

Occurrence and Mass Flows of Fluorochemicals in the Glatt Valley Watershed, Switzerland

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Fluorochemicals are persistent contaminants that are globally distributed in air, water, sediments, and biota. Wastewater treatment plants (WWTPs) play an important role in mitigating pollutant releases from municipalities to aquatic and terrestrial environments. However, because WWTPs are point sources of fluorochemicals, it is important to understand their contribution to fluorochemical burdens in the greater context of watersheds. To this end, over a 1 week period, the mass flows of 11 fluorochemicals from seven WWTPs that discharge effluent into the Glatt River in Switzerland were measured and compared to the measured mass flows within the Glatt River. Overall, the fluorochemicals were not removed efficiently during wastewater treatment. Effluents from WWTPs and Glatt River water were dominated by perfluorooctane sulfonate, which was detected in all samples, followed by perfluorohexane sulfonate and perfluorooctanoate. The mass flows of fluorochemicals emanating from WWTPs were found to be conserved within the 35 km Glatt River, which indicates that input from the WWTPs is additive and that removal within the Glatt River is not significant. Per capita discharges of fluorochemicals were calculated from the populations served by the WWTPs studied; the values determined also account for the fluorochemical content of Lake Greifen (Greifensee), which is a lake at the headwaters of the Glatt River that also receives treated wastewater.

Introduction

Measurements of direct inputs of fluorochemicals to the environment via the discharge of municipal wastewater treatment plant (WWTP) effluents indicate that WWTPs are point sources of fluorochemicals. Municipal wastewaters

contain fluorochemicals due to the use of fluorochemicals in household cleaners (1) and products applied to improve stain resistance (2, 3), and in some cases, municipalities treat landfill leachates that contain high levels of fluorochemicals (4). Unfortunately, conventional biological/mechanical wastewater treatment has limited effectiveness in removing fluorochemicals from aqueous waste streams, and therefore, WWTPs are point sources for fluorochemicals that enter the environment (3, 5, 6). Sinclair and Kannan attributed increases in perfluorocarboxylates in effluent to the degradation of precursor compounds during secondary treatment without significant removals (6). A study of 10 WWTPs across the U.S. showed inconsistent removal of fluorochemicals even among plants with the same types of treatment processes, and in some cases, wastewater treatment resulted in the production of fluorochemicals (5).

Relatively few studies have placed the discharge of fluorochemicals by WWTPs into a broader context. Boulanger et al. (7) conducted a mass budget of perfluorooctane sulfonyl fluoride (POSF)-based fluorochemicals in Lake Ontario and estimated that the most significant inputs were inflows to the system from Lake Erie and WWTP effluents, while removal through sorption, volatilization, or degradation was determined not to be significant. Other studies traced unusually high levels of fluorochemicals to an upstream input, as in Skutlarek et al., where waste containing fluorochemicals was inadvertently land applied and the resulting runoff caused high levels of contamination in the local watershed (8). A study of fluorochemicals in a North Carolina watershed suggested inputs from local sources, including fire-fighting foams used at military bases (9). Surface and drinking waters in northern Italy also were analyzed for fluorochemical contamination; probable sources of fluorochemicals included urban and industrial wastewater inputs, while analysis of precipitation proved to be an additional input to this system (10). The annual flux of perfluorocarboxylates (PFCAs) estimated from concentrations measured in 14 major European rivers was found to be the highest in watersheds that had known fluorochemical manufacturing facilities or large populations (11). Recent papers suggest nonpoint sources including urban runoff waters as the sources of fluorochemicals to aqueous urban systems (12, 13). While the sources of fluorochemicals to watersheds have been implied, the quantitative contribution of wastewater effluent to the total loads of receiving waters has not been quantified.

The objective of the present study was to quantify fluorochemicals present in the aqueous phase in the Glatt River of Switzerland and to compute the contribution of WWTPs to the river's mass flow. In the pursuit of this objective, the relative efficiency of seven WWTP's removal of fluorochemicals was evaluated. The concentrations of four perfluoroalkyl sulfonates (C₄–C₈), five perfluoroalkyl carboxylates (C₆–C₁₀), one fluorotelomer sulfonate, and one perfluoroalkyl sulfonamide were measured in aqueous, 24 h, composite samples over a period of 1 week in WWTP effluents and in Glatt River water. From WWTP effluent concentrations and flow data, WWTP contributions to the Glatt River mass flows were computed and compared to the actual measured mass flows.

Experimental Procedures

Standards and Reagents. Standards of potassium perfluorobutane sulfonate (PFBS), potassium perfluorohexane sulfonate (PFHxS), potassium perfluorooctane sulfonate (PFOS), perfluorooctane sulfonamide (FOSA), and dual labeled ¹⁸O₂-perfluorooctane sulfonate (¹⁸O₂PFOS) were donated by the

