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Attenuation of Wastewater-Derived Contaminants in an Effluent-Dominated River†

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Although wastewater-derived chemical contaminants undergo transformation through a variety of mechanisms, the relative importance of processes such as biotransformation and photolysis is poorly understood under conditions representative of large rivers. To assess attenuation rates under conditions encountered in such systems, samples from the Trinity River were analyzed for a suite of wastewater-derived contaminants during a period when wastewater effluent accounted for nearly the entire flow of the river over a travel time of approximately 2 weeks. While the concentration of total adsorbable organic iodide, a surrogate for recalcitrant X-ray phase contrast media in wastewater, was approximately constant throughout the river, concentrations of ethylenediamine tetraacetate, gemfibrozil, ibuprofen, metoprolol, and naproxen all decreased between 60% and 90% as the water flowed downstream. Comparison of attenuation rates estimated in the river with rates measured in laboratory-scale microcosms suggests that biotransformation was more important than photolysis for most of the compounds. Further evidence for biotransformation in the river was provided by measurements of the enantiomeric fraction of metoprolol, which showed a gradual decrease as the water moved downstream. Results of this study indicate that natural attenuation can result in significant decreases in concentrations of wastewater-derived contaminants in large rivers.

Introduction

Municipal wastewater effluent contains chemical contaminants that can pose risks to public health and aquatic ecosystems (*1*−*3*). In many locations, wastewater effluent is diluted by water from other sources and the concentrations of wastewater-derived contaminants (WWDCs) decrease below levels of concern for downstream water users or aquatic organisms within a short distance of the outfall. However, during low-flow conditions and in densely populated areas, wastewater effluent can account for a significant fraction of the overall flow in some surface waters for distances up to several hundred kilometers (*4*). In these systems, the concentrations of WWDCs will be controlled by rates of in-stream attenuation processes.

Numerous researchers have demonstrated that WWDCs are attenuated by photochemical reactions (*5*, *6*) and biotransformation (*7*−*9*) under laboratory conditions similar to those expected in surface waters. The effect of in-stream attenuation on concentrations of WWDCs often is simulated using models that include parametrized attenuation rates derived from laboratory studies (*10*, *11*). However, an attempt to corroborate one such model by comparison of monitoring data with model predictions suggested that in-stream attenuation rates of triclosan were significantly slower than those derived from laboratory experiments (*11*). Although it is possible to estimate in-stream attenuation rates from monitoring data, accurate estimates require large data sets and are complicated by uncertainties regarding assumptions about sources of WWDCs, wastewater treatment plant performance, and hydrologic data.

To obtain estimates of attenuation rates in surface waters, several researchers have studied relatively small rivers and lakes in which the effluent from one or more wastewater treatment plants accounted for the majority of the overall volume prior to dilution with water from other sources (*9*, *12*−*16*). In these simple systems, phototransformation of WWDCs often serves as the dominant attenuation mechanism, with half-lives for compounds such as naproxen and diclofenac of less than 1 h reported in sunlit river water under near-surface conditions (*14*, *15*). Despite the importance of phototransformation in these systems, this process may be much less important in larger rivers where light is rapidly attenuated by dissolved organic matter and suspended particles.

To assess the importance of in-stream attenuation under the conditions expected in large rivers, we have studied the Trinity River, a waterway in which more than 90% of the flow consists of wastewater effluent during the dry summer months (Figure 1). Rates of in-stream attenuation were estimated by analysis of WWDCs in samples collected at five locations downstream of the effluent discharge points for four consecutive days during low-flow conditions. To assess the relative importance of different attenuation mechanisms, these estimates were compared with rates of attenuation measured in laboratory experiments using water samples collected from the river.

Materials and Methods

Materials. Hexachlorocyclobenzene (HCB) (99%) and all WWDCs (>98%) were obtained from Sigma-Aldrich (St. Louis, MO), except iopromide and iopamidol (99%), which were obtained from United States Pharmacopeia (Rockville, MD). All reagents were obtained from Fisher Scientific (Pittsburgh, PA). Deionized water treated with a Barnstead Nanopure II system was used for all experimental procedures requiring water.

