Riverbank filtration potential of pharmaceuticals in a wastewater-impacted stream

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Abstract
Pharmaceutical contamination of shallow groundwater is a substantial concern in effluent-dominated streams, due to high aqueous mobility, designed bioactivity, and effluent-driven hydraulic gradients. In October and December 2012, effluent contributed approximately 99% and 71%, respectively, to downstream flow in Fourmile Creek, Iowa, USA. Strong hydrologic connectivity was observed between surface-water and shallow-groundwater. Carbamazepine, sulfamethoxazole, and immunologically-related compounds were detected in groundwater at greater than 0.02 μg L⁻¹ at distances up to 6 m from the stream bank. Direct aqueous-injection HPLC-MS/MS revealed 43% and 55% of 110 total pharmaceutical analytes in surface-water samples in October and December, respectively, with 16% and 6%, respectively, detected in groundwater approximately 20 m from the stream bank. The results demonstrate the importance of effluent discharge as a driver of local hydrologic conditions in an effluent-impacted stream and thus as a fundamental control on surface-water to groundwater transport of effluent-derived pharmaceutical contaminants.

1. Introduction

Wastewater reuse is necessary to meet current and future downstream-flow requirements and other water-supply demands (National Research Council, 2012), but inevitably increases the risks of aquatic ecosystem impairment (Jobling et al., 2008; Kidd et al., 2007; Kramer et al., 1998; McGee et al., 2009; Nash et al., 2004; Painter et al., 2009; Rosi-Marshall et al., 2013; Vajda et al., 2008) and contamination of surface-water and groundwater drinking-water supplies (Diaz-Cruz and Barcelo, 2008; Foster and Chilton, 2004; Lapworth et al., 2012; Lewandowski et al., 2011). Wastewater contaminants raise fundamental concerns due to the chemical and biological complexity of wastewater mixtures (Barber et al., 2011a, 2013; Kolpin et al., 2002), the potential for introduction into water resources (Barber et al., 2013; Glassmeyer et al., 2005), and the wide range of ecological and human health impacts (Jobling et al., 2008; Kidd et al., 2007; Kramer et al., 1998; McGee et al., 2009; Nash et al., 2004; Painter et al., 2009; Rosi-Marshall et al., 2013; Vajda et al., 2008). Wastewater pharmaceuticals are especially challenging due to their: relative solubility and high mobility in aqueous environments compared with many other wastewater contaminants; designed high bioactivities and long shelf-lives (biorecalcitrance); and wide range of potential ecological endpoints including, toxicity (Han et al., 2006; Quinn et al., 2008; Rosi-Marshall et al., 2013), endocrine disruption (Kidd et al., 2007; Painter et al., 2009; Vajda et al., 2008), immunomodulation (Canesi et al., 2007; Gust et al., 2013), antibiotic resistance selection (Haack et al., 2012; Martinez, 2009), as well as cytotoxicity and mutagenesis (Buerge et al., 2006; Johnson et al., 2008). Consequently, improved understanding of the environmental fate and transport of wastewater-derived contaminants is
essential for effective protection of vital aquatic ecosystem services, environmental health, and drinking water supplies.

Several assessments have documented substantial downstream transport of wastewater contaminants including pharmaceuticals, illustrating the threat to downstream drinking water supplies in effluent-impacted streams (Barber et al., 2013; Brown et al., 2009; Fono et al., 2006; Kunkel and Radke, 2011; Lin et al., 2006; Radke et al., 2010; Writer et al., 2012). Considerable attenuation of pharmaceutical contaminants was reported in effluent-impacted streams in the United States (Brown et al., 2009; Fono et al., 2006; Lin et al., 2006), but half-lives on the order of hours to days, nevertheless, represented substantial downstream transport. A tracer study conducted in a small stream in Sweden with six pharmaceuticals, representing a range of expected environmental fates, documented elimination of two compounds (ibuprofen and clofibric acid) but no attenuation of the remaining four (bezafibrate, diclofenac, metoprolol, and naproxen) over a 16.4 km study reach (Kunkel and Radke, 2011). Recent spatio-temporal (Lagrangian sampling of the same approximate parcel of water during downstream progress) field studies (Barber et al., 2013; Brown et al., 2009; Writer et al., 2012) likewise indicated substantial downstream transport and varied attenuation efficiencies for a number of bioactive wastewater contaminants, including pharmaceuticals. These studies demonstrate the considerable stream-to-stream and within-stream spatio-temporal variability of longitudinal contaminant attenuation and illustrate the critical need for improved understanding of fate and transport for a range of wastewater-impacted streams and hydrologic conditions.