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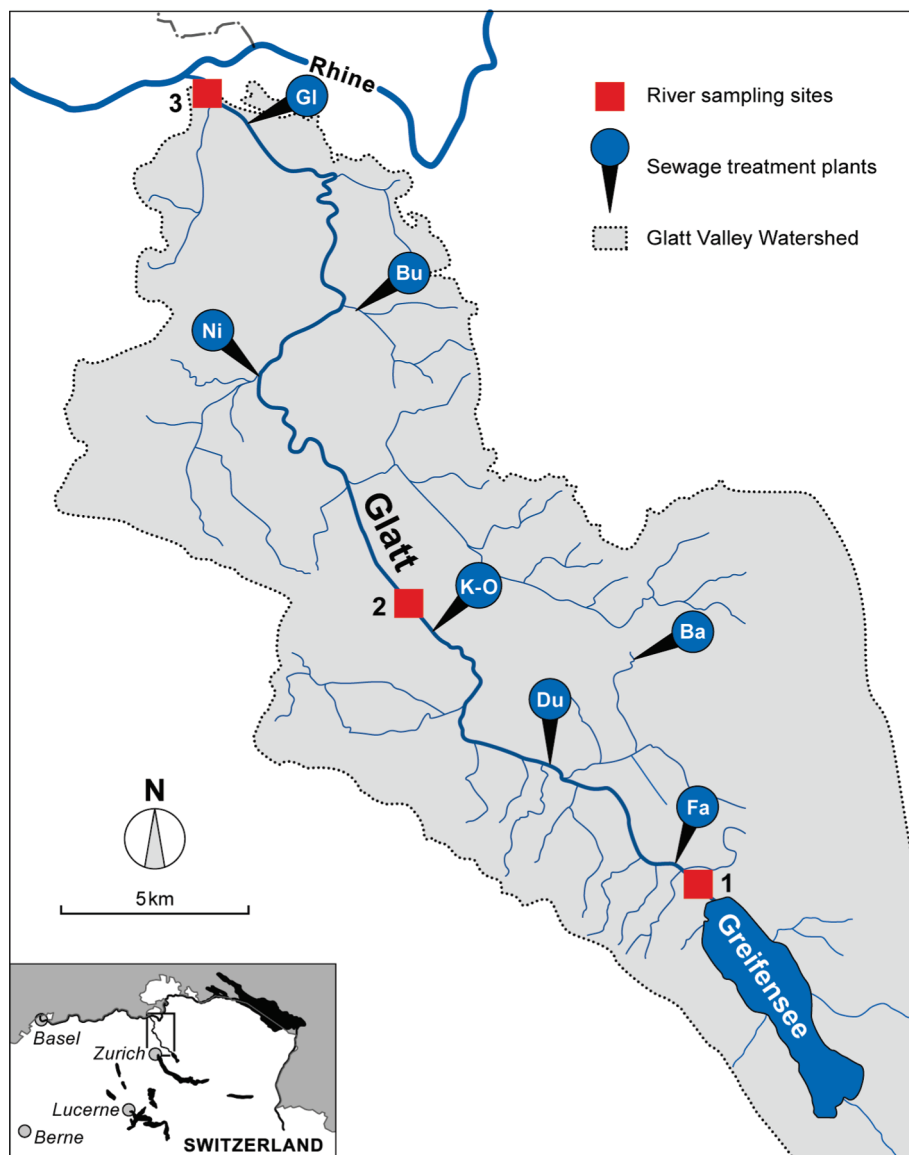


FIGURE 1. Map of Glatt River area of Switzerland with three river sampling stations and seven WWTPs.

3M Company (St. Paul, MN). Standards of the ammonium salts of perfluorodecane sulfonate (PFDS), perfluorodecanoate acid (PFDA), perfluorononanoate (PFNA), perfluorooctanoate acid (PFOA), and perfluoroheptanoate (PFHpA) were purchased from Aldrich Chemical (Milwaukee, WI). Perfluorohexanoic acid (PFHxA) was obtained from Fluka (Buchs, Switzerland). 1*H*,1*H*,2*H*,2*H*-tridecafluorooctane sulfonate (6:2 FtS) was acquired from Apollo Scientific Limited (Derbyshire, U.K.). Dual labeled [1,2-¹³C₂]-perfluorooctanoic acid (¹³CPFOA) was purchased from PerkinElmer (Wellesley, MA). Stock solutions of fluorochemicals were corrected for purities of the standards (Supporting Information Table S1). Optima grade methanol (MeOH) from Fischer was used as a HPLC solvent. Ammonium acetate (NH₄OAc) was purchased from Mallinckrodt (Phillipsburg, NJ).

River and WWTP Sampling. The Glatt River (Figure 1) is located in northern Switzerland, east of Zurich, and is a watershed inhabited by 284 000 residents. The Glatt River flows 35 km from its origin at Greifensee to the Rhine River and receives effluent from eight WWTPs (Table 1) (14, 15). The selection of the Glatt River for a mass flow study resulted from the availability of composite sample collection points along the river and at each WWTP discharging to the Glatt River.

The WWTPs of the Glatt Valley employ several methods of treatment (Table 1). WWTP Glattfelden is a nitrifying plant, while the WWTP at Bassersdorf and Niederglatt operate as denitrifying plants. Buelach, Duebendorf, Kloten-Opfikon, and Faellanden are denitrifying with additional filtration. Flow-proportional, 24 h composite samples of WWTP influent and effluent were collected daily for seven consecutive days from seven out of the eight municipal WWTPs that discharge into the Glatt River (Table 1 and Figure 1); the eighth WWTP is small (serves 1% of population of catchment) and was not included in this study. The 24 h, flow-proportional composite samples from WWTPs were taken volume-proportionately where the volume sampled is adjusted according to the total volume of wastewater per day to take approximately 100 samples per 24 h period. At each WWTP, the composite samplers and collection containers were housed under refrigerated conditions to minimize microbial activity.

