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Occurrence of organic wastewater compounds in effluent-dominated streams in Northeastern Kansas

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Abstract

Fifty-nine stream-water samples and 14 municipal wastewater treatment facility (WWTF) discharge samples in Johnson County, northeastern Kansas, were analyzed for 55 compounds collectively described as organic wastewater compounds (OWCs). Stream-water samples were collected upstream, in, and downstream from WWTF discharges in urban and rural areas during base-flow conditions. The effect of secondary treatment processes on OWC occurrence was evaluated by collecting eight samples from WWTF discharges using activated sludge and six from WWTFs samples using trickling filter treatment processes. Samples collected directly from WWTF discharges contained the largest concentrations of most OWCs in this study. Samples from trickling filter discharges had significantly larger concentrations of many OWCs (p -value < 0.05) compared to samples collected from activated sludge discharges. OWC concentrations decreased significantly in samples from WWTF discharges compared to stream-water samples collected from sites greater than 2000 m downstream. Upstream from WWTF discharges, base-flow samples collected in streams draining predominantly urban watersheds had significantly larger concentrations of cumulative OWCs (p -value = 0.03), caffeine (p -value = 0.01), and tris(2-butoxyethyl) phosphate (p -value < 0.01) than those collected downstream from more rural watersheds.

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Keywords: Wastewater; Activated sludge; Trickling filter; Urbanization; Detergent surfactants; DEET

1. Introduction

During the last 5 years, analytical methods have been developed that allow the quantification of organic chemicals typically used in the house, yard, or roadway that include compounds associated with food, detergents, fragrances, cleaners, insecticides, as well as with natural and fossil fuels (Zugg et al., 2002). Wastewater treatment facilities (WWTFs) have been identified as the primary sources of these chemicals, termed organic wastewater compounds (OWCs) (Miao et al., 2004; Glassmeyer et al., 2005). OWCs have been found to decrease in stream-

water downstream from WWTF discharges, eventually becoming statistically indistinguishable from samples collected upstream from discharges (Glassmeyer et al., 2005). Secondary treatment processes in WWTFs have been found to affect the occurrence of OWCs (Phillips et al., 2005); specifically, activated sludge treatment processes have been shown to be more efficient at removal of selected cosmetics, hormones, and pharmaceuticals (Cabella et al., 2004).

Wastewater discharges (Huggett et al., 2003) have estrogenic properties, and chronic exposures to individual as well as combinations of organic compounds within WWTF discharges have been linked to increased vitellogenin production in fish (Jobling and Sumpter, 1993; Solé et al., 2000; Petrovic et al., 2002) and have been

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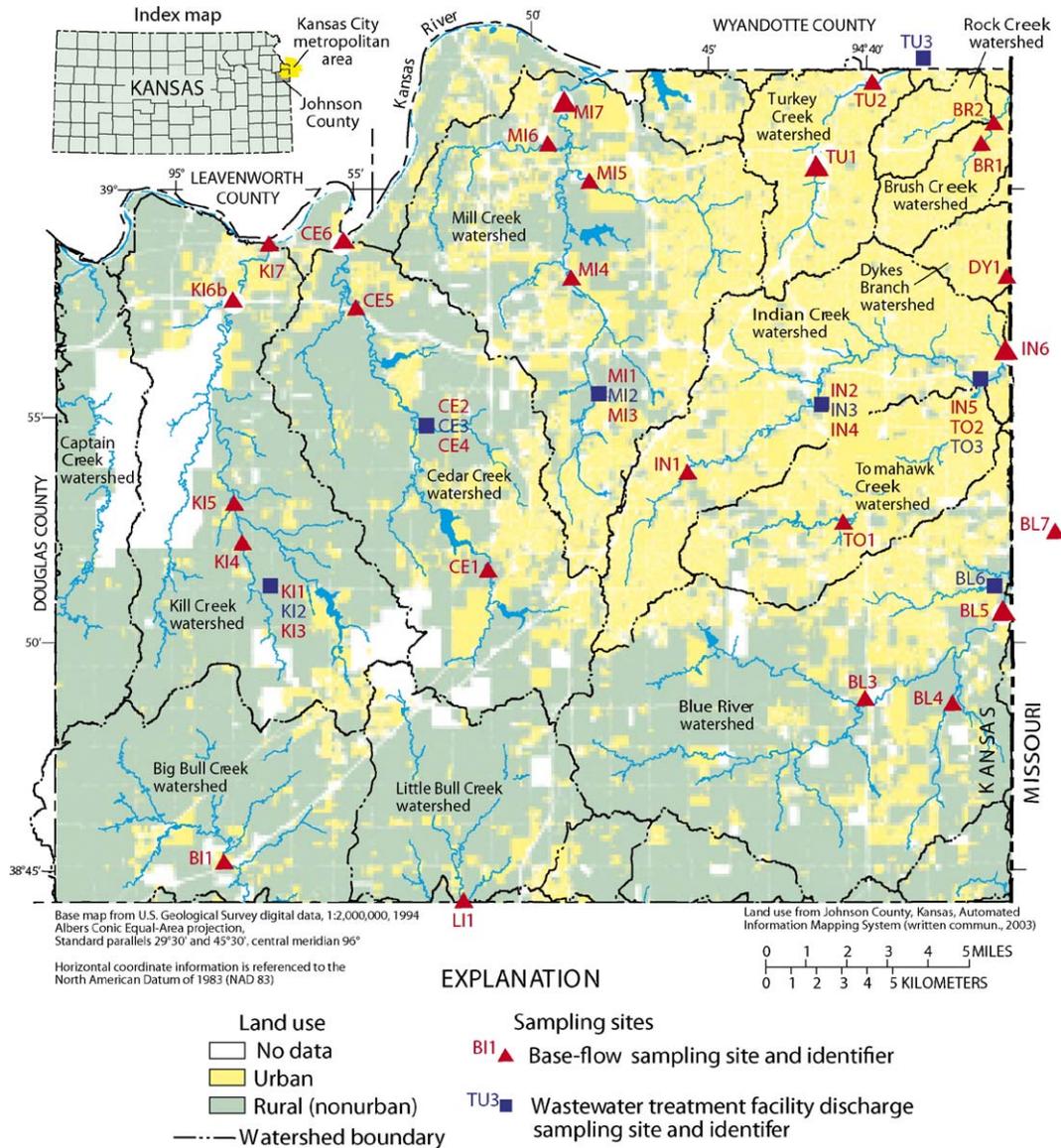


