

## **Changes in Nutrient Structure of the Cuyahoga River**

A Technical Report to the Ohio Lake Erie Commission, Ohio Lake Erie Protection Fund

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### **Abstract**

[1] Recent increasing occurrence of disruptive eutrophic conditions in Lake Erie highlights a shortcoming of our understanding on the dynamics of nutrients in aquatic ecosystems. In spite of significant reduction in point-source nutrient discharge, the loadings of bioavailable nutrients such as ammonia ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and soluble reactive phosphorus (SRP) from tributaries are still large enough to sustain such harmful events. But little is known about how much and how the structure of nutrients changes along the Cuyahoga River. We hypothesize that there are significant changes in nutrient structure in the Cuyahoga River. To test this hypothesis, we proposed to achieve three major objectives: 1) examine the stream hydrology through stable isotopic analysis, 2) determine the concentrations of various nutrient variables, and 3) evaluate the bioavailability of P in river bed sediments by chemical extraction tests. River waters and sediments were collected in a dozen locations from the Cuyahoga River and its major tributary. As a result, we found that 1) river water becomes isotopically heavier from upstream to downstream, 2) nutrient concentrations increase stepwise downstream, and 3) changes in water soluble phosphorus (WSP) of river bed sediments are consistent with those of nutrient concentrations in river waters.

## Activities and Timeline

[2] To better understand the structure and dynamics of nutrients in the Cuyahoga River, we conducted a preliminary study of isotope hydrology, water nutrient chemistry, and the mobility and bioavailability of phosphorus in river bed sediments. Specifically, we have 1) collected riverbed sediments and river waters at a dozen locations along the main stem of the Cuyahoga River and its largest tributary- Tinkers Creek, 2) analyzed isotopic composition of river waters collected, 3) performed chemical and nutrient analyses (pH, TDS, total phosphorus, soluble reactive phosphorus, total Kjeldahl nitrogen, chloride, sulfate, fluoride, nitrite, nitrate, ammonia and silica dioxide) of river waters, 4) conducted a series of chemical extraction tests on river bed sediment samples for phosphorus mobility and bioavailability, and 5) explored the mechanisms that control phosphorus transfer and cycling across the watershed.

[3] The Cuyahoga River receives water from a drainage area of ~1,800 km<sup>2</sup>, with 30-40% of agricultural fields, 40-50% of wooded areas, and ~10% of urban areas (Baker, 2006). Water samples were collected from over a dozen locations along the Cuyahoga River and its major tributary for oxygen and hydrogen isotopic and geochemical analyses. The water sampling was carried out five times (July 29, 2007; September 3, 2007; October 30, 2007; March 15, 2008; May 23, 2008). Most of the sediment sampling sites coincide with the sites for water sampling. Consideration for site selection includes 1) the proximity to existing gauging stations of the U.S. Geological Survey and 2) the degree of accessibility.

[4] These water samples were collected in 500ml HDPE wide-mouth round bottles for isotopic and chemical analyses. Prior to sampling, the HDPE bottles were treated with 10% HCl, washed with deionized water at least three times, and re-washed three times in-situ using stream water. Water samples were hand-dipped along the river shore at a water depth of 10cm where relatively clean and flowing water presented. Sample bottles were filled slowly in full to minimize post-sampling alteration in water isotopic composition.

[5] The chemical analyses of the water samples collected were performed at National Center for Water Quality Research, Heidelberg College, in accordance with the EPA and SW 846 Solid Waste method procedures (USEPA, 1974). The isotopic compositions ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) of the samples were determined at the Environmental Stable Isotope Laboratory of the Duke University, using a Thermo Finnigan TC/EA with GC-PAL autosampler attached to a Thermo Finnigan Delta Plus XL continuous flow mass spectrometer via a Conflo III interface. The isotopic values are reported using the standard  $\delta$  notion relative to the NIST / IAEA reference materials V-SMOW. The analytical precision was  $\pm 0.1\text{‰}$  and  $\pm 1.5\text{‰}$  for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , respectively.

