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Environmental impact statement

Wastewater treatment plant (WWTP) effluents are the primary source of emerging contaminants in a receiving river system in Ontario, Canada. Example contaminants include the artificial sweetener acesulfame-K (ACE-K) and the pharmaceutical compounds carbamazepine (CBZ), caffeine (CAF), sulfamethoxazole (SMX), ibuprofen (IBU), gemfibrozil (GEM), and naproxen (NAP). ACE-K was the most persistent compound at concentrations at least one order of magnitude higher than the pharmaceuticals over a 31 km stretch of the river. Concentrations of ACE-K, CBZ, GEM, NAP, and Cl^- were strongly correlated, suggesting these compounds can be used as co-tracers of wastewater. The use of multiple tracers, such as artificial sweeteners combined with pharmaceutical compounds, greatly increases the confidence of tracking wastewater in aquatic environments.

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ARTICLE

Acesulfame-K and pharmaceuticals as co-tracers of municipal wastewater in a receiving river

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Wastewater treatment plant (WWTP) effluents are important sources of emerging contaminants at environmentally-relevant concentrations. In this study, water samples were collected from a river downstream of two WWTPs to identify practical tracers for tracking wastewater. The results of the study indicate elevated concentrations of Cl^-, nutrients (NH_3-N and NO_2^-), the artificial sweetener acesulfame-K (ACE-K), and the pharmaceuticals carbamazepine (CBZ), caffeine (CAF), sulfamethoxazole (SMX), ibuprofen (IBU), gemfibrozil (GEM), and naproxen (NAP) in the river close to the WWTPs that decreased with distance downstream. A correlation analysis using the Spearman Rank method showed that ACE-K, CBZ, GEM, NAP, and Cl^- were strongly correlated with each other over a 31 km stretch of the river in the study area. The strong correlations of these target compounds indicate that the artificial sweetener ACE-K and the pharmaceuticals CBZ, GEM, and NAP can potentially be used as co-tracers to track wastewater.

Introduction

Sewage effluents are considered the primary source of emerging contaminants in the environment.[1] Chemical tracers for wastewater contamination should be conservative and present in most wastewaters, and ideally be derived only from wastewater. In addition, the concentrations of tracers should be well above analytical detection limits and not vary greatly over time.[2, 3] Chloride and nutrients have been used as conventional tracers of wastewater contamination; however, other anthropogenic sources, such as road salts and fertilizer, can contribute to loadings in surface and ground waters thus making these constituents potentially less reliable as tracers.

Artificial sweeteners such as acesulfame-K (ACE-K) and sucralose are particularly widespread and persistent in surface water and groundwater, and therefore have been suggested as ideal tracers of domestic wastewater in the environment.[4-6] In addition, some pharmaceuticals, such as carbamazepine (CBZ) and caffeine (CAF), have been proposed as indicators of wastewater contamination in the environment.[7-9] However, CBZ and naproxen (NAP) can adsorb to sediment[10, 11] and CAF tends to biodegrade[12]. These natural attenuation processes make these pharmaceuticals less ideal as wastewater tracers. Therefore, the use of multiple tracers would greatly increase the confidence of identifying wastewater in aquatic environments.[3, 13]

In this study, samples of river water were collected and analyzed for several potential tracers to track wastewater from two WWTPs in the Grand River watershed. The Grand River is the largest watershed in southwestern Ontario, Canada, flowing 300 km through a number of municipalities before discharging to Lake Erie. The persistence of several target compounds—ACE-K, CBZ, CAF, NAP, sulfamethoxazole (SMX), 3,4-methylenedioxyamphetamine (MDA), 3,4-methylenedioxymethamphetamine (MDMA), ibuprofen (IBU), and gemfibrozil (GEM)—was compared to conventional wastewater parameters to determine the potential use of these compounds as tracers.

