Use of a Water Quality Triad Approach to Investigate Waters Impaired by "Unspecified Pollutants" Due to Urban Runoff

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Abstract

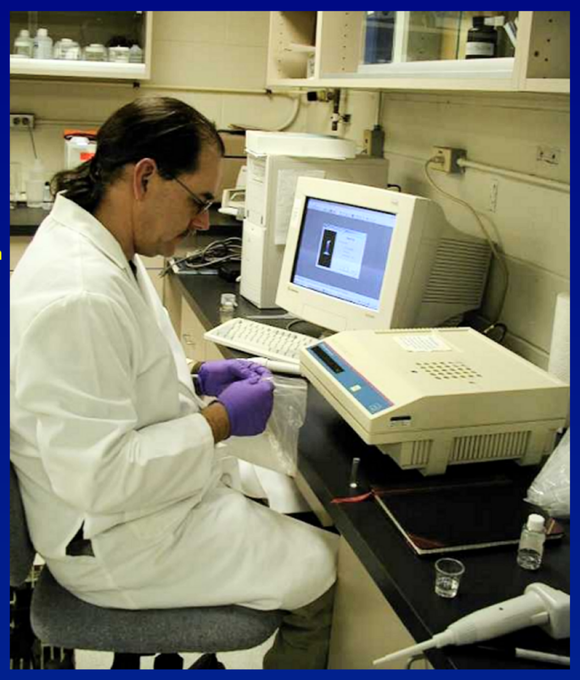
The Missouri Department of Natural Resources evaluated a 14-mile segment of Hinkson Creek that had been placed on the 1998 list of impaired waters designated under section 303(d) of the federal Clean Water Act for "unspecified pollutants" due to urban runoff. Urbanization concerns include the potential for water quality degradation, increased flow intensity due to storm water runoff of impervious surfaces, and effects of development on stream channel and riparian areas.

Because the type of pollutant(s) were listed as unknown, a water quality triad approach was used to document impairments to the aquatic community and identify pollutants that are likely contributing to those impairments. The water quality triad is an integrated assessment of infomation obtained from the aquatic community, chemical analyses, and toxicity testing. The steps in the triad include documenting that impairment to the aquatic community still exists, testing a variety of in-stream and storm water samples for toxicity using a bioluminescent microorganism (*Vibrio fischeri*) and in some cases a freshwater daphnid (*Ceriodaphnia dubia*). The purpose of this was to correlate effects of laboratory test organisms with in-stream effects on the biological community. Toxic samples were further manipulated using standard Toxicity Identification Evaluation procedures that allowed us to determine what broad classes of chemical compounds (e.g., metals, organics) might be causing or contributing to the observed toxicity. The final step in the triad was to analyze the samples for the chemical constituents indicated through the Toxicity Identification Evaluation procedures.

Toxicity Screening

The toxicity of surface waters, and stormwaters were determined for samples collected during the study using the Microtox bacterial bioluminescence test (APHA 1998). Establishing a connection between observed toxicity in waters and documented impairments in the aquatic community is a critical step when the potential for toxic components exists. Microtox has been shown to correlate well with other standard toxicity test organisms, including fathead minnows (*Pimephales promelas*) and daphnids (*Ceriodaphnia dubia*) (Bulich et al. 1981, Kaiser and Palabrica 1991, Munkittrick, K.R. et al. 1991). In Microtox, the commercially available freeze-dried strain of the bacterium *Vibrio fischeri* is exposed to water samples. Under suitable conditions, the bacteria convert a portion of their metabolic respiratory energy into visible light that can be measured by a photometer. Under adverse (toxic) conditions, this rate of light production is affected and is typically reduced in proportion to the toxicity of the test sample. The greater the toxicity, the greater the percent effect level that is recorded by the photometer.

