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Seasonal Variation in the Occurrence of Pharmaceuticals in Effluents from a Sewage Treatment Plant and in the Recipient Water

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The occurrence of five pharmaceuticals (ibuprofen, naproxen, ketoprofen, diclofenac, and bezafibrate) in the influent and effluent water of a sewage treatment plant (STP) in the recipient river water and in a drinking water treatment plant (DWTP) located downstream from the STP was followed during three seasons: winter, spring, and summer. In the STP, the elimination of the pharmaceuticals decreased significantly (an average of 25% compared to spring and summer) in wintertime leading to increased concentrations of pharmaceuticals in the effluent water. The total concentration of all the studied pharmaceuticals in the effluent water was 3−5 times higher in wintertime (about 2500 ng L^{-1}) than during the other seasons (about 500−900 ng L^{-1}). Accordingly, the highest concentrations (up to 129 ng L^{-1}) in the recipient river were measured in the wintertime. Pharmaceuticals were carried longer distances downstream from the STP when the river was covered by ice and snow. During a drastic increase in water flow rate (i.e., during snowmelting), a fast transportation of the pharmaceuticals was observed. The DWTP located downstream from the STP produced water that contained about 8 ng L^{-1} of ibuprofen and ketoprofen in the winter sample, whereas in spring and summer the studied pharmaceuticals could not be detected in the drinking water. The results show that cold seasons in boreal areas can severely increase the environmental risk of pharmaceuticals and the risk for contamination of drinking water.

Introduction

The consumption of human pharmaceuticals is increasing and concern has been raised about their environmental fate. A significant proportion of the consumed pharmaceuticals are excreted via feces and urine to the wastewater, and many of the compounds are incompletely removed by the sewage treatment plants (STPs). Several studies have measured μg L^{-1} concentrations of pharmaceuticals in the treated effluents (*1*−*4*). In the recipient surface waters, the pharmaceuticals and their metabolites have been detected in concentrations of some nanograms to several micrograms per liter (*1*, *4*−*9*).

We have previously shown that ibuprofen, naproxen, ketoprofen, diclofenac, and bezafibrate are ubiquitous in STP effluents in our country (*1*). Also in the studies performed in other countries, the compounds have been detected in STP effluents and in surface waters and are among the major pharmaceutical pollutants in recipient waters (concentrations up to μg L^{-1} level) (*2*). In STPs, the studied pharmaceuticals have been suggested to be eliminated by biodegradation and sorption (*10*, *11*). In surface water, the main elimination processes are biodegradation, sorption, and photodegradation. Ibuprofen could undergo biodegradation (*12*, *13*) and because of the relatively high sorption coefficient of the compound, it may also be eliminated by sedimentation (*14*). Diclofenac has been proved to be readily photodegradable but negligibly adsorbed to sediments (*14*−*16*). The sediment type has been shown to significantly affect the sorption of ibuprofen and diclofenac (*17*). Therefore, elimination of pharmaceuticals by sorption can be very site specific. For naproxen and ketoprofen, photodegradation and biodegradation have been suggested to be possible elimination processes (*14*, *18*, *19*). Bezafibrate is effectively removed in bank filtration (*20*) suggesting that it could also be adsorbed to particles in surface waters.

The aim of our study was to find out the effect of the seasonal variation in climate conditions on the elimination of pharmaceuticals in an STP and on the occurrence of pharmaceuticals downstream from the STP in the recipient river water and in drinking water produced by a downstream plant. As far as we know, no studies have been performed where seasonal variation in temperature and light intensity has been regarded as a factor determining the fate of pharmaceuticals. Especially, the boreal climate conditions with low temperature and short time of daylight in the wintertime may decrease the biodegradation and the photodegradation of pharmaceuticals. These processes are likely to be even less effective in rivers covered by ice and snow. Thus, risk for drinking water contamination is likely to be the highest in the wintertime.

Materials and Methods

The Pharmaceuticals. Ibuprofen, ketoprofen, bezafibrate, and diclofenac were purchased from Sigma-Aldrich, and naproxen was purchased from Fluka. Surrogate standard fenoprop was purchased from ICN Biomedicals. The studied compounds are presented in Table 1. Standard solutions of 2000 mg L^{-1} were prepared in methanol and stored at −18 °C. From these, working solutions were prepared in methanol.

Sampling Procedure. The samples were taken from the Aura STP, the River Aura, and the drinking water treatment plant (DWTP) of the city Turku (population 170 000) in March, May, and August 2004 (Figure 1). From the STP, one sample was taken from the influent and the effluent water at each sampling month. The Aura STP samples were collected as 24-h composite samples so that 70 mL of the influent water and 105 mL of the effluent water were collected every 10 min. During the samplings, the plant worked normally. The inflow to the Aura STP was about 650 m^3 h^{-1}, and the plant served a population of 3000 inhabitants. Of the inflow, 14% is composed of wastewaters from the food industry. The STP is a so-called ditch oxidation plant which consists of activated sludge compartment with simultaneous addition of ferric salt to precipitate phosphorus. The wastewaters from the food industry are pretreated together with part of the municipal wastewater (∼17% of the inflow) to add phosphorus and nitrogen. The pretreatment consists of aeration and sedimentation. The rest of the municipal wastewater