Materials and Methods

Water sampling and field analyses

Samples of river water were collected at 10 locations over a distance of 32.1 km along the Grand River near the cities of Waterloo and Kitchener (southwestern Ontario, Canada) in August 2012 and July 2013. Winter samples were not available due to the weather limitations. The 10 sampling locations are labeled GR 1 to GR 10 (Figure 1). GR 8 and GR 1 are upstream of GR 2 (the location of the first WWTP; WWTP-1), then GR 3, 9, 10, 4, 5, 6, 7 are located sequentially downstream. GR 5 is located at the intake of a Water Treatment Plant-1 (WTP-1) where Grand River water is treated to provide a drinking water supply, and GR 6 is located 0.1 km downstream of the effluent of WWTP-2. The average discharge of the Grand River measured at a gauge station near GR 6 (Grand River near DOON, station number 02GA048)[14] was 9.8 $m^3\ s^{-1}$ for the sampling dates in 2012 (August 9-10) and 56.7 $m^3\ s^{-1}$ for the sampling dates in 2013 (July 8-9).

All river water samples were collected in a consistent manner 5 m away from the river bank on the side of the river into which WWTP-1 and WWTP-2 effluents are discharged.

Additional samples were collected directly from the effluent discharge pipe from the wastewater treatment plant (WWTP-1), and from the water treatment plant (WTP-1) influent reservoir. These locations were selected to provide samples most representative of the WWTP-1 effluent and of the intake of WTP-1. Samples were obtained using Teflon tubing (6.5 m in length) connected to a peristaltic pump (MasterFlex, Cole-Parmer Instrument Company, CA). All samples, except those for pH, Eh, and electrical conductivity (EC) measurements, were filtered through 0.45 µm Thermopor membrane filters to determine alkalinity and concentrations of Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, NH_3-N, PO_4-P, and the target pharmaceuticals and artificial sweetener. Determination of pH, Eh, alkalinity, and EC was performed on site immediately after sample collection. The samples for NH_3-N, PO_4-P, pharmaceuticals, and artificial sweetener were acidified on site with H_2SO_4 to pH<2 while samples for anions (Cl^-, SO_4^{2-}, NO_3^-, NO_2^-) were not. All samples were stored at 4 °C until analysis.

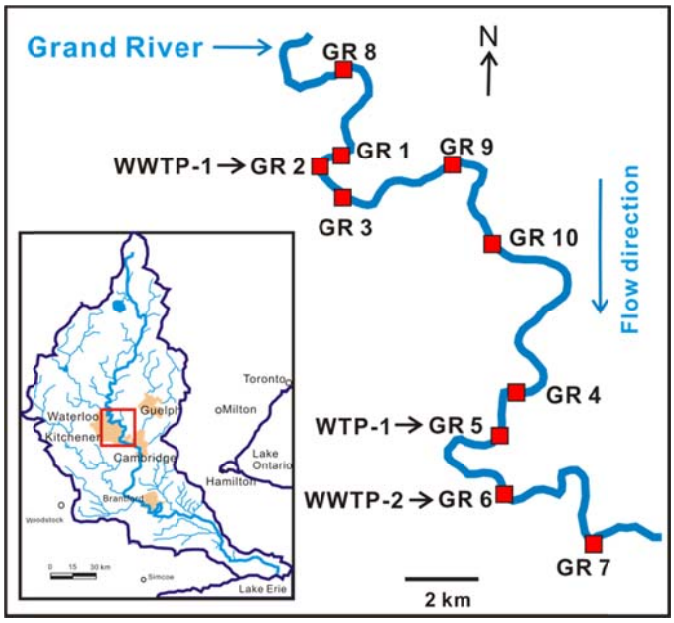

Figure 1. Sampling locations along the Grand River, southwestern Ontario, Canada.

Analysis of water samples

Primary wastewater parameters

Values of pH were determined using a pH electrode (Ross combination, Orion 815600) calibrated with standard pH 7.0 and pH 10.0 buffers prior to each measurement, and checked with a pH 7.0 buffer after each measurement. Values of Eh were determined using an Eh electrode (Pt-billeted Ag/AgCl combination, Orion 9678BNWP) checked using Zobell's[15] solution before and after each measurement. Electrical conductivity was measured using an Orion 013005MD conductivity cell. The performance of the EC cell was checked with a 0.01M KCl solution prior to each measurement. Alkalinity values were determined using standardized H_2SO_4 and a Hach digital titrator following Titration Method 2320 B[16].

