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Research Plan and Preliminary Results—A Field Research Site for Emerging Contaminants in Iowa

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Research has recently documented the prevalence of a wide variety of pharmaceuticals and other emerging contaminants (ECs) in streams across the United States. Wastewater treatment plants (WWTPs) have been found to be an important source and collection point of ECs to streams as many ECs are incompletely removed during treatment. To investigate the complex instream processes (e.g., dilution, sorption, degradation, dispersion, etc.) that can affect ECs following their input from a WWTP and determining if such input is having an effect on the aquatic ecosystem requires the integration of multi-disciplinary efforts at a carefully selected field site. Preliminary work has identified an 8-km reach of Fourmile Creek in central Iowa as an ideal research site to investigate such important research questions pertaining to ECs. Unique aspects of Fourmile Creek included: (1) a single source effluent-dominated stream, (2) background data document the input of a wide variety of ECs from WWTP discharge, (3) small basin size, (4) relatively simple flow system, (5) background data suggest that undefined processes are taking place decreasing the level of select ECs during stream transport, (6) the WWTP uses a treatment technology (activated sludge) typical of many towns in Iowa and the United States (7) a hydrogeologic setting of a low-gradient, small stream (average discharge less than 1.41 m³/s) in glacial drift is typical of many areas in Iowa and across the Midwest, and (8) the existence of a low-head dam approximately 2 km upstream of the WWTP outfall allowing more accurate "above WWTP" and "below WWTP" comparisons in aquatic ecosystems. Furthermore, the WWTP is scheduled to close by 2011 providing a unique opportunity to determine how stream hydrology, water chemistry and aquatic biota react to the removal of the primary source of flow and ECs in this system. This will allow a novel "before" and "after" assessment not previously available in EC research. Research to date at the site has included installation of a streamflow gauging station, dye-tracing tests (to determine water travel times), Lagrangian water-quality sampling at two flow/water temperature regimes, and sampling for ECs in bed sediment. Selected fish have been collected for analysis and identification. In addition, basic fish community and fish health assessment for different seasons and spawning conditions are being analyzed. The research "framework" is unique at Fourmile Creek for investigating the important question of how ECs are transported through the environment and if the presence of such compounds is having a deleterious effect on aquatic ecosystems.

INDEX DESCRIPTORS: Emerging contaminants, endocrine disruption, antibiotics, pharmaceuticals, surface water, wastewater.

Emerging Contaminants-Chemicals of Concern

A wide variety of chemicals are used everyday in today's society (homes, industry, agriculture, etc.). Recent research has shown that compounds not previously considered as contaminants are present in the environment (Halling-Sørenson et al. 1998, Kolpin et al. 2002). These include a number of compounds such as human and veterinary prescription drugs, diagnostic agents, hormones, cosmetics, dyes, preservatives, detergents, and numerous other organic compounds. There are increasing concerns about the potential environmental effects that may inadvertently occur from such "emerging contaminants" (ECs) (Thibaut et al. 2006; Gooding et al. 2006). What are ECs? A useful working definition follows:

The term emerging contaminants can be broadly defined as any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment, but has the potential to enter the environment and can cause suspected adverse ecological and/or human health effects. In some cases, release of emerging chemical or microbial contaminates to the environment has likely occurred for a long time, but may not have been recognized until new detection methods were developed. In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of emerging contaminants. (U.S. Geological Toxic Substances Hydrology 2005).

Most ECs are not routinely monitored. Indeed, water-quality monitoring in the United States is largely driven by regulations of the Clean Water Act and Safe Drinking Water Act. Therefore, most monitoring programs are focused on compounds that are assigned standards by federal or state agencies (U.S. Environmental Protection Agency 2003, U.S. Environmental Protection Agency 2004). During the past three decades, water-quality monitoring has focused almost exclusively on the conventional "priority pollutants," which are only one piece of the larger environmental puzzle (Daughton and Ternes 1999). Only recently have ECs been examined using new laboratory analytical methods and techniques. Furthermore, the likelihood that environmental contaminants may be present as complex mixtures that can interact synergistically or antagonistically has increased the need to understand ECs found in our waters.

In order to minimize ecological effects from ECs, it is essential to understand how a contaminant moves and is altered in the environment. Investigations of processes influencing transport (e.g., sorption, dispersion, degradation, etc.) require a systematic evaluation of a variety of hydrologic, landscape, and anthropogenic factors (Barber et al. 2006). The purpose of this paper is to provide a short synopsis of ECs as potential contaminants of concern and to highlight preliminary results from an 8-km reach of Fourmile Creek in central Iowa. Establishing an on-going field research site to investigate the transport, fate, and effects from an urban source of ECs at Fourmile Creek is presented. Furthermore, it is hoped that a field research site for ECs in Iowa will foster collaboration among various researchers within the State and elsewhere.

Analytical development, diverse chemicals, and complex pathways

Recent advances in sample extraction and analytical instrumentation now permit the environmental measurement of ECs at unprecedented detection levels (e.g., Sedlak et al. 2000, Kolpin et al. 2002, Cahill et al. 2004, Burkhardt et al. 2005). Quantification for many ECs was first reported in the parts per billion (microgram per liter) range, but now results are commonly reported in the parts per trillion (nanogram per liter) range. By comparison, many common pesticide compounds (atrazine, metolachlor, acetochlor, etc.) are routinely analyzed and reported in the parts per billion range and common inorganic substances (sodium, chloride, nitrate, etc.) are analyzed and reported in the parts per million (milligrams per liter) range. The low detection levels allow researchers to better define the range of compounds present in the environment and to properly gauge the importance of ECs. Improvements in analytical methods allow policy makers to better determine potential health-based thresholds (Focazio et al. 2004, p. 92).