Sample Site. Most of the wastewater effluent enters the Trinity River near Dallas, TX, from where it flows for a distance of approximately 500 km, with few other sources of wastewater effluent or flows from tributaries, before discharging into Lake Livingston. The reaches of the river sampled in this study had an average depth of 2 m and an average width of 50 m (*17*). River discharge at the time of sampling ranged from 21 to 23 m^3/s (*18*). Employees of the Trinity River Authority routinely measure water quality parameters (*19*), but there have not been any detailed studies of the occurrence and fate of wastewater-derived organic contaminants in the Trinity River.

Sample Collection. Samples were collected at six of the largest Dallas-area WWTPs during March, July, and September 2005 as 24 h composites (see Table SI 1 (SI indicates Supporting Information) for additional information about

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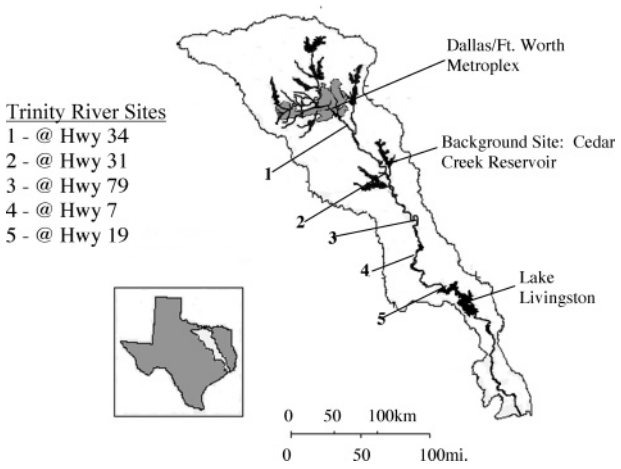

FIGURE 1. Map of Trinity River sampling locations.

the WWTPs). Samples to be analyzed for pharmaceuticals and total adsorbable organic iodide (TAOI) were stored in 4 L glass bottles, and samples to be analyzed for ethylenediamine tetraacetate (EDTA) and hormones were collected in either 10 or 1 L FEP-lined polyethylene bottles. No preservative was used for the WWTP samples, because wastewater effluent was sampled after disinfection.

Surface water samples were collected from five sites on the Trinity River between Dallas and Lake Livingston between Sept 12 and Sept 15, 2005, as well as at one upstream background site in a nearby reservoir that did not receive wastewater effluent (Figure 1). Samples were collected between 8 a.m. and 6 p.m. on four consecutive days. To avoid potential artifacts related to the time of day when samples were collected, we sampled from north to south on days 1 and 3 and from south to north on days 2 and 4. No relationship was observed between the time of day of sample collection and the concentration of WWDCs. Samples were taken from bridges at the centroid of flow, approximately 25 cm below the surface of the water, using LDPE plastic bottles and were immediately transferred to glass bottles (for total adsorbable organic iodide and pharmaceutical analysis) or PTFE-lined bottles (for EDTA analysis) for transport back to the laboratory. River water samples to be analyzed for pharmaceuticals and TAOI were preserved with 2 g/L sodium azide. Because the concentrations of hormones were mostly below the limit of detection of 0.1 ng/L in the effluent samples from WWTPs and in the preliminary samples collected from the river during July 2005, hormone analysis was not performed on the September river water samples. After collection, all samples were immediately put on ice and shipped overnight to the laboratory, where they were filtered within 12 h of arrival, stored at 5 °C, and extracted within 5 days. EDTA samples were filtered with 12 h of arrival and stored for 7−10 days prior to analysis.