Fig. 1. Urban and nonurban land use, and location of sampling sites in Johnson County, northeastern Kansas.

shown to affect the structure and function of algal communities (Wilson et al., 2003). However, many of the individual and cumulative effects from complex mixtures of OWCs in streams have not been identified, and their transport and fate in the environment need more study (Daughton and Ternes, 1999; Kolpin et al., 2002; Frick and Zaugg, 2003). Identification of other potential OWC sources (other than WWTF discharge) also is needed (Daughton and Ternes, 1999).

The purpose of the study described herein was to determine the occurrence of a variety of OWCs upstream, in, and downstream from WWTF discharges as well as to determine any relations between land use and OWC occurrence in freshwater streams. To that end, 55 OWCs were analyzed in 59 stream-water samples collected during base-flow conditions and in 14 samples from WWTF discharges in Johnson County, northeastern Kansas (Fig. 1).

1.1. Study area

Watershed size ranged from 6.6 (Dykes Branch) to 123 km² (Blue River), and 1.0 (Captain Creek) to 30.9% (Turkey Creek) of land cover in each watershed was occupied by impervious surfaces (houses, roads, driveways, and parking lots). Urbanization in Johnson County generally has progressed from the northeastern corner of the county (nearest metropolitan Kansas City) outward, with the older urban sections in the northeast and newer urban developments in the west and south (Fig. 1). Percentage impervious surface (buildings, courtyards, paved and unpaved roads) has been shown to be a good indicator of watershed urbanization (Arnold and Gibbons, 1996) and is used in this study to distinguish urban and rural watersheds.

To facilitate a statistical comparison of the occurrence of OWCs along an urbanization gradient, watersheds with greater than 15% impervious surface were defined as urban; less than 15% were defined as rural. This distinction appeared to most accurately define watersheds that had already experienced urban development and those which were either undergoing development or had experienced little urban development. There were no combined sewers in the study area; however, bypasses of WWTFs were known to occur because of infiltration and inflow of stormwater into sewage lines.

The geology of Johnson County is characterized by sedimentary rock with alternating limestone and shale and minor amounts of fine-grained sandstone. Soils in the study area generally consist of loess, glacial deposits, and residual from the weathering of bedrock (Plinsky et al.,

Table 1

Wastewater treatment facilities sampled in Johnson County, northeastern Kansas, their designed flow capacity and secondary treatment processes

Wastewater treatment facility	Discharge sampling site (Fig. 1)	Design flow (million gallons per day)	Secondary treatment processes
Blue River Main	BL6	3.0	Extended aeration and activated sludge
Cedar Creek	CE3	3.0	Activated sludge
Indian Creek Middle Basin	IN3	9.0	Complete mix activated sludge
Kill Creek	KI2	2.5	Activated sludge
Harold Street (Mill Creek)	MI2	3.2	Trickling filter
Tomahawk Creek	TO3	10	Trickling filter
Myron Nelson Complex (Turkey Creek)	TU3	7.0	Trickling filter

Information from E. Hack, Johnson County Wastewater and Public Works Department, written commun., 2003.

1975). Northern streams in the county are known to have steeper gradients and greater relief than the east- and south-flowing streams (O'Connor, 1971).

Nine of the 12 watersheds in Johnson County contained active WWTFs that discharged into streams. The seven largest of these WWTFs were sampled during this study (Table 1). Four of these discharges were from WWTFs that used activated sludge secondary treatment processes to remove organic matter from the waste stream; three of the discharges were from WWTFs that used trickling filter secondary treatment processes. Wastewater treatment facilities with trickling filter secondary treatment processes force wastewater to flow over a medium enriched with microorganisms that degrade organic material in the wastewater stream. Activated sludge secondary treatment processes are typically used at more modern facilities and use microorganisms in a mixed sludge in combination with aeration to degrade organic material in the wastewater stream.

1.2. Study design

OWCs were analyzed in stream-water samples collected during base-flow conditions (streamflow contributed by wastewater discharges and groundwater) using a synoptic sampling network in which samples were collected at 31 sites during November 4–7, 2002, and at 42 sites from July 14–18, 2003. Fourteen of these samples were collected directly from WWTF discharges; eight samples from four WWTFs with activated

Table 2

Organic wastewater compounds analyzed in base-flow samples collected from selected Johnson County streams, northeastern Kansas, November 4–7, 2002, and July 14–18, 2003