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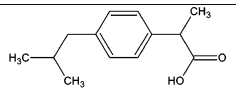
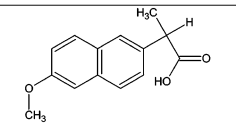
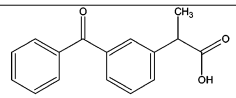
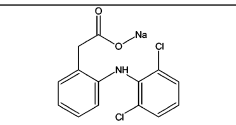
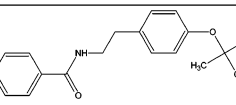
TABLE 1. The Studied Pharmaceuticals

compound	CAS-number	chemical structure	application
---	---		
ibuprofen	15687-27-1		antiphlogistics
naproxen	22204-53-1		antiphlogistics
ketoprofen	22071-15-4		antiphlogistics
diclofenac	15307-86-5		antiphlogistics
bezafibrate	41859-67-0		lipid regulator

and the pretreated water is led to the ditch oxidation where ferric salt is added to precipitate phosphorus. The average sludge retention time was 20 days and hydraulic retention time was 1.5 days. The plant removes an average of 98% of BOD_7 and 64% of nitrogen. The effluent was discharged to the River Aura which served as a raw water source for the DWTP of Turku. The characteristics of the river are presented in Figure 1 and Table 2.

The river samples (one sample from each sampling point) were collected as grab samples (500 mL) from eight points along the river (Figure 1) at 0.5 km upstream of the Aura STP, at the discharge point of the Aura STP, and at 1, 5, 8, 14, 23, and 32 km downstream of the plant. The river flow rate at the time of sampling was taken into consideration and the same plume of water was followed along the river. The volume of the river basin at various locations was estimated from the information gathered from the Finnish Environment Institute (*21*) and the River Aurajoki Foundation (*22*). Using these values and the flow rates (obtained from the Finnish Environment Institute, ref *21*), the water retention time was

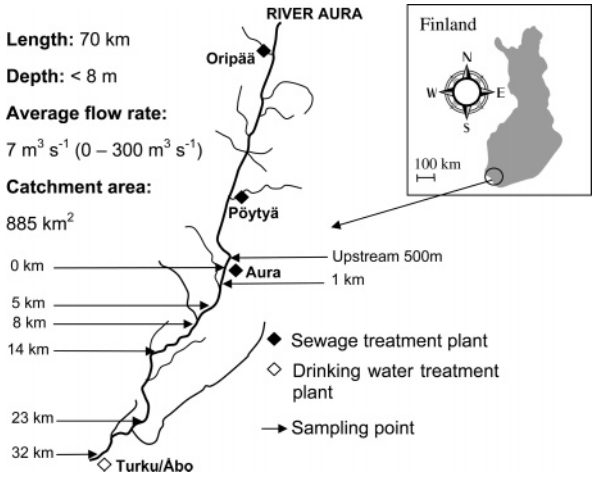


FIGURE 1. Characteristics of the River Aura. The flow rate given is based on long-term statistics provided by the Finnish Environment Institute.

TABLE 2. Characteristics of the River Aura during Samplings

	March	May	August
temperature (°C)	+1	+10	+21
pH	6.2	5.9	5.9
DOC (mg L^{-1})	9.0 ± 1.4 ($n = 5$)	11.0 ± 0.5 ($n = 7$)	14.5 ± 1.5 ($n = 4$)
	Flow Rate (m^3 s^{-1})[a]		
Aura	6.5 (0.43)[b]	0.32	0.23
Turku	14.7 (0.69)[b]	0.93	0.55

[a] Average flow rate during sampling period. [b] The increase in flow rate at the end of the sampling period because of melting ice increased the average flow rate, and the values in the parenthesis are flow rates in the beginning of the sampling.

estimated. At the periods of sampling of the river water, the raw water source of the Turku DWTP (32 km downstream from the STP) was sampled every other day for 2 weeks. This was done to study the concentration fluctuation of the pharmaceuticals.

Turku DWTP consisted of two-stage ferric coagulation, granular activated carbon (GAC) filtration, and chlorination. The first coagulation was performed in acidic and the second one in basic conditions. Flocs were removed by flotation in the first stage and by flotation or sedimentation in the second stage. The particles and organic compounds were further removed by GAC filters. Finally, chlorine was added to water, and pH was adjusted to 8.2−8.5. Grab samples (one sample from each sampling point) were collected from the raw water, after the first and second coagulation and after two GAC filters, and from the purified water. The volume of the samples collected from the DWTP was 500 mL.

Analytical Methods. Solid-phase extraction (SPE) was used for separation of the pharmaceuticals from the water phase. Extraction volumes were 100 mL and 300 mL for STP influent and effluent. The volume for the surface water samples and for samples from the DWTP was 500 mL. The samples were passed through a 0.45-μm glass fiber filter (GF 6, Schleicher & Schuell), which had been prewashed with *n*-hexane, acetone, methanol, and MilliQ water. Following filtration, the pH of the samples was adjusted to 2.0 with concentrated HCl, and 500 ng of fenoprop was added as a surrogate standard.

