2010 Project Abstract
For the Period Ending June 30, 2014

PROJECT TITLE: Understanding Sources of Aquatic Contaminants of Emerging Concern
PROJECT MANAGER: Deborah L. Swackhamer, PhD
AFFILIATION: University of Minnesota
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: ML 2010, Chap. 362, Sec. 2, Subd. 5a., M.L. 2013, Chapter 52, Section 2, Subdivision 17

APPROPRIATION AMOUNT: $640,000

Overall Project Outcome and Results

Pharmaceuticals, hormones, and other contaminants of emerging concern (CECs) are found in surface waters in Minnesota and nationally, and may result in potential ecological and health effects. This project addressed three objectives: to (1) determine what CECs are associated with specific land-uses; (2) identify indicator compounds to be used as monitoring tools; and (3) provide science-based recommendations for more effective monitoring strategies. The Zumbro River watershed in southeastern Minnesota provided a unique opportunity to study CECs because each of its sub-watersheds has a dominant land use.

Generally, agricultural herbicides and non-prescription drugs were more commonly detected that prescription drugs or phytoestrogens. The most commonly detected CECs were atrazine, caffeine, acetaminophen, the mosquito repellent DEET, and metalochlor. Erythromycin and sulfamethoxazole were not found as frequently as other compounds, but were found in the greatest concentrations. Detection frequencies of the five most detected CECs were similar across the four subwatershed sites. Urban pharmaceuticals and personal care products (PCPPs) exhibited higher concentrations during low-flow periods, while run-off associated pesticides had higher concentrations during spring and summer high flow periods. PCPPs were significantly elevated in water or sediment at sites with greater population density and percentage of developed land use. We found unique marker compounds that would differentiate agricultural sources from non-agricultural sources. Cotinine, DEET, carbamazepine, erythromycin and sulfamethoxazole were found to be good markers for urban wastewater-derived sources, and atrazine, metolachlor and acetochlor were found to be good markers for agricultural sources. Caffeine and acetaminophen have been associated historically with human use, but they were not associated with all land use categories and thus are not good source markers.

All of these results can be used to help policy-makers and stakeholders develop strategies to reduce their occurrence, and design more effective targeted sampling and monitoring programs.

Project Results Use and Dissemination

1. The results of this research have been submitted for publication in three peer-reviewed journals (two accepted in press, one in review), with two more in preparation. This work was part of a Masters project paper, and a PhD dissertation. In addition, this work has been presented at several international and state professional meetings. This research

received a best poster award at the 13th IUPAC International Congress of Pesticide Chemistry in August, 2014.

2. A summary factsheet on CECs that includes how they should be used for monitoring has been prepared to assist state agency staff in designing more effective, efficient, and targeting monitoring programs. This draft document is under review by key agency staff and will be revised after receiving their comments. In addition, this research was featured in the *New York Times* (http://mobile.nytimes.com/blogs/well/2014/09/25/a-rising-tide-of-contaminants/) which subsequently appeared in the print edition of the Science Times section.

2010 Environment and Natural Resources Trust Fund (ENRTF) Work Program Final Report

Date of Report: submitted September 8, 2014, revised submitted February 6, 2015, Amendment submitted February 6, 2015, Amendment approved February 12, 2015, Final Report submitted February 17, 2015.
Final Report
Date of Work Program Approval:
Project Completion Date: June 30, 2014

I. PROJECT TITLE: Understanding Sources of Aquatic Contaminants of Emerging Concern
Project Manager: Deborah L. Swackhamer, PhD
Affiliation: University of Minnesota
Mailing Address: Water Resources Center, 173 McNeal Hall, 1985 Buford Ave
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Web Site address: wrc.umn.edu
Location: Zumbro River watershed, Rochester, Olmstead County

Total ENRTF Project Budget:	**ENRTF Appropriation**	**$640,000**
	Minus Amount Spent:	**$638,703**
	Equal Balance:	**$ 1,296**

Legal Citation: ML 2010, Chap. 362, Sec. 2, Subd. 5a., M.L. 2013, Chapter 52, Section 2, Subdivision 17

Appropriation Language:

$640,000 is from the trust fund to the Board of Regents of the University of Minnesota to identify chemical markers to characterize sources of endocrine disruptors and pharmaceuticals entering surface waters in the Zumbro River Watershed. This appropriation is available until June 30, 2013, by which time the project must be completed and final products delivered. The availability of the appropriations for the following projects are extended to June 30, 2014: (2) Laws 2010, chapter 362, section 2, subdivision 5, paragraph (a), Understanding Sources of Aquatic Contaminants of Emerging Concern.

II. FINAL PROJECT SUMMARY AND RESULTS:

Pharmaceuticals, hormones, and other contaminants of emerging concern (CECs) are found in surface waters in Minnesota and nationally, and may result in potential ecological and health effects. This project addressed three objectives: to (1) determine what CECs are associated with specific land-uses; (2) identify indicator compounds to be used as monitoring tools; and (3) provide science-based recommendations for more effective monitoring strategies. The Zumbro River watershed in southeastern Minnesota provided a unique opportunity to study CECs because each of its sub-watersheds has a dominant land use.

Generally, agricultural herbicides and non-prescription drugs were more commonly detected that prescription drugs or phytoestrogens. The most commonly detected CECs were atrazine, caffeine, acetaminophen, the mosquito repellent DEET, and metalochlor. Erythromycin and sulfamethoxazole were not found as frequently as other compounds, but were found in the greatest concentrations. Detection frequencies of the five most detected CECs were similar across the four subwatershed sites. Urban pharmaceuticals and personal care products (PCPPs) exhibited higher concentrations during low-flow periods, while run-off associated pesticides had higher concentrations during spring and summer high flow periods. PCPPs were significantly elevated in water or sediment at sites with greater population density and percentage of developed land use. We found unique marker compounds that would differentiate agricultural sources from non-agricultural sources. Cotinine, DEET, carbamazepine, erythromycin and sulfamethoxazole were found to be good markers for urban wastewater-derived sources, and atrazine, metolachlor and acetochlor were found to be good markers for agricultural sources. Caffeine and acetaminophen have been associated historically with human use, but they were not associated with all land use categories and thus are not good source markers.

All of these results can be used to help policy-makers and stakeholders develop strategies to reduce their occurrence, and design more effective targeted sampling and monitoring programs.

III. PROGRESS SUMMARY AS OF:

January, 2011

We have conducted the contractor selection process (issued a Request for Proposals; reviewed proposals, selected best proposal, established contract through the U of M) and contracted with McGhie and Betts in Rochester, MN. They are advising us on site selection for sample collection, preparing GIS maps, and gathering existing flow data.

We have begun the development and validation of analytical methods. This involves the selection and purchase of analytical standards, and laboratory method development. Analyte selection is key to this project; we are interviewing Extension staff, local livestock veterinarians, and further reviewing the literature to ensure a broad selection of potential analytes to maximize project success.

