations in the aquatic system and bioconcentration as the main uptake process by fish.

The relative contributions of wastewater to the total water throughflow of the rivers were calculated from the average dry weather effluent discharge of the respective WWTPs (Q_{T}) and the flow rate of the rivers (Q_{347}) as Q_{T} divided by ($Q_{\mathrm{T}} + Q_{347}$). The relative wastewater contribution was between 5% (river #4) and 56% (river #7). *P*/*Q* ratios estimated from population equivalents based on biological oxygen demand (BOD5) and available waterflow data (Q_{347}) ranged from 0.15 to 1.53 persons m^{-3} day, as shown in Table 1. These ratios are mostly larger than those of typical Swiss lakes (maximum *P*/*Q* for lake Greifensee: 0.3 persons m^{-3} day) (*9*), and higher exposure of fish toward anthropogenic contaminants from WWTPs is anticipated. The *P*/*Q* ratios calculated here represent maximum values for the anthropogenic burden from the WWTP under investigation. Because there are further WWTPs upstream and/or downstream of actual sampling sites in some river systems, in particular for river #5 with two WWTP upstream and river #2 with lake Greifensee and one additional WWTP upstream, the actual burden, and therefore the *P*/*Q* ratios may differ from those reported in Table 1. Consequently, migrating fish from these rivers may have experienced different exposures during their lifetime than indicated by the *P*/*Q* ratios reported.

For lake fish, a correlation was observed between the methyl triclosan concentration and the *P*/*Q* ratio of the lake (*4*). In principle, a similar correlation is expected for river fish with concentrations increasing with the contribution of wastewater to a river or *P/Q*, respectively. However, no such correlation was detected with river fish when using the data from Table 1. A possible explanation for the missing correlation is that the Q_{347} based *P*/*Q* ratios do not reflect actual integrated hydraulic throughflow data (which are not available from the rivers investigated) with sufficient accuracy. Furthermore, individual fish from some rivers showed larger differences in concentrations of UV filters and methyl triclosan than lake fish, suggesting greater variability in the actual exposure in such rivers. Nevertheless, the presence of methyl triclosan in all these fish clearly indicates that all fish were exposed to lipophilic contaminants from WWTPs, and it can be concluded that river fish are exposed to higher levels of these chemicals than lake fish.

Different Concentrations of UV Filters in River and Lake Fish. Most river fish showed higher lipid based tissue concentrations of 4-MBC, OC, and methyl triclosan than lake fish. This may be due to (i) higher contaminant concentrations (P/Q) in these rivers than in lakes, (ii) higher bioaccumulation of these contaminants in fish from rivers than in fish from lakes, (iii) species differences with respect to metabolic processes, or (iv) a combination of such reasons.

In a previous study, we used semipermeable membrane devices (SPMDs) as a model system to investigate the bioaccumulation potential of 4-MBC and methyl triclosan (*2*). SPMDs are designed for integrative sampling of nonpolar organic chemicals from water and air. They consist of a neutral, high molecular weight lipid (triolein), encased in a layflat polyethylene membrane tube (e.g., refs *10* and *11*). In this earlier study, we observed lower concentrations of 4-MBC relative to methyl triclosan in fish (roach) from lakes with inputs from WWTPs than measured by SPMDs in the respective lakes. This suggested that 4-MBC is less bioaccumulated in lake fish than expected, likely as a result of metabolism in fish or less uptake of the compound from water, resulting in ratios of 4-MBC to methyl triclosan between 0.3 and 1. The very similar ratios of 4-MBC to methyl triclosan observed now in most although not all river fish suggest similar exposure routes for these fish.

The situation is different for OC in river and lake fish. Whereas OC was observed in lake fish in only one case, OC was observed in all river fish at concentrations sometimes exceeding those of 4-MBC. This suggests a very different bioaccumulation behavior of this more lipophilic compound by different fish (biomagnification) and/or lower concentrations of OC relative to 4-MBC in lakes than in rivers and probably also a lower bioavailabilty of this compound. Assuming that the relative inputs of these UV filters from WWTPs into rivers are similar to that into lakes, lower concentrations of OC relative to 4-MBC in lakes would require the selective elimination of the more lipophilic UV filter (OC) from water. Such elimination cannot be due to flushing (or dilution) because this would affect both compounds in the same way. However, other processes such as sorption/sedimentation could favor an elimination of the more lipophilic OC. Estimates for sedimentation rates in lakes, based on K_{OC} values (estimated from log K_{OW} values of 5.1 for 4-MBC and 6.9 for OC), typical particle concentrations (particulate organic carbon POC, 0.2−0.5 mg L^{-1}), and settling velocities, do indicate much higher rates for OC (0.008−0.07 day^{-1}) than for 4-MBC (0.0001−0.002 day^{-1}), the rates for OC clearly exceeding those for flushing from the lakes (Zürichsee and Greifensee, $k_w = 0.0023$ and 0.0024 day^{-1}, respectively (*12*), as calculated according to ref *13*). Presently, however, we have no information on the relevance of this or other potential elimination processes (chemical, biological, photochemical degradation, vaporization) for UV filters in surface waters. With the exception of vaporization, all these processes, however, seem to be less important in rivers than in lakes, due to the longer residence times in lakes.