The pharmaceuticals were isolated using Oasis MCX 3 cm^3 (60 mg) SPE cartridges from Waters. The cartridges were preconditioned sequentially with 2 mL of *n*-hexane, 2 mL of acetone, 10 mL of methanol, and 10 mL of noncontaminated groundwater (pH adjusted to 2.0 with concentrated HCl). The samples were allowed to pass through the cartridges at a flow rate of approximately 8 mL min^{-1}. After passage of the samples, the cartridges were dried under a stream of nitrogen for 1 h and the analytes were extracted with four 1-mL portions of acetone. The extracts were evaporated to a volume of 100 μL under a nitrogen stream, and 100 μL of methanol was added. Evaporation was continued until a volume of 50 μL and 10 mM ammonium hydroxide was added to reach the final volume of 500 μL. The samples were stored at −18 °C until analysis.

The chromatographic separation was carried out with an Agilent 1100 HPLC system (Agilent Technologies, Espoo, Finland) consisting of a binary pump, a vacuum degasser, an autosampler, and a thermostated column oven kept at 30 °C. The analytes were separated on a 5 μm, 2.1 × 50 mm reversed phase C18 analytical column equipped with a 5 μm, 2.1 × 12.5 mm narrow-bore guard column (Zorbax Extend-C18, Agilent Technologies, Espoo, Finland). The mobile phase consisted of acetonitrile and 10 mM ammonium hydroxide and the flow rate was 250 μL min^{-1}. The column was eluted isocratically for 3 min with 5% acetonitrile and then with a

TABLE 3. Retention Times on HPLC and MS/MS Parameters for the Studied Pharmaceuticals Using Electrospray Ionization at Negative Mode

	retention time [min]	precursor ion [*m*/*z*]	product ion [*m*/*z*]	cone voltage [V]	collision energy [eV]
Fenoprop[a]	10.5	266.8	194.8	24	15
Ibuprofen	11.3	205.1	161.0	15	8
Naproxen	6.6	229.0	169.9	15	16
Ketoprofen	9.6	253.0	209.0	14	8
Diclofenac	12.9	293.8	249.9	16	12
Bezafibrate	11.5	360.0	273.9	21	16

[a] Surrogate standard.

gradient to 35% acetonitrile over the course of 12 min. Finally, the mobile phase was raised to 100% acetonitrile within 1 min, held at this percentage for 5 min, and lowered back to 5% in 1 min. Prior to the next injection, the column was allowed to equilibrate for 8 min. The injection volume was 50 μL and retention times were between 6.6 and 12.9 min for the five analytes and the surrogate standard (Table 3).

Mass spectrometry was performed using Quattro Micro triple-quadrupole mass spectrometer (Micromass, Manchester, U.K.) equipped with an electrospray ionization source. The mass spectrometer was operated in the multiple reaction monitoring mode, and the cone voltage and collision energy were optimized for each analyte in negative ion mode (Table 3). Nitrogen was used as the desolvation and nebulizing gas at flow rates of 639 and 30 L h^{-1}, respectively. Argon was used as the collision gas, at a collision cell pressure of 2.8×10^{-3} mbar. The source and desolvation temperatures were 130 and 325 °C, respectively. The precursor and product ions for each analyte and the surrogate standard were determined by direct infusion of pure compounds to the MS/MS compartment (Table 3). A dwell time of 0.2 s per ion pair was used, and the interchannel delay was 0.2 s.

Detailed information about quality parameters of the method, such as recoveries and detailed description of calibration, is presented in ref *1*. For ibuprofen, diclofenac, and bezafibrate, the LOQ was 1 ng L^{-1} in ground and river waters and 5 ng L^{-1} in the STP influent and effluent. For naproxen and ketoprofen, the respective LOQs were 5 ng L^{-1} and 25 ng L^{-1}.

Results and Discussion

The River Aura. The River Aura is a relatively narrow (the average width is about 30 m) and shallow (the average depth is about 3 m) river in southwestern Finland. The length of the river is about 70 km, and it empties into the Baltic Sea. The catchment area of the river is 885 km^2, and it consists mainly of forests and agricultural land. The river receives discharges from three STPs (Figure 1). The largest discharge volumes (average 650 m^3 d^{-1}) are due to the STP of the municipal Aura. This treatment plant serves a population of about 3000 inhabitants. Upstream of Aura, there are two STPs serving populations of about 600 (Oripää) and 1500 (Pöytyä) inhabitants and having discharges of 160 and 350 m^3 d^{-1}, respectively. Along the river, there are no discharges from industrial activities. About 32 km downstream of the Aura STP is located the drinking water treatment plant of the city Turku (170 000 inhabitants), which uses the river water as the raw water source.

Sewage Treatment Plant. The studied pharmaceuticals were determined in the influent and effluent water of the Aura municipal STP in samples collected in September 2003 (data from ref *1*) and in March, May, and August 2004 (Figure 2). When taking into account all samples, the mean influent concentrations of ibuprofen, naproxen, ketoprofen, diclofenac, and bezafibrate were 23.4, 8.6, 2.9, 0.46, and 2.2 μg L^{-1}, respectively, while the corresponding mean concentrations in the effluent water were 0.04, 0.42, 0.23, 0.40, and 0.14 μg L^{-1}. Although ibuprofen was the major pharmaceutical in the influent water, in the effluent water this was not the case. The reason for this was the difference in elimination efficiency of the pharmaceuticals, that is, ibuprofen was more efficiently eliminated than the other compounds. The high elimination efficiency for ibuprofen has also been reported in previous studies (*1*, *4*).