The use of ECs for both human and veterinary purposes result in complex fate pathways through the environment (Fig. 1). Wastewater treatment plants (WWTPs) are an important collection point and source of ECs to the environment (Heberer 2002, Carballa et al. 2004, Joss et al. 2005, Miao et al. 2004, Xia et al. 2005). WWTPs have multiple pathways to the environment including direct discharge of treated effluent to surface water bodies (Ashton et al. 2004, Glassmeyer et al. 2005), land application of treated effluent (Kinney et al. 2006), and land application of treated biosolids (Yang and Metcalf 2005). Thus, as sinks for ECs, WWTPs are ideal locations to reduce the loading of these compounds to the environment. Early research comparing influent and effluent concentrations at select WWTPs in New York has shown that treatment technologies vary in their ability to reduce EC concentrations (Phillips et al. 2005).

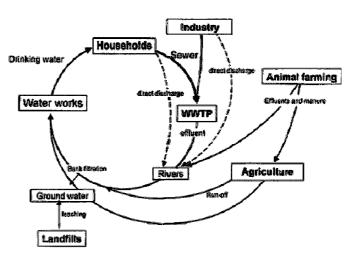


Fig. 1. Potential sources, pathways, and sinks of emerging contaminants in the environments. Modified from Halling-Sørenson et al., 1998.

Possible effects of ECs—Endrocrine disruption and antibiotic resistance

The potential toxicological behavior of ECs and mixtures of ECs is largely unknown. In particular, the effects of ECs on aquatic organisms are difficult to measure because the concentrations of these compounds are generally low (nanogram per liter range) and may produce no acutely toxic effects during the life of the organism. However, detrimental effects to organisms from ECs may be subtle and go unnoticed until some cumulative threshold is reached. In recent years, the presence and effects of endocrine disrupting compounds (EDCs) in the environment has become an important issue (Keith 1997). The endocrine system is the "key control system" of most organisms as hormones are secreted that interact with specific receptors on cells that enable functions to be controlled (Global Water Research Coalition 2003). A working definition of an EDC as defined by the World Health Organization (WHO) is "an exogenous substance that alters the function of the endocrine system and consequently causes adverse health effects in an organism, or its progeny, or (sub)populations" (U.S. Environmental Protection Agency, web page http://epa.gov/endocrine/Pubs/smithrep.html accessed August, 2005). The presence of low concentrations of some chemicals in the environment (e.g., natural and synthetic hormones, alklyphenols, pesticides, solvents, and pharmaceuticals) could affect or damage the function of the endocrine system (Global Water Research Coalition 2003). For example, nonylphenol (a detergent degradation product), and AHTN (a polycyclic musk) have been shown to disrupt reproduction and growth in fish by affecting endocrine systems (Thorpe et al. 2001, Schreurs et al. 2004). A variety of ECs have been shown to bioaccumulate in fish tissue (Brooks et al. 2005, Kukrunthachalam et al. 2005). Data from laboratory experiments suggest that EDCs in the aquatic environment may impact the reproductive health of fish populations (Mills and Chichester 2005, Bistodeau et al. 2006). Linking EDCs to observed changes in fish populations, however, remains an open challenge (Mills and Chichester 2005). Although less is known about potential effects to other aquatic species, early research suggests that effects to

Ankeny, Iowa, 2002 (Glassmeyer et al. 2005). [WWTP, wastewater treatment plant; µg/L; micrograms per liter].						
Site (locations shown on figures 2 and 5)		Total concentration of selected emerging contaminants (µg/L)				
Upstream (site 1)	11	2.75				
$\hat{W}WTP$ effluent (site 2)	50	27.5				

Table 1. Number of compounds and total concentration of analytes found in samples collected from Fourmile Creek near

aquatic organisms are possible (Flaherty and Dodson 2005, Oetken et al. 2005, Wilson et al. 2003). Indeed, ecological risk assessment for EDCs in the environment is in its infancy (Hartemann 2004, p. 267).

2.9 km downstream of WWTP (site 4)

8.4 km downstream of WWTP (site 5)

Antibiotics are an important class of pharmaceuticals and their prevalence and use in the last 60 years has brought dramatic and often even "miraculous" progress in fighting bacterial infections in humans and animals. In livestock farming, sub-therapeutic doses of antibiotics are often used to promote more rapid animal growth (Alexy et al. 2004). Despite their widespread use, antibiotics have only recently received attention as environmental contaminants. However, the increase of resistant bacterial strains and the spread of bacterial resistance have become a worldwide concern (Kummerer, 2004b). Concerns also exist for antibiotic use and increasing antibiotic resistance in livestock confined feeding operations (Boxall et al. 2003, Osterberg and Wallinga 2004). Many antibiotics are only partially metabolized after administration to humans or animals (Hamscher et al. 2004). Concentrations of select antibiotics in animal manure have been reported at mg/L levels (Hamscher et al. 2004, p. 140, Meyer 2004).

Antibiotics can reach streams and groundwater via a variety of mechanisms (Fig. 1) and the potential for the aquatic environment to promote or maintain antibiotic resistance is largely unknown. Some chemicals, such as triclosan (an antimicrobial disinfectant found in many liquid soaps, dishwasher powders, and plastics), are suspected of increasing the antibiotic resistance of bacteria in the environment (McMurry et al. 1998), reducing algae diversity in streams (Wilson et al. 2003), and affecting natural ecosystem functions such as soil microbial activity (Thiele-Bruhn and Beck 2005). In addition, research has shown effects of mixtures of antibiotics to aquatic organisms (Brain et al. 2005).