Site selection has been finalized, based on consultations with our contractor and actual site visits to the area. The final sites will be at the South Fork of the Zumbro River (SFZR) at the WWTP, SFZR at Hwy 14, Willow Creek, Bear Creek at the confluence with the SFZR. This will allow us to isolate the residential signal from several agricultural signals and still allow us to have access and flow data. The sampling plan also reflects the changes made in response to the review of our Research Addendum.

We have ordered and/or gathered together and tested all field sampling equipment. Our initial sampling event will be a “shakedown” sampling to test field deployment and performance in the field. This will take place in February.

July, 2011

We are on track with the first year of the project. We have conducted the contractor selection process (issued a Request for Proposals; reviewed proposals, selected best proposal, established contract through the U of M) and contracted with McGhie and Betts in Rochester, MN. They have advised us on site selection for sample collection, preparing GIS maps, and gathering existing flow data.

We have selected our analytes, based on their known use, physical chemical properties, availability and cost. We are developing and validating analytical methods

Site selection has been finalized, based on consultations with our contractor and actual site visits to the area. The final sites are the South Fork of the Zumbro River (SFZR) at the WWTP, SFZR at Hwy 14, Willow Creek, Bear Creek at the confluence with the SFZR. This will allow us to isolate the residential signal from several agricultural signals and still allow us to

have access and flow data. The sampling plan also reflects the changes made in response to the review of our Research Addendum.
We have acquired and tested all field sampling equipment. We completed a “shakedown” sampling event in February, and have conducted two more sampling trips. Samples have been extracted and are waiting for instrumental analysis.

January, 2012

We are on track with the timeline of the project. We have conducted the contractor selection process (issued a Request for Proposals; reviewed proposals, selected best proposal, established contract through the U of M) and contracted with McGhie and Betts in Rochester, MN. They have advised us on site selection for sample collection, preparing GIS maps, and gathering existing flow data.

We have selected our analytes, based on their known use, physical chemical properties, availability and cost. We are developing and validating analytical methods

Site selection has been finalized, based on consultations with our contractor and actual site visits to the area. The final sites are the South Fork of the Zumbro River (SFZR) at the WWTP, SFZR at Hwy 14, Willow Creek, Bear Creek at the confluence with the SFZR. This will allow us to isolate the residential signal from several agricultural signals and still allow us to have access and flow data. The sampling plan also reflects the changes made in response to the review of our Research Addendum.

We have acquired and tested all field sampling equipment. We completed a “shakedown” sampling event in February, and have conducted two more sampling trips in the spring of 2011.Samples have been extracted and are waiting for instrumental analysis.

We continue to collect field samples, and extract them. Instrumental analysis is underway and ongoing.

July, 2012

We continue to collect field samples, and extract them. Instrumental analysis is underway and ongoing. Preliminary data assessment has begun.

January, 2013

We have completed all field sample collections, and all sample laboratory extractions. All extracts have undergone instrumental analysis for selected compounds of interest. All samples have undergone analysis for suspended solids, major ions, nutrients, and major elements. All data are being reviewed carefully for quality assurance purposes, and final concentrations and loadings of compounds are being calculated and interpreted. Final GIS maps are near completion for detailed land use and land cover characterization.

July, 2013

All laboratory work is complete, and we are exploring, processing, and examining the data using a number of statistical approaches.

January, 2014

Data interpretation continues, and results compared to land use patterns, time and space, are being evaluated.

August, 2014

Data interpretation is complete, and the analyses of these data for correlation with land use patterns, and spatial and temporal correlations, are now complete. Our outreach document has been designed, providing advice on CEC sampling and monitoring programs, and it is being reviewed by state agency staff for effectiveness.

Amendment Request (2/6/2015)

We request funds be shifted between categories for Activity 1. As the project progressed, it became clear that additional funds were needed for personnel to process the laboratory data, and for instrumental analyses. We did not require all the budgeted funds for the contract, for supplies, for "other", for printing, and for travel in Activity 1. We request that these small amounts of funds that were not spent in these categories be shifted to cover the costs of personnel and instrument analyses (other). The total requested shifts are confined to Activity 1, and are as follows:

increased personnel by $9828 – we required more effort to analyze the data
decreased contract by $5400 - it came in under budget
increased "other" by $1500 – the instrument analyses were greater than anticipated
decreased supplies by $3828 – costs came in under budget
decreased travel by $1700 – costs came in under budget
decreased printing by $400 – these costs were included under supplies

These changes are also reflected in the final overall budget.
Amendment Request Approved by LCCMR 2/12/2015.

IV. OUTLINE OF PROJECT RESULTS:

RESULT/ACTIVITY 1: Characterization of CECs from different land uses

Description:

Water samples will be collected from 4 sub-watersheds of the Zumbro River watershed in the spring, summer, and fall over two years. These 4 sub-watersheds include the South Fork of the Zumbro River (SFZR) at the WWTP, SFZR at Hwy 14, Willow Creek, Bear Creek at the confluence with the SFZR. They have land uses differing in percent and type of agriculture and percent of urban sewered or suburban septic-systems. All relevant land uses can be sampled upstream of the wastewater treatment plant. Samples will be analyzed for ~30 selected target compounds associated with wastewater discharge, personal care product use, human pharmaceutical use, pesticide application, animal agriculture, and row crop agriculture. Surface water samples will be collected in accordance with the protocols and procedures as outlined in the USGS National Field Manual for the Collection of Water-Quality Data. Sample collection techniques, quality control/quality assurance, contaminant prevention, sample preservation and handling, chain-of-custody procedures will be conducted in accordance with USGS and University of Minnesota protocol. Analysis will be performed with established methods developed and used by the USGS that are validated in our laboratory. Sample analyses will be conducted using equipment made available by the USDA laboratory at the University of Minnesota.

Summary Budget Information for Result/Activity 1:	**ENRTF Budget:**	**$361,221**
	Amount Spent:	**$361,210**
	Balance:	**$ 11**

Deliverable/Outcome	Completion Date	Budget
1. Collection of field samples from subwatersheds (yrs 1 and 2)	Fall 2012	$206,116
2. Analysis of field samples (yrs 1 and 2)	Spring 2012	$128,596
3. Data compilation and analysis	Spring 2013	$26,509

Result Completion Date: Summer, 2013

Result Status as of January 2011:

We have completed the contractor selection process. A Request for Proposals (RFP) was issued in August, 2010 by the University's Office of Purchasing Services that was prepared by the Project Team, and reviewed and approved by the Office of Purchasing Services (attached as separate file). Two bids were received (MSA, $16,994 and McGhie Betts, $44,529) and forwarded to us, and evaluated and scored according to criteria previously established by the Project Team that had been approved by the Office of Purchasing Services. The criteria were as follows: how well the respondent can meet the needs of the project (50%); the respondent's level of expertise and qualifications (20%), cost of bid (20%), and references (10%). Based on the final scores of the two bids, the Project Team recommended that the contract be awarded to McGhie and Betts in Rochester, MN. This recommendation was accepted by the Office of Purchasing Services, and the contract was issued by the University in October, 2010. They are currently advising us on site selection for sample collection, preparing GIS maps, and gathering existing flow data. The final costs for this came in under bid.