Organic wastewater compound	Laboratory reporting level (µg/l)	Base-flow samples (Freq %)	Base-flow samples Median (µg/l)	Base-flow samples Max (µg/l)	Typical use (Zaugg et al., 2002)
<i>Detergent metabolites</i>					
4-Cumylphenol	1	0	ND	ND	Nonionic detergent metabolite
4-Nonylphenol	5	59	e1	E17	Nonionic detergent metabolite
4-Octylphenol	1	0	ND	ND	Nonionic detergent metabolite
4-Tert-octylphenol	1	0	ND	ND	Nonionic detergent metabolite
Nonylphenol-diethoxylate (NPEO2)	5	71	e4	E63	Nonionic detergent metabolite
Octylphenol-diethoxylate	1	0	ND	ND	Nonionic detergent metabolite
Octylphenol-ethoxylate	1	5.5	ND	e1	Nonionic detergent metabolite
<i>Flame retardants</i>					
Bisphenol A	1	0	ND	ND	Manufactured polycarbonate resins, anti-oxidant, flame retardant
Tributylphosphate	0.5	60	e0.1	e0.3	Antifoaming agent, flame retardant
Triphenyl phosphate	0.5	29	ND	e0.2	Plasticizer, resin, wax, finish, roofing paper, flame retardant
Tris(2-butoxyethyl) phosphate (TBEP)	0.5	64	e0.3	27	Plasticizer, floor polish, flame retardant
Tris(2-chloroethyl) phosphate (Fyrol CEF)	0.5	44	ND	0.6	Flame retardant, plasticizer
Tris(dichlorisopropyl) phosphate (Fyrol PCF)	0.5	64	e0.1	0.6	Flame retardant
<i>Fragrances</i>					
3-methyl-1(H)-indole (Skatol)	1	0	ND	ND	Fragrance, stench in feces and coal tar
Acetophenone	0.5	1.4	ND	e0.4	Fragrance in detergent and tobacco, flavor in beverages
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	0.5	49	ND	2.3	Musk fragrance (widespread usage)
D-limonene	0.5	4.1	ND	e0.1	Fungicide, antimicrobial, antiviral, fragrance
Hexahydro-hexamethyl-cyclopentabenzopyran (HHCB)	0.5	34	ND	0.5	Musk fragrance (widespread usage), persistent in ground water
Indole	0.5	23	ND	e0.4	Pesticide inert ingredient, fragrance in coffee
Isoborneol	0.5	4.1	ND	e0.1	Fragrance in perfumery, disinfectants
Isophorone	0.5	2.7	ND	e0.3	Fragrance in perfumery, disinfectants
Isoquinoline	0.5	0	ND	ND	Flavors and fragrances
<i>Herbicides/pesticides/insecticides</i>					
1,4 Dichlorobenzene	0.5	8.2	ND	e0.2	Moth repellent, fumigant, deodorant metabolite
Bromacil	0.5	22	ND	1.1	Herbicide
DEET	0.5	23	ND	3.7	Insecticide, mosquito repellent
Pentachlorophenol	2	0	ND	ND	Herbicide, fungicide, wood preservative, termite control
<i>PAHs and compounds associated with fossil fuels</i>					
1-Methylnaphthalene	0.5	2.7	ND	e0.2	2–5% of gasoline, diesel fuel, or crude oil
2,6-Dimethylnaphthalene	0.5	0	ND	ND	Present in diesel/kerosene (trace in gasoline)
2-Methylnaphthalene	0.5	2.7	ND	e0.2	2–5% of gasoline, diesel fuel, or crude oil
9, 10-Anthraquinone	0.5	32	ND	e0.3	Bird repellent, manufactured dye/textiles, PAH degradate

Table 2 (continued)

Organic wastewater compound	Laboratory reporting level (µg/l)	Base-flow samples (Freq %)	Base-flow samples Median (µg/l)	Base-flow samples Max (µg/l)	Typical use (Zaugg et al., 2002)
Anthracene	0.5	2.7	ND	e0.1	PAH, wood preservative, component of tar, diesel, or crude oil, combustion product
<i>PAHs and compounds associated with fossil fuels</i>					
Benzo A Pyrene	0.5	0	ND	ND	PAH, combustion product
Carbazole	0.5	11	ND	e0.1	Component of coal tar, oil, petroleum products
Fluoranthene	0.5	9.6	ND	e0.1	PAH, component of coal tar and asphalt, combustion product
Naphthalene	0.5	4.1	ND	e0.2	PAH, fumigant, moth repellent, major component of gasoline
Phenanthrene	0.5	2.7	ND	e0.1	PAH, component of tar, diesel fuel, crude oil, combustion byproduct
Pyrene	0.5	4.1	ND	e0.1	PAH, component of coal tar and asphalt (only traces in gasoline or diesel fuel), combustion product
<i>Sterols and stanols</i>					
3-Beta-coprostanol	2	16	ND	5	Carnivore fecal indicator
Beta-Sitosterol	2	29	ND	3	Plant sterol
Beta-Stigmastanol	2	21	ND	4	Plant sterol
Cholesterol	2	36	ND	10	Often a fecal indicator, plant sterol
<i>Others</i>					
3-Tert-butyl-4-hydroxy anisole (BHA)	5	0	ND	ND	Antioxidant, general preservative
5-Methyl-1H-benzotriazole	2	12	ND	4	Antioxidant in antifreeze and deicers
Benzophenone	0.5	38	ND	0.5	Fixative for perfumes and soaps
Caffeine	0.5	78	e0.1	12	Beverages, diuretic
Camphor	0.5	6.8	ND	e0.1	Flavor, odorant, ointments
Cotinine	1	36	ND	e0.8	Primary nicotine metabolite
Isopropyl benzene (Cumene)	0.5	0	ND	ND	Manufactured phenol/acetone, fuels, and paint thinner
Menthol	0.5	15	ND	E1.4	Cigarettes, cough drops, liniment, mouthwash
Methyl salicylate	0.5	15	ND	E.2	Liniment, food, beverage, ultraviolet-absorbing lotion
Para-cresol	1	4.1	ND	8	Wood preservative
Phenol	0.5	0	ND	ND	Disinfectant, manufacture of several products, leachate
Tetrachloroethylene	0.5	0	ND	ND	Solvent, degreaser, veterinary anthelmintic
Triclosan	1	5.5	ND	e2	Disinfectant, antimicrobial
Triethyl citrate	0.5	38	ND	e0.3	Cosmetics, pharmaceuticals