Microtox acute toxicity tests were used to screen water samples for further toxicity and/or chemical analyses. Surface water and stormwater samples were screened using the Microtox SOLO acute toxicity test or the Microtox Basic tests (Microtox Omni 1999). A finding of toxicity in these screening tests resulted in further Microtox analyses of portions of the toxic sample that were manipulated using standard Toxicity Identification Evaluation procedures (US EPA 1991). The purpose of manipulating toxic samples prior to additional testing was to attempt to determine broad classes of chemicals that might be causing or contributing to the toxicity. Toxicity that is reduced or eliminated following filtration, might indicate that the toxic component was adhering to suspended particles. Toxicity that is reduced or eliminated in the presence of a strong chelating agent, such as EDTA, might indicate that metals are a toxic component. Toxicity that is reduced or eliminated following passage of the sample through a Solid Phase Extraction (C18) column might indicate that non-polar organic chemicals are contributing to the toxicity.

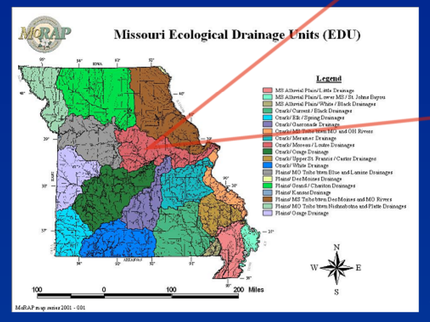


Passing a sample through a Solid Phase Extraction (C18) column.

In addition to using the Microtox test system, selected water samples were also analyzed for toxicity using the freshwater daphnid, *Ceriodaphnia dubia*. *C. dubia* is a standard toxicity test organism utilized by the state of Missouri as part of its National Pollutant Discharge Elimination System program. During the study, spikes in chloride and conductivity levels at specific locations occurred during the chemical monitoring of stormwater and surface water samples. Since the Microtox organisms are marine bacteria, they are less sensitive to the presence of chlorides, especially sodium and calcium salts, while, *C. dubia* are relatively sensitive to the presence of these salts (US EPA 1991, MoDNR unpublished reference toxicity data). Therefore it was decided to utilize both the Microtox and *C. dubia* tests. The use of both organisms provided an opportunity to obtain data from organisms with known differences in sensitivity to these chemicals.

Hinkson Creek

Hinkson Creek originates northeast of Hallsville, MO in Boone County, and flows approximately 26 miles in a southwesterly direction to its mouth at Perche Creek. The Hinkson Creek watershed is approximately 88.5 square miles. The land use in the upper portion of the watershed consists of rural pastureland and wooded areas, whereas the lower portion of the watershed is within the urbanized section of Columbia, MO. The upper reaches of Hinkson Creek are classified as a Class C stream, where the stream may cease flowing in dry periods but maintains permanent pools that support life. The beneficial uses in this reach consist of "livestock and wildlife watering" and "protection of warm water aquatic life and human health associated with fish consumption." The lower reaches of Hinkson Creek are classified as a Class P stream, where the stream is capable of maintaining permanent flow even in drought periods. The beneficial uses in this reach consist of "livestock and wildlife watering", "protection of warm water aquatic life and human health - fish consumption" and "boating and canoeing." During this study, the main Hinkson Creek sampling locations were located within the Class C reach.



Hinkson Creek is considered a Missouri Ozark border stream. It is located in a unique area that is characterized as a transitional zone between the Glaciated Plains and Ozark Natural Divisions (Thom and Wilson 1980). Pfleiger (1989) stated that streams within this region generally originate on level uplands underlain by shales and descend into rolling to hilly terrain underlain by limestone. The soil type within the Hinkson Creek watershed drains soils located geographically in the Central Clay Pan and Central Mississippi Valley Wooded Slopes regions (USDA 1978). According to the "Characteristics of Ecoregions of Iowa and Missouri" map (Chapman et al. 2002), the soil type within the upper segments of Hinkson Creek is characterized as being loamy till with well developed clay pan. Pennsylvanian sandstone, limestone, and shale also characterize this region. The soil types within the lower segments of Hinkson Creek are characterized as being thin cherty clay and silty to sandy clay. Mississippian and Pennsylvanian limestones, sandstones, and shales with considerable bedrock exposure characterize this region.