Microcosm Studies. A mixture of river water from each of the sites along the Trinity River, which had been stored at 5 °C, was composited and divided into three, 1 L Pyrex beakers between 25 and 28 days after sample collection. A fourth beaker was filled with Nanopure water. Prior to the addition of water, 1 μg each of metoprolol, ibuprofen, naproxen, and gemfibrozil in 200 μL of methanol was plated onto the walls of the beaker. Water was added to the beakers after the methanol had fully evaporated. Two of the beakers containing river water were covered with aluminum foil and stored in the dark at 22 ± 3 °C, and one of the two beakers was sterilized with 1 mM mercuric chloride as a control. One of the beakers containing river water and the beaker containing Nanopure water were placed on the roof of a building at the University of California at Berkeley campus in direct sunlight, in a 25 °C constant-temperature bath, during the second half of October 2005. The water in the beakers had a depth of 13 cm. Aliquots of 200 mL were removed from all four beakers at 0, 4, 9, and 14 days and analyzed for acidic drugs and metoprolol. After each sample aliquot was removed, the volume removed was replaced by an equal quantity of river water or Nanopure water without any added WWDCs. Before each sample was extracted, 250 ng/L flurbiprofen and 250 ng/L propranolol were added to monitor the recovery of acidic drugs and metoprolol, respectively. After analyses, concentrations were corrected for dilution. An interfering peak made it impossible to measure EDTA in the microcosm experiments.

An additional experiment was performed to ascertain whether the speciation of FeEDTA changed over time. The concentrations of FeEDTA and total EDTA were measured in a mixture consisting of 4 mL of final effluent from WWTP 6 and 12 mL of unfiltered Trinity River water. The mixture was split into two 10 mL borosilicate glass test tubes. One of the test tubes was irradiated by a 500 W medium-pressure mercury lamp for 30 min to remove the FeEDTA. The concentrations of FeEDTA and non-FeEDTA in both test tubes were measured after storage of the samples in the dark at room temperature for 2 and 6 days.

Analyses. Analytical methods for TAOI (*20*), EDTA (*21*), hormones (*22*), and β-blockers (*8*) have been described previously. The GC/MS/MS method used for analysis of acidic pharmaceuticals is described in the Supporting Information.

Results and Discussion

Attenuation of WWDCs in the Trinity River. During the sampling period, the effluent from the six WWTPs sampled as part of this study accounted for approximately 83% of the flow of the Trinity River (*18*). Most of the remaining flow was attributable to smaller WWTPs that were not sampled. Concentrations of WWDCs detected in wastewater effluent samples (Tables SI 2−3) were consistent with values reported at other WWTPs in North America (*22*−*26*). Concentrations of WWDCs in effluent samples exhibited considerable temporal and spatial variation, which is consistent with observations from other monitoring studies (*22*, *27*). Because the discharges of the Dallas-area WWTPs mix prior to sampling site 1, the impact of plant-to-plant variations in the WWDC concentrations did not affect concentrations in samples collected from the river. The effects of day-to-day variations in the loading of WWDCs was assessed by averaging the concentration measured in samples collected on four consecutive days.

With the exception of TAOI and FeEDTA, concentrations of WWDCs decreased substantially with distance downstream in the Trinity River (Figures 2 and 3). Most of the TAOI in wastewater effluent consists of triiodinated aromatic X-ray contrast media (*28*−*30*), which are recalcitrant in WWTPs and surface waters (*28*, *31*). TAOI has been used as a surrogate for this family of compounds at groundwater recharge sites where the concentration of TAOI remains constant over long travel distances (*20*, *32*). Thus, TAOI serves as a good tracer for the fraction of the overall flow of the river that was derived from wastewater. Assuming conservative mixing, where wastewater effluent is diluted by water containing TAOI at a concentration equal to the average detected at the background site, we calculate that if the percentage of wastewater effluent in the Trinity River decreased from 100% to 75% by dilution with background water, the concentration of TAOI concentration would have decreased by 1.7 μg/L. The uniformity of the TAOI data among sites was consistent with a hydrological model developed by the Texas Commission for Environmental Quality (*17*) that indicated no significant inputs of water downstream of the Dallas metropolitan area during the sampling period. As a result, we