We have begun the development and validation of analytical methods. This involves the selection and purchase of analytical standards, and laboratory method development. Analyte selection is key to this project; we are interviewing Extension staff, local livestock veterinarians, and further reviewing the literature to ensure a broad selection of potential analytes to maximize project success.

Site selection has been finalized, based on consultations with our contractor and actual site visits to the area. The final sites will be at the South Fork of the Zumbro River (SFZR) at the WWTP, SFZR at Hwy 14, Willow Creek, Bear Creek at the confluence with the SFZR. This will allow us to isolate the residential signal from several agricultural signals and still allow us to have access and flow data. The sampling plan also reflects the changes made in response to the review of our Research Addendum.

We have ordered and/or gathered together and tested all field sampling equipment. Our initial sampling event will be a "shakedown" sampling to test field deployment and performance in the field. This will take place in February of 2011.

Result Status as of July 2011:

We have acquired and tested all field sampling equipment. Our initial sampling event was a "shakedown" sampling to test field deployment and performance in the field (February 10, 2011). This included testing water sampling methods and equipment. Water grab samples were collected to represent pre-snow melt. Additional water grab samples were obtained on March 18, 2011 to represent post-snow melt. On May 26-27, 2011 we deployed the ISCO samplers and POCIS samplers (6 per site). On June 3, 2011 we collected the water samples from the ISCO samplers, collected 3 POCIS from each site (all deployed 1 week). There had been a power failure at the Willow Creek site, and no samples or flow data were collected. The ISCO samplers for Willow Creek and Bear Creek locations were reset, and 3 POCIS for each location re-deployed for a second week. We collected composite sediment samples at each location. We also collected water grab samples at each location (as a back up). On June 10, we collected ISCO water samples at the Willow Creek and Bear Creek sites. We collected the POCIS from all 4 sites (3 POCIS per site, represent deployment for 2 weeks). We collected 3 composite sediment samples from each of the 4 locations. We collected water grab samples at each location (as a back up).

All samples were returned to the laboratory following collection. All water and POCIS samples were extracted and stored in a freezer to preserve them until analysis. Sediment samples are stored in a refrigerator until extraction and analysis. Planning for additional sampling is underway.

Result Status as of January 2012:

We have continued sampling our four sites – two sampling periods occurred in mid- and late-August, and two sampling periods occurred in mid- and late-November. The November ISCO samples were not full volume due to freezing conditions. Samples include ISCO water samples, water grab samples as backup, POCIS samples, and sediment samples.

All of the water samples to date from the project have been extracted using the HLB SPE cartridges. All POCIS samples have been extracted manually using glass SPE syringes. Sediment samples are being stored in the freezer until extraction at a future date.

A set of spiked samples (29 compounds) have been prepared to use for ongoing method assessment.

Result Status as of July 2012:

We continue to sample out four sites. Three sampling periods were included in this time period, including January, March, and May 2012.

MBI has provided an initial “test” assessment of land use for one sub-watershed and is in process of completing the assessment for the entire study area.

All backlogged samples have been analyzed for total suspended solids and have been submitted to STRAL for nutrient, major ions, and elemental analysis. All water samples have been extracted using Oasis HLB SPE cartridges. POCIS samples were extracted manually using glass SPE syringes. Sediment samples are stored in the freezer; extractions of these samples have begun.

Result Status as of January 2013:

This task is nearly complete. All sampling is completed. All samples have been analyzed for suspended solids, nutrient, major ions, and major elements. All samples (water, POCIS, and sediment) have been extracted and run for selected compounds of interest. Data from these analyses are undergoing quality assurance review, and once completed, will be further analyzed to meet the goals of the project. Additional effort was required to complete the data analyses and the instrumental analyses.

Result Status as of July 2013:

This task is now completed. We are proceeding to Activities 2 and 3.

Result Status as of January 2014:

This task is now completed. We are proceeding to Activities 2 and 3.

Final Report Summary:

We contracted with McGhie Betts to do the land use analysis and GIS mapping. Water samples were collected over 4 seasonal periods for two years. Sample sites included the South Fork of the Zumbro River (SFZR) at the wastewater treatment plant, SFZR at Hwy 14, Willow Creek, and Bear Creek at the confluence with the SFZR. Grab samples, composite samples, and Polar Organic Chemical Integrated Samples (POCIS) were collected each time from each site, and sediment samples were collected once from each site. Samples were extracted to isolate the compounds of interest, and were then analyzed by high pressure liquid chromatographic mass spectrometry. All data were reviewed for acceptability and then used in Activity 2 and 3.

RESULT/ACTIVITY 2: Development of "source signature" for CECs in water
Description:

Results of water sample analyses will be interpreted using the diverse expertise and experience of our research team. We anticipate the detailed characterization of contaminant concentrations and temporal occurrences for each subwatershed (Result 1) will reflect the surrounding land use and provide contaminant signatures associated with specific land uses. By this we mean that specific contaminants will show up in samples associated with specific land uses and thus serve as markers for that land use. A variety of statistical methods will be used to facilitate identification of "grouped" CECs associated with particular land uses. Source signatures (unique combinations of target chemicals that are specific to a given source) and individual chemical markers will be developed that can be used by others to characterize the sources of CECs to additional surface waters.

Summary Budget Information for Result/Activity 2: **ENRTF Budget: $207,758**
Amount Spent: $207,661
Balance: $ 97

Deliverable/Outcome	Completion Date	Budget
1. Interpretation of water sample data to determine source signature & marker compounds associated with specific land uses	Fall 2013	$207,758

Result Completion Date: Fall, 2013

Result Status as of January 2011:

No data are yet available to determine source signatures. This deliverable depends on completing Activity 1.

Result Status as of July 2011:

No data are yet available to determine source signatures. This deliverable depends on completing Activity 1.

Result Status as of January 2012:

No data are yet available to determine source signatures. This deliverable depends on completing Activity 1.

Result Status as of July 2012:

No data are yet available to determine source signatures. This deliverable depends on completing Activity 1.

Result Status as of January 2013:

Completion of this task requires final, quality-assured data to evaluate and determine source signatures and patterns. In preparation of having final data, we have begun analyzing patterns in the data based on location, time of collection, year, and subwatershed.

Result Status as of July 2013:

The final concentration and mass loading data for each compound are being explored for trends across time, space, source, using both parametric and non-parametric statistical techniques.

Result Status as of January 2014:

The final concentration and mass loading data for each compound are being explored for trends across time, space, source, using both parametric and non-parametric statistical techniques.

Final Report Summary:

Generally, agricultural herbicides and non-prescription drugs were more commonly detected that prescription drugs or phytoestrogens. The most commonly detected CECs were atrazine, caffeine, acetaminophen, the mosquito repellent DEET, and metalochlor. Monensin (vet antibiotic), genistein (phytoestrogen) and iprodione (fungicide) were not detected in any samples. Erythromycin and sulfamethoxazole (both mixed use prescription antibiotics) were not found as frequently as other compounds, but were found in the greatest concentrations. Detection frequencies of the five most detected CECs were similar across the four subwatershed sites. Urban pharmaceuticals and personal care products (PCPPs) exhibited higher concentrations during low-flow periods, while run-off associated pesticides had higher concentrations during spring and summer high flow periods. The full description of the data was prepared for publication in a peer-reviewed journal, and accepted. The will be provided to LCCMR under separate cover (Fairbairn et al., 2014a).