Anion (Cl^-, SO_4^{2-}, NO_3^-, NO_2^-) concentrations were determined by ion chromatography (Dionex ICS-5000+, Mississauga, CA). Ammonia (NH_3-N) and ortho-phosphate (PO_4-P) concentrations were determined using a Hach spectrophotometer DR/8400 following the salicylate method (4500-NH_3)[17] and ascorbic acid method (4500-P: E)[18], respectively.

Trace wastewater parameters

ACE-K and the eight pharmaceutical compounds were analyzed using solid-phase extraction and high-performance liquid chromatography (HPLC) followed by tandem mass spectrometry using previously published methods[6, 19, 20], with slight modifications such as inclusion of isotope dilution techniques for each study compound and optimization of instrument operating conditions. Native compounds were supplied by Sigma-Aldrich (Oakville, Canada) with the exception of ACE-K obtained from Toronto Research Chemicals Inc. (Toronto, Canada). Isotope-labeled standards, including ACE-K-d4 and SMX-d4 (Toronto Research Chemicals Inc., Toronto, Canada), MDA-d5 and MDMA-d5 (Cerilliant Inc., Texas, USA), and CBZ-d10, CAF-d3, IBU-d3, GEM-d6, and [^{13}C]-NAP (Cambridge Isotope Laboratory Inc., Cambridge, USA) were obtained as dry powders. Standard stock solutions of ~1000 µg L^{-1} were prepared by dissolving each compound in methanol. Working standard solutions containing all analytes were prepared by serial dilution in methanol:water 50:50 vol:vol. HPLC-grade ammonium acetate and formic acid were obtained from Sigma-Aldrich (Oakville, Canada). Ultrapure (Type 1) water was generated using a MilliQ A10 water system (18.2 MΩ.cm @ 25 °C).

Prior to analysis, 600 mL aliquots of aqueous samples were spiked with a consistent amount of internal standard mixture. These samples were passed through solid-phase extraction (SPE) cartridges (Oasis HLB 6 mL glass cartridges; Waters Corp., Mississauga, Canada) pre-conditioned with 3 × 2 mL methanol and then equilibrated with 3 × 2 mL ultrapure water. After loading the 600 mL samples, the cartridges were washed using 3 × 2 mL 5 vol. % methanol then eluted with 3 × 2 mL methanol. The eluate was collected in an amber glass vial and stored at 4 °C until analysis.

The extracts were analyzed using an Agilent 1100 HPLC (Agilent Technologies, Mississauga, Canada) followed by electrospray tandem mass spectrometry (MS/MS; 4000 Q TRAP, Applied Biosystems, Foster City, USA). Caffeine, SMX, CBZ, MDA, and MDMA were analyzed in electrospray ionization positive (ESI+) mode, while IBU, GEM, NAP, and ACE-K were analyzed in ESI negative (ESI-) mode. The gradient and mobile phases were changed from previous methods based on the HPLC analytical columns and mass spectrometer (MS) requirements. The compound and source-dependent parameters of the MS were modified to obtain an optimum signal response. The mobile phases for analysis in ESI+ mode consisted of 0.1% formic acid and 5 mM ammonium acetate in water (phase A) and 99.9% MeOH with 0.1% formic acid (phase B). A gradient elution started at 10% B for 3 min, increased to 90% B in 10 min, and then held at 90% B min for 10 min. The flow rate was 1000 µL min^{-1} and the injection volume was 15 µL. The mobile phases for analysis in ESI- mode consisted of 6.9 mM acetic acid in 300 mL acetonitrile and 700 mL water (phase A) and 100% acetonitrile (phase B). A gradient elution started at 12% B, then increased linearly to 40% in 10 min and held at 40% for 10 min. The injection volume was 10 µL and the flow rate was 1000 µL min^{-1}. For ACE-K analyzed in ESI- mode, the mobile phases consisted of 20 mM ammonium acetate in water (phase A) and 20 mM ammonium acetate in methanol (phase B). The gradient elution started at 2% B, then increased linearly to 75% in 8 min

and held at 75% for 8 min. The injection volume was 10 µL and the flow rate was 1000 µL min^{-1}.