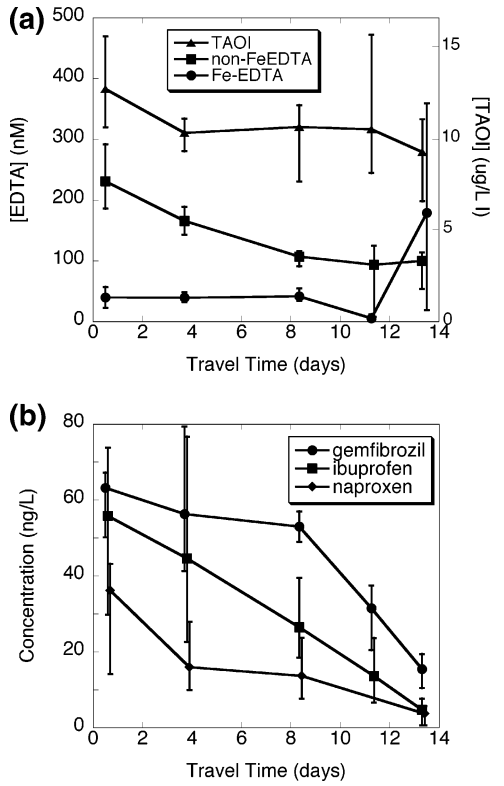

FIGURE 2. Average (symbols) and range (bars) of concentrations of WWDCs in the Trinity River. All data are included in Table SI 2.

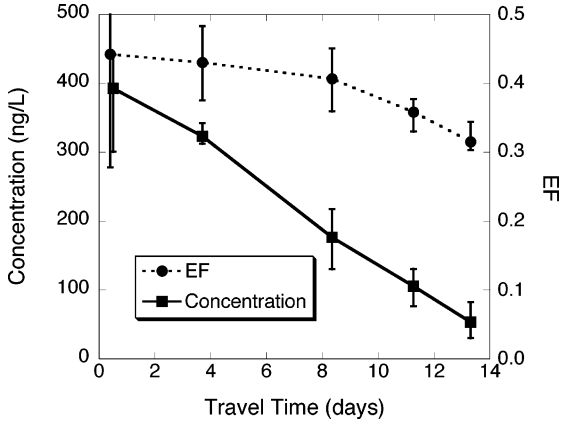

FIGURE 3. Average (symbols) and range (bars) of concentrations and enantiomer fractions (EFs) of metoprolol in the Trinity River.

are confident that the decreases in the concentrations of other WWDCs were not attributable to dilution.

Although it would have been preferable to conduct a true synoptic study and follow parcels of water downstream over the travel time of the river, this was not feasible due to logistical constraints. To ascertain whether apparent decreases in concentration were due to WWDC attenuation or to a pulse of elevated concentrations of WWDCs from the WWTPs at the upstream sites, we compared concentrations of the apparently reactive compounds in samples representing the same parcel of water at adjacent sites separated by 2 or 3 days (Figure SI 1). The comparison indicated that WWDC concentrations in the downstream samples were lower than the concentrations in the upstream samples.

EDTA is a synthetic chelating agent that is always associated with a metal in wastewater. FeEDTA complexes undergo direct photolysis in sunlight with a half-life of approximately 10 min under near-surface conditions (*33*). Other metal−EDTA complexes are not photolabile and therefore are much more persistent in surface waters (*16*). Under the conditions encountered in the Trinity River (i.e., pH 6.5−8.1) FeEDTA is thermodynamically unstable and should slowly be converted into complexes such as $ZnEDTA^{2-}$ and $CuEDTA^{2-}$ (*34*). When a mixture of metal−EDTA complexes in wastewater effluent was mixed with Trinity River water in the laboratory, the concentration of FeEDTA complexes decreased by less than 5% over a period of 6 days (Figure SI 2), which is consistent with previous studies of EDTA exchange kinetics in surface waters (*34*). A small amount (i.e., <10% of the total EDTA) of FeEDTA was formed over 6 days when FeEDTA initially present in the sample was eliminated through photolysis prior to incubation.