In this study, Principal Components Analysis was used to identify sources of emerging organic contaminants in the Zumbro River watershed in southeastern Minnesota. Principal components analysis served as a powerful technique in categorizing the CECs according to the structure of their concentration patterns across different sites and seasons, revealing patterns that were not clearly apparent from detection frequencies. Two main principal components were identified, which together explained more than 50% of the variance in the data. Principal Component1 (PC1) was attributed to urban wastewater-derived sources, including the effects from municipal wastewater and urban/residential septic tank effluents, while Principal Component 2 (PC2) was attributed to agricultural sources. Cotinine, DEET and the prescription drugs carbamazepine, erythromycin and sulfamethoxazole were best explained by the first principal component, while agricultural pesticides atrazine, metolachlor and acetochlor were best explained by the second principal component. Mixed use compounds carbaryl, iprodione and daidzein did not specifically group with either PC1 or PC2. Furthermore, despite the fact that caffeine and acetaminophen have been historically associated with human use, they could not be attributed to a single dominant land use category (e.g., urban/residential or agricultural). Contributions from septic systems did not clarify the source for these two compounds, suggesting that additional sources, such as runoff from biosolid-amended soils, may exist. Based on these results, Principal Components Analysis may be a useful way to broadly categorize the sources of new and previously uncharacterized emerging contaminants or may help to clarify transport pathways in a given area. Acetaminophen and caffeine were not ideal markers for urban/residential contamination sources in the study area and may need to be reconsidered as such in other areas as well. This work is described in a paper accepted for publication, which is attached to this report (Karpuzcu et al. 2014).

This study confirms that CECs are present in urban and agricultural stream sediments, including those CECs that would typically be thought of as non-sorptive based on their physical chemical properties. Thus the detection frequencies, concentrations, and distributions of CECs in sediment were not governed by the principles of hydrophobic partitioning, such as legacy contaminants. Seasonality in CEC concentrations was seen in water but was not seen in sediments, although sediment concentrations of three CECs varied between years.

Multivariate analyses indicated that PCPPs are significantly elevated in water or sediment at sites with greater population density (> 100 people/km2) and percentage of developed land use (> 8% of subwatershed area) compared with less population density and land area development. The multivariate analyses and interpretation have been finalized for submittal to a peer-reviewed journal for publication (Fairbairn et al., 2014b, submitted). We will provide the draft of this manuscript under separate cover.

RESULT/ACTIVITY 3: Development of recommendations to policy-makers
Description:

We will engage policymakers, resource managers, and regulatory communities in discussions where our findings will be the scientific basis of recommendations for strategies (legislative, voluntary, incentive-based, etc) to reduce sources, mitigate sources, and remediate sources of CECs in the state. These discussions will includes state agency regulators and managers, water resource managers at the county and watershed scale, selected non-governmental organizations, and legislative policymakers.

Summary Budget Information for Result/Activity 3:	**ENRTF Budget:**	**$ 71,021**
	Amount Spent:	**$ 69,832**
	Balance:	**$ 1,189**

Deliverable/Outcome	Completion Date	Budget
1. Develop recommendations for CEC source reduction, and hold workshop with policymakers to discuss strategies	Fall 2013	$36,862
2. Final Project Report	August 2014	$34,159

Result Completion Date: August 1, 2014

Result Status as of January 2011:
No recommendations can be made until Activities 1 and 2 are completed.

Result Status as of July 2011:
No recommendations can be made until Activities 1 and 2 are completed.

Result Status as of January 2012:
No recommendations can be made until Activities 1 and 2 are completed.

Result Status as of July 2012:
No recommendations can be made until Activities 1 and 2 are completed.

Result Status as of January 2013:
No recommendations can be made until Activities 1 and 2 are completed.

Result Status as of July 2013:
No recommendations can be made until Activities 1 and 2 are completed.

Result Status as of January 2014:
While no public recommendations can be made until Activities 1 and 2 are completed, we have begun to examine possible options for completing Activity 3.

Final Report Summary:

Our results indicate that the variability in time and location, and fluctuation of sources, of diverse CECs makes it very difficult to design a one-size-fits-all monitoring study or protocol. Currently many studies by the state and others attempt to sample for more chemicals than they need to and in more places and media than they need to, in an attempt to capture as much data as possible. This ends up being inefficient, expensive, and does not provide more information than a more targeted program might. The variability is different for different compounds, making an all-encompassing standardized approach difficult and perhaps would lead to incorrect interpretations. For example, many compounds thought to be associated only with wastewater treatment plant effluent can be found in watersheds dominated by septic systems. Not all compounds co-vary with stream flow. Not all compounds occur in water; some are found in sediment. Thus monitoring programs must clearly define their objectives and design sampling protocols for specific classes of CECs.

To this end we have prepared a two-page factsheet that summarizes which compounds should be included for a given monitoring objective, and provided recommendations for the type of sample collection depending on the monitoring objective. This factsheet includes whether the compound of interest should be monitored in water or sediment or both, and whether the water samples should be composite or grab samples. It indicates whether there is a seasonal component to the compound's occurrence. It also indicates whether the compound is of interest because of potential ecosystem effects or potential human health effects or both. This summary has been shared with the appropriate monitoring and CEC program staff in the Minnesota Department of Health and the Minnesota Pollution Control Agency. The draft summary factsheet is provided under separate cover; we will provide a final version when all comments are received and incorporated into the final factsheet.

V. TOTAL ENRTF PROJECT BUDGET:

UM Personnel:

D Swackhamer ($28,541)
P Novak ($24,017)
W Arnold ($21,221)
B barber ($98,174)
Students ($313,058)
TOTAL: $ 485,012

Contracts: (to be determined by RFP) $ 44,600

Equipment/Tools/Supplies:

Includes supplies associated with sample collection; laboratory supplies for sample extractions; supplies needed for instrumental analyses and instrument maintenance; supplies associated with data analysis and report preparation; supplies needed for policymaker workshop	$ 108,969
Acquisition (Fee Title or Permanent Easements):	$ -
Travel: includes in-state travel, such as mileage between UM-TC to SE MN watersheds and food and lodging for overnights as needed	$ 1,420
Additional Budget Items:	$ -
TOTAL ENRTF PROJECT BUDGET:	**$640,000**

Explanation of Capital Expenditures Greater Than $3,500: N/A

VI. PROJECT STRATEGY:

A. Project Partners:

All investigators are from the University of Minnesota, and include the following (project funding in parentheses).