The comparative lack of information on vertical and lateral transport (infiltration) of wastewater contaminants from surface-water to hyporheic and shallow groundwater compartments is a critical scientific data gap, given the potential for contamination of groundwater supplies in effluent-impacted systems (Foster and Chilton, 2004; Hughes et al., 2013; Lapworth et al., 2012; Lewandowski et al., 2011; Michael et al., 2013). Groundwater represents the largest and most reliable perennial source of freshwater globally (Oelkers et al., 2011; Schwartz and Ibaraki, 2011), and in many parts of the world is the most important source of drinking water (Oelkers et al., 2011; U.S. Geological Survey, 2009). Importantly, the hydrologic conditions created by wastewater releases to surface-water systems increase the potential for surface-water contamination of unconfined aquifers in arid, semi-arid, and drought-impacted environments, in which contributions of wastewater treatment facility (WWTF) effluent to downstream flow are substantial and often predominate (Foster and Chilton, 2004; Lapworth et al., 2012; Lewandowski et al., 2011). In such water-limited circumstances, WWTF outfalls represent important groundwater recharge zones, creating substantial hydraulic gradients that favor water and solute transport to the adjacent aquifer (Lapworth et al., 2012; Lewandowski et al., 2011). Growing dependencies on bank filtration and artificial recharge applications for release of wastewater to the environment and for pretreatment of poor-quality surface-water for drinking water (Diaz-Cruz and Barcelo, 2008; Eckert and Irmscher, 2006; Grunheid et al., 2005; Heberer et al., 2004; Irmscher and Teermann, 2002; Jekel and Grunheid, 2005; Maeng et al., 2010, 2008; Tufenkji et al., 2002) further emphasize the critical need to better understand the exchange of wastewater contaminants, like pharmaceuticals, between surface-water and groundwater compartments.

Herein the potential transport of effluent-derived pharmaceutical contaminants from surface-water to hyporheic-water and

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**Fig. 1.** Map of Fourmile Creek study area in Ankeny, Iowa.
shallow groundwater compartments is examined in a WWTF-impacted stream in Ankeny, Iowa under effluent-dominated (71–99% of downstream flow) conditions. Spatio-temporal variations in vertical (surface-water to shallow hyporheic zone) and lateral (surface-water to adjacent shallow groundwater zone) gradients in hydrology and chemistry were assessed by continuous water level monitoring and by synoptic assessment of pharmaceutical contaminant concentrations in surface-water and in shallow hyporheic and groundwater piezometer networks.

2. Material and methods

2.1. Site description

The study site (Fig. 1) was an approximate 100 m reach of Fourmile Creek adjacent to the WWTF (46 million liter per day; activated sludge treatment) in Ankeny, Iowa, United States (Barber et al., 2013, 2011b). The Ankeny WWTF ceased operations in November 2013, providing a rare opportunity to investigate ecosystem hydrologic, chemical, and biological responses to the removal of a long-term effluent source of water as well as chemical and biological contaminants. To assess these ecological responses to WWTF shutdown, surface water sampling locations and corresponding networks of in-stream and out-of-channel piezometers were established prior to shut down and sampled with pre-shutdown data loggers. Pre-shutdown monitoring began in October 2011. Post-shutdown monitoring will continue through at least 2014. This paper presents pharmaceutical concentration data for two pre-shutdown, synoptic sampling events in October and December of 2012 along with continuous water level data for the entire October–December 2012 period.

2.2. Piezometer networks

Networks of piezometers (25 total; 5 cm diameter; 30 cm screened interval) for monitoring of surface-water to groundwater hydraulic and wastewater-chemical gradients were installed by hand auger and slide hammer within the stream and on both banks at three locations near the WWTF outfall. Networks are identified by position (upstream, U; downstream, D) and nominal distance (m) relative to the WWTF outfall (Fig. 1). The study reach stream width was approximately 6 m. Effluent contributed approximately 99% and 71% of downstream flow during the October 2012 and December 2012 synoptic sampling events, respectively.