SUMMARY OF PREVIOUS WORK

29.9 10.6

47

35

Following a national stream reconnaissance study (Kolpin et al. 2002), water samples were collected in 2001 upstream and downstream of select towns and cities in Iowa during low-, normal-, and high-flow conditions to determine the contribution of urban centers to concentrations of ECs in streams under varying flow conditions (Kolpin et al. 2004). That study found that the number of ECs detected decreased as streamflow increased from low- (51 ECs detected) to normal- (28) to highflow (24) conditions. Fourmile Creek near Ankeny, Iowa was sampled for ECs for the first time during this study and results showed that a strong gradient in EC detections during low-flow conditions between samples collected upstream of Ankeny (three ECs detected) compared to samples collected downstream (31 ECs detected).

The initial EC results from Fourmile Creek (Kolpin et al. 2004), led to including this stream as part of collaborative research between the U.S. Geological Survey (USGS) and the U.S. Environmental Protection Agency to better understand the fate of ECs following their discharge from WWTPs (Glassmeyer et al. 2005). This research involved collecting four samples at each of 10 WWTPs across the nation: upstream of the WWTP, at the WWTP where effluent was being discharged into the stream, at a location in close proximity downstream of the WWTP, and at a location farther downstream from the WWTP. All samples were measured for 110 ECs and found between 28 and 50 ECs in treated wastewater effluent being discharged to streams (Glassmeyer et al. 2005). The similarity in chemical concentrations between WWTP effluent and proximal downstream sampling points clearly shows the contribution of WWTPs to EC concentrations in streams. Additional knowledge gained from Fourmile Creek during this study included:

Selected compounds detected, primary use, reporting level, and concentrations-upstream, at source, and Table 2. downstream-from samples collected at Fourmile Creek near Ankeny, Iowa, 2002. (Glassmeyer et al. 2005; written communication, June 2005, Susan Glassmeyer, U.S. Environmental Protection Agency). [µg/L, micrograms per liter; WWTP, wastewater treatment plant; location of sites shown on Figs. 2 and 5].

Compound	Primary Use	Reporting level (µg/L)	Concentration upstream (site 1) of WWTP (µg/L)	Concentration at source (site2) WWTP (µg/L)	Concentration 8.4 km downstream (site 5) of WWTP (µg/L)
Cimetidine	Antacid	0.012	Not detected	0.123	0.107
Dehydronifedipine	Antianginal	0.015	Not detected	0.202	0.018
Diltiazem	Antihypertensive	0.016	Not detected	0.053	0.029
Diphenhydramine	Antihistamine	0.015	Not detected	0.218	Not detected
Sulfamethozole	Antibiotic	0.064	Not detected	0.589	0.321
Tonalide (AHTN)	Fragrance, musk	0.5	Not detected	2.3	0.7
Trimethoprim	Antibiotic	0.013	Not detected	0.353	0.093

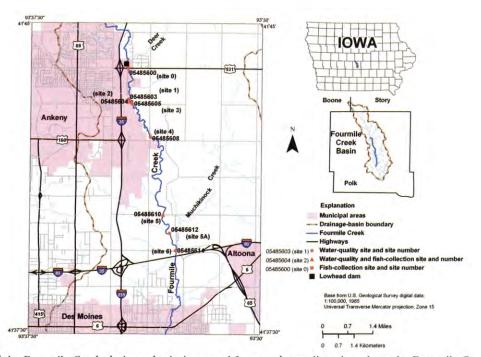


Fig. 2. Location of the Fourmile Creek drainage basin in central Iowa and sampling sites along the Fourmile Creek stream reach.

- 1) the ECs detected in Fourmile Creek during the previous study (Kolpin et al. 2004) were primarily derived from the Ankeny WWTP (Table 1),
- 2) there were significant reductions of the number of ECs detected and total EC concentrations through the 8.4 km study reach (Table 1) by undefined natural processes (e.g., sorption, microbial degradation, photolysis, etc.),
- 3) ECs vary in their type of transport (conservative versus nonconservative) through the study reach (Table 2), at lowflow conditions greater than 90 percent of the streamflow is derived from WWTP discharge (Glassmeyer et al. 2005).

In 2003, the USGS EC Project (http://toxics.usgs.gov/regional/ emc/index.html) attempted to identify a real-world setting to investigate the complex in-stream processes (e.g., dilution, sorption, degradation, dispersion, etc.) that can affect ECs following their discharge from a WWTP and to determine if such input is having an effect on the aquatic ecosystem. The fate and transport of ECs involves the integration of multidisciplinary efforts at a carefully selected field site. Knowledge gained from previous research (Kolpin et al. 2004, Glassmeyer et al. 2005) and other unique aspects of Fourmile Creek lead to its selection as a field setting to help answer these important research questions. Critical aspects of Fourmile Creek included the following:

- (1) A single-source, effluent-dominated stream. A singlesource, effluent-dominated stream allows for the examination of EC concentrations as water moves downstream without complications from additional inputs.
- (2) Background data document the input of a wide variety of ECs from WWTP discharge. Previous research found between 3 and 10 ECs present upstream of the WWTP and between 30 and 50 ECs downstream (Kolpin et al. 2004, Glassmeyer et al. 2005). Detectable concentrations are

necessary to determine longitudinal patterns with down-stream transport.