Deborah Swackhamer, Project Manager, Water Resources Center, School of Public Health, and Hubert H. Humphrey Institute of Public Affairs. ($381,566; includes salary and portion of supplies, students and travel budgets; also contract costs which will be administered by WRC)

Pamela Rice, Department of Soil, Water and Climate, and USDA Agricultural Research Service. ($56,060; includes portion of costs associated with sample analysis and interpretation)

William Koskinen, Department of Soil, Water and Climate, and USDA Agricultural Research Service. ($56,060; includes portion of costs associated with sample analysis and interpretation)

Paige Novak, Civil Engineering. ($74,555; includes salary and portion of supplies, students and travel budgets)

William Arnold, Civil Engineering. ($71,759; includes salary and portion of supplies, students and travel budgets)

We will be issuing a Request for Proposals for two specific tasks (funds currently included under Swackhamer), including $10,000 for hydrologic flow measurements (water volume per time) at each site at the time of sampling, and $40,000 for GIS mapping (to relate the contaminant analyses back to the land use via maps and illustrate the source signature findings).

B. Project Impact and Long-term Strategy:

This project grew out of previous work demonstrating the role that wastewater treatment plants (WWTP) play as a source of CECs and in reducing estrogenicity during certain processes. This project is part of a larger initiative to expand the capacity for CEC research in Minnesota, and to build capacity for synthesis of information coming from many different efforts (well monitoring data from Minnesota Pollution Control Agency, data from U.S. Geological Survey, newly published toxicology information, etc). Our long-term goal is to characterize all CEC sources and place this knowledge into a larger context (fate, transport, effects) so that more effective management strategies for the state can be developed.

C. Other Funds Proposed to be Spent during the Project Period: none

D. Spending History:

We expended $29,844 in the first 6 months of work. This included $19,658 in salaries, $5,055 in fringe benefits, and $5,131 in supplies. We expended $70,580 in the second six months. This included $26,804 in salaries, $14,646 in fringe benefits, $12,143 in contracts; $16,347 in supplies, and $640 in travel. In the first half of the second year, we expended $81,520. This included $65,418 in personnel, $5,993 in contracts; $9,532 in supplies, and $577 in travel. In the second half of the second year, we expended $84,978. This included $66,742 in personnel, $15,720 in contracts; $2,386 in supplies, and $130 in travel. In the first half of the third year, we expended $91,258. This included $76,777 in personnel, $10,672 in contracts; and $3,809 in supplies. In the second half of the third year, we expended $77,357, including $36,659 in salaries, $26,606 in benefits, $14,092 in supplies and services. We received a no-cost extension for FY2014. In the first half of the fourth year, we expended $71,729. This included $54,478 in personnel, and $17,251 in supplies. In the second half of the fourth year we expended $131,436. Corresponding financial reports have been submitted to LCCMR staff from the UM Financial Reporting of the Sponsored Projects Office. The final financial report has been submitted by UM Financial Reporting for this project.

VII. DISSEMINATION:

The results of this study will be disseminated through professional and non-professional oral presentations, briefings to LCCMR as requested, peer-reviewed publications, and our website. The data will be freely shared after acceptance for publication. We will also present progress on the project periodically in the quarterly newsletter of the Water Resources Center, the *Minnegram*. The results will also contribute to the graduate theses of 2-3 graduate students.

VIII. REPORTING REQUIREMENTS: Periodic Work Program progress reports will be submitted not later than January 31, 2011; July 30, 2011; January 31, 2012; July 30, 2012; January 31, 2013; July 30, 2013; January 31, 2014. A final Work Program report and associated products will be submitted between June 30 and August 1, 2014.

IX. RESEARCH PROJECTS: Please refer to the appended Research Addendum.

Attachment A: Budget Detail for 2010 Projects

Project Title: Understanding Sources of Aquatic Contaminants of Emerging Concern

Project Manager Name: Deborah Swackhamer

Trust Fund Appropriation: $ 640,000
1) See list of non-eligible expenses, do not include any of these items in your budget sheet
2) Remove any budget item lines not applicable

2010 Trust Fund Budget [1]	**Revised Result 1 Budget (2/6/2015):**	**Amount Spent to date**	**Balance (July 2014)**	**Result 2 Budget:**	**Amount Spent to date**	**Balance (July 2014)**	**Result 3 Budget:**	**Amount Spent to date**	**Balance (July 2014)**	**REVISED TOTAL (2/6/2015) BUDGET**	**TOTAL AMOUNT SPENT**	**TOTAL BALANCE**
	Characterization of CECs from different land uses			**Development of "source signature" for CECs in water**			**Development of recommendations to state policy-makers**					
BUDGET ITEM												
Total Personnel	$ 229,529	$ 230,459	$ (930)	$ 187,758	$ 187,661	$ 97	$ 67,724	$ 66,832	$ 892	$ 485,011	$ 484,952	$ 59
Personnel: wages and benefits												
Deborah Swackhamer, PI (4%)	$ 9,210	$ 2,000	$ 7,210	$ 14,230	$ 26,648	$ (12,418)	$ 5,102	$ 5,084	$ 18	$ 28,541	$ 33,732	$ (5,191)
Paige Novak (4%)	$ 7,750	$ 15,240	$ (7,490)	$ 11,974	$ 7,904	$ 4,070	$ 4,293	$ 2,367	$ 1,926	$ 24,017	$ 25,511	$ (1,494)
William Arnold (4%)	$ 6,848	$ 12,726	$ (5,878)	$ 10,580	$ 2,625	$ 7,955	$ 3,793	$ 7,488	$ (3,695)	$ 21,221	$ 22,839	$ (1,618)
Brian Barber (50%)	$ 98,174	$ 86,800	$ 11,374	$ -	$ 16,019	$ (16,019)	$ -	$ 15,500	$ (15,500)	$ 98,174	$ 118,319	$ (20,145)
3 graduate students (50% each)	$ 107,547	$ 113,693	$ (6,146)	$ 150,975	$ 134,465	$ 16,510	$ 54,536	$ 36,393	$ 18,143	$ 313,058	$ 284,551	$ 28,507
Contracts		$ -	$ -									
Professional/technical *(for hydrology and GIS; TBD by RFP)*	$ 44,600	$ 44,529	$ 71	$ -	$ -	$ -	$ -	$ -	$ -	$ 44,600	$ 44,529	$ 71
Other direct costs (*instrument analysis, workshop costs)*	$ 21,500	$ 21,092	$ 408	$ 20,000	$ 20,000	$ -	$ 3,000	$ 3,000	$ -	$ 44,500	$ 44,092	$ 408
Printing	$ -	$ -	$ -		$ -	$ -	$ 297	$ -	$ 297	$ 297	$ -	$ 297
Supplies *(sampling supples, laboratory sample extraction supplies)*	$ 64,172	$ 63,783	$ 389		$ -	$ -		$ -	$ -	$ 64,172	$ 63,783	$ 389
Travel expenses in Minnesota	$ 1,420	$ 1,347	$ 73		$ -	$ -		$ -	$ -	$ 1,420	$ 1,347	$ 73
COLUMN TOTAL	$ 361,221	$ 361,210	$ 11	$ 207,758	$ 207,661	$ 97	$ 71,021	$ 69,832	$ 1,189	$ 640,000	$ 638,703	$ 1,296