The downstream network (D10; 13 piezometers) was positioned to assess the vertical and lateral hydraulic and wastewater-chemical gradients created by local effluent discharge and associated hydraulic overlying normal to low streamflow conditions. The majority of effluent-stream-water flow under these conditions was directed toward the left bank approximately 10–20 m downstream of the outfall, because the outfall was located on the right bank and oriented downstream at an approximate 45° angle. A surface-water (SW) sampling point and three nested, hyporheic-water piezometers were installed (in-stream, IS) approximately 10 m downstream of the outfall within the centroid of effluent-stream-water flow (normal to low upstream flow conditions), with piezometer screen depths ranging from 15 to 45 cm (shallow, S), 45–75 cm (intermediate, I), and 75–105 cm (deep, D) below the water/bed-sediment interface. Three piezometer transects were installed at the left bank (LB) 10 m (transect 1, 2, and 3) downstream, adjacent to in-stream surface-water and piezometer location, 15 m (transect 2, T2) and 20 m (transect 3, T3) downstream from the outfall to provide insight into the longitudinal variability of the hydraulic and chemical gradients created in the left bank, shallow groundwater system in this high effluent impact zone (D10; Fig. 1). Left bank piezometers were emplaced at distances of 1, 2, 3, 5, 6, and 20 m (corresponding rows, R1–R5) from the bank at T1 and at distances of 1 and 2 m (corresponding rows 1 and 2) from the bank at T2 and T3 to assess lateral groundwater hydraulic and chemical gradients associated with effluent discharge. A single piezometer was emplaced on the right bank (RB) for comparison of left bank and right bank gradients. All out-of-channel (groundwater) piezometers were installed with top of screen positioned below the water table (approximately 30 cm during the study period) at depths of 2.25–2.50 m below land surface.

A piezometer network (US5; 8 piezometers), consisting of a RB piezometer (1 m from bank), a single in-stream (shallow) piezometer, and two LB piezometer transects (5 m apart, with piezometers located 1, 2, and 3.5 m from the bank), was emplaced 50 m upstream of the outfall to provide a comparison for downstream, effluent-driven hydraulic and chemical gradients. A second reference network (UB0; 4 piezometers), consisting of a RB piezometer (1 m from bank), a single in-stream (shallow) piezometer, and a single LB piezometer transect (with piezometers located 1 and 2 m from the bank), was installed in December 2012 approximately 80 m upstream of the outfall. In-stream and out-of-channel reference piezometers were installed as described for the downstream, effluent-impacted locations.

2.3. Hydrologic assessment

USGS has operated a streamflow gaging station (05485605) at Fourmile Creek approximately 330 m downstream of the WWTF outfall since 2003 (U.S. Geological Survey, 2013a, b). Continuous streamflow data were computed using standard USGS stage/discharge techniques and stored in the USGS National Water Information System database (U.S. Geological Survey, 2013b). During the October 2012 sampling event, instantaneous stream discharge (Q) was measured by Acoustic Doppler Velocimetry (FlowerTracker [SonTek, 2013]) during surface water sampling at locations approximately 80 m upstream (U80) and 50 m downstream of the WWTF outfall (40 m downstream of D10-IS-SW), in order to quantify the contribution of effluent to downstream flow. The effluent contribution to downstream flow during the December 2012 sampling event was estimated as the reported average WWTF discharge expressed as a percentage of streamflow at the gage.

Water level data loggers (Global Water WL16 [Global Water, 2013]; HOBO U20 [Onset HOBO Data Loggers, 2013]) were deployed in the water column, and in the screened intervals of in-stream and out-of-channel piezometers, respectively, to provide continuous water pressure data. In-stream sampling locations and all piezometers were surveyed to provide elevations in m relative to the North American Vertical Datum 1988 (NVD88). Level logger pressure data were corrected for barometric pressure changes based on a baro-logger deployed in the D10-RB piezometer at a depth of 0.5 m below land surface (approximately 2 m above the water table). Continuous pressure data were then converted to continuous water level elevations in m NVD88 based on the depth to water table measured (electric water-level tape) in each piezometer immediately before the respective logger was removed for data download. Based on replicate measurements of fixed survey locations within the sample area, differences in water level elevations which were 1 cm or less were not considered significant.