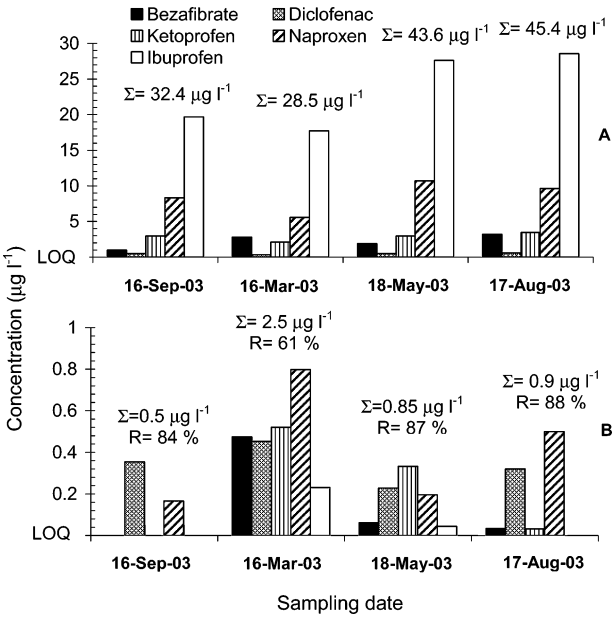


FIGURE 2. Study pharmaceuticals in the influent (A) and the effluent (B) of the sewage treatment plant of Aura. Σ is the sum of all the studied pharmaceuticals. *R* is the average removal of the pharmaceuticals in the treatment process calculated from the measured influent and effluent concentrations.

Although the March influent sample had the lowest total concentration of the studied compounds ($\Sigma = 28.5$ μg L^{-1}), the corresponding effluent sample contained higher concentrations of pharmaceuticals ($\Sigma = 2.5$ μg L^{-1}) than the effluent samples collected during the other months. Obviously, the reason for this discrepancy is that the elimination processes in the treatment plant did not work as efficiently during the winter months as during the other sampling periods. In the study of Tauxe-Wuersch et al. (*23*), the removal of ibuprofen and ketoprofen were found to deteriorate in wintertime. They suggested that the reason was the lower biodegradation in the plant because of heavy rainfall. In our case, however, the lower removal was most probably because of low water temperature in wintertime (~7 °C) and consequently lower rate of biodegradation. Although the mechanism for the elimination of the pharmaceuticals in STPs is not known exactly, biodegradation and sorption are likely to be the major elimination processes, biodegradation being the dominant one (*10*, *11*, *24*). Both mechanisms are temperature dependent. For many compounds, sorption increases with decreasing temperature (*25*) whereas biodegradation works with a lower efficiency at lower water temperatures. In March, the water temperature in the treatment plant was 7 °C. In May, August, and September, the temperature was around 13, 21, and 17 °C, respectively, and the elimination rates of pharmaceuticals were much higher. During the winter season (November−March), also the removal of BOD_7 and COD was impaired (data not shown). No nitrification occurred in the plant in winter because of low water temperature resulting in poor nitrogen removal. Previously, efficient nitrogen removal has been associated

TABLE 4. Weather Characteristics in Turku during the Sampling Periods[d]

	March	May	August
temperature (°C)[a]	+1	+9	+15
rainfall (mm)[b]	21	11	44
solar radiation (MJ m^{-2} d^{-1})[c]	8.1	17.5	14.4

[a] Calculated from daily average. [b] Cumulative during the study. [c] Measured in 60°49′N, 23°30′E. [d] Data provided by Finnish Meteorological Institute.

with high removal of biodegradable pharmaceuticals (*24*). In the Aura STP, the lack of nitrifying microorganisms in the wintertime may also have caused the poor removal of pharmaceuticals.

It could be argued that the reason for the higher effluent concentration of pharmaceuticals in the March sample is due to a higher consumption during wintertime (for example, because of flu epidemics). Obviously, this is not the case, since the influent water contained a lower amount of pharmaceuticals in March than during the other months. The results clearly show that the treatment process applied by the STP was not eliminating the studied pharmaceuticals from the wastewater. Further, the elimination was less effective during the cold season. This was probably due to a lower rate of biodegradation during the wintertime. Thus, the highest risk for river water contamination is during the cold season.

The River Water. The weather conditions and the river water temperature varied greatly between the sampling months (Tables 2 and 4). In March, the river was covered by ice and snow, and the water temperature was near 0 °C. In May, the ice cover had melted, the water temperature was around 10 °C, and the solar radiation was 17.5 MJ m^2 d^{-1}. In August, the water temperature had increased to 21 °C and the solar radiation was 14.4 MJ m^2 d^{-1}.

The river water samples were collected in such a way that the same plume of the STP discharge was followed down the river. Since the rate of the water flow in the river was known (see discussion concerning drinking water treatment plant), it was possible to determine the approximate time for the plume to reach the sampling points.

In March, the concentrations of the studied pharmaceuticals at the discharge point of the Aura STP effluent were drastically higher than in the samples collected in May and August (Figure 3). The total concentration of the compounds at the discharge point was 320 ng L^{-1} in March, while the concentration was 90 ng L^{-1} in May and 85 ng L^{-1} in August. One obvious reason for the extremes noted for the March sample is that the discharges from the treatment plant contained high concentrations of the compounds at this time of the year. Second, the river water was already contaminated because of discharge from the two STPs located upstream of the discharge point (Figure 1). The contamination altered the concentration profile of the pharmaceuticals so that it was not the same at the discharge point as in the effluent of the Aura STP. When the concentration profile observed 0.5 km upstream was subtracted from the profile observed at the discharge point, the outcome was a profile which was very similar to that of the Aura STP effluent presented in Figure 2. This shows that the compounds ketoprofen, diclofenac, and bezafibrate mainly originated from the Aura STP while ibuprofen and naproxen were mainly due to the discharges from the treatment plants located further upstream. The influence of the upstream discharge was much lower during the other sampling months and thus the May and August concentration profiles at the discharge point were very similar to those in the Aura STP effluent.