µg/l, micrograms per liter; %, percent; e, estimated below laboratory reporting level or; E, estimated due to <95% standard purity; ND, not detected; PAH, polycyclic aromatic hydrocarbon.

sludge secondary treatment processes, six samples from three WWTFs with trickling filter secondary treatment processes. Samples were collected during a single week to approximate an instantaneous view of base-flow conditions. Sampling sites were selected to provide spatial coverage of each watershed and to differentiate between effects of WWTF discharges and those associated with varying land use on the occurrence of OWCs in the study area (Lee et al., 2005).

Water samples were classified in terms of whether they were collected upstream ($n=31$), directly from ($n=14$),

immediately downstream (<500 m; $n=8$) and farther downstream (>2000 m; $n=20$) from WWTF discharges during base-flow conditions. Due to site accessibility problems, site TU3 (Fig. 1) was classified as a direct WWTF discharge sample although it was collected in-stream less than 10 m downstream from the actual discharge (mean WWTF discharge was greater than 95% of streamflow). Additionally, because of study limitations, samples were not collected directly downstream (<500 m) of all sampled WWTF discharges. Discharges from six of the seven WWTFs during base-flow conditions composed

Table 3

Results of commonly detected organic wastewater compounds in base-flow samples related to wastewater treatment facility discharges

Organic wastewater compound (OWC)	Median concentration ($\mu\text{g/l}$)				Maximum concentration ($\mu\text{g/l}$)				Level of significance (p -values) from Mann–Whitney			
	Up ($n=31$)	WWTF ($n=14$)	D1 ($n=8$)	D2 ($n=20$)	Up	WWTF	D1	D2	Nonparametric test of independent groups			
									Up/ WWTF	WWTF/ D1	WWTF/ D2	Up/ D2
Total OWC concentration	4.2	14.8	15.2	6.1	32.1	146	57	44	<0.01	0.62	0.01	0.13
3-beta coprostanol	ND	e0.6	ND	ND	e1	5	e2	e2	<0.01	0.30	<0.01	0.32
4-nonylphenol	ND	e1.5	e1.5	e1	e3	E17	E6	e2	<0.01	0.67	0.03	0.02
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	ND	1.6	1.2	e0.1	e0.1	2.3	1.6	0.5	<0.01	<0.01	<0.01	<0.01
Caffeine	e0.1	e0.1	0.5	e0.1	6.9	12	3.3	2.5	0.92	0.56	0.62	0.21
Cholesterol	ND	1.1	1	ND	2	10	4	6	0.02	0.91	0.18	0.25
Nonylphenol diethoxylate (NPEO2)	e3	E6	E6.5	e4	E22	E63	E34	E14	<0.01	0.78	0.13	0.04
Tris(2-butoxyethyl) phosphate (TBEP)	e0.1	1.3	1.6	e0.2	7.4	27	6.2	6.6	0.02	0.71	0.03	0.91
Tris(dichloroisopropyl) phosphate	ND	e0.4	e0.4	e0.1	e0.2	0.6	0.5	e0.4	<0.01	0.75	<0.01	<0.01

Up, sites upstream from wastewater discharge; WWTF, wastewater treatment facility discharge samples; D1, Samples from sites <500 m downstream from WWTF discharges; D2, Samples from sites >2000 m downstream from WWTF discharges; n , number of samples; ND, not detected; e, estimated below laboratory reporting level; E, estimated due to <95% standard purity.

the majority of streamflow exiting the county (Lee et al., 2005).

2. Methods

Fifty-five organic compounds were analyzed from stream-water samples which have known wastewater sources as well as available laboratory methods (Zaugg et al., 2002). Stream-water and WWTF discharge samples were collected by submerging an amber glass bottle at the centroid of flow. Onsite measurements of specific conductance and turbidity indicated equal mixing of water-quality conditions across the cross section during base-flow sampling. Stream-water samples were filtered using a 0.7- μm glass fiber filter; samples were refrigerated and shipped for analysis. Filtered water methodologies have been found to approximate values reported by whole-water analysis methods (slope of 0.80; Lee et al., 2004). Additionally, suspended-sediment concentrations were relatively small (median=8 mg/L) during base-flow conditions, thus filtered samples should closely approximate total OWC concentrations. All samples were collected in accordance with U.S. Geological Survey protocols for the collection of wastewater and pharmaceutical compounds with the exception of the final methanol rinse (Lewis and Zaugg, 2003). Stream-water samples were analyzed at the U.S. Geological Survey National Water-Quality Laboratory in Lakewood, Colorado, using methods described by Zaugg et al. (2002). Compounds were extracted using solid-phase extraction and analyzed by capillary-column gas chromatography/mass spectrometry (GC/MS). Most

laboratory reporting levels for OWCs in stream-water samples were 0.5 $\mu\text{g/l}$ but were as high as 5 $\mu\text{g/l}$ for selected compounds (Table 2). Detections determined as less than the laboratory reporting limits are denoted with an “e” value, whereas all detections of nonylphenol diethoxylate and 4-nonylphenol are denoted with an “E” to symbolize that standards used to develop this method are of less than 95% purity (standards are of 90% purity) (S. Zaugg, written commun, 2006).