2.4. Water chemistry assessment

Direct aqueous injection, high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) was used to determine 110 pharmaceutical, pharmaceutical degrade, and anthropogenic indicator compounds (Furlong et al., 2014). Unfiltered water samples were collected in combusted amber glass vials, shipped on ice to the lab, and stored frozen until analyzed (Furlong et al., 2014). Samples were filtered in the lab (0.45 μm pore size glass-fiber filter) prior to analysis. The complete list of analytes with Chemical Abstracts Services (CAS) registry numbers and reporting limits is given in the supporting information (Table S1-1).

HPLC-MS/MS analysis offers high selectivity and sensitivity for a broad range of pharmaceuticals, but did not address potential environmental metabolites expected to occur in situ. For this reason, two model pharmaceuticals (carbamazepine and sulfamethoxazole) with distinct environmental impact mechanisms were also analyzed in unfiltered water samples by commercial enzyme-linked immunosorbent assays (ELISA) according to manufacturer’s instructions (Abraxis, 2013a, b). ELISA assays for both compounds responded to immunologically similar compounds (cross-reactivity) including related metabolites (Abraxis, 2013a, b), offering the

![Fig. 2. Spearman Rank Order Correlations between concentrations (ng L⁻¹) of carbamazepine (CBZ) and sulfamethoxazole (SMX) as determined by enzyme-linked immunosorbent assay (ELISA) and by direct aqueous injection HPLC-MS/MS in samples collected during the study period. Dashed lines indicate laboratory reporting limits (same reporting limit for CBZ and SMX ELISA) for analyte and method. Solid symbols below analytical reporting limits are estimated values. Open symbols indicate half detection limits for non-detections of at least one method.](image-url)
advantage of detection of the primary target compound and associated metabolites. For this reason ELISA results were expected to be higher than but strongly correlated to the more selective HPLC-MS/MS results for carbamazepine and sulfamethoxazole. Plots illustrating the significant correlations between ELISA concentrations and HPLC-MS/MS concentrations for carbamazepine (p < 0.8; p < 0.0001) and sulfamethoxazole (p = 0.79; p < 0.0001) are presented in Fig. 2. ELISA samples were collected and filtered in the same way as samples for HPLC-MS/MS analysis. Redox parameters were assessed in in-stream and out-of-channel piezometers as described (Chapelle et al., 2005, 2009, 2012).

Surface-water grab samples were collected from the centroid of flow (thalweg) at each network. In-stream and out-of-channel piezometer samples were collected by peristaltic pump (flow approximately 200 mL min\(^{-1}\)) after purging the screened interval by pumping for 10 min (as described in Bradley et al., 2012). A preliminary assessment of water quality parameters (pH, conductivity, and temperature) over time was conducted to verify stream-water entrainment did not occur in in-stream piezometers under these flow conditions.

2.5. Quality assurance quality control (QAQC)

HPLC-MS/MS analysis of pharmaceutical contaminants included a single fortified sample as well as addition of surrogate standards to all samples to evaluate whole-method recovery (Table SI-1). For all surrogates, recoveries ranged between 30 and 188%, with a mean of 106% and a relative standard deviation (RSD) of 11%. Recovery statistics for individual surrogates are given in the supporting information (Table SI-2). A sample (D10-LB-T1-R1) was collected in December 2012 and fortified with a standard mixture (250 ng/L for all 110 analytes) to further assess method recovery efficiency and matrix interference. All spiked compounds were detected, with recoveries ranging between 30 and 214% (mean = 96%; RSD = 28%).

The field quality-assurance program consisted of field triplicates and field blanks. Piezometers in left bank rows 1 and 2 of network D10 (Fig. 1) represented spatial triplicates reflecting longitudinal variations in shallow groundwater parameters. Concentrations in the LB effluent-high-impact area. Triplicate surface-water and groundwater samples were collected in December 2012 from the D10-IS-SW (in-stream surface water) location and from the D10-LB-T1-R1 piezometer, respectively, to provide insight into sample collection variability. The mean detection percentage of compounds in triplicates was 55% (RSD = 11%) for surface-water and 19.7% (RSD = 33%) for groundwater. The mean cumulative concentration of detections in triplicates was 24.4 µg L\(^{-1}\) (RSD = 68%) for surface-water and 3.8 µg L\(^{-1}\) (RSD = 84%) for groundwater. Finally, surface-water collection blanks consisting of organic-free reagent water were prepared for HPLC-MS/MS and ELISA analyses by decanting blank water directly into sample vials and then handling as for environmental samples. To ensure that peristaltic sampling procedures did not result in sample cross-contamination, corresponding groundwater collection blanks for ELISA and HPLC-MS/MS pharmaceutical analyses were prepared by pumping (flow approximately 200 mL min\(^{-1}\)) blank water through the same peristaltic pump and tubing used previously to sample piezometers for a period of 10 min (equivalent to the screen purge), filling blank sample vials, and then handling as for environmental samples. No pharmaceuticals were detected in either blank with HPLC-MS/MS or ELISA methods, indicating no contamination issues associated with sample collection, handling, or analysis.