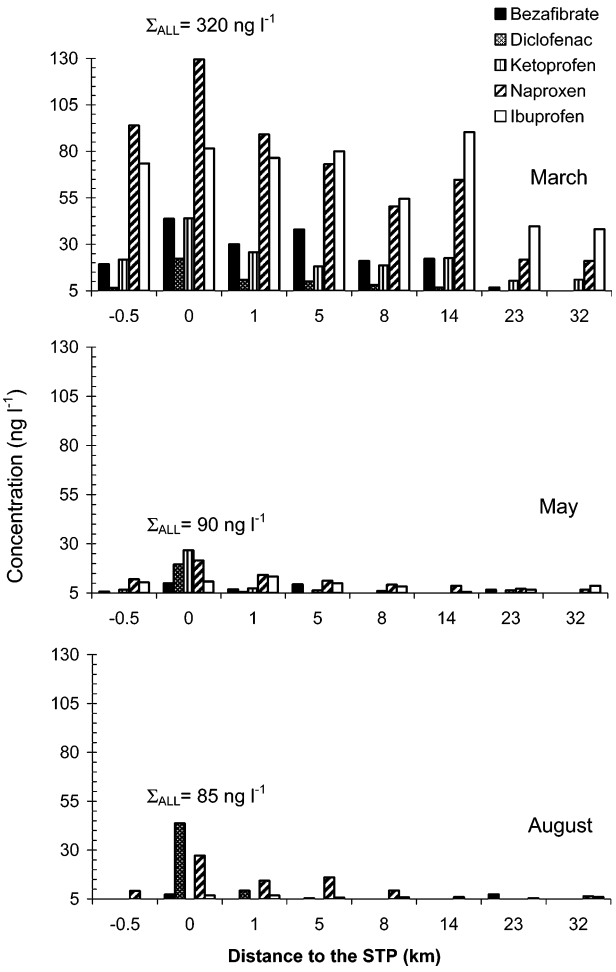


FIGURE 3. Concentrations of pharmaceuticals in River Aura at different distances to the sewage treatment plant of Aura.

Elimination in the River. In March, all the samples collected along the river contained pharmaceuticals in easily detectable amounts (the mean concentration of all pharmaceuticals along the river was 41 ng L^{-1}), but in May and August, concentrations near the quantification limit for all compounds were observed already 5 km downstream of the Aura STP (Figure 3). The higher concentrations noted along the river during wintertime must be due to the higher load of the compounds from the upstream STPs. The concentrations decreased as the compounds were carried downstream. This was partly due to further dilution of the compounds to the river water but may also have been due to some elimination processes working during the downstream transportation. The main elimination processes in river are the same as in STPs, sorption and biodegradation, and an additional factor is the UV light penetrating the water (*12*−*18*). As mentioned previously, higher temperature usually decreases the sorption (*25*). However, the effect of temperature on sorption is very compound specific and at the moment there is no information available in the literature on the effect of temperature on sorption of the studied pharmaceuticals. Biodegradation is known to increase as the temperature rises. Photodegradation is an elimination process that cannot be in effect during wintertime when the river is covered by ice and snow.

Ibuprofen has been reported to be biodegradable in surface water (*12*, *13*), but the graph in Figure 4 shows no significant difference in rate of elimination of the compound along the river during winter-, spring-, and summertime. The degradation of the pharmacologically active *S*-enantiomer of ibuprofen has been reported to occur much faster

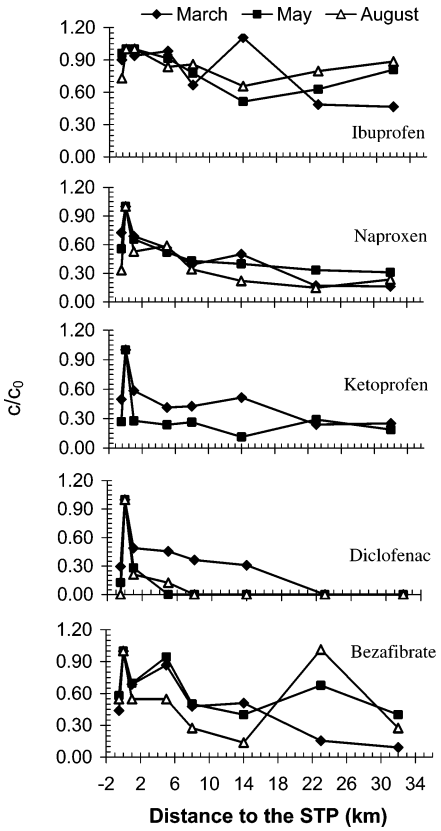


FIGURE 4. Relative concentrations of selected pharmaceuticals at different sampling points. In August, the concentration of ketoprofen was <LOQ at all points. In March, melting of the ice diluted the samples collected at 23 and 32 km causing decrease of the concentrations. c = concentration at the sampling point, c_0 = concentration at the STP effluent discharge point.