- (3) Small basin size (less than 160 km² size, average discharge less than 1.41 m³/s). A small basin size facilitates an increased understanding of the transport and fate of environmental contaminants as larger basins tend to have more complex interactions and flows that can obscure existing trends.
- (4) Relatively simple flow system. Discharge measurements indicate little to no ground or surface water inputs to stream flow exist in Fourmile Creek during normal flow conditions. Changes in EC concentrations observed with transport downstream can be attributed to in-stream processes taking place rather than from simple dilution of additional flow inputs from groundwater or surface water sources.
- (5) Background data document that ECs vary in their type of transport. Within an 8 km stretch of Fourmile Creek, some compounds were found to behave relatively conservatively while others exhibited substantial decreases in concentration as water migrated downstream (Table 2). Thus, currently undefined processes are taking place within the stream that can affect EC concentrations.
- (6) The WWTP uses a treatment technology (conventional activated-sludge) typical of many towns and cities across the United States. Thus, the source is representative of many similar sources in the United States.
- (7) The hydrogeologic setting (low-gradient stream, glacial deposits, rowcrop agriculture) is typical of the Midwest.
- (8) A low-head dam exists approximately 2 km upstream of the WWTP outfall. The low-head dam provides a physical barrier to fish migration. Thus, "above WWTP" and "below WWTP" comparisons in fish community structure and fish health assessment can be made to more accurately determine potential effects from the input of ECs by the WWTP. Research has found a range of abnormalities in



Fig. 3a. Injection of dye at Fourmile Creek near Ankeny, Iowa at the wastewater treatment plant outfall, March, 2005. Fig. 3b. Leading edge of the dye concentration at Fourmile Creek near Ankeny, Iowa, site 3, March 2005. Fig. 3c. Peak dye concentration at Fourmile Creek near Ankeny, Iowa, site 3, March 2005. Fig. 3d. Trailing edge of the dye concentration at Fourmile Creek near Ankeny, Iowa, site 3, March 2005.

fish populations (e.g., vitellogenin induction in males and juvenile females, development of oocytes in testes) downstream of WWTPs (Mills and Chichester 2005, Diniz et al. 2005, Gagne et al. 2006).

(9) Closure of the WWTP in 2011. In 2011, the WWTP will close and the waste will be piped to a larger WWTP in Des Moines, Iowa. This closure provides a unique opportunity to determine how stream hydrology, water chemistry, and aquatic biota react to the removal of the primary source of flow and ECs in this system. This will allow a novel "before" and "after" assessment that has not been previously available in EC research.

METHODS AND PRELIMINARY RESULTS

Fate and Effects Research at Fourmile Creek

A first step in an investigation of chemical transport and fate is the collection of streamflow data critical to understanding the

flow dynamics of a stream system (Barber et al. 2006). Streamflow-the amount of water (volume) passing through a stream cross-section in a given point in time—is important for understanding the types of flow (droughts to floods) and patterns of flow (diurnal to seasonal) that can occur at a site and within a drainage basin. Streamflow in a basin often displays a unique "pattern" over time based on numerous factors including: land use, vegetation, water inputs, soil types, and slope. Streamflow is the primary transport mechanism for the movement of chemicals in a drainage basin once input into the stream. Knowledge of streamflow and chemical concentrations in a stream makes it possible to determine mass fluxes or chemicals loads in the stream under various flow conditions. Early tasks for the Fourmile Creek study site included the installation of a USGS gauging station (station number 05485606, site 3) downstream of the WWTP and a USGS staff plate (for measuring stream stage) at the first bridge upstream of the WWTP (station number 05485600, site 0) (Fig. 2).

Another critical component for research on chemical transport is determining how long it takes for water to flow through a stream reach under varying flow conditions. The most accurate method of determining travel times in a stream is by direct measurement using dve tracers (Kilpatrick and Wilson 1989, Jobson 2000). Typically, dye tracing and time of travel involves the injection of a known volume of dye at an upstream location and the measurement of the dye plume at strategic locations downstream. Fluorescent, nontoxic dyes are used in dye tracing studies and the degree of fluorescence in the water sample can be determined with a fluorometer (Wilson 1967). The concentration of dye in the sample is directly proportional to its fluorescence. A plot of concentration against time defines the dye-response curve, between sampling sites. The time of travel is measured by observing the time required for the movement of the "dye cloud," as defined by the response curve, between sampling sites. It is then possible to extrapolate travel times to other flow conditions within the stream (Jobson 2000) and to more accurately predict travel times over a range of flow conditions. In addition, the dye tracing provides accurate time-of-travel data that can be used in various chemical transport models over a range of flow conditions. To accurately determine travel times between strategic locations along the study reach, dve-tracing tests were conducted at Fourmile Creek in August of 2003 and in March of 2005 (Figs. 3 and 4) during differing seasons and flow regimes.

Time-of-travel studies provide critical information for Lagrangian sampling of streams. Lagrangian transport examines the transport of any number of dissolved constituents that move with water in a stream. In a Lagrangian sample set, the same mass of water is tracked and sampled as the water migrates downstream. Once the time of travel information is established for a particular stream reach, the timing of the Lagrangian sample collection sets can readily be determined over a range of flow conditions. Lagrangian sample sets are more useful than traditional samples sets for constructing transport models of dissolved chemicals and suspended sediment (Meade and Stevens 1990, Moody 1993) and for identifying in-stream processes that affect stream chemistry (Hanor 1988). For example, Lagrangian sample sets have been used to better understand the magnitude of subsequent in-stream transformations of nitrate (NO₃) in the Mississippi River (Battaglin et al. 2001) and the fate of atrazine in Roberts Creek (Kolpin and Kalkhoff 1991, Kolpin and Kalkhoff 1993).