2.1. Quality assurance

One field blank and two process blank water samples were collected and analyzed for OWCs. Field blank samples were collected using laboratory-grade organic-free water and were subjected to the same collection and processing procedures as stream-water samples. Process blank samples were collected using laboratory-grade organic-free water and were subjected to the same sample processing procedures as stream-water samples. Phenol was the only compound detected (3.4 $\mu\text{g/l}$ in the field blank) larger than laboratory reporting levels (0.5 $\mu\text{g/l}$) and was larger than values determined from any water sample in this study. Nine other compounds (1,4-dichlorobenzene, acetophenone, benzophenone, caffeine, camphor, DEET, isophorone, phenanthrene, and tris(2-chloroethyl) phosphate) were detected at concentrations less than laboratory reporting levels in the field blank sample. Nonylphenol-diethoxylate was the only compound detected in process blank samples at an estimated detection of 2 $\mu\text{g/l}$ (less than the laboratory reporting limit

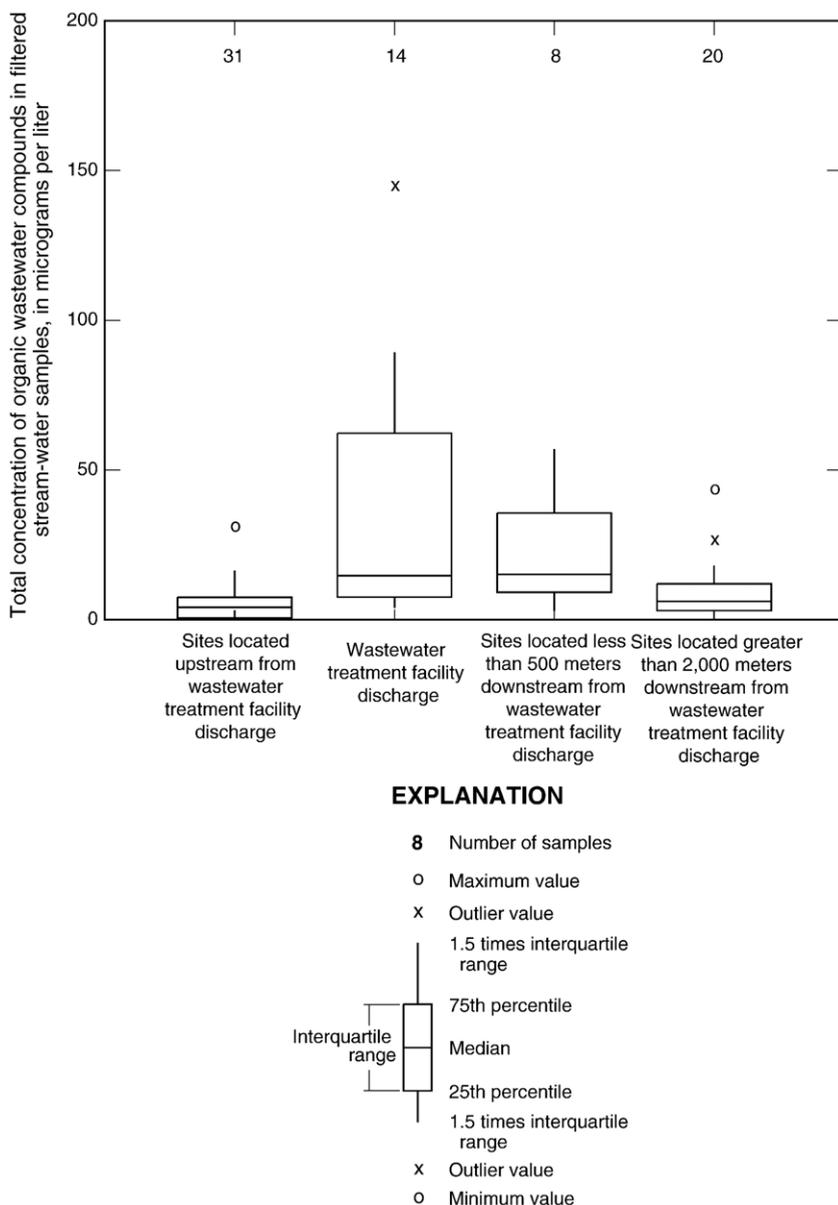


Fig. 2. Total organic wastewater compound concentrations in relation to wastewater discharges during base-flow conditions.

of 5 $\mu\text{g/l}$). Stream-water concentrations of compounds at the same or less than each respective blank concentration were reported as less than the laboratory reporting level. Five sequential replicate samples were analyzed for OWCs, all of which had mean relative percentage differences (RPDs) less than 30%.

2.2. Statistical methods

Because data were not normally distributed, the non-parametric Mann–Whitney U test was used (as opposed

to the parametric student's t test) to determine statistical differences between two independent groups. OWCs that were not detected were assigned values one-tenth of the laboratory level (less than any possible detections) for this analysis. Probability of error (p) was used in this study to determine the significance for all statistical methods. A p -value of less than 0.05 (95% confidence that the statistical test was valid or that the compared data sets were different) is used in this manuscript to indicate if a statistical test was significant (Helsel and Hirsch, 1992).

3. Results

For each stream-water and WWTF discharge sample, the concentrations of all 55 OWCs were summed to provide a total concentration per sample. Only one sample (site KI7, Fig. 1) did not record a detection of any OWCs. For comparative purposes, 0.1 $\mu\text{g}/\text{l}$ (the minimum total OWC concentration of all the other samples) was assigned to this sample.