A mixed standard containing ACE-K, CBZ, CAF, SMX, IBU, NAP, and GEM was used for method calibration. The same amount of isotope-labeled compounds was added to the calibration standards, method standards, and unknown samples. The recovery of the isotope-labeled compounds was used to correct the response of the instrument to each compound. Nine-point calibration curves from 5 to 10,000 ng L^{-1} were established by analysis of standard mixtures prepared in 50% methanol: 50% water. Tap water samples spiked with the analyte mixtures and internal standards and extracted following the same procedure as the unknown samples were used to evaluate the addition of the SPE step to the method. The limits of detection (LOD) and quantification (LOQ) were calculated at three and 10 times the signal-to-noise values, respectively. The method detection limits (MDL) were determined by extracting 14 deionized water samples fortified with labeled analytes at concentrations three to five times the LOD, depending on the expected MDL and internal standard at the same concentration level used in the method. The MDL was calculated by multiplying the standard deviation of the replicate measurements by the Student's t value for n-1 degrees of freedom. The MDLs determined were 41.9 ng L^{-1} for ACE-K, 99 ng L^{-1} for CAF, 10.4 ng L^{-1} for SMX, 17.1 ng L^{-1} for CBZ, 38.8 ng L^{-1} for MDA, 3.9 ng L^{-1} for MDMA, 29.6 ng L^{-1} for IBU, 3.1 ng L^{-1} for GEM, and 9.7 ng L^{-1} for NAP. The LOQs determined were four to 230 times lower than MDL values.

Methanol:water samples (continuous calibration verification samples) were analyzed at initial instrument calibration and after every 10 unknown samples. Quality assurance/quality control results showed that the concentrations of all target compounds in the calibration standard blanks and method standard blanks were consistently below detection limits. The absolute analyte and internal standard recovery for continuous calibration verification samples ranged from 84 to 116%. Relative method recovery for ACE-K ranged from 94 to 118% across the standard curve from 0.1 to 100 µg L^{-1}. The relative internal standard recovery of ACE-K for unknown samples ranged from 71 to 95%. Relative method recovery for CAF, SMX, CBZ, MDA, and MDMA ranged from 84 to 120% across the standard curve (0.01-10 µg L^{-1} for SMX and MDMA, 0.05-10 µg L^{-1} for CBZ and MDA, 1-10 µg L^{-1} for CAF). Relative internal standard recovery of CAF, SMX, CBZ, MDA, and MDMA for unknown samples ranged from 70 to 109%; CBZ had the best absolute internal standard recovery (84-97%) for unknown samples. Relative method recovery for IBU, GEM, and NAP ranged from 91 to 110% across the standard curve (0.02-10 µg L^{-1}); the corresponding relative internal standard recovery for unknown samples was 94-119%. The recovery of duplicated, spiked, and repeated samples was 75-121%.

Results and Discussion

Grand River sampling results

The average pH of the river water samples was ~7.9 during the 2012 and 2013 sampling events, with lower values of 7.6-7.8 observed near the effluent of WWTP-1. Eh varied over the sampling distance of the river in 2012, with lower values observed near the effluents of both WWTP-1 and WWTP-2; however, values were relatively constant (~350 mV) in 2013 likely due to the larger discharge of the river at the time of sampling. The highest alkalinity and EC values over the sampling distance in both 2012 and 2013 were observed near the effluent of WWTP-1, and higher values were observed in 2013 (alkalinity, ~330 as $CaCO_3$ mg L^{-1}; EC, ~870 µS cm^{-1}) than in 2012 (Fig. 2).