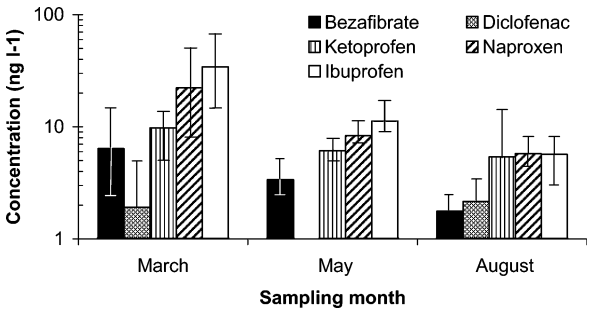


FIGURE 5. Two weeks average concentrations (with variation of minimum and maximum value, $n = 7$) of studied pharmaceuticals 32 km downstream from the sewage treatment plant. When no minimum value is presented in the figure, the value was below the quantification limit.

than the *R*-enantiomer (*13*). In our case, most of the (*S*)-ibuprofen may have already been biodegraded in the STP, and therefore biodegradation is not noticed in the river. For naproxen, the most likely elimination mechanism has been suggested to be photodegradation (*14*, *19*), and in our case, we should expect a higher elimination rate especially in May, but also in August, than in March. However, the difference in elimination rate between the sampling periods was not drastically different. The lower level of ibuprofen and naproxen at the last sampling points can therefore be mainly attributed to dilution and sorption to particles and sedimentation (*14*, *17*). The slightly higher elimination of naproxen compared to ibuprofen may be attributed to sorption process effective for naproxen, and therefore ibuprofen will gradually become the major pharmaceutical as the water flows further away from the discharge point (Figure 3).

Ketoprofen and diclofenac were compounds found to be eliminated more readily in summertime than in wintertime. Both ketoprofen and diclofenac have been suggested in the literature to undergo photodegradation (*14*−*16*, *19*), and this is a likely reason for their elimination in the river. Also, bezafibrate seemed to be readily eliminated especially in August. However, in the case of bezafibrate, the concentrations in the river were close to the limit of quantification, and therefore no firm conclusions can be made concerning its elimination.

The conclusion of this discussion is that the main reason for the higher contamination level in the river water during the cold season was the higher discharge load from STPs. This in turn was due to poor elimination in the STPs when processing water at a low temperature. In the river, the pharmaceuticals were subjected to elimination processes, of which photodegradation seemed to be the most important. However, this elimination process is not in effect in rivers covered by ice and snow. Therefore, during the cold season, pharmaceuticals are found in the river at enhanced concentrations, and because of the lower elimination rates, they are carried further away from the discharge point than in warmer seasons. This increases the risk to the aquatic environment and for the contamination of the drinking water.

Drinking Water Treatment Plant. The drinking water treatment plant was located at the sampling point of 32 km downstream from the Aura STP. Therefore, this point was studied in more depth, and seven samples were collected during two week periods in March, May, and August. The results confirmed those obtained from the study of the river water, that is, a significantly higher level of pharmaceuticals were present in the samples collected in March than in May and August (Figure 5). Total mass flows of the studied pharmaceuticals in Turku were also highest in March (Figure 6). In the case of a steady and stable discharge from STP, the mass flow should stay fairly equal. The higher the flow rate, the larger is the dilution, and the total mass of pharmaceuticals that passes one sampling point in a certain time should be roughly the same. Figure 6 shows that this was not the case in the River Aura at the time of the study. When the flow increased, the total mass flow of the pharmaceuticals also increased. The pattern was consistent throughout the study but was most evident in March where mass flow of pharmaceuticals up to 2100 μg s^{-1} was observed. The most evident reason for higher mass flows is that at the times of high flow rate, the water residence time in river is less than 1 day, and there is not enough time for elimination of pharmaceuticals. On the contrary, at low flow rate, more time is available for the elimination to take place.

In the raw water samples collected in March, the mean concentrations of ibuprofen, naproxen, ketoprofen, and bezafibrate were 34, 22, 10, and 6 ng L^{-1}, respectively (Figure 5). The maximum concentration of the major compound, ibuprofen, was determined to be 67 ng L^{-1}. The reason for the large variation in concentrations in the March samples was the large fluctuation in the water flow in the river because of days of snow melting. In May and August, the concentrations of the compounds were near or under the LOQ. Accordingly, the highest risk for drinking water contamination was in the wintertime.

The fate of the pharmaceuticals was followed in the DWTP. The major processes applied in the plant was a two-step coagulation (coagulation I and II, both using ferric coagulant) followed by filtration on granular activated carbon (GAC) and disinfection with chlorine. At the time of the samplings, the raw water samples contained pharmaceuticals at concentrations of 7−17.5 ng L^{-1}, respectively (Table 5). The concentrations of bezafibrate and diclofenac were under the