Summary of Key Contaminants of Emerging Concern (CECs) and Their Use in Monitoring Programs

CEC	Description	Physiologic Endpoint	Why Might this CEC be Important?[1,2,3,4,5]	Media in which this CEC was detected most/Best Media to Sample	Seasonality of Water Concentration Evident?[6,7,9]	Best Type of Sample	Best Time to Sample	Source Marker/Indicator[8,9]
Atrazine	Herbicide - Agricultural, triazine	Reproductive and Endocrine Systems; Possible Mutagen	Possible ecological effects; possible health effects; possible endocrine effects	Water (99%)	Yes (Early Summer is highest)	Grab or Composite. High flow grab if peak loads/concentrations are of interest	Early Summer will show maxima, but this CEC is evident year round.	Possible indicator but not a specific marker. Detection is common (>90% at all sites and in 75% of WWTP effluent samples), but agricultural sites and seasons have greater water concentrations. Correlated with other agricultural pesticides but with lesser variability than these in water. Vast majority of load comes via non-WWTP sources.
Acetochlor	Herbicide - **Agricultural,** chloroacetanilide	Mutagen; Reproductive and Endocrine Systems	Possible ecological effects; possible health effects	Sediment (57%) and Water (47%) / Either[13]	Yes (early summer highest, spring also elevated)	Grab or Composite. High flow grab if peak loads/concentrations are of interest	Early Summer and Spring show maxima in water, but this CEC is evident year round.	Indicator but not a specific marker. Detected at all sites, but agricultural sites and seasons have greater water concentrations. Correlated with other agricultural pesticides. Correlated more strongly than atrazine to periods of application and runoff. Vast majority of load comes via non-WWTP (wastewater treatment plant) sources.
Metolachlor	Herbicide - **Agricultural,** chloroacetanilide	Nervous system; Possible Mutagen	Possible ecological effects	Water (88%)	Yes (early summer highest, spring also elevated)	Grab or Composite. High flow grab if peak loads/concentrations are of interest.	Early Summer and Spring show maxima, but this CEC is evident year round.	Indicator but not a specific marker. Detection is common (>70%) at all sites, but agricultural sites and seasons have greater water concentrations. Correlated with other agricultural pesticides. Correlated more strongly than atrazine to periods of application and runoff. Vast majority of load comes via non-WWTP sources.
Carbaryl	Insecticide - Mixed-Use, Carbamate	Nervous, Reproductive, and Endocrine Systems	Possible ecological effects; possible endocrine effects; possible health effects	Water (10%)	No, but indications[10] of greater water concentrations during periods of greater usage (early summer).	Grab or Composite	Early summer	Yes; indications[1] of urban/residential association. Majority of load comes via WWTP.
Mecoprop (MCPP)	Herbicide - Mixed-use, Post-emergent	Nervous system	Possible endocrine effects	Water (46%)[12]	No	Grab or Composite. High flow grab if peak loads/concentrations are of interest.	Spring through fall	Yes; strong association with urban/residential sites, with greatest concentrations near the WWTP. Load is balanced between WWTP and other sources.
Daidzein	Plant hormone (phytoestrogen)	Endocrine Systems	Possible ecological effects; indicator of harmful co-contaminants; possible endocrine effects	Water (40%)	Yes (early summer/spring highest)	Grab or Composite	Spring, but is detectable in other seasons (fall is worst).	Not specific (found equally across sites). Majority of load comes via non-WWTP sources.
4-Nonylphenol	Detergent metabolite	Reproductive and Endocrine Systems	Possible ecological effects; possible endocrine effects	Water (28%)[12]	No, but indications[10] of greater water concentrations in low-flow seasons.	Grab or Composite	Any because it was detected year-round, but greater concentrations may be evident during low flow seasons.	Yes; detected most frequently and in greatest concentrations near WWTP, with some detections at other sites. Majority of load comes via WWTP
Acetaminophen	Non-prescription PPCP - Analgesic/antipyretic	Nervous system	Possible ecological effects; possible health effects; indicator of harmful co-contaminants; possible endocrine effects	Water (90%) and Sediment (88%) / Either[14]	Yes (early summer highest, spring also elevated)	Grab or Composite	Any because it was detected year-round, but temporal trends may be evident during high-flow and runoff events.	Not specific. Detection is common (>80%) at all sites, but urban/residential sites have greater concentrations than agricultural sites. This CEC also shows an association with precipitation runoff, indicating mixed sources or transport. Load is balanced between WWTP and other sources.
DEET	PPCP - Insect Repellant	Nervous system	Indicator of harmful co-contaminants	Water (88%)	No, but indications[10] of greater water concentrations during periods of greater usage (early summer).	Grab[11]	Any because it was detected year-round, but temporal trends may be evident during summer due to increased use.	Indicator but not a specific marker. Detection is common (>80%) at all sites, but concentration at WWTP is at least doubled compared to other sites. Majority of load comes via WWTP.
Caffeine	Nonprescription PPCP - Stimulant	Nervous system	Indicator of harmful co-contaminants; p*ossible ecological effects*	Water (98%) and Sediment (100%) / Either[14]	No, but indications[10] of greater water concentrations in low-flow seasons, especially late summer.	Grab or Composite	Any because it was detected year-round, but greater concentrations may be evident during low flow seasons.	Indicator but not a specific marker. Detection is common (>80%) at all sites, but urban/residential sites have greater concentrations than agricultural sites. Majority of load comes via non-WWTP sources.
Cotinine	Nonprescription PPCP - Nicotine metabolite	Nervous system	Indicator of harmful co-contaminants; Possible ecological effects	Water (27%)	No	Grab or Composite	Any	Yes; detected most frequently and in greatest concentrations near WWTP, with some detections at other sites. Load is balanced between WWTP and other sources.
Trimethoprim	Prescription PPCP - Antibiotic	Systemic	Possible ecological effects	Water (72%)[12]	No	Grab or Composite	Any because it was detected year-round, but temporal trends may be evident during high-flow and runoff events.	Indicator but not a specific marker. Detection is common (>50%) at all sites, but concentration at WWTP is at least doubled compared to other sites. Majority of load comes via WWTP.
Carbamazepine	Prescription PPCP - Antiepileptic	Nervous system	Possible ecological effects; indicator of harmful co-contaminants; possible endocrine effects	Water (46%)	No	Grab or Composite	Any because it was detected year-round, but greater concentrations may be evident during low flow seasons.	Yes; strong association with urban/residential sites, with much greater concentrations near the WWTP. Vast majority of load comes via WWTP.
Erythromycin	Prescription PPCP - Antibiotic	Systemic	Possible ecological effects; possible endocrine effects	Water (24%)	No, but indications[10] of greater water concentrations in low-flow seasons.	Grab or Composite	Any because it was detected year-round, but greater concentrations may be evident during low flow seasons.	Yes; almost exclusively associated with WWTP. Vast majority of load comes via WWTP.
Sulfamethoxazole	Prescription PPCP - Antibiotic	Systemic	Possible ecological effects; possible endocrine effects	Water (27%)	No, but indications[10] of greater water concentrations in low-flow seasons.	Grab or Composite	Any because it was detected year-round, but greater concentrations may be evident during low flow seasons .	Yes; almost exclusively associated with WWTP. Vast majority of load comes via WWTP.
Tylosin	Prescription PPCP - Antibiotic	Systemic	Possible ecological effects	Water (19%)[12]	No, but indications[10] of greater water concentrations in low-flow seasons.	Grab or Composite	Summer through fall	Yes; almost exclusively associated with WWTP. Vast majority of load comes via WWTP.