The rapid photolysis of FeEDTA complexes and the slow formation of FeEDTA from the non-FeEDTA complexes (i.e., $[EDTA_{total}] - [FeEDTA]$) had two effects on the EDTA data. First, the relatively low concentrations of FeEDTA complexes (i.e., <60 nM) detected at sites 1−4 may be attributable to conversion of a fraction of the non-FeEDTA complexes into FeEDTA during the 7−10 day period between sample collection and analysis (i.e., actual FeEDTA concentrations in the river may have been significantly lower than those measured after storage). Second, the slow conversion of non-FeEDTA complexes into FeEDTA could have provided a mechanism for loss of the normally recalcitrant non-FeEDTA complexes. In other words, the modest decrease in non-FeEDTA complexes observed as the water moved downstream may have been attributable to slow formation of FeEDTA complexes followed by rapid photolysis. Because the rate of FeEDTA formation that we measured in our mixing experiment (Figure SI 2) accounts for less than half of the EDTA loss that we measured in the Trinity River, we cannot rule out the possibility of EDTA biotransformation in the river.

The relatively high concentrations of FeEDTA complexes detected in the furthest downstream site on Sept 13 and 14 (i.e., 357 and 345 nM compared to <60 nM in all other samples) are indicative of a source unrelated to the Dallas WWTPs because FeEDTA would be photolyzed during the 13 day transit from Dallas, and an elevated concentration of FeEDTA was not detected in samples from the previous upstream site (i.e., site 4) on Sept 12. The unexpectedly high concentration of FeEDTA at the downstream site was not accompanied by increases in the concentrations of other WWDCs, and therefore, it is unlikely that it was attributable to wastewater effluent or sewage. It is possible that the FeEDTA was related to an agricultural source, such as chelated iron in fertilizer. However, such sources cannot be proven because no information on spills or local discharge of EDTA is available for this section of the river.

Among the pharmaceuticals measured, only gemfibrozil, ibuprofen, metoprolol, and naproxen were consistently detected in wastewater effluent and in the Trinity River. Propranolol and indometacine were observed sporadically in wastewater effluent and in the river, while ketoprofen and diclofenac were detected in about half of the wastewater effluent samples, but not in any river water samples. The average concentration of gemfibrozil, ibuprofen, metoprolol, and naproxen decreased by 75−90% as the water traveled downstream (Figure 2). Their respective half-lives, derived by fitting the data depicted in Figure 2 to a first-order disappearance, were 8.9, 4.6, 5.3, and 4.2 days, respectively.

In addition to data on concentrations of metoprolol, the analytical method (*8*) provided data on the concentration of the two enantiomers of metoprolol (Figure SI 3). Changes in the relative concentration of enantiomers are often quantified by use of an enantiomer fraction (EF), which is defined as

$$EF = \frac{[\text{isomer 1}]}{[\text{isomer 1}] + [\text{isomer 2}]} \quad (1)$$

TABLE 1. First-Order Rate Constants (day^{-1}) ($\pm$ Standard Deviation) for Dissipation of Pharmaceuticals in Microcosms and in the Trinity River

	microcosms			
	sunlight		dark	in situ
	deionized water	Trinity River water	Trinity River water	in situ river
gemfibrozil	0.08 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	0.08 ± 0.03
ibuprofen	0.11 ± 0.06	0.12 ± 0.05	0.04 ± 0.02	0.15 ± 0.04
naproxen	0.37 ± 0.09	0.50 ± 0.11	0.04 ± 0.02	0.16 ± 0.02
metoprolol	0.09 ± 0.05	0.11 ± 0.03	0.013 ± 0.002	0.13 ± 0.02

where isomers 1 and 2 are the first and second isomers to elute from a GC column. Although metoprolol, which is administered as a racemate, is partially metabolized prior to excretion and is removed to a small extent in municipal wastewater treatment plants, it does not appear to undergo a net enantiomer shift during these processes (i.e., an average EF of 0.52 was observed in wastewater effluent by Wong et al. (*35*)). In the effluent of the Dallas-area WWTPs, we measured an average EF for metoprolol of 0.50 ± 0.03 (n = 18). The average EF in the river decreased with distance downstream from 0.44 at site 1 to 0.31 at site 5 (Figure 3).

Enantioselective degradation only occurs when a chiral contaminant interacts with another chiral compound such as an enzyme during biotransformation (*36*, *37*). Other attenuation mechanisms that could result in a decrease in metoprolol concentration, such as photolysis and sorption to mineral surfaces, should not affect the EF. As a result, the change in EF for metoprolol provides strong evidence that biotransformation occurred in the Trinity River.