Chloride (Cl^-) reached its highest concentration of ~150 mg L^{-1} near the effluent of WWTP-1 in both 2012 and 2013, and reached a second peak concentration (~87 mg L^{-1}) near the effluent of WWTP-2 in 2012. Elevated concentrations of SO_4^{2-} and PO_4-P were observed near the effluents of both WWTPs in 2012, but were less variable in 2013 likely due to the much larger river discharge in that year. Incomplete removal of nitrogen (nitrification and denitrification) by WWTP-1 likely resulted in the generally low observed concentrations of NO_3^- and higher concentrations of NO_2^- and NH_3-N in the effluent. Concentrations of NO_3^- decreased from a background concentration of ~15 to 8.5 mg L^{-1} at the effluent of WWTP-1, where the highest concentrations of NO_2^- (4.6 mg L^{-1}) and NH_3-N (3.0 mg L^{-1}) were observed in July 2013 (Fig. 2). In addition, small increases in the concentrations of NO_2^- and NH_3-N were observed near the effluent of WWTP-2. Elevated concentrations of NH_3-N near WWTPs have also been observed in other studies[21].

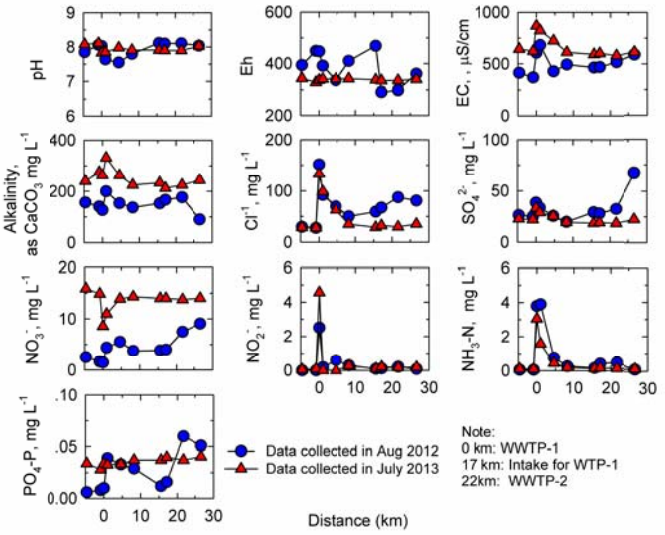

Figure 2. Concentrations of pH, Eh, alkalinity, EC, Cl^-, NO_3^-, NO_2^-, NH_3-N, SO_4^{2-}, and PO_4-P as a function of sampling distance.

The concentrations of ACE-K and the target pharmaceuticals were observed to follow a similar trend over the sampling distance, with the highest concentrations observed near the effluent of WWTP-1 in both 2012 and 2013; this is consistent with other studies of pharmaceutical compounds in southwestern Ontario rivers.[22] The concentrations of the target compounds downstream of WWTP-1 deceased gradually with distance and, when discharge from WWTP-2 entered the river, a secondary concentration peak of target compounds was noted, especially in 2012 (Fig. 3). The concentrations of target compounds 10 km downstream of WWTP-1 were at least one order of magnitude lower than those observed at the effluent of WWTP-1, likely as a result of dilution and dispersion and other natural attenuation processes[23, 24].

Concentrations of ACE-K (~6500 ng L^{-1} in 2012 and ~4000 ng L^{-1} in 2013) were consistent with those observed at the effluent of WWTP-1 in 2007-2009[22]. ACE-K is particularly conservative and recalcitrant, and has been proposed as an ideal marker for wastewater in the environment.[4, 25] Furthermore,

observed ACE-K concentrations were well above the MDL (~40 ng L^{-1}), and were one or two orders of magnitude higher in concentration than other target pharmaceuticals (Fig. 3). Its conservative behavior and high detectable concentrations suggest that ACE-K may be a suitable tracer of wastewater in river systems.

Concentrations of CAF at the effluent of WWTP-1 in 2012 were ~3300 ng L^{-1}, which is one order of magnitude larger than observed in 2013 (~280 ng L^{-1}). Caffeine is extensively ingested in food, beverage, and drugs, and has been reported as a stable compound under variable environmental conditions. Caffeine has been widely used as an anthropogenic indicator of domestic wastewater contamination.[9, 12, 26] Metcalfe et al.[27] report that CAF is detectable in most sewage treatment plants and surface waters in Lake Ontario and Lake Erie in Canada. Buerge et al.[12] observed CAF concentrations of up to 9.5 µg L^{-1} in WWTP effluents in Switzerland, and up to 250 ng L^{-1} in downstream lakes and rivers.