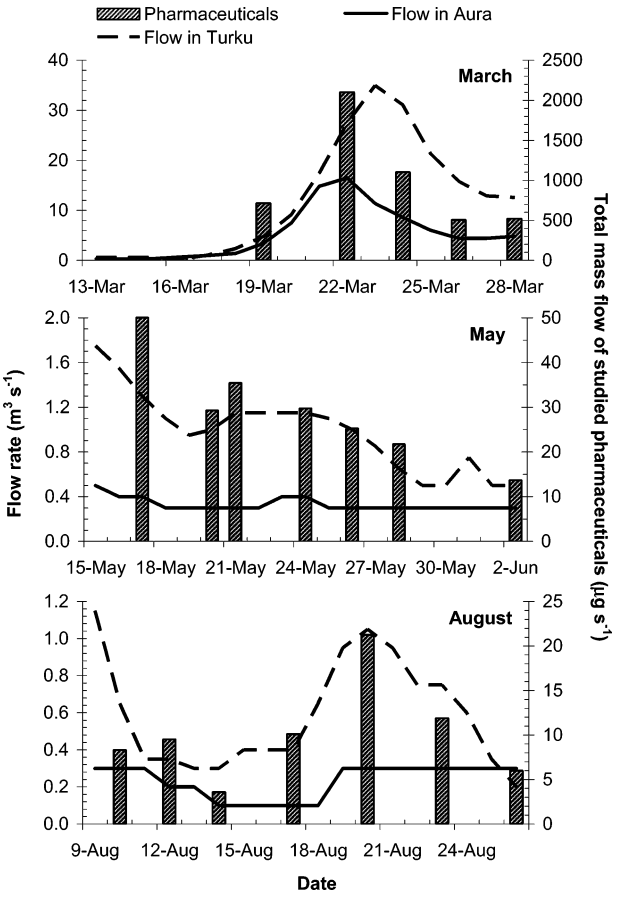


FIGURE 6. Flow rate of the River Aura in Aura and in Turku (32 km downstream) during the sampling periods. Columns represent the total mass flow of studied pharmaceuticals in Turku at the days of sampling.

TABLE 5. Measured Concentrations of the Studied Pharmaceuticals in Raw Water and after Every Major Step of the Treatment Process of Turku DWTP[c]

sample	raw water	coagulation I[a]	coagulation II[b]	GAC	purified water
			Ibuprofen		
March	17.5	16.5	13.5	9.0	8.5
May	8.5	8.0	8.0	<LOQ	<LOQ
August	8.5	8.0	8.5	<LOQ	<LOQ
			Naproxen		
March	7.5	6.0	<LOQ	<LOQ	<LOQ
May	7.0	5.5	<LOQ	<LOQ	<LOQ
August	7.5	6.0	<LOQ	<LOQ	<LOQ
			Ketoprofen		
March	7.0	5.0	6.5	5.0	8.0
May	7.5	7.5	7.5	<LOQ	<LOQ
August	11.5	10.0	10.5	<LOQ	<LOQ

[a] Ferric salt in acidic pH followed by flotation. [b] Ferric salt in basic pH followed by flotation or sedimentation. [c] Concentrations of Diclofenac and Bezafibrate were always <LOQ.

LOQ. During the two-step coagulation, naproxen was effectively eliminated to a concentration of <5 ng L^{-1} (LOQ), while the elimination of ibuprofen and ketoprofen was only marginal (13% and 8%, respectively). The elimination of ibuprofen and ketoprofen is in accordance with previous work where it has been found that pharmaceuticals are poorly removed by coagulation (*26*, *27*). Adams et al. (*26*) reported no significant removal of many antibiotics with alum or ferric salt coagulation. Similarly, Ternes et al. (*27*) reported no significant elimination of pharmaceuticals using iron chloride coagulation. In our study, it was found that granular activated carbon filtration decreased the level of ibuprofen and ketoprofen to <LOQ (1 ng L^{-1} and 5 ng L^{-1}, respectively) in May and August. In March, however, the removal was incomplete, 33% for ibuprofen and 23% for ketoprofen. Previously, activated carbon has been found to significantly reduce the level of some pharmaceuticals in water (*26*−*28*). Several factors, for example, amount of humic substances, the height of the filtration bed, and the age of the carbon, however, considerably affect the removal (*27*, *28*). Because of incomplete removal in GAC filtration in March, ibuprofen and ketoprofen were detected at concentrations of 8.5 and 8 ng L^{-1}, respectively, in the drinking water.

Although the study on the fate of the pharmaceuticals in a DWTP was conducted on single samples collected after each of the main purification processes, the study gives insight into the eliminations that may take place in a DWTP. Our results are in accordance with those reported in previous studies on the fate of pharmaceuticals in DWTPs (*26*, *27*).

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Supporting Information Available