Microcosm Experiments. The microcosm experiments were performed to provide insight into the relative importance of different attenuation mechanisms for gemfibrozil, ibuprofen, metoprolol, and naproxen in the river (Table 1 and Figure SI 3). The microcosm experiments in which deionized water and Trinity River water were exposed to sunlight established the occurrence of direct and indirect photolysis, while the experiments with Trinity River water incubated in the dark established the occurrence of biotransformation. The absence of degradation in the dark, sterilized controls eliminated the possibility of losses in the river through other abiotic processes (e.g., hydrolysis or sorption).

To assess the relative importance of photolysis and biotransformation, it is necessary to consider the ways in which the microcosm treatments were different from the conditions encountered in the Trinity River. With respect to photolysis, there are differences in solar irradiance both due to season and latitude and due to light screening with depth (i.e., the microcosm was 0.13 m deep, while the river was typically about 2 m deep). As indicated by the results of our calculations (SI calculations a−c), the rate of photolysis in the sunlit microcosms should have been about an order of magnitude faster than the rates in the river. With respect to biotransformation in the dark microcosm, the microbes present may have been less active because they were deprived of labile organic carbon related to primary production (e.g., the decay of dead algae), which is likely to be considerable under the eutrophic conditions encountered in the Trinity River (*38*). Additionally, storage of the river water in the refrigerator for 28 days prior to initiation of the experiment may have decreased the concentration of labile organic carbon and shifted the microbial communities to favor more psychrophilic organisms rather than the mesophilic community normally present in the river. As a result, the rates of biotransformation observed in the microcosms may have been slower than those in the river.

Despite the uncertainties associated with extrapolating results of the microcosms to conditions encountered in the river, the data provide insight into the relative importance of the different attenuation mechanisms. Without correcting for the effects of light screening with depth, dissipation rates through photolysis were higher for all compounds in the river than in the microcosms, with the exception of naproxen (Table 1). Given the approximate order of magnitude decrease in photolysis rates in the river relative to the microcosms, it is unlikely that photolysis can explain dissipation observed in the river. Additionally, if phototransformation were the dominant attenuation mechanism in the river, the rate of dissipation of naproxen in the river would have been substantially faster than the rates observed for the other three compounds, as was the case in the two sunlit microcosms. Because photolysis cannot explain the absolute or relative rates of dissipation and the rates of dissipation in the dark were all comparable, albeit slower than those observed in the river, we conclude that biotransformation is a more likely explanation for the observed dissipation than photolysis.

We did not observe a change in the EF of metoprolol in any of the microcosms. This was due to the limited extent of biotransformation of metoprolol in the dark treatments. We calculate that if the EF of metoprolol had changed at the same rate in the microcosm as in the Trinity River, the final EF would have been about 0.47, which could not be differentiated from that of racemic metoprolol with our analytical method (SI calculation d). Additionally, EF values are sensitive to environmental conditions, and differences in pH, microbial communities, and many other factors can influence enantioselectivity (*37*). It may be difficult to reproduce the conditions in the river closely enough to observe the same pattern of enantioselectivity in a microcosm.

Relative Importance of Phototransformation and Biotransformation in Surface Waters. Most in-stream attenuation studies have downplayed the importance of biotransformation because the systems that are the easiest to study have typical hydraulic retention times that are too short for such processes to have a noticeable effect on concentrations of most WWDCs (*15*, *16*). Because the section of the Trinity River that we studied had a hydraulic retention time of almost 2 weeks and considerable light attenuation over its depth, biodegradation was as important as or more important than photolysis for most of the compounds that we analyzed. For more photolabile compounds, such as FeEDTA and diclofenac, photodegradation may still be the dominant loss mechanism in deeper rivers.