To date, two sets of Lagrangian samples have been collected from Fourmile Creek representing low-flow/warm water conditions (August 2003) and medium-flow/cold water conditions (March 2005) (Fig. 5). A comparison of the water-quality results between two flow/temperature regimes will provide an increased understanding of in-stream processes (e.g., dilution, degradation, sorption, etc.) taking place affecting chemical concentrations within Fourmile Creek. A select subset of chemicals measured during the Lagrangian sampling is provided in Table 3. These results document that the degree and type of transport (conservative versus nonconservative) varies by chemical and hydrologic condition. The complete suite of analyses for these Lagrangian samples is still in progress and will be published in a forthcoming report.

Sediment has also been shown to be a reservoir for ECs (Furlong et al. 2004). Thus, both water and bed sediment samples were collected and measured for ECs during the two Lagrangian sampling events. These data are not yet completed and will also be published in a forthcoming interpretive report. In addition, two types of passive samplers were deployed at Fourmile Creek to compliment the set of data from the Lagrangian water samples and streambed sediment samples:

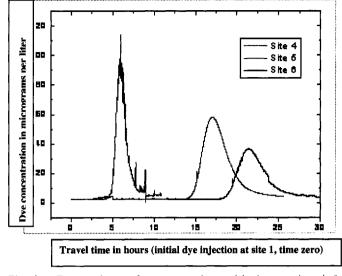


Fig. 4. Dye tracing peak concentrations with time at sites 4, 5, and 6 at Fourmile Creek near Ankeny, August 2003, as dye cloud moves downstream.

a semipermeable membrane device (SPMD) for accumulating hydrophobic contaminants such as PCBs, PAHs, and organochlorine pesticides over time (Huckins et al. 2002, http:// wwwaux.cerc.cr.usgs.gov/spmd/spmd_overview.htm), and a polar organic chemical interactive sampler (POCIS) for hydrophilic contaminants such as antibiotics and other pharmaceuticals (Alvarez et al. 2004, 2005, http://www.cerc.usgs.gov/pubs/ center/pdfDocs/POCIS.pdf). Both the SPMD and POCIS passive samplers were deployed for 28 days at select sampling sites on Fourmile Creek in March of 2005. These passive samplers have the advantage of integrating large volumes of water for an extended period of time and can identify the presence of extremely low concentrations of contaminants (by accumulating them through time). Such contaminants may only be present during episodic events or may be missed by instantaneous water samples. Time-weighted average concentrations are also fundamental to ecological risk assessment for chemical stressors. The analysis of the extracts generated from these passive samplers is currently in progress.

To determine potential EC effects on fish, research on community structure (Moulton et al. 2002) and fish health assessment (Schmitt et al. 1999) was conducted at three sites in the stream reach (Fig. 2) twice (July 2005 and April 2006)

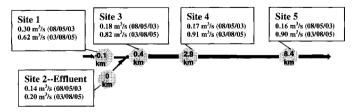


Fig. 5. Schematic diagram of streamflow system at Fourmile Creek near Ankeny, Iowa and sampling sites during the Lagrangian sampling 5 August 2003 and 8 March 2005.

Compound	Primary use	August 2003			March 2005		
		Site 1	Site 2	Site 5	Site 1	Site 2	Site 5
Nitrate (mg/L)	Nutrient	3.2	13.9	10.2	17.1	10.7	15.2
Chloride (mg/L)	Common anion	80	113	109	49.4	121.1	59.3
Tonalide (µg/L)	Fragrance, musk	< 0.40	1.20	E.22	E0.02	4.40	E0.42
Triclosan (µg/L)	Disinfectant	< 0.80	E0.15	E0.06	<1.0	1.20	0.05
Ofloxacin (µg/L)	Antibiotic	< 0.05	0.37	< 0.05	< 0.05	2.18	0.08

Table 3. Selected compounds from the Lagrangian samples collected at Fourmile Creek sites (Fig. 2) near Ankeny, Iowa. [LRL, laboratory reporting limit; E, estimated]

during differing season and spawning conditions. Fish health assessment is being conducted on two native species: white sucker (*Catostomus commersoni*) and fathead minnow (*Pimephales promelas*).

FUTURE WORK

Future work on ECs will identify not only the presence or absence of these compounds, but also their fate, transport, and possible effects in the environment. Several large-scale studies in the United States by the USGS Toxic Substances Hydrology Program have already documented the occurrence of ECs in the environment (Kolpin et al. 2002, Barnes et al. 2002, Furlong et al. 2004, Focazio et al. 2004, Barnes et al. 2005). These studies have shown that a wide variety of ECs are commonly detected in streams, streambed sediment, and groundwater as complex mixtures of compounds. Other studies have documented the occurrence of ECs globally (Kummerer 2004a). Indeed, the data on ECs collected at Fourmile Creek near Ankeny, Iowa to date are consistent with similar national studies (Kolpin et al. 2002). However, the effects of long-term, low-level exposure to these mixtures of emerging contaminants on aquatic life and humans are currently unknown. Research on the effects of ECs in the environment is only in the beginning stages.

The field research site established at Fourmile Creek near Ankeny, Iowa will build a framework for understanding of the transport, fate, and effects of ECs in the environment. A goal of the field research site is to move beyond documenting the occurrence of these compounds and to examine what happens to them in the environment and the potential effects to aquatic ecosystems. Work to date has proceeded with streamflow data, dye tracing/time of travel studies, Lagrangian water-quality sampling, and fish community and fish health assessment. The integration of chemical and biological research within the same stream reach will allow a greater understanding of the fate and effects of ECs.