Footnotes:
Color codes indicate the primary usage of the CEC: agricultural (green), mixed (brown), non-prescription PPCPs (pink), prescriptions PPCPs (blue)
Abbreviations: PPCP - Pharmaceuticals and Personal Care Products
[1] Categories include possible ecological effects; possible health effects; and/or indicator of harmful co-contaminants)
[2] www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html
[3] water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm
[4] toxnet.nlm.nih.gov/
[5] www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm
[6] This column refers to seasonality in water, as seasonality was not evident for any CECs in sediment
[7] Fairbairn et al. (in press)
[8] Kapuzcu et al. (2014)
[9] Fairbairn et al. (2015)
[10] This trend appears evident but is not significant in our data set
[11] DEET appears to exhibit strong differences due to sample type (i.e. apparent artifact in composite samples but not grab samples)
[12] Not assessed in sediment
[13] Choose media to sample based on study goals (water may demonstrate acute issues; sediment may demonstrate chronic issues)
[14] Choose media to sample based on study goals (both media exhibit high detection frequencies and land use sensitivity, but water may indicate seasonal trends)

How to use this table

- If your objective is to get a general sense of water quality and the potential presence of CECs from specific sources, then monitor according to “Source Marker/Indicator” and “Best Time to Sample” column
  - You may wish to refer to the color codes in Column A, which correspond to observed groupings based in part on CEC type and occurrence patterns [1-3]
- If your objective is to understand relative occurrence patterns among different CECs, then refer to and monitor according to the columns “Media in which this CEC was detected most”, "Seasonality of Concentration Evident?", and “Source Marker/Indicator”.
- If your objective is to understand changing inputs of CECs to a water body over time, then monitor the media indicated in the "Best Media to Sample" column according to the season that provides the highest detection (see "Seasonality of Concentration Evident?" and “Best Time to Sample” columns) over multiple years
- If specific seasonal or hydrologic conditions are of interest, then monitor CECs that have strong signals during these periods based on "Best Time to Sample" and "Seasonality of Concentration Evident?" columns.
- If a specific CEC is of interest, then monitor according to the relevant row.

References

1. Karpuzcu, M.E., D. Fairbairn, W. Arnold, B.L. Barber, E. Kaufenberg, W. Koskinen, P. Novak, P. Rice, and D.L. Swackhamer. Identifying sources of emerging organic contaminants in a mixed use watershed using principal components analysis. Environmental Science: Processes & Impacts 2014.
2. Fairbairn, D.J., M.E. Karpuzcu, W.A. Arnold, B.L. Barber, E.F. Kaufenberg, W.C. Koskinen, P.J. Novak, P.J. Rice, and D.L. Swackhamer. Sediment–water distribution of contaminants of emerging concern in a mixed use watershed. Science of the Total Environment 2015. 505; 0; 896-904.
3. Fairbairn, D.J., M.E. Karpuzcu, W.A. Arnold, B.L. Barber, E.F. Kaufenberg, W.C. Koskinen, P.J. Novak, P.J. Rice, and D.L. Swackhamer. Contaminants of Emerging Concern in a Mixed Land Use Watershed: A Two Year Study of Occurrence and Seasonal Variation. in press.

This work was supported by the Minnesota Environment and Natural Resources Trust Fund as recommended by the Legislative-Citizen Commission on Minnesota Resources (LCCMR).

Summary of Key Contaminants of Emerging Concern (CECs) and Their Use in Monitoring Programs

Guidance on designing monitoring programs based on field research examining occurrence, seasonality and sources of CECs

D.L. Swackhamer, P. Novak, P. Rice, W. Arnold, D. Fairbairn

University of Minnesota, St. Paul. MN

How to use this table

- If your objective is to get a general sense of water quality and the potential presence of CECs from specific sources, then monitor according to “Is Compound an Indicator” and “Best Time to Sample” column.
- If your objective is to understand relative occurrence patterns among different CECs, then refer to and monitor according to the columns “Best Media to Sample" and "Seasonality of Concentration Evident?".
- If your objective is to understand changing inputs of CECs to a water body over time, then monitor the media indicated in the "Best Media to Sample" column according to the season that provides the highest detection (see "Seasonality of Concentration Evident?" and “Best Time to Sample” columns)over multiple years
- If specific seasonal or hydrologic conditions are of interest, then monitor CECs that have strong signals during these periods based on "Best Time to Sample" and "Seasonality of Concentration Evident?" columns.
- If a specific CEC is of interest, then monitor according to the relevant row.

References

1. Karpuzcu, M.E., D. Fairbairn, W. Arnold, B.L. Barber, E. Kaufenberg, W. Koskinen, P. Novak, P. Rice, and D.L. Swackhamer. Identifying sources of emerging organic contaminants in a mixed use watershed using principal components analysis. Environmental Science: Processes & Impacts 2014.
2. Fairbairn, D.J., M.E. Karpuzcu, W.A. Arnold, B.L. Barber, E.F. Kaufenberg, W.C. Koskinen, P.J. Novak, P.J. Rice, and D.L. Swackhamer. Sediment–water distribution of contaminants of emerging concern in a mixed use watershed. Science of the Total Environment 2015. 505; 0; 896-904.
3. Fairbairn, D.J., M.E. Karpuzcu, W.A. Arnold, B.L. Barber, E.F. Kaufenberg, W.C. Koskinen, P.J. Novak, P.J. Rice, and D.L. Swackhamer. Contaminants of Emerging Concern in a Mixed Land Use Watershed: A Two Year Study of Occurrence and Seasonal Variation. in press.

This work was supported by the Minnesota Environment and Natural Resources Trust Fund as recommended by the Legislative-Citizen Commission on Minnesota Resources (LCCMR).