In addition, 24 h, time-proportional composites were collected at the point at which the Glatt River flows out of Lake Greifen (Greifensee, R1 (Figure 1) and a point 15 km downriver (R2), while a 24 h, flow-normalized composite sample was collected at a point just before the Glatt River joins the Rhine River (R3). The time-proportional composite samples were taken at these three points to investigate the

TABLE 1. Sampling Locations; Populations Served by Each Wastewater Treatment Plant; Average, Minimum, and Maximum Flow for Each Station; Treatment Type; Sludge Age; and Volume of Activated Sludge Tank

sampling station ^a	inhabitants × 1000 ^b	av flow (1000 m ³ /day)	min flow (1000 m ³ /day)	max flow (1000 m ³ /day)	type of treatment ^c	typical sludge age (day)	vol activated sludge tank (m ³)
WWTP							
Faellanden (Fa)	29.8	12	9	17	D/F	17	6800
Bassersdorf (Ba)	15.7	9	6	16	D	18	4120
Duebendorf (Du)	36.2	18	15	26	D/F	13	12100
Kloten-Opfikon (K-O)	30.9	21	17	32	D/F	9	6880
Niederglatt (Ni)	33.3	22	14	39	D	15	7260
Buelach (Bu)	25.1	12	8	2	D/F	16	5916
Glattfelden (Gl)	3.1	1	1	2	N	14	560
Glatt River							
Schwerzenbach (R1)	110	359	321	428			
Oberglatt (R2)	222	457	382	641			
Rheinsfelden (R3)	284	659	520	1100			

^a See Figure 1 for sampling station locations. ^b No. of inhabitants as of 2006. ^c N = nitrifying plant; D = denitrifying plant; and D/F = denitrifying with additional filtration.

river system as a whole and to account for any changes in flow or composition over the course of daily sampling. Additional sampling details are included in the Supporting Information.

Composite WWTP and river samples were collected in glass bottles present in the sampling equipment currently in place and operated by the Swiss water authority. Composite WWTP and river samples were collected in glass bottles and transferred to plastic bottles for transport back to the laboratory where further aliquots were removed; samples destined for fluorochemical analysis were aliquoted into high density polyethylene bottles and frozen until shipment to minimize any microbial degradation. Additionally, river water samples were filtered through Whatman GF/D filters (Whatman, Maidstone, U.K.). All samples were shipped frozen to minimize losses due to degradation during transport and were stored frozen (−20 °C) until analysis.

Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Frozen samples were thawed to room temperature, shaken, and aliquoted into 2 mL microcentrifuge tubes and centrifuged at 10 000 rpm (or 6700g) for 15 min. The supernatant was removed (1.2 mL) and transferred to a 2 mL glass autosampler vial that was then spiked with 30 pg each of the ¹⁸O₂PFOS and ¹³CPFOA internal standards and analyzed immediately. Glass autosampler vials did not cause reductions in aqueous fluorochemical concentrations and were used for all samples.

Separations were performed on an Agilent 1100 HPLC system (Agilent, Palo Alto, CA). A 900 µL volume of sample was injected directly onto a 2.0 mm × 4.0 mm C18 Security Guard cartridge (Phenomenex, Torrance, CA) that preceded a 150 mm × 2.1 mm Targa C18 column (Higgins Analytical, Mountain View, CA). The mobile phase system (2 mM ammonium acetate with 5% methanol (A) and methanol (B)) was pumped through the column at a temperature of 25 °C and a flow rate of 200 µL/min. The initial mobile phase (10% A and 90% B) was held for 4 min, ramped linearly to 45% B over 6.5 min, held for 2 min, ramped to 90% B over 1 min, and finally held at this last composition until 18 min total had elapsed.

The HPLC was interfaced to a Quattro Micro tandem mass spectrometer (Waters, Milford, MA) through an electrospray ionization source operated in negative mode. Quantification of analytes was performed through multiple reaction monitoring with one transition monitored for each analyte. Details of the mass spectrometry conditions and transitions monitored are provided in Table S1 in the Supporting Information.

Calibration curves were prepared daily in blank well water obtained near Corvallis, OR that gave no fluorochemical

background signal and was run before and after each batch of (~20) samples. Linear, 1/X-weighted regressions, not forced through the origin, were based on internal standard calibration and typically had *R*² values of 0.97 or greater. The internal standard ¹⁸O₂PFOS was used for quantification of PFBS, PFHxS, PFOS, PFDS, 6:2 FtS, and FOSA, while ¹³CPFOA was used for the quantification of PFHxA, PFHpA, PFOA, PFNA, and PFDA. Calibration curves ranged from 1 to 300 ng/L (or higher as necessary) with internal standard concentrations of 25 ng/L.

Quality Control. To assess the effect of filtering the river water, two samples of nanopure water were filtered with the same GF/D filters used to filter river water samples into HDPE bottles and shipped with the rest of the samples. Two samples of unfiltered nanopure water in HDPE bottles were sent along with the treatment plant and river water samples to serve as travel blanks.

Method blanks, which were used to ensure clean sample preparation, consisted of deionized water prepared in the same manner as samples (including internal standard spikes) and analyzed with every batch of samples. Instrumental blanks were used to monitor for any instrumental background and carryover from samples and standards. Quality control standards, which were used to evaluate the chromatographic and quantitative performance during analysis, were prepared at 30 or 75 ng/L in the same manner as calibration standards and were analyzed within each batch of samples, with one analyzed for every 10 injections. Any deviation by quality control standards of greater than 20% caused the reanalysis of all samples preceding the faulty standard. Replicate measurements were performed on randomly selected samples comprising 20% of the entire set, and the results were averaged.