[6] A dozen riverbed sediment samples collected were wet-sieved, air dried, and homogenized for the fine fraction ( $d < 63\mu\text{m}$ ) prior to chemical extraction tests. About 0.05g of sediment mass was used for each test with different extraction solutions; using deionized water (~18M $\Omega$ ) for water soluble phosphorus (WSP), 0.01M CaCl<sub>2</sub> solution for readily desorbable phosphorus (RDP), 0.05M NaOH solution for algal available

phosphorus (AAP), and 0.5M NaHCO<sub>3</sub> solution for Olsen-P (Olsen et al., 1954; Zhou et al., 2001). Supernatants were collected for phosphorus measurements through the classic colorimetric method- USEPA Method 365.3.

[7] Oxygen and hydrogen isotope composition ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) of river waters have been commonly used as environmental tracers for hydrologic investigations. Analysis of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in the Cuyahoga River and Tinkers Creek shows both seasonal and spatial variations. In general, the values of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  increase from upstream to downstream but there is a relatively large magnitude of variations during winter/snow melting period, indicating the presence of isotopically distinct water components (e.g., reservoir water, groundwater baseflow, and bank storage, etc). This indicates the complexity of the hydrologic system of the Cuyahoga River.

[8] Major anion concentrations increase progressively from upstream to downstream. For example, SO<sub>4</sub> concentration increased from 20 mg L<sup>-1</sup> in the headwater region to 40 mg L<sup>-1</sup> in the downstream near the bridge on Harvard Ave. Interestingly, the increase in anion concentrations coincides with the increase in stream flow from upper basin downward. It is worth noting that the concentration of chloride was relatively high during the wintertime, indicating the presence of road salt in stream waters. On the other hand, nutrient concentration increased stepwise from upstream to downstream. For example, the lower Cuyahoga River has higher nutrient contents than the upper Cuyahoga River. The Tinkers Creek also has a similar increasing trend of nutrient concentrations. The nutrient concentrations in the East Branch appear to be higher than those in the West Branch. The nutrient loading anomalies are found to be associated with wastewater treatment plant (WWTP) effluents. But it is not clear how much of nutrient loading is from the historical nutrient releases or due to reduced capacity of nutrient processing resulted from human disturbances.

[9] To probe the mobility and bioavailability of phosphorus in riverbed sediments, we have conducted a series of chemical extract tests. The test results show that the WSP content increases from upstream to downstream. This pattern of spatial WSP variability in riverbed sediments is similar to that of spatial nutrient variability in river waters across the Cuyahoga River. This suggests that there exists some degree of geochemical equilibrium between stream waters and bed sediments. Interestingly, other extractable phosphorus such as AAP, RDP, and Olsen-P displays an opposite pattern of variability, in which their concentrations appear to be higher in the upper Cuyahoga River than in the lower basin. More chemical extraction tests are needed.

[10] This project was designed to examine the spatial nutrient variability across the Cuyahoga River. Originally we planned to collect soils, sediments, and river waters only once during the project period. We extended the sample frequency to five times over one project year in order to account for the seasonal variations in stream variables (e.g., temperature, microbial activity, and streamflow discharge, etc). We were unable to perform  $\delta\text{D}$ ,  $\delta^{13}\text{C}$ , and  $\Delta^{14}\text{C}$  analyses for particular organic matter (POM) in soils, sediments, and river waters because collection of POM turned out to be a difficult task.

Instead, we focused on isotopic analyses of river waters as their isotopic compositions are usually indicative of water sources and associated hydrologic processes.

### **Work Products**

[11] Over the course of project implementation, we involved three undergraduates (Erick Butler, Michael Albert, and Derek Wojcik) and collaborators at other institutions (Steve Tuckerman at Ohio EPA and David Baker at Heidelberg College). We developed one poster for COS Research Day and one powerpoint presentation for the site visit in June. There is at least one manuscript for journal publication in preparation. We have appended these documents in the following pages.

[12] Yuan, F. 2008 Changes in nutrient structure of the Cuyahoga River-a preliminary study, CSU COS Research Day Poster

[13] Yuan, F. 2008 Changes in nutrient structure of the Cuyahoga River, PPT presentation for the project site visit in June

### **Reference:**

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USEPA, 1974. Methods for Chemical Analysis of Water and Wastes. U.S. EPA Environmental Monitoring & Support Laboratory, Cincinnati, OH.

Zhou, Q., Gibson, C.E. and Zhu, Y., 2001. Evaluation of phosphorus bioavailability in sediments of three contrasting lakes in China and the UK. *Chemosphere*, 42(2): 221-225.