Aquatic Toxicity

Chemical Analysis

Water Quality Triad

Aquatic Community

Macroinvertebrates were collected using a multi-habitat sampling method. The sampling was done in a stream reach approximately twenty times the average width of the stream and encompassed two riffle sequences or two meander sequences. Hinkson Creek is considered a "riffle/pool" predominant stream and, therefore, macroinvertebrate samples were collected from three predominant habitats: flowing water over coarse substrate (e.g. riffle); non-flowing water over depositional substrate (e.g. pool); and rootmat substrate. Each macroinvertebrate sample was a composite of six subsamples within each habitat. The sampling periods occurred during periods of stable base-flow before peak periods of aquatic insect emergence. In general, macroinvertebrate sampling occurs in the spring from mid-March through mid-April and fall from mid-September through mid-October.

Biological Assessment

Samples from each major habitat were collected and preserved with 10% formalin. Habitat samples were kept separate to provide the ability to factor out habitat differences between sites. Macroinvertebrate identifications were made to the lowest possible taxonomic level (usually genus or species). The macroinvertebrates from each habitat were evaluated using the following metrics:

- Taxa Richness (TR)
  Reflects the health of the community through a measurement of the number of taxa present. In general, the total number of taxa increases with improving water quality, habitat diversity, and habitat suitability. Taxa Richness is calculated by counting all taxa from the subsampling effort.
- Ephemeroptera/Plecoptera/Trichoptera Taxa (EPT Taxa)
  Is the total number of distinct taxa within the orders Ephemeroptera, Plecoptera, and Tricoptera. This value summarizes taxa richness within the insect taxonomic orders that are generally considered to be pollution sensitive. The EPT taxa index generally increases with higher water quality.
- Biotic Index (BI)
  Developed as a means to detect organic pollution. Tolerance values for each taxon range from 1 to 10, higher values indicating increased tolerance.
- Shannon Diversity Index (SDI)
  Is a measure of community composition that takes into account both richness and evenness. It assumed that a more diverse community is a more healthy community. Diversity increases as the number of taxa increases and as the distribution of individuals among those taxa is more evenly distributed.

Ephemeroptera

Plecoptera

Tricoptera

The four metrics were aggregated into a single value and a stream condition index (SCI) calculated according to Semi-Quantitative Macroinvertebrate Stream Bioassessment project procedure for each season and year. The SCI score is based upon data collected from reference streams within the same EDU as the study stream and is divided into three categories. Study reaches that scored from 16-20 were considered fully biologically supporting, scores from 10-14 were considered partially biologically supporting, and scores of 4-8 were considered non-biologically supporting of aquatic life.

Latchat Quick Chem 8000
--Used in analysis of nutrients and chloride

Flow Injection Mercury System 100 cold vapor analyzer

Focused Analysis

Attempting to identify the "unknown pollutants" impairing Hinkson Creek required numerous sampling events and vast numbers of chemical analyses. Chemical parameters needed to be evaluated both qualitatively and quantitatively from various stream locations (main stem, tributaries, storm drainages, etc.) and conditions (base flow and high flow/storm events). Nutrients, chloride, E. coli and non-filterable residue were consistently collected and analyzed to provide background information for longitudinal comparison. Total recoverable metals, qualitative organic analyses, volatile organic analysis, petroleum fractions and base neutral/acid extractables were only analyzed when Toxic Identification Evaluation (TIE) procedures indicated the presence of that pollutant class. This screening approach minimized analysis cost and time while identifying potential unknown pollutants.

Varian Saturn 2000R
Ion Trap GCMS
--Used for analysis of organic constituents

IDEXX
Colilert Quantitray System
--Used for analysis of E. coli