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Organic Wastewater Chemicals in Silver Bow Creek - Butte to Warm Springs Ponds

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Introduction

Organic wastewater chemicals (OWCs) originate from human or animal wastewater discharges to the environment. These compounds represent a broad range of contaminants, including hormones, pharmaceuticals, industrial chemicals, pesticides, and personal care products. Many of these chemicals have been shown to interfere with the endocrine system of both animals and humans at very low concentrations.

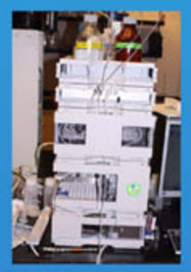
Problems:
- Many OWCs have no guidelines in place
- OWC distribution, transportation, and environmental behavior are not highly understood

Objectives:
- Detail/analyze distribution, concentration, and loads of 5 organic compounds along Silver Bow Creek (starts at Municipal Wastewater treatment plant) to Warm Springs Ponds
  1. Carbamazepine (pharmaceutical)
  2. Sulfamethoxazole (antibiotic)
  3. Thiabendazole (antibiotic)
  4. Miconazole (fungicide)
  5. Ciprofloxacin (antibiotic)
- Begin the 2 year study to analyze 6 additional compounds (11 compounds total)
- Develop effective method to detail and analyze OWCs using Mass Spectrometer/Liquid chromatography system
- Aid in assessment of aquatic health; aid in ongoing restoration work
- EPA method 1694 used for analysis

Liquid Chromatography-Mass Spectrometry and Method Development

Heidi Reid operating the LC-MS in the Department of Chemistry and Geochemistry (July 2013).

Mass Spectrometer component of system.



Liquid Chromatography system.

Liquid Chromatography
- uses a mobile liquid phase (eluant) to move the compound of interest (analyte) through a stationary phase (chromatography column)
- Analyte divides and moves between mobile and stationary phase with a characteristic retention time
  - Retention time determined by chemical structure
- Analytes detected by UV and visible light exposure after exiting column, and move on to the mass spectrometer

Mass Spectrometer
- Parent/daughter ions identified based on mass/charge ratio
- Extremely sensitive detection method
- Each compound has unique characteristic mass/structure
- These results include only positive ion electrospray
  - Analytes are compounds that can accept a hydrogen ion and gain positive charge
- Charged particles collected in an ion trap using a radio frequency field
- From RF field ions are moved selectively out of the trap and accelerated into mass spectrometer detector

Previous results from Butte Summit Valley and Silver Bow Creek

- Selected OWCs found in groundwater in un-sewered sections of valley (Timmer et al, in prep) and in Blacktail Creek (upstream of SBC)
  - Enzyme-Linked Immunosorbent Assay (ELISA) analytical technique used for ground and surface water
  - ELISA uses specific immune response to detect and quantify the presence of target compounds
  - 2 samples from stream in developed area showed 2 antibiotics and 2 hormones in addition to traditional inorganic water-quality parameters
  - Results show widespread presence of OWCs in this area
  - Every site sampled showed sulfamethoxazole, and 40% of samples showed 17β-estradiol
- Other studies show high nitrate levels in Summit Valley groundwater (LaFave, 2008)
  - Attributed to human/animal waste discharge, likely from septic systems

SBC to Areas Downstream
- Elevated nutrient levels shown to originate from discharge of wastewater treatment plant (WTP; Plum, 2009; Gammons et al, 2011)
- Most nitrogen discharged in reduced form (ammonia/ammonium), oxidizes as it goes downstream
- Changes in the amplitude of daily cycles/concentration of nitrogenous compounds with distance downstream show processing of these nutrients

Silver Bow Creek with thick growth of macrophytes at SBC3 sampling site in Aug. 2007 (from Plum, 2009).

Silver Bow Creek at Miles Crossing (MilesX) site in July 2013. Notice the heavy attached macrophytes including Ranuculus Aquatilus (river buttercups). [S. Parker picture]

Field sampling – July 2013

Katie Hailer and Heidi Reid installing the datasonde at Miles Crossing in July 2013. Notice the vegetation along this "resotred" section of SBC. [S. Parker picture]