Standard-addition experiments were performed since peak areas for the internal standards were ~50% less for wastewater and river water samples than those for the standards and method blanks. To investigate the possibility of matrix effects and to evaluate precision and accuracy, standard-addition experiments were performed in an identical manner for each of the three separate sample matrices of the study and included WWTP influent, WWTP effluent, and river water. For each matrix, a total of eight aliquots was prepared, and each was spiked with 30 pg of the ¹⁸O₂PFOS and ¹³CPFOA internal standards. Four of the eight aliquots were then analyzed directly by LC-ESI/MS/MS. The four remaining aliquots were then spiked with fluorochemical standards to increase each fluorochemical analyte's response 1.5–3 times that of the background signal(16) and then analyzed by LC-ESI/MS/MS. The first step in data analysis

was the quantification of background concentrations and 95% confidence intervals (CIs) in the four aliquots that received only internal standards; concentrations were determined from solvent-based calibration curves. The second step in data analysis was to use linear regression on the data (ratio of fluorochemical analytes to its internal standard vs concentration of analyte added to the aliquot) for all eight aliquots to determine the background concentration and 95% CI for each fluorochemical analyte by standard addition (16).

Selected WWTP influent samples gave levels of background interferences in the transition time windows that made peak identification ambiguous, and the problem was not resolved by employing secondary transitions for the affected analytes. Therefore, only when necessary, WWTP influent samples were treated with single-point spike-addition experiments to aid in correctly assigning peak identities for PFBS, PFHxS, and PFDS.

Limits of Detection. The instrumental limits of detection (LOD) were determined using a NIOSH method (17). In short, an estimation of the detection limit was made based on a signal-to-noise ratio of 3:1, and then 12 standard solutions were prepared spanning the range from 10 times less to 10 times more than the estimated detection limit. These 12 standards were analyzed, their responses were used to generate a linear regression, and the LOD was calculated using both the standard error and the slope of the regression (17). Additionally, the signal-to-noise (S/N) ratio for low level detections was calculated, and measurements with S/N < 10 were assigned a concentration of twice the LOD.

Results and Discussion

Chromatography and Quality Control. The solvent gradient employed was a modification of that described by Schultz et al. (5). It allowed for more rapid elution of analytes, and by maintaining the column at 90% MeOH during injections and between samples, it provided the added benefit of reducing any background in fluorochemical leaching from instrument components, and while initial solvent conditions were 90% in methanol, the analytes were injected in a volume of aqueous sample (900 μ L) that was large relative to the analytical column volume (<100 μ L); it is for this reason that the analytes are well-focused on the analytical column. The large volume injections were used to increase sensitivity without additional sample preparation (e.g., solid phase extraction) (5).

The filtered and unfiltered nanopure (blank) samples, which were prepared at the same time as the river water samples, contained no fluorochemicals above the detection limit. Filtration of a composite river water sample containing PFOA, PFOS, and PFHxS did not affect concentrations, indicating that filtration contributed neither positive nor negative artifacts. Plastic filter holders containing PTFE components were avoided because they were discovered to contain PFOA; glass filter holders were used instead. Method and instrumental blanks prepared with each batch of samples did not contain any measurable level of fluorochemicals. Field spikes, which are usually prepared by introducing a known quantity of analyte into the collected sample in the field, were not performed in this study due to the logistics of collecting the samples in Switzerland and performing the fluorochemical analysis in Oregon. Previously, wastewater samples were collected in similar containers, and recoveries ranged from 82–100% (5); therefore, losses during sampling and transport were assumed to be minimal.

A series of standard-addition experiments indicated that matrix effects did not affect analyte quantification from solvent-based calibration curves. Concentrations determined from solvent-based calibration curves and by standard addition gave statistically equivalent values at the 95% CI (Supporting Information Table S2), which indicates the

acceptable precision and accuracy of the method. For some WWTP influents, it was difficult to assign the identities of PFBS, PFHxS, and PFDS, and the situation was not ameliorated by the use of a secondary transition, as the signal for the secondary transitions was much weaker. Consequently, single-point spike additions revealed the appropriate peak for quantification. The instrumental LODs were determined to vary from 1.2 to 9.4 ng/L (Supporting Information Table S1). Fluorochemical concentrations greater than or equal to their LOQ (Supporting Information Table S1) were tabulated, analyte concentrations greater than or equal to the LOD but less than the LOQ were assigned a concentration twice that of the LOD, and analytes at or below the LOD were assigned a value of zero.

Fluorochemicals in Wastewater and Inputs to the Glatt River. Over the course of the week, there were no consistent removal or production trends when we compared daily influent and effluent values (data not shown). Therefore, fluorochemical removal by each WWTP was evaluated using weekly average influent and effluent concentrations (Table 2). Computed average influent and effluent concentrations indicated few statistically significant differences at the 95% CI between effluent and influent concentrations (Table 2), which indicates inefficient removal of fluorochemicals during wastewater treatment when averaged over the week. For additional clarity, concentration ranges also are reported in the Supporting Information as box plots (Supporting Information Figure S1) and in Supporting Information Table S3 along with the number of observations >LOD.