CEC	Description	Physiologic Endpoint	Why Might this CEC be Important?[1,2,3,4,5]	Best Media to Sample	Best Type of Sample	Seasonality of Water Concentration Evident?[6,7,9]	Best Time to Sample	Is Compund an Indicator of a Specific Source?[8,9]
Atrazine	Herbicide - Agricultural, triazine	Reproductive and Endocrine Systems; Possible Mutagen	Possible ecological effects; possible health effects	Water	Grab or Composite. High flow grab if peak loads/concentrations are of interest	Yes (Early Summer is highest)	Early Summer will show maxima, but this CEC is evident year round.	Possible indicator. Detection is common (>90% at all sites and in 75% of WWTP effluent samples), but agricultural sites and seasons have greater water concentrations. Correlated with other agricultural pesticides but with less variability than other pesticides in water. Vast majority of load comes via non-WWTP sources.
Acetochlor	Herbicide - Agricultural, chloroacetanilide	Mutagen; Reproductive and Endocrine Systems	Possible ecological effects; possible health effects	Water or Sediment[13]	Grab or Composite. High flow grab if peak loads/concentrations are of interest	Yes (early summer highest, spring also elevated)	Early Summer and Spring show maxima in water, but this CEC is evident year round.	Yes. Detected at all sites, but agricultural sites and seasons have greater water concentrations. Correlated with other agricultural pesticides. Correlated more strongly than atrazine to periods of application and runoff. Vast majority of load comes via non-WWTP (wastewater treatment plant) sources.
Metolachlor	Herbicide - Agricultural, chloroacetanilide	Nervous system; Possible Mutagen	Possible ecological effects	Water	Grab or Composite. High flow grab if peak loads/concentrations are of interest.	Yes (early summer highest, spring also elevated)	Early Summer and Spring show maxima, but this CEC is evident year round.	Yes. Detection is common (>70%) at all sites, but agricultural sites and seasons have greater water concentrations. Correlated with other agricultural pesticides. Correlated more strongly than atrazine to periods of application and runoff. Vast majority of load comes via non-WWTP sources.
Carbaryl	Insecticide - Mixed-Use, Carbamate	Nervous, Reproductive, and Endocrine Systems	Possible ecological effects; possible health effects	Water	Grab or Composite	No, but indications[10] of greater concentrations in water during periods of greater usage (early summer).	Early summer	Yes. Indications[1] of urban/residential association. Majority of load comes via WWTP.
Mecoprop (MCPP)	Herbicide - Mixed-use, Post-emergent	Nervous system	Possible ecological effects; possible health effects	Water[12]	Grab or Composite. High flow grab if peak loads/concentrations are of interest.	No	Spring through fall	Yes. Strong association with urban/residential sites, with greatest concentrations near the WWTP. Load is balanced between WWTP and other sources.
Daidzein	Plant hormone (phytoestrogen)	Endocrine Systems	Possible ecological effects; indicator of harmful co-contaminants	Water	Grab or Composite	Yes (early summer/spring highest)	Spring, but is detectable in other seasons (fall is worst).	Not specific (found equally across sites). Majority of load comes via non-WWTP sources.
4-Nonylphenol	Detergent metabolite	Reproductive and Endocrine Systems	Possible ecological effects; possible endocrine effects	Water[12]	Grab or Composite	No, but indications[10] of greater water concentrations in low-flow seasons.	Found year-round, but greater concentrations may be evident during low flow seasons.	Yes. Detected most frequently and in greatest concentrations near WWTP, with some detections at other sites. Majority of load comes via WWTP
Acetaminophen	Non-prescription pharmaceutical - Analgesic/antipyretic	Nervous system	Possible ecological effects; possible health effects; indicator of harmful co-contaminants	Water or Sediment[14]	Grab or Composite	Yes (early summer highest, spring also elevated)	Found year-round, but temporal trends may be evident during high-flow and runoff events.	Not specific. Detection is common (>80%) at all sites, but urban/residential sites have greater concentrations than agricultural sites. This CEC also shows an association with precipitation runoff, indicating mixed sources or transport. Load is balanced between WWTP and other sources.
DEET	Insect Repellant	Nervous system	Indicator of harmful co-contaminants	Water	Grab[11]	No, but indications[10] of greater water concentrations during periods of greater usage (early summer).	Found year-round, but temporal trends may be evident during summer due to increased use.	Yes. Detection is common (>80%) at all sites, but concentration at WWTP is at least doubled compared to other sites. Majority of load comes via WWTP.
Caffeine	Stimulant	Nervous system	Indicator of harmful co-contaminants; possible ecological effects	Water or Sediment[14]	Grab or Composite	No, but indications[10] of greater water concentrations in low-flow seasons, especially late summer.	Found year-round, but greater concentrations may be evident during low flow seasons.	Yes. Detection is common (>80%) at all sites, but urban/residential sites have greater concentrations than agricultural sites. Majority of load comes via non-WWTP sources.
Cotinine	Nicotine metabolite	Nervous system	Indicator of harmful co-contaminants; Possible ecological effects	Water	Grab or Composite	No	Found year-round	Yes. Detected most frequently and in greatest concentrations near WWTP, with some detections at other sites. Load is balanced between WWTP and other sources.
Trimethoprim	Prescription pharmaceutical - Antibiotic	Systemic	Possible ecological effects	Water[12]	Grab or Composite	No	Found year-round, but temporal trends may be evident during high-flow and runoff events.	Yes. Detection is common (>50%) at all sites, but concentration at WWTP is at least doubled compared to other sites. Majority of load comes via WWTP.
Carbamazepine	Prescription pharmaceutical - Antiepileptic	Nervous system	Possible ecological effects; indicator of harmful co-contaminants	Water	Grab or Composite	No	Found year-round, but greater concentrations may be evident during low flow seasons.	Yes. Strong association with urban/residential sites, with much greater concentrations near the WWTP. Vast majority of load comes via WWTP.
Erythromycin	Prescription pharmaceutical - Antibiotic	Systemic	Possible ecological effects	Water	Grab or Composite	No, but indications[10] of greater water concentrations in low-flow seasons.	Found year-round, but greater concentrations may be evident during low flow seasons.	Yes. Almost exclusively associated with WWTP. Vast majority of load comes via WWTP.
Sulfamethoxazole	Prescription pharmaceutical - Antibiotic	Systemic	Possible ecological effects	Water	Grab or Composite	No, but indications[10] of greater water concentrations in low-flow seasons.	Found year-round, but greater concentrations may be evident during low flow seasons .	Yes. Almost exclusively associated with WWTP. Vast majority of load comes via WWTP.
Tylosin	Prescription pharmaceutical - Antibiotic	Systemic	Possible ecological effects	Water[12]	Grab or Composite	No, but indications[10] of greater water concentrations in low-flow seasons.	Summer through fall	Yes. Almost exclusively associated with WWTP. Vast majority of load comes via WWTP.

Footnotes:

Color codes indicate the primary usage of the CEC: agricultural (green), mixed (brown), non-prescription PPCPs (pink), prescriptions PPCPs (blue)

[1] Categories include possible ecological effects; possible health effects; and/or indicator of harmful co-contaminants)

[2] www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html

[3] water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

[4] toxnet.nlm.nih.gov/

[5] www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm

[6] This column refers to seasonality in water, as seasonality was not evident for any CECs in sediment

[7] Fairbairn et al. (in press)

[8] Kapuzcu et al. (2014)

[9] Fairbairn et al. (2015)

[10] This trend appears evident but is not significant in our data set

[11] DEET appears to exhibit strong differences due to sample type (i.e. apparent artifact in composite samples but not grab samples)

[12] Not assessed in sediment

[13] Choose media to sample based on study goals (water may demonstrate acute issues; sediment may demonstrate chronic issues)

[14] Choose media to sample based on study goals (both media exhibit high detection frequencies and land use sensitivity, but water may indicate seasonal trends)