Data from compounds detected most frequently, and (or) at the largest concentrations (Table 2) during base-flow conditions are summarized relative to WWTF discharge in Table 3. During base-flow conditions, samples collected directly from WWTF discharges had the largest cumulative OWC concentrations of all base-flow samples; concentrations were significantly greater ($p < 0.01$) than upstream samples (Fig. 2, Table 3). Sample medians decreased slightly immediately downstream but were not significantly different from WWTF discharge samples ($p = 0.62$). Sample medians collected farther downstream (> 2000 m) had significantly less cumulative OWCs ($p = 0.01$) than WWTF discharges, likely due to degradation of compounds, adsorption to streambed sediment, uptake by aquatic biota, or dilution of WWTF sources. However, dilution was likely not a large factor due to the large magnitude of streamflow contributed by

WWTF discharges relative to other sources (Lee et al., 2005). Samples collected farther downstream from WWTFs were not significantly different ($p = 0.13$) than those collected upstream from discharges, suggesting that many of the OWCs only had significantly larger concentrations at, and immediately downstream from, WWTF point-source discharges. Similar patterns in total concentrations of OWCs have been observed by Glassmeyer et al. (2005). The sampling design did not take travel time into account; thus, definitive OWC elimination rates could not be computed from the data.

Of the WWTF discharges sampled, six water samples from the three facilities with trickling filter secondary treatment processes had significantly larger ($p < 0.01$) total OWC concentrations than eight samples collected from four activated sludge WWTFs (Fig. 3, Table 4). Similar findings have been made by Carbella et al. (2004) and Phillips et al. (2005). Due to consistent differences in OWC occurrence between WWTFs with different secondary treatment processes and larger sample numbers at activated sludge treatment facilities ($n = 8$), median concentrations tended to underestimate the concentrations of many OWCs.

Mean comparisons are used to characterize the magnitude of compound loss between the eight WWTF discharges and eight sites with samples immediately

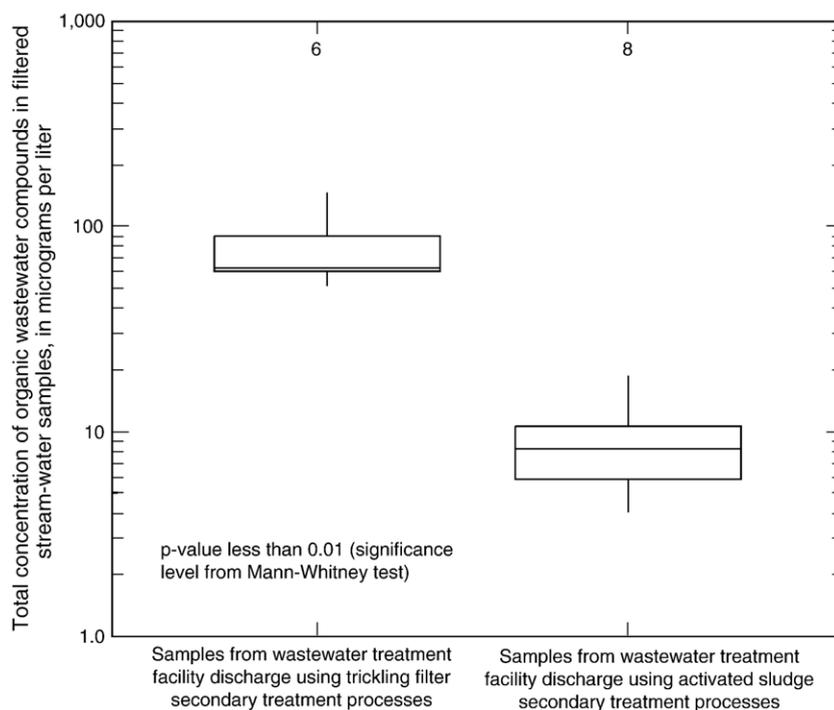


Fig. 3. Total organic wastewater compound concentrations in discharges from wastewater treatment facilities with trickling filter and activated sludge secondary treatment processes.

Table 4
Organic wastewater compounds in wastewater treatment facilities with activated sludge or trickling filter secondary treatment processes

Organic wastewater compound (OWC)	Detection frequency (percent)		Median concentration ($\mu\text{g/l}$)		Maximum concentration ($\mu\text{g/l}$)		Level of significance (p -values) from Mann–Whitney nonparametric test of independent groups
	WWTFs with activated sludge secondary treatment processes ($n=8$)	WWTFs with trickling filter secondary treatment processes ($n=6$)	WWTFs with activated sludge secondary treatment processes ($n=8$)	WWTFs with trickling filter secondary treatment processes ($n=6$)	WWTFs with activated sludge secondary treatment processes	WWTFs with trickling filter secondary treatment processes	
Total OWC concentration	–	–	8.2	62	18.6	146	<0.01
3-beta coprostanol	13	100	ND	e2	e1	5	<0.01
4-Nonylphenol	83	100	e1	E9	e2	E17	<0.01
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	100	100	1.4	1.8	1.8	2.3	0.24
Beta-sitosterol	13	83	ND	e2	e2	3	0.02
Beta-stigmastanol	13	67	ND	e1.5	e2	3	0.06
Caffeine	25	100	ND	7.2	e0.1	12	<0.01
Cholesterol	13	100	ND	3	e2	10	<0.01
DEET	13	83	ND	1.4	e0.3	3.7	0.01
Menthol	0	67	ND	0.9	ND	1.4	0.01
Nonylphenol-diethoxylate (NPEO2)	83	100	e3.5	E26	E7	E63	<0.01
Tris(2-butoxyethyl) phosphate	63	100	e0.3	10	2.5	27	<0.01
Tris(2-chloroethyl) phosphate	100	100	e0.4	e0.4	0.6	0.6	0.84
Tris(dichloroisopropyl) phosphate (TBEP)	100	100	0.5	e0.4	0.6	0.5	0.47

n , number of samples; WWTF, wastewater treatment facility; ND, not detected; e estimated below laboratory reporting level; E, estimated due to <95% standard purity.