The concentrations of fluorochemicals in the effluents of seven WWTPs that discharge to the Glatt River followed a general trend of PFOS > PFHxS > PFOA (Table 2). PFOS was detected in every wastewater effluent (and influent) collected in this study and was the fluorochemical present at the highest concentrations (Table 2). Concentrations of PFOS at Duebendorf (up to 790 ng/L) were among the highest we have found for wastewater since the 2002 phaseout of PFOS-related chemistry (12); higher reports for wastewater collected prior to 2002 reach up to 5000 ng/L (18). The high concentrations of PFOS at Duebendorf were not correlated with significantly higher levels of other fluorochemicals. Industries engaged in electroplating, surface treatment, and carpet manufacturing are located in the Duebendorf catchment and may be responsible for the elevated PFOS concentrations since such activities are known to involve fluorochemicals (19). At this time, there are no PFOS regulations yet in Switzerland, but there are preparations for Switzerland to follow the European Union regulations for PFOS (20). PFHxS was detected in 90% of the effluents in the present study with an average concentration (27 ng/L; Table 3) 5–10 times higher than what previously was reported (5, 6, 21, 22). PFOA was detected in 98% of effluents tested at concentrations (Table 2) similar to those in Scandinavia (22), the U.S. (5), and in Austria (23) but are lower than the values reported for other WWTPs in the U.S. (6, 21).

Other fluorochemicals were detected in effluents with less frequency including PFDS, but when it was detected, it was at higher concentrations than previously reported for municipal wastewater (5, 24). Fluorochemicals including 6:2 FtS, PFBS, PFHxS, PFHpA also were only frequently detected in effluents and at concentrations lower than those observed by Schultz et al. (5), which is the only other report containing data on these fluorochemicals in wastewater. PFNA and PFDA were infrequently detected at concentrations similar to those for some WWTPs in the U.S. (5, 21, 24) but were lower than for other WWTPs in the U.S. (6).

Concentrations of Fluorochemicals in Glatt River. PFOS, PFHxS, and PFOA were each detected in 100% of the Glatt River samples at average concentrations of 49, 12, and 7.4 ng/L, respectively (Table 2). PFBS and PFHpA also were

TABLE 2. Average Weekly^a(n = 7) Concentration (ng/L) ± 95% CI of Analytes at each WWTP and River Station

station	type	PFBS	PFHxS	PFOS	PFDS	6:2 Fts	FOSA	PFHxA	PFHpA	PFOA	PFNA	PFDA
WWTP												
Faellanden (Fa)	Influent	3.9 ± 3.6	0.5 ± 1.3	71 ± 36	26 ± 46	1.9 ± 4.6	ND	ND	16 ± 36	4.9 ± 9.8	ND	ND
	Effluent	4.0 ± 6.8	3.0 ± 3.2	103 ± 32	ND	3.8 ± 3.3	3.4 ± 5.3	0.7 ± 1.7	0.6 ± 1.0	28 ± 12	ND	ND
Bassersdorf (Ba)	Influent	2.6 ± 5.0	12 ± 4.7	18 ± 10	ND	6.5 ± 9.1	ND	ND	6.7 ± 5.0	5.1 ± 3.5	ND	1.9 ± 3.0
	Effluent	1.8 ± 4.5	2.8 ± 2.9	16 ± 3.3	ND	1.9 ± 3.0	ND	5.6 ± 8.9	6.3 ± 3.8	17 ± 6.6	ND	2.8 ± 3.3
Duebendorf (Du)	Influent	5.8 ± 5.5	45 ± 33	449 ± 200	ND	6.6 ± 0	3.4 ± 5.3	1.4 ± 2.2	1.1 ± 1.0	35 ± 11	5.1 ± 8.4	ND
	Effluent	7.2 ± 9.3	53 ± 31	303 ± 120	ND	0.9 ± 2.3	1.7 ± 4.1	11 ± 19	4.1 ± 5.9	35 ± 8.8	0.4 ± 0.9	ND
Kloten-Opfikon (K-O)	Influent	7.3 ± 5.7	54 ± 34	134 ± 50	36 ± 41	3.8 ± 3.3	5.1 ± 5.8	ND	1.8 ± 0.7	25 ± 21	ND	ND
	Effluent	7.8 ± 4.4	88 ± 99	119 ± 37	4.5 ± 7	1.9 ± 3.0	8.4 ± 5.3	2.1 ± 3.6	3.9 ± 4.5	27 ± 15	0.8 ± 2.0	2.4 ± 5.9
Niederglatt (Ni)	Influent	1.3 ± 1.8	9.7 ± 3.3	76 ± 30	18 ± 33	2.8 ± 3.3	ND	0.7 ± 1.7	2.2 ± 3.0	8.9 ± 8.3	ND	1.9 ± 3.0
	Effluent	1.1 ± 1.7	11 ± 5.5	92 ± 30	ND	1.9 ± 3.0	3.4 ± 5.3	0.7 ± 1.7	1.8 ± 1.4	12 ± 9.7	ND	1.9 ± 3.0
Buelach (Bu)	Influent	0.6 ± 1.3	5.0 ± 4.7	33 ± 23	130 ± 150	7.3 ± 4.9	3.4 ± 5.3	1.4 ± 3.4	9.9 ± 20	9.0 ± 11	ND	1.9 ± 3.0
	Effluent	2.2 ± 1.9	9.0 ± 3.9	23 ± 6.3	ND	0.9 ± 2.3	ND	ND	0.8 ± 1.9	27 ± 16	ND	ND
Glattfelden (Gl)	Influent ^b	2.3 ± 2.6	16 ± 16	117 ± 38	160 ± 120	6.6 ± 0	ND	ND	1.2 ± 1.4	9.0 ± 8.0	ND	ND
	Effluent	ND	19 ± 11	144 ± 46	2.2 ± 5	2.8 ± 3.3	ND	33 ± 19	0.3 ± 0.7	13 ± 9.4	ND	ND
Glatt River												
Schwerzenbach (R1)	River ^c	7.7 ± 12	8.9 ± 3.1	44 ± 7.3	ND	ND	ND	ND	0.7 ± 1.1	7.0 ± 3.4	ND	ND
Oberglatt (R2)	River ^c	2.8 ± 1.7	14 ± 5.6	60 ± 22	ND	ND	ND	ND	0.9 ± 1.0	7.7 ± 3.3	ND	ND
Rheinsfelden (R3)	River	2.3 ± 1.9	14 ± 4.9	43 ± 14	ND	ND	ND	ND	2.7 ± 6.0	7.6 ± 3.3	ND	ND