2.6. Statistical analyses

The laboratory reporting level (URL) for individual pharmaceuticals in the HPLC-MS/MS analysis was equal to twice the method detection limit (MDL, as defined in U.S. Environmental Protection Agency, 2005). The probability of falsely reporting “nondetection” for a sample that contained an analyte at a concentration equal to or greater than the URL is estimated to be less than 1 percent (Childress et al., 1999). Detections greater than or equal to the URL were considered quantitative. Detections between the URL and MDL were considered semi-quantitative and reported as nondetection greater than or equal to the MDL were considered quantitative. Detections greater than the MDL is estimated to be less than 1 percent (Childress et al., 1999). MS/MS analysis was equal to twice the method detection limit (MDL; as defined in Childress et al., 1999).

Diurnal streamflow patterns demonstrate the importance of Ankeny WWTF effluent discharge as a primary driver of downstream streamflow and longitudinal hydraulic gradients in Fourmile Creek. The continuous streamflow gage (05485605) located 330 m downstream of the WWTF outfall reveals a consistent effluent-driven diurnal pattern (U.S. Geological Survey, 2013a, b). Excluding precipitation-driven high-flow events, this diurnal pattern includes a ubiquitous morning peak flow, a secondary late afternoon peak (shoulder) most evident during week days, and an overnight minimum (see for example Fig. 3); all reflect urban water-use and associated WWTF discharge patterns. The relative (expressed as a percentage of mean daily streamflow) diurnal variability increases as streamflow decreases, being most evident under baseflow conditions. The relative diurnal ranges were approximately 63% and 33% for the October and December 2012 sampling events, respectively.

Numerous paired upstream—downstream streamflow measurements made since 2003 verified the importance of WWTF effluent discharge as a contributor to downstream flow, ranging from 15% under normal to high-stream-flow conditions up to greater than 90% under low-flow conditions (Barber et al., 2011a, 2013; Bradley et al., 2009; Bradley et al., 2007, 2008; Glassmeyer et al., 2005). Sampling assessments conducted in Fourmile Creek in summer 2003 and spring 2005 documented effluent contributions to downstream flow of 81% and 28%, respectively (Barber et al., 2011b). Additional published studies conducted during 2004 and 2008, respectively, documented 98% effluent contribution to downstream flow, under low-flow conditions (Glassmeyer et al., 2005) and approximately 15% under high-flow conditions (Bradley et al., 2009). During 2011–2013, effluent contributions to downstream flow varied from 90 to 99% in fall and 11–17% in spring (unpublished results). During the 2012 study period
addressed herein, effluent contributed approximately 99% and 71% to downstream flow during October and December sampling events, respectively. Thus, multiple lines of evidence demonstrate that, during the October to December 2012 study period, the Fourmile Creek study reach was appropriate for assessing the potential for surface-water to groundwater transport of pharmaceutical contaminants under effluent-dominated flow conditions.

3.2. Potentiometric evidence for lateral surface-water/groundwater exchange

Multiple lines of evidence also indicate that effluent discharge was a primary driver of hydrologic conditions in the adjacent shallow groundwater system (Fig. 3). Over the period of October to December 2012, diurnal variations in groundwater levels in D10-LB-T1 piezometers coincided closely with effluent-driven surface-water fluctuations (Fig. 3A). The close correspondence in water level fluctuations indicates strong hydrologic connectivity between surface-water and the adjacent shallow groundwater system.