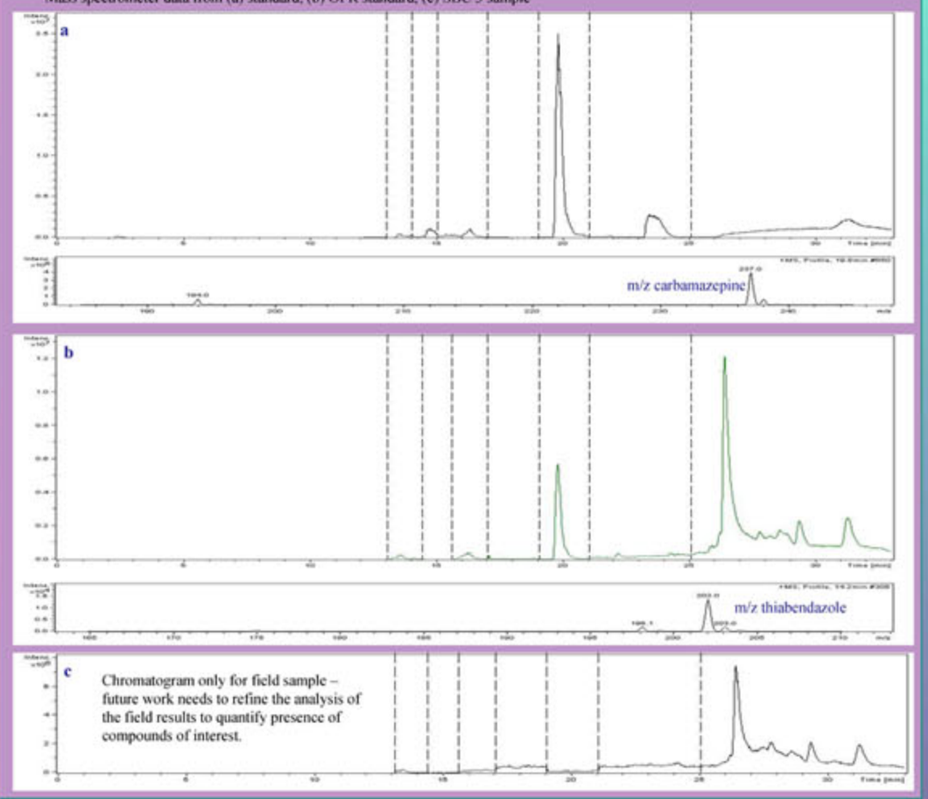
Katie Hailer and Heidi Reid recording field data along Silver Bow Creek at Miles Crossing (MilesX) site in July 2013. [S. Parker picture]

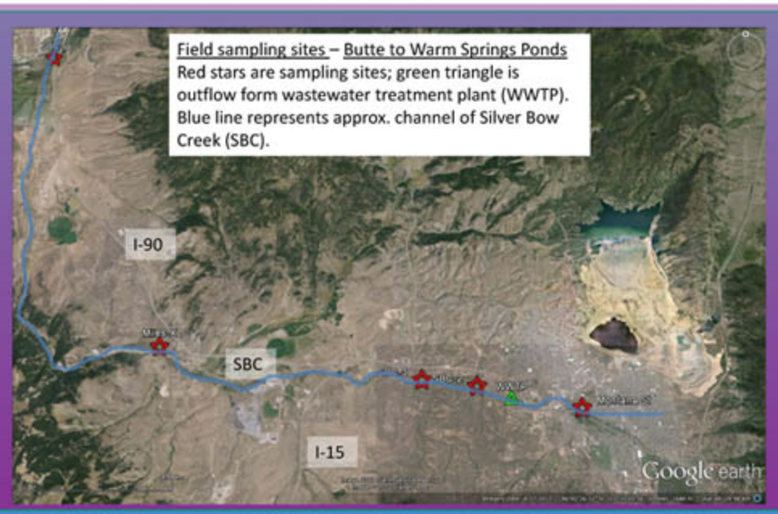
Field work took place on 23-July-2013. Five sites were sampled along Silver Bow Creek (SBC):
1) Montana Street (above wastewater outfall);
2) SBC2 site (about 1.2 km below wastewater outfall);
3) SBC3 (about 3.1 km below outfall);
4) Miles Crossing (13 km below outfall) and
5) SBC6 (just upstream of Warm Springs Ponds).

- Integrated (cross channel) 2.5 L water samples were collected in glass, amber bottles that had been washed according to the EPA method for collection of OWCs.
- All samples filtered on-site (0.45 µm) using peristaltic pump and tubing previously rinsed with methanol/deionized water
- Individual samples collected for analyses of dissolved organic carbon, dissolved inorganic carbon isotopes, water isotopes and OWCs.
- At time of collection temperature (°C), pH, dissolved oxygen, specific conductivity, and oxidation-reduction potential were recorded using a Hydrolab MS5 datasonde.
- Alkalinity titrations performed at collection site using standardized acid and bromocresol green-methyl red indicator
- All samples stored in ice in cooler, immediately taken back to lab after completion of work

Results and Discussion

Mass spectrometer data from (a) standard, (b) OPR standard, (c) SBC 3 sample





Future work
- Improve/refine understanding of mass spectrum analysis
- Quantify results of mass spectrometer analysis
- Collect/analyze sediments from Silver Bow Creek and Warm Springs Ponds

Acknowledgements

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