(<500 m) downstream (Table 5). Mean concentrations of most OWCs decreased by approximately 40–60% within 500 m downstream from the discharge. Mean and maximum concentrations of tris(dichloroisopropyl) phosphate did not decrease immediately downstream; however, it was the only compound with mean values less than laboratory reporting levels.

Nearly all OWCs (with the exception of caffeine) had significantly larger concentrations in WWTF discharges than in samples collected upstream (Table 3). Caffeine differed from most OWCs in that it was detected in a majority of samples collected upstream from WWTF discharges (Table 3), and concentrations from activated sludge discharges were similar to those detected at upstream sites (Table 4). Only AHTN exhibited significant compound loss immediately (<500 m) downstream from WWTF discharges based on median comparisons. AHTN was one of the few compounds observed at similar concentrations in WWTF discharges irrespective of treatment

process (Table 4), allowing for a more consistent comparison between WWTF discharges and sites immediately downstream. Additionally, AHTN is one of the most hydrophobic (Koc ~ 3.93; Meylan et al., 1992) of the compounds sampled. However, mean comparisons (Table 5) indicate that OWCs detected above laboratory reporting levels (regardless of adsorptive capacity) began decreasing less than 500 m downstream from WWTF discharges.

Several individual OWCs were observed at significantly larger concentrations in trickling filter discharges (Table 4). 3-beta coprostanol, 4-nonylphenol, beta-sitosterol, caffeine, cholesterol, DEET, menthol, nonylphenol diethoxylate, and tris(2-butoxyethyl) phosphate had significantly larger concentrations ($p < 0.05$) in samples from trickling filter discharges than in samples from activated sludge discharges. Other compounds that were detected frequently did not show significant differences (AHTN, beta-stigmastanol, tris(2-chloroethyl)

Table 5

Mean concentrations of commonly detected organic wastewater compounds at and immediately downstream from wastewater treatment facility discharges

Organic wastewater compound (OWC)	Mean concentration (µg/l)		Maximum concentration (µg/l)	
	WWTF	D1	WWTF	D1
	(n=8)	(n=8)		
Total OWC concentration	38	23	89	57
3-Beta coprostanol	1.4	0.5	5	2
4-Nonylphenol	3.8	2.3	9	6
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	1.7	1.1	2.3	1.7
Caffeine	2.4	0.9	12	3.3
Cholesterol	2.5	1.3	10	4
Nonylphenol diethoxylate (NPEO2)	E17	E11	E32	E34
Tris(2-butoxyethyl) phosphate (TBEP)	4.4	2.0	15	6.2
Tris(dichloroisopropyl) phosphate	e0.4	e0.4	0.6	0.6

[WWTF, wastewater treatment facility discharge samples; D1, samples from sites <500 m downstream from WWTF discharges; n, number of samples; e, estimated below laboratory reporting level; E, estimated due to <95% standard purity].

phosphate, tris(dichloroisopropyl) phosphate. AHTN has shown improved removal in activated sludge than in trickling filter treatment facilities (Simonich et al., 2002; Carbella et al., 2004); statistically insignificant differences of this and other compounds may be because of the limited number of samples and (or) small concentrations in WWTF discharges relative to laboratory reporting levels.

The majority of OWCs had significantly smaller concentrations at sites farther downstream (>2000 m) than WWTF discharges, indicating that loss of the majority of compounds sampled in this study continued

farther downstream from WWTF point sources. Exceptions include caffeine, cholesterol, and nonylphenol diethoxylate (Table 3). All three of these compounds had significantly smaller concentrations in WWTF discharges with activated sludge secondary treatments, decreasing the magnitude of potential compound loss at downstream sites (Tables 3 and 4). Persistent concentrations of caffeine downstream from WWTF discharges also may be due to hydrophilic properties (Koc ~ 1.00; Meylan et al., 1992). These compounds may have additional sources (such as leaking sewage lines or unauthorized discharges) downstream from WWTF discharges, as larger concentrations of caffeine are linked to urban land uses upstream from WWTF discharges (Table 6).

Upstream samples were compared to those collected >2000 m downstream from WWTF discharges to characterize compounds that continued to have WWTF discharge sources farther downstream. 4-nonylphenol, AHTN, nonylphenol-diethoxylate, tris(2-chloroethyl) phosphate, and tris(dichloroisopropyl) phosphate were detected at significantly larger concentrations farther downstream from WWTF discharges than upstream from discharges, indicating that WWTFs likely continue to be the primary source of these compounds farther (>2000 m) downstream. Caffeine, cholesterol, and tris(2-butoxyethyl) phosphate concentrations were statistically insignificant in upstream samples, indicating that WWTF discharges may not be the predominant source of these compounds in downstream detections. Both caffeine and tris(2-butoxyethyl) phosphate had significantly larger concentrations in urban areas upstream from WWTF discharges (Table 6), providing further evidence of the presence of nonpoint sources of these compounds. In addition, DEET was detected at significantly larger

Table 6

Organic wastewater compounds detected in a majority of urban or rural base-flow samples upstream from WWTF discharges

Organic wastewater compound	Median concentration (µg/l)		Maximum concentration (µg/l)		Level of significance (p-values) from Mann–Whitney nonparametric test of independent groups
	Rural base-flow samples upstream from WWTF discharges (n=11)	Urban base-flow samples upstream from WWTF discharges (n=20)	Maximum value from rural base-flow samples upstream from WWTF discharges	Maximum value from urban base-flow samples upstream from WWTF discharges	
Total OWC concentration	0.4	4.8	32.1	16.4	0.03
Caffeine	e0.1	e0.2	e0.1	6.9	0.01
Nonylphenol-diethoxylate (NPEO2)	ND	E3	E22	6	0.34
Tris(2-butoxyethyl) phosphate (TBEP)	ND	e0.4	e0.3	7.4	<0.01

n, number of samples; WWTF, wastewater treatment facility; ND, not detected; e, estimated below laboratory reporting level.