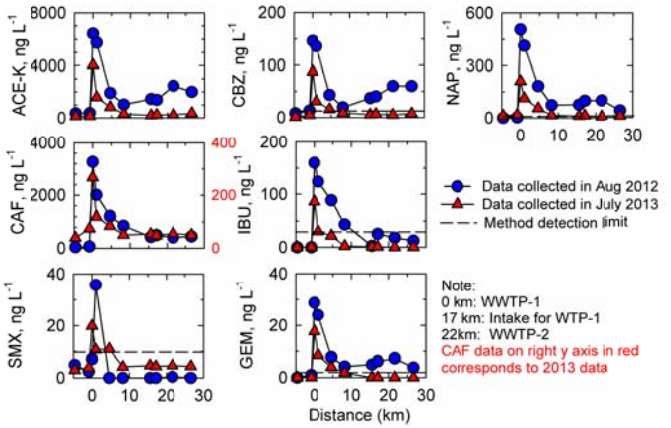

Figure 3. Concentrations of acesulfame-K (ACE-K), caffeine (CAF), sulfamethoxazole (SMX), carbamazepine (CBZ), ibuprofen (IBU), gemfibrozil (GEM), and naproxen (NAP) as a function of sampling distance. The method detection limits of ACE-K and CAF were too low to appear in the figure.

The average discharge of the Grand River over the sampling distance in 2013 was about six times larger than in 2012, indicative of a relatively larger dilution factor. The 2012:2013 concentration ratios of six of the target compounds were consistent for WWTP-1 effluent, with values of 1.6 for ACE, 1.7 for CBZ, 1.8 for IBU, 1.7 for GEM, and 2.4 for NAP. However, the corresponding concentration ratio of CAF was 11.8, which is a full order of magnitude larger than for the other target compounds. The difference in CAF concentrations at WWTP-1 between 2012 and 2013 can be partially, but not completely, attributed to the larger dilution factor in 2013. Many other factors, such as variability in CAF consumption in the contributing watershed and the stability of the performance of the WWTP can also account for the differences.

Illicit amphetamine compounds, including MDA and MDMA, are used as recreational and empathogenic drugs. The concentrations of MDA and MDMA in the study area over the entire sampling distance were below the MDLs in both 2012 and 2013. However, these compounds have been widely detected in wastewaters at ng L^{-1} levels, with MDMA observed to exhibit relatively higher detectable concentrations and frequencies than MDA.[28-30] In addition, Metcalfe et al.[31] report MDMA at concentrations up to 35 ng L^{-1}, but MDA at concentrations below the detection limit in treated and untreated wastewaters from three Canadian cities.

Sulfamethoxazole (SMX), a sulfonamide antibiotic, has been widely used in human and veterinary medicine. The highest concentration of SMX (~37 ng L^{-1}) was observed near WWTP-1 in 2012 with a somewhat lower concentration (~20 ng L^{-1}) observed in 2013. Sulfamethoxazole has been frequently detected in environmental water samples.[32-35] Yargeau et al.[36] report up to 578 ng L^{-1} of SMX downstream of a WWTP in the Yamaska River, Quebec, Canada.

Carbamazepine (CBZ), an antiepileptic drug, was observed near WWTP-1 in the Grand River at a concentration of ~146 ng L^{-1}; this is similar to concentrations observed in another Canadian river[36]. Carbamazepine has been found to be recalcitrant in conventional and biological WWTPs[37, 38] and is widespread in the environment. Miao et al.[39] report the ubiquitous and persistent nature of CBZ and its five metabolites through different stages of treatment in a Canadian WWTP.