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LITERATURE CITED

- ALVAREZ, D. A., J. D. PETTY, J. N. HUCKINS, T. L. JONES-LEPP, D. T. GETTING, J. P. GODDARD, and S. E. MANAHAN. 2004. Development of a passive, *in situ*, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environmental Toxicology and Chemistry 23:1640–1648.
- ALEXY, R., A. SCHOLL, T. KUMPEL, and K. KUMMERER. 2004. What do we know about antibiotics in the environment?, Chapter 17. In: Pharmaceuticals in the Environment. Klaus Kummerer (ed.). Springer-Verlag, Berlin, Germany. 527 pp.
- ALVAREZ, D. A., J. D. PETTY, J. N. HUCKINS, T. L. JONES-LEPP, D. T. GETTING, J. P. GODDARD, and S. E. MANAHAN. 2004. Development of a passive, *in situ*, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environmental Toxicology and Chemistry 23(7):1640–1648.
- ASHTON, D., M. HILTON, and K. V. THOMAS. 2004. Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom. Science of the Total Environment 333: 167–184.
- BARBER, L. B., S. F. MURPHY, P. L. VERPLANCK, M. W. SANDSTROM, H. E. TAYLOR, and E. T. FURLONG. 2006. Chemical loading into surface water along a hydrological, biogeochemical, and land use gradient: A holistic watershed approach. Environmental Science and Technology 40:475–486.
- BARNES, K. K., D. W. KOLPIN, M. T. MEYER, E. M. THURMAN, E. T. FURLONG, S. D. ZAUGG, and L. B. BARBER. 2002. Waterquality data for pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000. U.S. Geological Survey Open-File Report 02–94, 7 pp.
- BARNES, K. K., D. W. KOLPIN, E. T. FURLONG, S. D. ZAUGG, M. T. MEYER, L. B. BARBER, and M. J. FOCAZIO. 2005. Studies examine contaminants-Pharmaceuticals, hormones and other organic wastewater contaminants in ground water resources. National Driller Magazine 26(3):38-39.
- BATTAGLIN, W. A., C. KENDALL, C. CECILY, Y. CHANG, S. R. SILVA, and D. H. CAMPBELL. 2001. Chemical and isotopic evidence of nitrogen transformation in the Mississippi River, 1997– 98. Hydrological Processes 15:1285–1300.
- BISTODEAU, T. J., L. B. BARBER, S. E. BARTELL, R. A. CEDIEL, K. J. GROVE, J. KLAUSTERMEIER, J. C. WOODARD, K. E. LEE, and H. L. SCHOENFUSS. 2006. Larval exposure to environmentally relevant mixtures of alkylphenolethoxylates reduces reproductive competence in male fathead minnows. Aquatic Toxicology 79:268–277.
- BOXALL, A. B. A., L. A. FOGG, P. KAY, P. A. BLACKWELL, E. J. PERBERTON, and A. CROXFORD. 2003. Prioritization of veterinary medicines in the United Kingdom environment. Toxicology Letters 142:207–218.
- BRAIN, R. A., C. J. WILSON, D. J. JOHNSON, H. SANDERSON, K. BESTARI, M. L. HANSON, P. K. SIBLEY, and K. R. SOLOMON. 2005. Effects of a mixture of tetracyclines to *Lemna gibba* and *Myriophyllum sibiricum* evaluated in aquatic microcosms. Environmental Pollution 138:425-442.

- BROOKS, B. W., K. C. CHAMBLISS, J. K. STANLEY, A. RAMIREZ, K. E. BANKS, R. D. JOHNSON, and R. J. LEWIS. 2005. Determination of select antidepressants in fish from an effluentdominated stream. Environmental Toxicology and Chemistry 24(2):464-469.
- BURKHARDT, M. R., R. C. REVELLOW, S. G. SMITH, and S. D. ZAUGG. 2005. Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for industrial and anthropogenic waste-indicator compounds in sediment. Analytica Chimica Acta 534:89–100.
- CAHILL, J. D., E. F. FURLONG, M. R. BURKHARDT, D. W. KOLPIN, and L. G. ANDERSON. 2004. Determination of pharmaceutical compounds in surface- and ground-water samples by solid-phase extraction and high-performance liquid chromatography-electrospray ionization mass spectrometry. Journal of Chromatography A 1041:171–180.
- CARBALLA, M., F. OMIL, J. M. LEMA, M. LLOMPART, C. BARCIA-JARES, I. RODRIGUEZ, M. GOMEZ, and T. TERNES. 2004. Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. Water Research 38:2918–2926.
- DAUGHTON, C. G. and T. T. TERNES. 1999. Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? Environmental Health Perspectives 107, supplement 6:907-938.
- DINIZ, M. S., I. PERES, I. MAGALHAES-ANTOINE, J. FALLA, and J. C. PIHAN. 2005. Estrogenic effects in crucian carp (*Carassius carassius*) exposed to treated sewage effluent. Ecotoxicology and Environmental Safety 62:427–435.
- FLAHERTY, C. M. and S. I. DODSON. 2005. Effects of pharmaceuticals on *Daphnia* survival, growth, and reproduction. Chemosphere 61:200-207.
- FOCAZIO, M. J., D. W. KOLPIN, and E. T. FURLONG. 2004. Occurrence of human pharmaceuticals in water resources of the United States: A Review, Chapter 7. *In*: Pharmaceuticals in the Environment. Klaus Kummerer (ed.). Springer-Verlag, Berlin, Germany. 527 pp.
- FURLONG, E. T., C. A. KINNEY, S. L. WERNER, and J. D. CAHILL. 2004. Presence and behavior of wastewater-derived pharmaceuticals in soil samples irrigated by reclaimed water. *In:* Proceedings of the 4th International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water, Minneapolis, Minnesota, October 13–15, 2004: National Ground Water Association, 292–293. CD-ROM.
- GAGNE, F., C. BLAISE, and C. ANDRE. 2006. Occurrence of pharmaceutical products in a municipal effluent and toxicity to rainbow trout (*Oncorhynchus mykiss*) hepatocytes. Ecotoxicology and Environmental Safety 64:329–336.
- GLASSMEYER, S. T., E. T. FURLONG, D. W. KOLPIN, J. D. CAHILL, S. D. ZAUGG, S. L. WERNER, M. T. MEYER, and D. D. KRYAK. 2005. Transport of chemical and microbial compounds from known wastewater discharges: Potential for use as indicators of human fecal contamination. Environmental Science and Technology 39:5157–5169.
- GLOBAL WATER RESEARCH COALITION. 2003. Endrocrine disrupting compounds—An overview of the sources and biological methods for measuring EDCs, prepared by Kiwa Water Research (Netherlands), BTO 2003.008, Alliance House, 12 Canton Street, London, United Kingdom, 16 pp.
- GOODING, M. P., T. J. NEWTON, M. R. BARTSCH, and K. C. HORNBUCKLE. 2006. Toxicity of synthetic musks to early life stages of the freshwater mussel *Lampsilis cardio*. Archives of Environmental Contamination and Toxicology 51(4):549–558.
- HALLING-SØRENSON, B., S. N. NIELSEN, P. F. LANZKY, F. L. INGERSLEV, H. C. LUTZHOFF, and S. E. JORGENSEN. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment–A review. Chemosphere 36:357–393.
- HAMSCHER, G., H. T. PAWELŻICK, H. HOPER, and H. NAU. 2004. Antibiotics in Soil: Routes of Entry, Environmental Concentrations, Fate, and Possible Effects, Chapter 11. In: Pharmaceuticals in the Environment. Klaus Kummerer (ed.). Springer-Verlag, Berlin, Germany. 527 pp.