During the October sampling event (Fig. 3B), the approximate 1–2 h delay between the timing of surface-water and groundwater changes and the persistent hydraulic gradient (approximately 5 cm) from surface-water toward groundwater over a distance of 1 m from the stream bank throughout the daytime high effluent discharge hours indicated a resistance to flow at the channel bed. These observations were consistent with the visible presence of finer-grained bank-levee deposits. No detectable gradient or response lag was observed between groundwater piezometer locations, however, indicating strong hydrologic connectivity and minimal flow resistance within the shallow groundwater system. The surface-water to groundwater gradient disappeared during overnight water-level minima, but no gradient reversal was observed during the October event.

During the December sampling event, streamflow upstream of the outfall was significant and the effluent contribution to downstream flow was reduced to approximately 71%. Strong hydrologic connectivity between surface-water and groundwater compartments continued (Fig. 3C), but the surface-water to groundwater gradient during high effluent discharge hours was lower (approximately 2–3 cm) than in October. Again, no detectable gradient or response lag was observed between groundwater piezometer locations, indicating strong hydrologic connectivity and minimal flow resistance within the shallow groundwater system. A distinct reversal in the hydraulic gradient (from groundwater toward the surface-water compartment) was evident during the overnight low-effluent-discharge and corresponding low-streamflow period. This pattern was apparent in all D10 transects (supporting information Figure SI-1).

These results indicate substantial effluent-driven hydrologic exchange occurs between the surface-water and adjacent shallow groundwater compartments immediately downstream of the WWTF outfall. These observations in turn indicate a substantial potential for transport of soluble surface-water contaminants to the shallow groundwater system. The marked decrease in peak water levels observed at the stream bank compared with the lack of significant delay or gradient between groundwater piezometer locations, suggests that the greatest attenuation in the transport of surface-water solutes may occur at the stream bank.

3.3. Potentiometric evidence for vertical groundwater/surface-water exchange

A similarly strong correspondence in the timing and magnitude of diurnal fluctuations was also observed between water levels in the stream and in the shallow hyporheic-zone nested-piezometer at D10 (D10-IS-S; Supporting Information Figure SI-1). A tight, poorly-conductive, silt/clay sediment layer was present beginning at a depth of approximately 0.5 m below the surface-water/bed-sediment interface at D10. The deep in-stream piezometer (D10-IS-D; screened 75–105 cm below the sediment surface) did not produce water and was not sampled or monitored further. The intermediate piezometer (D10-IS-I; screened 45–75 cm below the sediment surface) did produce water at a slow rate, but very little diurnal water-level change was observed, indicating limited hydrologic connectivity with the shallow hyporheic zone and with the overlying surface-water compartment.

3.4. Surface-water/groundwater exchange of Pharmaceuticals-ELISA

ELISA analyses were employed to assess the presence of carbamazepine and, sulfamethoxazole in the adjacent shallow groundwater system in the vicinity of the WWTF outfall. Because both ELISA kits have recognized cross-reactivity, the results are estimated cumulative concentrations for target and immunologically-related compounds, including metabolites. Consistent with effluent-driven hydraulic gradients observed at network D10 during October and December 2012 sampling events, ELISA analyses indicated measurable concentrations of carbamazepine and sulfamethoxazole (and immunologically-related compounds) in the adjacent shallow groundwater systems on both banks (Fig. 4; Supplementary Information Tables S13 and S14). Concentrations observed in groundwater piezometers located 1 m from the stream banks (on both sides) were generally less than 42% of the concentrations observed in corresponding surface-water samples. The notable lack of difference in sulfamethoxazole concentrations observed in surface-water and 1 m groundwater samples in October was attributed to short-term fluctuations in effluent and, thus, surface-water sulfamethoxazole concentrations. Concentrations of both analytes were generally comparable in samples from 1 to 2 m piezometer locations, suggesting that the shallow
Concentrations of carbamazepine and sulfamethoxazole in groundwater were 8.6% and 15.4%, respectively. In surface-water samples, the relative standard deviations were 2.0% and 11.2%.