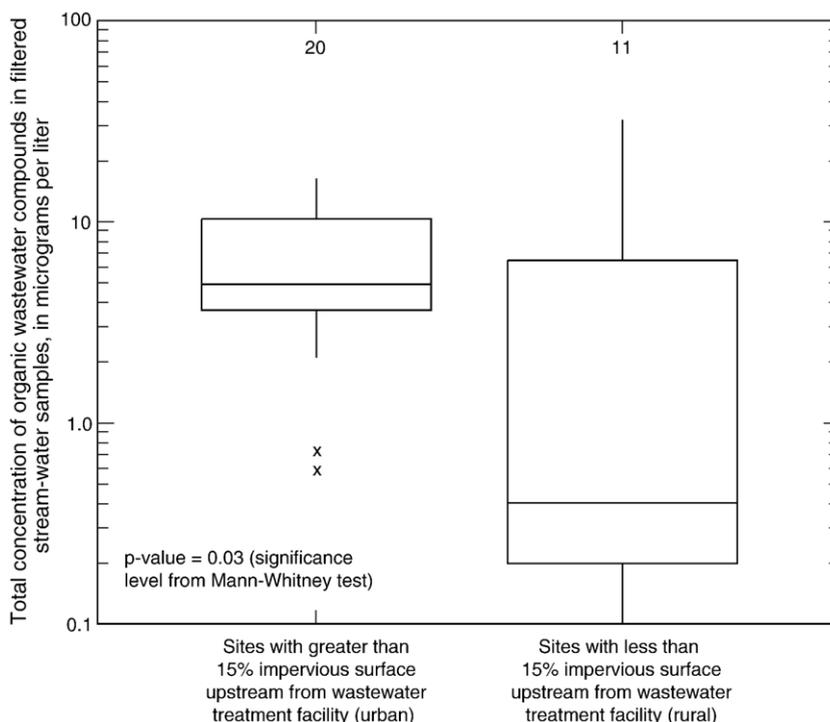


Fig. 4. Total organic wastewater compound concentrations in base-flow samples from urban and rural sites upstream from wastewater discharges.

($p < 0.01$) concentrations in summer (July 14–18) base-flow samples than in November 4–7, 2002 samples corresponding to increased summer usage.

OWCs were summed from base-flow samples collected upstream from WWTF discharges and compared to land use (Fig. 4; Table 6). Samples from sites with more urban land uses (>15% impervious surface) had significantly larger ($p = 0.03$) cumulative concentrations of OWCs than samples from sites with more rural (<15% impervious surface) land uses. Caffeine, nonylphenol diethoxylate, and tris(2-butoxyethyl) phosphate) were detected in a majority of urban or rural samples upstream from WWTF discharges during base-flow conditions. Caffeine ($p = 0.01$) and tris(2-butoxyethyl) phosphate ($p < 0.01$) were found at significantly larger concentrations in urban base-flow samples than in rural samples (Table 6). One rural site located upstream from WWTF discharges had relatively large nonylphenol diethoxylate concentrations (22 $\mu\text{g/l}$, Table 4) but was unique among rural sites in that this sample was collected directly downstream from a 4.1- km^2 rock quarry operation.

4. Discussion

These data suggest that although WWTF discharges were the largest source of OWCs, secondary treatment processes were among the most important factors

affecting the magnitude of OWCs contributed to streams. Because samples were not collected in the waste stream entering WWTFs, it is impossible to definitively isolate the effect of secondary treatment processes on OWC concentrations in WWTF discharges. However, discharges from trickling filter and activated sludge facilities with both large and small capacities were sampled in both urban and rural areas; indicating that secondary treatment processes are likely an important variable affecting concentrations of OWCs in WWTF discharge.

Comparisons of WWTF discharges to sites downstream indicate that decreases in compound concentrations begin immediately after discharge into streams and that concentrations of many compounds return to ambient (without WWTF discharges) levels farther downstream. Depending upon the hydrology of the receiving waters, statistically significant decreases in OWCs originating from WWTF discharges may not occur until some distance downstream. Additionally, larger concentrations of some OWCs at urban sites indicate that other nonpoint sources of OWCs exist during base-flow conditions, which can further mask comparisons between direct WWTF discharges and the receiving stream.

The results presented in this study indicate that a substantial portion of OWCs contributed to streams may be eliminated through upgrades in secondary treatment processes. As many parent and degradation products of

compounds analyzed in this study were not determined, the total concentrations of organic wastewater compounds likely exceed results presented in this study. Potential impacts to aquatic life are likely most pronounced immediately downstream from WWTF point sources, and to a lesser degree farther downstream from discharges and at sites downstream from urban land uses. Although selected OWCs found downstream from WWTFs in water, sediment, and fish tissue (Rice et al., 2003) have been correlated to vitellogenin increases in carp (Petrovic et al., 2002), cumulative impacts of these compounds in water and streambed sediment are often unknown. Additional study characterizing thresholds of aquatic impact in stream-water and streambed sediments would help determine potential effects at distances downstream from WWTF discharge points.

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