Ibuprofen (IBU) and naproxen (NAP) are two common non-steroidal anti-inflammatory drugs, and gemfibrozil (GEM) is widely used as a lipid regulator. The highest concentrations of IBU (160 ng L^{-1}), GEM (29 ng L^{-1}), and NAP (506 ng L^{-1}) were observed near the effluent of WWTP-1 in 2012; lower concentrations were observed in 2013. Widespread distribution of IBU, GEM, and NAP in wastewater and downstream river water at ng L^{-1} concentrations has been reported since 1998 and attributed to their variable removal (IBU, >90%; NAP, ~80%; GEM, ~55%) by conventional WWTPs.[40-42] IBU, GEM, and NAP have also been observed to persist in a subsurface receiving aquifer.[23]

Concentrations of ACE-K and most of the target pharmaceuticals were lower in 2013 than in 2012. Secondary concentration peaks of ACE-K, SMX, CBZ, IBU, GEM, and NAP observed near the effluent of WWTP-2 in 2012 were also not as apparent in 2013. This is likely due to either the larger discharge when sampling was conducted in 2013 vs. 2012 and/or implementation of a new ultraviolet (UV) facility at WWTP-2 in 2013 that enhanced effluent disinfection but also likely removed some target contaminants through UV photolysis[43-46].

Mechanisms affecting the transport of the target compounds

Natural attenuation processes account for a significant decrease in concentrations of wastewater-derived contaminants in surface water bodies[24] and groundwater[23]. During transport from WWTPs to downstream areas, the concentrations of the seven target compounds considered in this study can be affected by physical processes, primarily dilution and dispersion, but also potentially chemical and biological natural attenuation processes, such as sorption, hydrolysis, biotransformation, and photolysis[47]. It is important, therefore, to determine the relative importance of these processes in the Grand River and other rivers.

ACE-K has been reported to undergo photo-degradation in aqueous systems, following first-order rates of removal.[43] Benotti and Brownawell[48] report that CAF is biodegradable in estuarine and coastal waters, with an average half-life of 5.4 days. The antibiotic SMX has been reported to undergo biotransformation[49] and direct photolysis[50] in aqueous systems. In addition, direct photolysis is an important process for removing SMX from surface water.[51] CBZ is reported to be resistant to biodegradation but may undergo indirect photo-degradation[52] and adsorption reactions[53]. The indirect photo-

degradation rate of CBZ is limited ($t_{1/2}$ = 8-39 h), however, and strongly dependent on the dissolved organic carbon (DOC) concentration in solution.[52]

Removal of NAP through natural attenuation processes is more variable. Approximately 40% of NAP present in surface water during daylight hours has been reported to be removed through photolysis ($t_{1/2}$ = 1.7 h), with the remainder most likely removed via sorption.[54] Strong sorption of NAP to soils also has been observed.[55] Biotransformation reactions can be an important attenuating process for IBU and GEM in river water, with half lives of 5.4 h and 2.7 h respectively[24, 54]. IBU and GEM exhibit relatively longer photodegradation half-lives of ~15 h.[56]

Acesulfame-K and pharmaceuticals as co-tracers in the Grand River

The concentrations of the target compounds exhibited similar changes over the sampling distance, with a primary peak in concentrations observed at the effluent of WWTP-1 and a secondary peak near WWTP-2 (Fig. 3). Correlation analysis using Spearman Rank correlation coefficients (ρ) of the target compounds and Cl^- indicated that ACE-K and CBZ were very strongly correlated with Cl^- over the sampling distance downstream of WWTP-1, with ρ values ranging from 0.95 to 1.00 in both 2012 and 2013; GEM and NAP were strongly correlated with ACE-K, CBZ, and Cl^- with ρ values ranging from 0.69 to 0.89 in both 2012 and 2013; and CAF, SMX, and IBU were moderately correlated with ACE-K, CBZ, and Cl^- (Tables 1 and 2, Fig. 4). Concentrations of MDA and MDMA were below the MDLs in both 2012 and 2013, therefore no correlations could be determined. Similarly, the Spearman Rank correlation for SMX in 2012 was not calculated due to the low concentrations (<MDL) observed.

Table 1: Spearman rank correlation coefficients (ρ)[†] of the target compounds and Cl^- over the sampling distance in the Grand River in August 2012.