- HANOR, J. S. 1988. Effects of discharge of municipal waste on water quality of the lower Mississippi River. Environmental Geology and Water Sciences 12(3):163–175.
- HARTEMANN, P. 2004. Risk Assessment of Organic Xenobiotics in the Environment, Chapter 20. *In*: Pharmaceuticals in the Environment. Klaus Kummerer (ed.). Springer-Verlag, Berlin, Germany. 527 pp.
- HEBERER, T. 2002. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicology Letters 131:5–17.
- HUCKINS, J. N., J. D. PETTY, J. A. LEBO, F. V. ALMEIDA, K. BOOIJ, D. A. ALVAREZ, W. L. CRANOR, R. C. CLARK, and B. B. MOGENSEN. 2002. Development of the Permeability/Performance Reference Compound (PRC) Approach for in situ Calibration of Semipermeable Membrane Devices (SPMDs). Environmental Science and Technology 36:85–91.
- JOBSON, H. E. 2000. Estimating the variation of travel time in rivers by use of wave speed and hydraulic characteristics. U.S. Geological Survey Water-Resources Investigations Report 00-4187, 40 pp.
- JONES-LEPP, T. L., D. A. ALVAREZ, J. D. PETTY, and J. N. HUCKINS. 2004. Polar Organic Chemical Integrative Sampling (POCIS) and LC-ES/ITMS for assessing selected prescription and illicit drugs in treated sewage effluents. Archives of Environmental Contamination and Toxicology 42:427–439.
- JOSS, A., E. KELLER, A. C. ALDER, A. GOBEL, C. S. MCARDELL, T. TERNES, and H. SIEGRIST. 2005. Removal of pharmaceuticals and fragrances in biological wastewater treatment. Water Research 39:3139–3152.
- KEITH, L. H. 1997. Environmental endocrine disruptors: A handbook of property data. John Wiley and Sons, Inc., New York. 1232 pp.
- KILPATRICK, F. A. and J. F. WILSON, JUNIOR. 1989. Measurement of time of travel in streams by dye tracing: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 3, Chapter A9, 27 pp.
- KINNEY, C. A., E. T. FURLONG, S. L. WERNER, and J. D. CAHILL. 2005. Presence and distribution of wastewater-derived pharmaceuticals in soils irrigated with reclaimed water. Environmental Science and Toxicology 25:317–326.
- KOLPIN, D. W., E. T. FURLONG, M. T. MEYER, E. M. THUR-MAN, S. D. ZAUGG, L. B. BARBER, and H. T. BUXTON. 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000—A national reconnaissance. Environmental Science and Technology 36(6):1202–1211.
- KOLPIN, D. W. and S. J. KALKHOFF. 1991. Time of travel and dispersion in a selected reach of Roberts Creek, Clayton County, Iowa: U.S. Geological Survey Water-Resources Investigations Report 91-4145, 16 pp.
- KOLPIN, D. W. and S. J. KALKHOFF. 1993. Atrazine degradation in a small stream in Iowa. Environmental Science and Technology 27:134-139.
- KOLPIN, D. W., M. SKOPEC, M. T. MEYER, E. T. FURLONG, and S. D. ZAUGG. 2004. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. Science of the Total Environment 328:119–130.
- KUMMERER, K. 2004a. (ed.). Pharmaceuticals in the Environment. Springer-Verlag, Berlin, Germany. 527 pp.
- KUMMERER, K. 2004b. Resistance in the environment. Journal of Antimicrobial Chemotherapy 54:311-320.
- KURUNTHACHALAM, K., J. L. REINER, S. HUN YUN, E. E. PERROTTA, L. TAO, B. JOHNSON-RESTREPO, and B. D. RODAN. 2005. Polycyclic musk compounds in higher trophic level aquatic organisms and human from the United States. Chemosphere 61:693–700.
- MCMURRY, L. M., M. OETHINGER, and S. B. LEVY. 1998. Overexpression of marA, soxS, or acrAB produces resistance to triclosan in laboratory and clinical strains of *Escherichia coli*. FEMS Microbiology Letters 166(2):305–309.
- MEADE, R. H. and H. H. STEVENS. 1990. Strategies and equipment for sampling suspended sediment and associated toxic chemicals in large rivers—with emphasis on the Mississippi River. Science of the Total Environment 97–98:125–135.