^a Av weekly values that appear <LOD are the result of averaging concentrations using the following criteria: fluorochemical concentrations greater than or equal to their LOQ (Table S1) were tabulated, analyte concentrations greater than or equal to the LOD but less than the LOQ were assigned a concentration twice that of the LOD, and analytes at or below the LOD were assigned a value of zero. Bold values indicate a significant difference at the 95% CI between av weekly influent and effluent concentrations. ND = not detected.

^b Glattfelden influent n = 5 (two bottles out of seven broke during sample collection). ^c Schwerzenbach and Rheinsfelden n = 6.

TABLE 3. Av Weekly Mass Flows^a (g/day \pm 95% CI^b) of Fluorochemicals in WWTP Effluent and at Glatt River Stations

station	PFBS	PFHxS	PFOS	PFDS	6:2 FTS	FOSA	PFHxA	PFHpA	PFOA	PFNA	PFDA
Schwerzenbach (R1)	2.8 \pm 4.3	3.1 \pm 1.2	15.7 \pm 3.1	NC ^c	NC	NC	NC	0.25 \pm 0.4	2.5 \pm 1.3	NC	NC
Faellanden (Fa)	0.05 \pm 0.08	0.04 \pm 0.04	1.3 \pm 0.5	NC	0.05 \pm 0.04	0.04 \pm 0.07	0.01 \pm 0.02	0.01 \pm 0.01	0.33 \pm 0.17	NC	NC
Bassersdorf (Ba)	0.02 \pm 0.04	0.03 \pm 0.03	0.14 \pm 0.06	NC	0.02 \pm 0.03	NC	0.05 \pm 0.08	0.06 \pm 0.04	0.15 \pm 0.08	NC	0.03 \pm 0.03
Duebendorf (Du)	0.13 \pm 0.17	0.93 \pm 0.57	5.3 \pm 2.4	NC	0.02 \pm 0.04	0.03 \pm 0.07	0.19 \pm 0.34	0.07 \pm 0.10	0.61 \pm 0.2	NC	NC
Kloten-Opfikon (K-O)	0.16 \pm 0.10	1.8 \pm 2.1	2.5 \pm 1.0	0.09 \pm 0.15	0.04 \pm 0.06	0.18 \pm 0.12	0.04 \pm 0.08	0.08 \pm 0.10	0.56 \pm 0.35	0.02 \pm 0.04	0.05 \pm 0.12
Oberglatt (R2)	1.3 \pm 0.82	6.1 \pm 3.0	27.6 \pm 11.2	NC	NC	NC	NC	0.40 \pm 0.47	3.5 \pm 1.6	NC	NC
Niederglatt (Ni)	0.02 \pm 0.04	0.24 \pm 0.17	2.0 \pm 1.2	NC	0.04 \pm 0.07	0.07 \pm 0.12	0.02 \pm 0.04	0.04 \pm 0.04	0.26 \pm 0.25	NC	0.04 \pm 0.07
Buelach (Bu)	0.03 \pm 0.03	0.11 \pm 0.07	0.28 \pm 0.15	NC	0.01 \pm 0.03	NC	NC	0.01 \pm 0.02	0.33 \pm 0.24	NC	NC
Glattfelden (G1)	NC	0.02 \pm 0.02	0.16 \pm 0.10	NC	NC	NC	0.04 \pm 0.03	NC	0.01 \pm 0.01	NC	NC
Rheinsfelden (R3)	1.52 \pm 1.5	9.4 \pm 4.5	28.6 \pm 13.3	NC	NC	NC	NC	1.8 \pm 4.6	5.0 \pm 2.7	NC	NC

^a Mass flow values (g/day) calculated using av flows (Table 1) and av concentration (Table 2, footnote ^a) was not computed. ^b 95% CI calculated using pooled standard deviations for av concentrations and flow. ^c NC = Not computed because the av weekly concentration (Table 2, footnote ^a) was not computed.

detected in the Glatt River, but at lower frequencies (68 and 32%, respectively, and at lower average concentrations (4 and 1 ng/L, respectively) (Table 2). The average concentrations of fluorochemicals in the Glatt River were higher than values reported in surface waters in Scandinavia (22) and northern Italy (10). PFBS was the most abundant fluorochemical found in the Rhine by two separate studies, Skutlarek et al. (8) and Lange et al. (25), which was not the case for the Glatt. PFNA, PFOA, PFHpA, and PFHxA concentrations measured at the mouth of the Rhine River were all higher than the concentrations in the Glatt River (11), which indicates that the Glatt River is but one source of fluorochemicals in the Rhine River. Levels of perfluorocarboxylates in the Glatt were also lower than reports from other rivers in Europe (11), Japan (12), and North America (9) with some higher levels of PFCAs in the Rhine, Po, and Danube Rivers attributed to known fluorochemical industries in those watersheds (11). The concentrations of PFOS, PFOA, and other fluorochemicals in the Glatt River are in the same range as at other locations not having industrial sources (e.g., AFFF, fluorochemical manufacture) (26, 27).