Data of all the samples collected from the sewage treatment plant and the river. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Lindqvist, N.; Tuhkanen, T.; Kronberg, L. Occurrence of acidic pharmaceuticals in raw and treated sewage and in receiving waters. *Water Res.* **2005**, *39*, 2219−2228.
(2) Heberer, T. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. *Toxicol. Lett.* **2002**, *131*, 5−17.
(3) Stumpf, M.; Ternes, T.; Wilken, R−D.; Rodrigues, S. V.; Baumann, W. Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil. *Sci. Total Environ.* **1999**, *225*, 135−141.
(4) Ternes, T. Occurrence of drugs in German sewage treatment plants and rivers. *Water Res.* **1998**, *32*, 3245−3260.
(5) Gross, B.; Montgomery-Brown, J.; Naumann, A.; Reinhard, M. Occurrence and fate of pharmaceuticals and alkylphenol ethoxylate metabolites in an effluent-dominated river and wetland. *Environ. Toxicol. Chem.* **2004**, *23*, 2074−2083.
(6) Wiegel, S.; Aulinger, A.; Brockmeyer, R.; Harms, H.; Löffler, J.; Reincke, H.; Schmidt, R.; Stachel, B.; von Tümpling, W.; Wanke, A. Pharmaceuticals in the river Elbe and its tributaries. *Chemosphere* **2004**, *57*, 107−126.
(7) Calamari, D.; Zuccato, R.; Castiglioni, S.; Bagnati, R.; Fanelli, R. Strategic survey of therapeutic drugs in the Rivers Po and Lambro in Northern Italy. *Environ. Sci. Technol.* **2003**, *37*, 1241−1248.
(8) Metcalfe, C. D.; Miao, X.-S.; Koenig, B. G.; Struger, J. Distribution of acidic and neutral drugs in surface waters near sewage treatment plants in the lower great lakes, Canada. *Environ. Toxicol. Chem.* **2003**, *22*, 2881−2889.
(9) Weigel, S.; Kuhlmann, J.; Hühnerfuss, H. Drugs and personal care products as ubiquitous pollutants: occurrence and distribution of clofibric acid, caffeine and DEET in the North Sea. *Sci. Total Environ.* **2002**, *295*, 131−141.
(10) Urase, T.; Kikuta, T. Separate estimation of adsorption and degradation pf pharmaceutical substances and estrogens in the activated sludge process. *Water Res.* **2005**, *39*, 1289−1300.
(11) Ternes, T. A.; Herrmann, N.; Bonerz, M.; Knacker, T.; Siegrist, H.; Joss, A. A rapid method to measure the solid-water distribution coefficient (K_d) for pharmaceuticals and musk fragrances in sewage sludge. *Water Res.* **2004**, *38*, 4075−4084.
(12) Winkler, M.; Lawrence, J. R.; Neu, T. R. Selective degradation of ibuprofen and clofibric acid in two model river biofilm systems. *Water Res.* **2001**, *35*, 3197−3205.
(13) Buser, H.-R.; Poiger, T.; Müller, M. D. Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater. *Environ. Sci. Technol.* **1999**, *33*, 2529−2535.
(14) Tixier, C.; Singer, H. P.; Oellers, S.; Müller, S. R. Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen,

ketoprofen, and naproxen in surface waters. *Environ Sci Technol.* **2003**, *37*, 1061−1068.
(15) Andreozzi, R.; Marotta, R.; Paxéus, N. Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. *Chemosphere* **2003**, *50*, 1319−1330.
(16) Buser, H.-R.; Poiger, T.; Müller, M. D. Occurrence and fate of the pharmaceutical drug diclofenac in surface waters: rapid photodegradation in a lake. *Environ. Sci. Technol.* **1998**, *32*, 3449−3456.
(17) Scheytt, T.; Mersmann, P.; Lindstädt, R.; Heberer, T. Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments. *Chemosphere* **2005**, *60*, 245−253.
(18) Boreen, A. L.; Arnold, W. A.; McNeill, K. Photodegradation of pharmaceuticals in the aquatic environment: A review. *Aquat. Sci.* **2003**, *65*, 320−341.
(19) Boscá, F.; Marin, M. L.; Miranda, M. A. Photoreactivity of the nonsteroidal anti-inflammatory 2-arylpropionic acids with photosensitizing side effects. *Photochem. Photobiol.* **2001**, *74*, 637−655.
(20) Heberer, T.; Verstraeten, I. M.; Meyer, M. T.; Mechlinski, A.; Reddersen, K. Occurrence and fate of pharmaceuticals during bank filtration −preliminary results from investigations in Germany and the United States. *Water Resour. Update* **2001**. No *120*, 4−17.
(21) The Finnish Environment Institute. http:// www.environment.fi/ (accessed February 2004).
(22) The River Aurajoki Foundation. http://www.aurajoki.net/index_eng.htm (accessed February 2004).
(23) Tauxe-Wuersch, A.; De Alencastro, L. F.; Grandjean, D.; Tarradellas, J. Occurrence of several acidic drugs in sewagetreatment plants in Switzerland and risk assessment. *Water Res.* **2005**, *39*, 1761−1772.
(24) Clara, M.; Kruzinger, N.; Strenn, B.; Gans, O.; Kroiss, H. The solids retention time − a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. *Water Res.* **2005**, *39*, 97−106.
(25) Hulscher, Th. E. M. ten; Cornelissen, G. Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants − a review. *Chemosphere* **1996**, *32*, 609−626.
(26) Adams, C.; Wang, Y.; Loftin, K.; Meyer, M. Removal of antibiotics from surface and distilled water in conventional water treatment processes. *J. Environ. Eng.* **2002**, *128*, 253−260.
(27) Ternes, T. A.; Meisenheimer, M.; McDowell, D.; Sacher, F.; Brauch, H.-J.; Haist-Gulde, B.; Preuss, G.; Wilme, U.; Zulei-Seibert, N. Removal of pharmaceuticals during drinking water treatment. *Environ. Sci. Technol.* **2002**, *36*, 3855−3863.
(28) Yoon, Y.; Westerhoff, P.; Snyder, S.; Song, R.; Levine, B. A review on removal of endocrine-disrupting compounds and pharmaceuticals by drinking water treatment process. *Proceedings of Water Quality Technology Conference*, Seattle, WA, Nov 10−14, 2002, American Water Works Association: Denver, CO, 2002.

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