- MEYER, M. T. 2004. Use and Environmental Occurrence of Veterinary Pharmaceuticals in United States Agriculture: A Review, 2004, Chapter 13. *In*: Pharmaceuticals in the Environment. Klaus Kummerer (ed.). Springer-Verlag, Berlin, Germany. 527 pp.
- MIAO, X-S., F. BISHAY, M. CHEN, and C. D. METCALFE. 2004. Occurrence of antimicrobials in the final effluents of wastewater treatment plants in Canada. Environmental Science and Technology 28:3533-3541.
- MILLS, L. J. and C. CHICHESTER. 2005. Review of evidence: Are endocrine-disrupting chemicals in the aquatic environment impacting fish populations? Science of the Total Environment 343:1–34.
- MOODY, J. A. 1993. Evaluation of the Lagrangian scheme for sampling the Mississippi River during 1987–1990: U.S. Geological Survey Water-Resources Investigation Report 93-4042, 31 pp.
- MOULTON, II. S. R., J. G. KENNEN, R. M. GOLDSTEIN, and J. A. HAMBROOK. 2002. Revised protocols for sampling algal, invertebrate, and fish communities as part of the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 02-150.
- OETKEN, M., G. NENTWIG, D. LOFFLER, T. TERNES, and J. OEHLMANN. 2005. Effects of pharmaceuticals on aquatic invertebrates. Part I. The antiepileptic drug carbamazepine. Archives Environmental Contaminants Toxicology 49:353–361.
- OSTERBERG, D. and D. WALLINGA. 2004. Addressing externalities from swine production to reduce public health and environmental impacts. American Journal of Public Health 94(10):1703-1708.
- PHILLIPS, P. J., B. STINSON, S. D. ZAUGG, E. T. FURLONG, D. W. KOLPIN, K. M. ESPOSITO, B. BODNIEWICZ, R. PAPE, and J. ANDERSON. 2005. A multi-disciplinary approach to the removal of emerging contaminants in municipal wastewater treatment plans in New York State, 2003–2004: Water Environment Federation WEFTEC 78th Annual Technical Exhibition and Conference, Conference Proceedings, Washington DC, November 2005, Pp. 5095–5124.
- SCHMITT, C. J., V. S. BLAZER, G. M. DETHLOFF, D. E. TILLITT, T. S. GROSS, W. L. J. BRYANT, L. R. DEWEESE, S. B. SMITH, R. W. GOEDE, T. M. BARTISH, and T. J. KUBIAK. 1999. Biomonitoring of environmental status and trends (BEST) program: Field procedures for assessing the exposure of fish to environmental contaminants. USGS/BRD/ITR – 1999-0007.
- SCHREURS, R. M., J. LEGLER, E. ARTOLA-GARICANO, T. L. SINNIGE, P. H. LANSER, W. SEINEN, and B. VAN DER BURG. 2004. In vitro and in vivo antiestrogenic effects of polycyclic musks

in zebrafish. Environmental Science and Technology 38(4):997-1002.

- SEDLAK, D. L., J. L. GRAY, and K. E. PINKSTON. 2000. Understanding microcontaminants in recycled water. Environmental Science and Technology 34:508A-515A.
- THIBAUT, R., S. SCHNELL, and C. PORTE. 2006. The interference of pharmaceuticals with endogenous and xenobiotic metabolizing enzymes in carp liver: An in-vitro study. Environmental Science and Technology 40:5154–5160.
- THIELE-BRUHN, S. and I. C. BECK. 2005. Effects of sulfonamide and tetracycline antibiotics on soil microbial activity and microbial biomass. Chemosphere 59:457-465.
- THORPE, K. L., T. H. HUTCHINSON, M. J. HETHERIDGE, M. SCHOLZE, J. P. SUMPTER, and C. R. TYLER. 2001. Assessing the biological potency of binary mixtures of environmental estrogens using vitellogenin induction in juvenile rainbow trout (*Oncorbynchus mykiss*). Environmental Science and Technology 35(12):2476–2481.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. 2003. Ambient aquatic life water quality criteria for nonlyphenol-draft. U.S. Environmental Protection Agency Report 822-R-03-029, 71 pp.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. 2004. The 2004 edition of the drinking water standards and health advisories. U.S. Environmental Protection Agency Report 822-R-04-005, 13 pp.
- U.S. GEOLOGICAL SURVEY TOXIC SUBSTANCES HYDRO-GLOGY PROGRAM. 2005. Web Page URL: http://toxics.usgs. gov/regional/emc/ accessed 07/01/05.
- WILSON, J. F. JR. 1967. Time-of-travel measurements and other applications of dye tracing. *In*: Hydrologic aspects of the utilization of water: International Association of Scientific Hydrology Publication 76, pp. 252–265.
- WILSON, B. A., V. H. SMITH, F. DENOYELLES, and C. K. LARIVE. 2003. Effects of three pharmaceutical and personal care products on natural freshwater algal assemblages. Environmental Science and Technology 37(9):1713–1719.
- YANG, J. J. and C. D. METCALFE. 2006. Fate of synthetic musks in a domestic wastewater treatment plant and in an agricultural field amended with biosolids. Science of the Total Environment 363:149-165.
- XIA, K., A. BHANDARI, K. DAS, and G. PILLAR. 2005. Occurrence and fate of pharmaceuticals and personal care products (PPCPs) in biosolids. Journal of Environmental Quality 34:91–104.