Mass Flow of Fluorochemicals. The hypothesis of this study was that WWTP effluents are the principal contributor to the mass flows of fluorochemicals in the Glatt River. To test this hypothesis, the first step was to compute the mass flow of PFBS, PFHxS, PFOS, PFHpA, and PFOA for each WWTP and river sampling station (Table 3) using the average concentrations (Table 2) and flows (Table 1). A 95% CI was computed from the pooled standard deviation for the average concentrations and flows for each WWTP and river sampling station (16). Mass flow calculations were not performed for PFDS, 6:2 FTS, FOSA, PFHxA, PFNA, and PFDA because they occurred infrequently in WWTP effluents, and average weekly concentrations could not be computed for the Glatt River since concentrations were below detection (Table 2). The next step was to predict the mass flows at river sampling stations R2 and R3 from the measured mass flows for the nearest upstream river sampling station and the WWTPs located between the two river sampling stations. For example, to predict the mass flow at R2 (Figure 2), the mass flows for fluorochemicals at river sampling station R1 were added to the sum of the mass flows for the four WWTPs including Faellanden (Fa), Bassersdorf (Ba), Duebendorf (Du), and Kloten-Opfikon (K-O) that are located upstream of R2 but downstream of R1. In an analogous manner, the predicted mass flows at R3 (Figure 2) were computed as the sum of the mass flows at R2 and the three WWTPs (Niederglatt (Ni), Buelach (Bu), and Glattfelden (G1)) located downstream of R2 but upstream from R3 (Figure 1). This predicted mass flow was then compared to the measured mass flow measured at river sampling station R2 (Figure 2).

No statistically significant difference at the 95% CI was observed for any of the fluorochemical mass flows measured and predicted for R2 or R3 (Figure 2). No such comparison could be made between measured and predicted mass flows for R1 because there were no river sampling stations upstream of R1. River sampling station R1 is located at the outflow of Greifensee and is the headwater of the Glatt River. However, the mass flows for the Greifensee, as indicated by R1, are similar to the combined fluorochemical mass flows for all seven WWTPs investigated for this study (Table 3). The fluorochemicals in Greifensee likely result from the nine WWTPs that discharge to the Greifensee. This finding indicates that the Greifensee itself is a major source of fluorochemicals in the Glatt River. Furthermore, because R3 is the point where the Glatt River flows into the Rhine River, the Glatt River is a source term for the Rhine River for which others have reported the presence of fluorochemicals (8, 25).

The lack of statistically significant differences between measured and predicted mass flow at the two river sampling

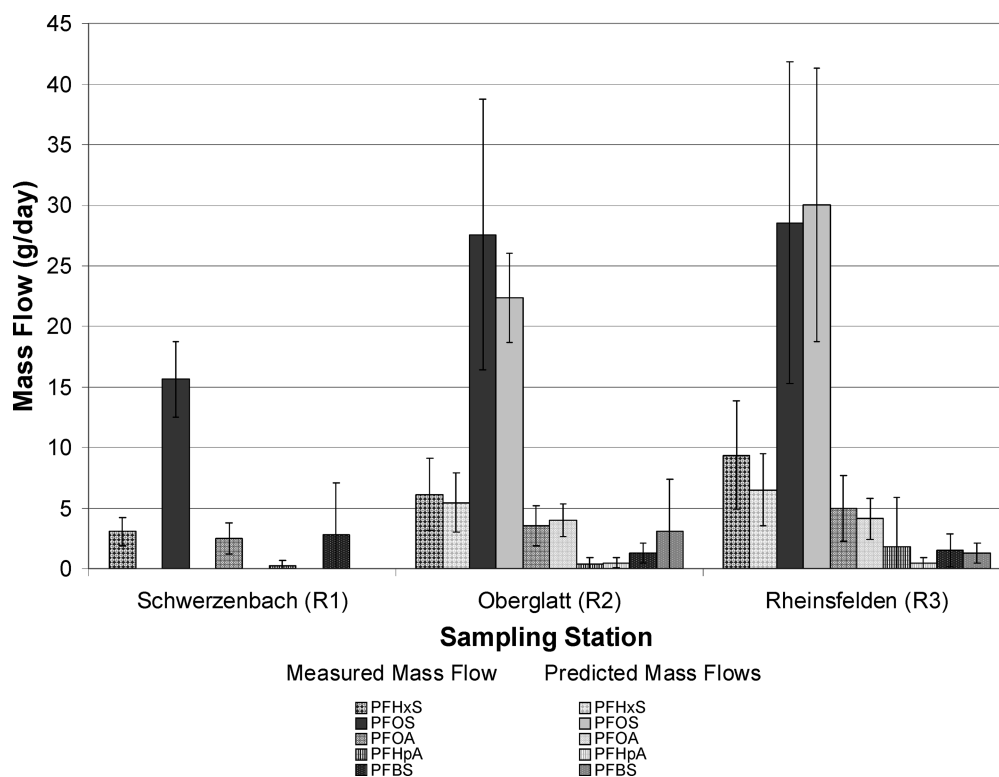


FIGURE 2. Measured and predicted mass flows of PFBS, PFHxS, PFOS, PFHpA, and PFOA (g/day \pm 95% CI) for Glatt River sampling stations R1 (only measured mass flows are indicated for river sampling station R1 because there are no river sampling stations upstream of R1), R2, and R3.