Our results suggest that biotransformation should be considered as a potentially important attenuation mechanism for WWDCs in large rivers, even if it is relatively unimportant in shallow surface waters. To illustrate the differences between these two types of systems, consider the fate of naproxen in river water with three different beam attenuation coefficients ranging from a low-DOC, particle-free river to a turbid, highly colored water (Figure 4). We assumed a near-surface direct photolysis rate (k_{surf}) of 0.37 day^{-1}, which is equivalent to the rate observed in the deionized water microcosm, and adjusted this number to 0.39 day^{-1} to

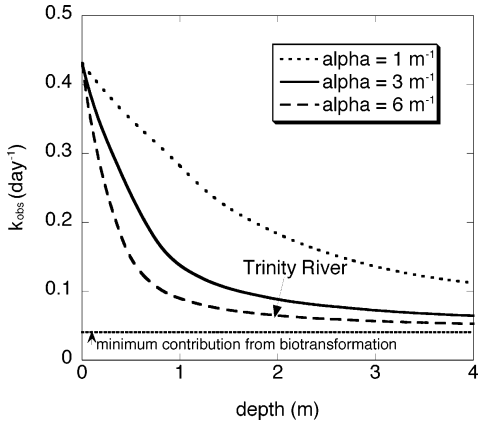

FIGURE 4. Calculated attenuation rates for naproxen for mid-September, 33°N.

account for differences in solar irradiation between Berkeley and Dallas (SI calculation a). We neglected indirect photolysis because the dissipation rates for all the compounds in this study were similar in deionized water and in river water.

To account for the effect of light attenuation due to scattering and absorption on photolysis rates in rivers of different depths, k_{surf} is adjusted by a screening factor (S) (*39*):

$$S = \frac{1 - e^{-\alpha z_{photic}}}{\alpha z_{photic}} \quad (2)$$

where z_{photic} is the depth of the photic zone. The rate of photolysis averaged over the depth of the photic zone is therefore

$$k_{photo} = Sk_{surf} \quad (3)$$

Finally, if the water depth (z_{tot}) is greater than the depth of the photic zone, the rate needs to be adjusted (*40*):

$$k_{photo(deep)} = \frac{k_{photo} z_{photic}}{z_{tot}} \quad \text{for} \quad z_{tot} > z_{photic} \quad (4)$$

Assuming a river in which photodegradation and biotransformation occur, the observed degradation rate (k_{obsd}) will be the sum of k_{bio} and k_{photo}.

The effects of depth and light attenuation differ considerably between the different types of surface waters. For a turbid river, photolysis rates for naproxen are approximately equal to biotransformation rates at a depth of 2 m, whereas photolysis is almost an order of magnitude faster than biodegradation at 0.2 m depth.

The calculations in Figure 4 (SI calculations e) likely exaggerate the importance of photodegradation as an attenuation mechanism for the WWDCs that we studied because naproxen has a relatively high propensity to undergo direct photolysis. In the Trinity River, for example, while we estimate that while biotransformation accounts for about half of the total attenuation rate for naproxen, we predict that it is responsible for over 80% of the total attenuation rate for ibuprofen (Figure SI 5). In deeper, more turbid rivers, the importance of photodegradation relative to biodegradation will be further diminished. Because many important effluent-impacted water resources are several meters deep (e.g., the Grand River in Canada (*41*) and the Passaic River in the U.S. (*4*)), we cannot assume that photolysis will be more important than biotransformation. In rivers where phototransformation is slow, management to increase the rate of biotransformation through the construction or restoration of wetlands may provide a means for enhancing the attenuation of WWDCs in such systems, while providing other benefits such as aquatic habitat and nutrient removal.

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Supporting Information Available

Information about WWTPs sampled, concentrations of WWDCs measured in wastewater effluent samples, concentrations of WWDCs measured in September in the Trinity River, a comparison of concentrations of reactive compounds upstream and samples from the Trinity River, speciation of EDTA during incubation of mixed Trinity River/WWTP effluent samples, chromatograms of the enantiomers of metoprolol, microcosm experiments for gemfibrozil, naproxen, metoprolol, and ibuprofen, calculated attenuation rates for ibuprofen for mid-September, procedures for the acidic pharmaceutical method, conditions used for analysis of acidic drugs, and relevant calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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