The spatial impacts of WWTF discharge within the Fourmile Creek study area were further emphasized by the recirculation of effluent upstream of the outfall (Fig. 5; Supplementary Information Tables SI3 and SI4). In October, concentrations of carbamazepine (1.18 μg L⁻¹) and sulfamethoxazole (1.47 μg L⁻¹) observed in surface-water samples collected 50 m upstream of the outfall at U50 were comparable to effluent concentrations (0.98 μg L⁻¹ and 1.65 μg L⁻¹, respectively). Trace level detections were also observed in groundwater piezometers on both banks in October. In December, both compounds were still detectable at U50 despite higher streamflow conditions. No pharmaceutical contaminants were observed in surface-water or groundwater samples collected 80 m upstream at U80 in December, verifying that WWTF effluent was the source of pharmaceutical contaminants in the system.

### 3.5. Surface-water/groundwater exchange of Pharmaceuticals-HPLC MS/MS

Surface-water and groundwater samples from D10 transect 1 were analyzed using HPLC-MS/MS to provide improved sensitivity and insight into compound-specific variations in pharmaceutical and anthropogenic indicator contaminant transport (Fig. 6; Supplementary Information Tables SI5 and SI6). Of 110 analytes, 48 and 61 ± 7 (mean ± standard deviation of triplicate samples) pharmaceutical and anthropogenic indicator compounds were detected in a single and in triplicate surface-water samples collected at D10 in October and December, respectively. In groundwater samples collected 1 m from the stream at transects 1–3, 19 ± 1 and 25 ± 6 pharmaceuticals were detected in October and December, respectively; a detection attenuation of approximately 60% within 1 m of flowpath. However, 18 and 7 compounds were detected approximately 20 m from the streambank in October and December, respectively; indicating substantial transport of pharmaceuticals within the groundwater system. Pharmaceutical compounds most commonly detected in LB groundwater piezometers included carbamazepine, carisoprodol, lidocaine, methocarbamol, sulfamethoxazole, and warfarin. Pharmaceuticals, which were detected in groundwater 20 m from the streambank at cumulative concentrations up to approximately 0.5 μg L⁻¹, included acyclovir, bupropion,
carbamazepine, caffeine, carisoprodol, desvenlafaxine, fexofenadine, lidocaine, metformin, meprobamate, methocarbamol, methotrexate, metoprolol, nicotine, sulfamethoxazole, temazepam, tramadol, and warfarin. These pharmaceuticals reflect diverse therapeutic and chemical classes and many different functional group elements, but all are water-soluble at concentrations orders of magnitude higher than measured in the current study. Thus, the hydrologic and chemical assessment results are consistent with the hydrologic transport of soluble wastewater contaminants from surface water to the shallow groundwater system. Moreover, while several of these compounds (e.g., carbamazepine and sulfamethoxazole) are considered recalcitrant (Barber et al., 2009; Clara et al., 2004; Haack et al., 2012) in groundwater, others (e.g., caffeine and nicotine) are generally considered readily biodegradable in surface-water systems under aerobic conditions (Bradley et al., 2007; Buerge et al., 2003; Swartz et al., 2009), like those observed here (Supplementary Information Table S17). These observations raise concerns that biodegradation of wastewater contaminants is markedly less efficient in groundwater than in surface-water sediment and, thus, that subsurface transport of surface-water pharmaceuticals is substantial, potentially exceeding the 20 m distance assessed here.

3.6. Implications for wastewater-impacted streams

These results demonstrate the importance of effluent discharge as a driver of local hydrologic conditions in a WWTF-impacted stream and thus as a fundamental control on surface-water to groundwater transport of effluent-derived pharmaceutical contaminants. Under water-limited (arid, semi-arid, and drought) conditions, WWTF outfalls create strong vertical and lateral hydraulic gradients resulting in unintentional and uncontrolled transport of effluent contaminants to the shallow groundwater system. The results of this study indicate that infiltration of effluent–contaminated surface-water can result in pharmaceutical contamination in groundwater tens of meters away from the stream at concentrations greater than established environmental concern levels (for example, 10 ng/L threshold safety value for pharmaceuticals; European Medicines Agency, 2006). Thus these results have important implications for a range of water-reuse applications that depend on efficient contaminant attenuation over short subsurface flowpaths, including bank filtration and artificial recharge applications for release of wastewater to the environment and for pretreatment of poor-quality surface-water for drinking water (Diaz-Cruz and Barcelo, 2008; Eckert and Irmscher, 2006; Grunheid et al., 2005; Heberer et al., 2004; Irmscher and Teermann, 2002; Jekel and Grunheid, 2005; Maeng et al., 2010, 2008; Tufenkji et al., 2002).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.06.028.

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