Therefore, it is presently still not clear whether selective elimination from surface water in lakes and/or different bioaccumulation or metabolic processes in different fish species are responsible for the generally higher concentrations and the changed UV filter composition in river and lake fish. Further studies will be needed to elucidate the actual processes that are involved and determine to what extent they affect the fate of these UV filters in the environment and in biota. Nevertheless, the data clearly indicate that river fish experience a much worse situation with respect to exposure to UV filters, methyl triclosan and, likely, to other lipophilic contaminants than lake fish do.

Acknowledgments

Patricia Burkhardt-Holm and Etienne Vermeirssen are acknowledged for sharing the brown trout samples taken for the project SAFE (endocrine disruption in Switzerland: assessment of fish exposure and effects). Caroline Joris, Richard Burki, Erwin Schäffer, Etienne Vermeirssen, and Andreas Gerecke are acknowledged for organization and contributions in the fishing campaign. We thank Etienne Vermeirssen for contributions to the manuscript, Caroline Joris for the age determination of the fish, and Andreas Gerecke for his contributions to sample preparation.

Literature Cited

(1) U.S. EPA: National lake fish tissue study 2005; http://epa.gov/waterscience/fishstudy/overview.htm.

(2) Balmer, M. E.; Buser, H.-R.; Müller, M. D.; Poiger, T. Occurrence of some organic UV filters in wastewater, in surface waters, and in fish from Swiss lakes. *Environ. Sci. Technol.* **2005**, *39*, 953−962.

(3) Schlumpf, M.; Cotton, B.; Conscience, M.; Haller, V.; Steinmann, B.; Lichtensteiger, W. In vitro and in vivo estrogenicity of UV screens. *Environ. Health Perspect.* **2001**, *109*, 239−244.

(4) Balmer, M. E.; Poiger, T.; Droz, C.; Romanin, K.; Bergqvist, P.-A.; Müller, M. D.; Buser, H.-R. Occurrence of methyl triclosan, a transformation product of the bactericide triclosan, in fish from various lakes in Switzerland. *Environ. Sci. Technol.* **2004**, *38*, 390−395.

(5) Vermeirssen, E. L. M.; Burki, R.; Joris, C.; Peter, A.; Segner, H.; Suter, M. J.-F.; Burkhardt-Holm, P. Characterization of the estrogenicity of Swiss Midland rivers using a recombinant yeast bioassay and plasma vitellogenin concentrations in feral male brown trout. *Environ. Toxicol. Chem.* **2005**, *24*, 2226−2233.

(6) Müller, S.; Schmid, P.; Schlatter, C. Occurrence of nitro and non-nitro benzenoid musk compounds in human adipose tissue. *Chemosphere* **1996**, *33*, 17−28.

(7) Fürst, P.; Fürst, C.; Meemken, H. A.; Groebel, W. Procedure for the determination of polychlorinated dibenzodioxines and dibenzofurans in breast milk. *Z. Lebensm.-Unters.-Forsch.* **1989**, *189*, 338−345.

(8) Boehmer, W.; Ruedel, H.; Wenzel, A.; Schroeter-Kermani, C. Retrospective monitoring of triclosan and methyl-triclosan in fish: Results from the German Environmental Specimen Bank. *Organohalogen Compd.* **2004**, *66*, 1516−1521.

(9) Buerge, I. J.; Poiger, T.; Müller, M. D.; Buser, H.-R. Caffeine, an anthropogenic marker for wastewater contamination of surface waters. *Environ. Sci. Technol.* **2003**, *37*, 691−700.

(10) Huckins, J. N.; Manuweera, G. K.; Petty, J. D.; Mackay, M.; Lebo, J. A. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **1993**, *27*, 2489−2496.

(11) Huckins, J. N.; Petty, J. D.; Lebo, J. A.; Orazio, C. E.; Prest, H. F.; Tillitt, D. E.; Ellis, G. S.; Johnson, B. T.; Manuweera, G. K. In *Techniques in aquatic toxicology*; Ostrander, G. K., Ed.; CRC Press: Boca Raton, FL, 1996; pp 625−655.

(12) Liechti, P. *Der Zustand der Seen in der Schweiz*; BUWAL: Bern, 1994; Vol. No. 237: Gewässerschutz.

(13) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley: New York, 1993.

Received for review October 20, 2005. Revised manuscript received December 7, 2005. Accepted December 7, 2005.

ES052088S