stations along the Glatt River indicates that the mass flows of these five fluorochemicals in the river are conserved and that, other than the WWTPs included in this study, there appear to be no significant, unaccounted for sources of fluorochemicals along the 35 km Glatt River. The perfluoroalkyl carboxylates and perfluoroalkyl sulfonates are known to be resistant to biotransformation (19, 28) and photodegradation without catalysis (29). Because of the low volatility of these fluorochemicals (30), losses to the atmosphere are predicted to be low. Sorption to suspended solids or sediments in the river is a possible loss mechanism (31), but the agreement between measured and calculated loads suggests that, if sorption occurs, it is not an important loss mechanism in this system. Other fluorochemical inputs to the system could include the degradation of precursor compounds potentially present in effluent or from other sources such as precipitation (32, 33), runoff from contaminated sites (8), or surface runoff, as demonstrated by a study in New York where runoff was the source of fluorochemicals to urban lakes in the system (13).

In comparison, fluoroquinolones showed a net removal along the Glatt River due to sorption (15), whereas clarithromycin was not removed significantly (34). Analysis of the mass flows of phenolic endocrine disruptors measured in a similar study indicated removal for bisphenol A along the course of the river but conservation of other endocrine disrupting compounds including, phenylphenol, nonylphenol, nonylphenol ethoxylates, nonylphenol ethoxy acetic acids, and parabens including methyl, ethyl, propyl, butyl, and benzyl (35).

Per Capita Discharge of Fluorochemicals in the Glatt Valley. The per capita estimates for the seven WWTP investigated in this study (Table S4 in the Supporting Information) were calculated from the average weekly concentrations for each fluorochemical, the flow of each WWTP (Table 1), and the population served by each WWTP (Table 1). The term per capita must be interpreted with caution since we cannot exclude the inputs of commercial

TABLE 4. Per Capita ($\mu\text{g/day/person}$) Estimates of Fluorochemical Discharges for WWTPs along the Glatt River in Switzerland and Other WWTPs (in the U.S.)

analyte	no. of WWTPs investigated and location by country			
	seven in Switzerland (this study) ($\mu\text{g/day/person}$)	10 in U.S. (5) ($\mu\text{g/day/person}$)	two in U.S. (6) ($\mu\text{g/day/person}$)	one U.S. (24) ($\mu\text{g/day/person}$)
PFBS	1.9	1.6	NR ^a	NR
PFHxS	15	13	6.8	0.64
PFOS	57	42	16	13
PFDS	0.54	0.63	NR	4.4
6:2 FtS	1.0	1.1	NR	5.2
FOSA	1.4	1.6	NR	2.5
PFHxA	3.2	2.7	NR	3.4
PFHpA	1.4	1.3	NR	NR
PFOA	12	11	220	5.9
PFNA	0.1	0.09	76	1.8
PFDA	0.64	0.71	27	1.2

^a NR = not reported.

or industrial sources. For example, electroplating, surface treatment, and carpet manufacturing small industries are known to be in the catchment served by the Duebendorf WWTP. To more readily compare the estimate to those of the few other published studies, that per capita data were averaged (Table 4). The average per capita estimates are in good agreement with those determined for 10 WWTPs in the U.S. (5). Per capita estimates are also in good agreement with those for a single WWTP in the U.S. (24) with the exception of PFBS and PFHxS, which are greater in the present study. In contrast, a report on two WWTPs located in New York with known industrial sources gave lower per capita estimates for PFHxS and PFOS but significantly larger per capita estimates for PFOA, PFNA, and PFDA (Table 4) (6).

The specific sources of fluorochemicals associated with human consumption and disposal of fluorochemicals (e.g., per capita discharges) are not well-understood. However, daily dietary intakes of 0.12 $\mu\text{g}/\text{day}$ for PFOS and 0.27 $\mu\text{g}/\text{day}$ PFOA estimated for a German cohort (36) were significantly smaller than per capita discharge values reported here at 57 $\mu\text{g}/\text{day}$ and 12 $\mu\text{g}/\text{day}$ for PFOS and PFOA, respectively, which indicates that nonfood sources of fluorochemicals contribute more to the estimated per capita discharges than food-derived sources (e.g., excretion).

Study Limitations. The precursor compounds such as fluorotelomer alcohols and fluoroalkyl sulfonamides that may degrade to yield perfluorinated acids (37) and sulfonates (38), respectively, were not measured in this study. Although mass balance was achieved between WWTP effluent and Glatt River, we were unable to preclude the possibility that the river system was at a pseudo-steady state with biodegradation of precursors balanced by the removal of sulfonate and carboxylate degradation products during transport in the river. Furthermore, other potential inputs to the Glatt River system including precipitation, tributaries to the Glatt River, and surface runoff that contributed significantly to urban lakes in New York (13) were not measured for this study. However, unless the system is at pseudo-steady state, these additional inputs do not appear to significantly add to the mass balance of fluorochemicals measured in the Glatt River.

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Supporting Information Available

Sample calculation for per capita discharge and additional analytical details and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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