	CAF	CBZ	IBU	GEM	NAP	Cl^-
ACE	0.36	0.98	0.45	0.69	0.69	0.98
CAF		0.40	0.93	0.64	0.64	0.40
CBZ			0.52	0.71	0.71	1.00
IBU				0.79	0.79	0.52
GEM					1.00	0.71
NAP						0.71

Note: [†] Positive values were interpreted as follows: 0.8-1.0 = very strong; 0.6-0.8 = strong; 0.4-0.6 = moderate; 0.2-0.4 = weak; 0.0-0.2 = weak or no relationship.

Table 2: Spearman rank correlation coefficients (ρ)[†] of the target compounds and Cl^- over the sampling distance in the Grand River in July 2013.

	CAF	SMX	CBZ	IBU	GEM	NAP	Cl^-
ACE	0.71	0.59	0.90	0.71	0.89	0.74	0.98
CAF		0.84	0.62	0.71	0.85	0.64	0.62
SMX			0.54	0.64	0.73	0.59	0.56
CBZ				0.90	0.92	0.93	0.95
IBU					0.92	0.98	0.76
GEM						0.92	0.89
NAP							0.81

Note: [†] Positive values were interpreted as follows: 0.8-1.0 = very strong; 0.6-0.8 = strong; 0.4-0.6 = moderate; 0.2-0.4 = weak; 0.0-0.2 = weak or no relationship.

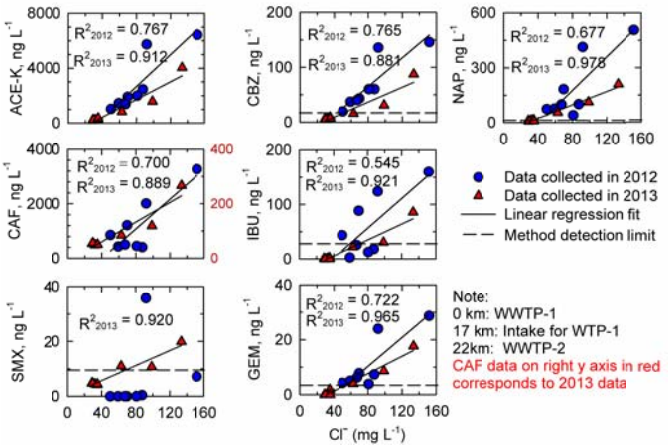

Figure 4. Concentrations of acesulfame-K (ACE-K), caffeine (CAF), sulfamethoxazole (SMX), carbamazepine (CBZ), ibuprofen (IBU), gemfibrozil (GEM), and naproxen (NAP) as a function of Cl^- concentration. The method detection limits of ACE-K and CAF were too low to appear in the figure.

The artificial sweetener ACE-K and pharmaceuticals CBZ, IBU, GEM, and NAP exhibited strong correlations over the sampling distance downstream of WWTP-1 in 2013, but weaker correlations in 2012. The pharmaceuticals CAF and SMX exhibited moderate correlations with other target compounds (Tables 1 and 2). This analysis indicates that ACE-K, CBZ, GEM, and NAP can potentially be used as co-tracers of the wastewater over the sampling distance considered. The very strong correlation between ACE-K, CBZ and Cl^-, however, suggests that Cl^- may also be used as a waste-water indicator. However, previous studies have indicated that Cl^- may be affected by other sources, including road salt application.[57]

Conclusions

This study indicates that the decline in concentrations of bulk wastewater constituents, ACE-K, and a suite of pharmaceutical compounds downstream from two WWTPs is due to dilution and, for some compounds, other attenuation mechanisms. Of the compounds studied, the artificial sweetener ACE-K and three pharmaceutical compounds (CBZ, GEM, and NAP) had the greatest persistence. These compounds dissipated at the same rate as the conservative anion Cl^-, indicating that declines in concentration were likely due to dilution alone. The use of multiple tracers, such as artificial sweeteners combined with pharmaceutical compounds, would greatly increase confidence when tracking wastewater in aquatic environments throughout the year.

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