Arsenic, Metals, and Nutrients in the Wallkill River, New Jersey: Natural and Induced Diurnal Cycles

Julia L. Barringer, Timothy P. Wilson, Zoltan Szabo, Jennifer L. Bonin, Jeffrey M. Fischer, Nicholas P. Smith

U.S. Geological Survey, New Jersey Water Science Center, in cooperation with the New Jersey Department of Environmental Protection
To aid NJDEP in implementation of an arsenic (As) TMDL for the Wallkill River in northwestern New Jersey, two sites on the river were sampled in September 2004, and one in September 2005, to determine the magnitude of diurnal variations in concentrations of As and metals, and to investigate the processes that controlled the diurnal cycles.

Both sampling sites are downstream from a mined area of the Franklin Marble, host to Zn ores and As and Mn minerals.

Concentrations of total As in streamwater downstream from the mined area ranged as high as 5 $\mu$g/L.
The river channel is underlain by glacial deposits over dolomite except near Franklin Pond, where it crosses the Franklin Marble, site of former zinc mining.

The sampling sites are about 2.5 and 10 km, respectively downstream from the mined area at Franklin.
Sampling site WAL-2 is on the upstream side of this bridge. It is in a rural area with farms and a few residences, and is next to a railroad line. The streambed is rocky.
Sampling site WAL-4 is in the National Wildlife Preserve. The streambed is muddy; rooted macrophytes are present. The river is ~10 m wide here.
September 2004
Unfiltered samples were collected at WAL-2 and WAL-4, using an automatic sampler and acid-washed equipment. Cycles of total (recoverable) metals peaked at night at both sites.

Cycles in total (recoverable) metals and arsenic concentrations during 24 hours at WAL-2, September 2004

Cycles in total (recoverable) metals and arsenic concentrations during 24 hours at WAL-4, September 2004,
Concentrations of total boron (B) were lowest and varied little over a 24-hour period at WAL-2, but showed two distinct peaks at WAL-4, indicating different inputs and/or processes affecting concentrations at the two sites.
September 2005

Samples—unfiltered and filtered—were collected manually at WAL-4, using a peristaltic pump and ultraclean techniques. Field parameters were collected using a data sonde.

Temperature (T), pH, and dissolved oxygen (DO) concentrations all peaked at or just after nightfall (at 2000 or 2200 h), which is later than the timing of peaks seen in most other diurnal studies.
The cycle for total metals was similar to that of the previous year, including a decrease in concentration at 0400 h. (Note scaling of concentrations.)
Fe and Al were virtually all in particulate form, but Mn and Zn were present in particulate and filterable ("dissolved") form. The filterable cycles for Mn and Zn differed from the particulate cycles.

Variation in concentrations of total, filterable, and particulate Mn over a 24-hour period, Wallkill River at WAL-4, September 2005

Variation in concentrations of total, filterable, and particulate Zn over a 24-hour period, Wallkill River at WAL-4, September 2005
What caused the observed particulate metals cycle?

Stream flow increased during the night, but did not fully coincide with either turbidity or the particulate metals cycle.

Other researchers have reported the nighttime maximum in a particulate metals cycle and ascribe it to suspension of particles by nocturnal activity of benthic organisms.
What about the As cycles?
The filterable As cycle was roughly opposite to those of filterable Mn and Zn. The total (recoverable) As cycle differed slightly from the total/particulate metals cycles, but was not opposite, as it had been the previous year.

Concentrations of arsenic and zinc (filtered samples) in water from the Wallkill River at WAL-4, over a 24-hour period, September 2005.

Concentrations of arsenic and zinc (unfiltered samples) in water from the Wallkill River at WAL-4, over a 24-hour period, September 2005.
Did pH affect the observed As and metals cycles? Concentrations of filterable Mn (also Zn—not shown), which are cations, decreased as pH increased in streamwater, whereas concentrations of As (predominantly as the As (V) anion) increased slightly in water as pH increased. Cations adsorb and anions desorb as pH increases.

Relation of filterable As, Mn, and Zn to pH over a 24-hour period, Wallkill River at WAL-4, September 2005
A set of cycles was observed for anions that has not, to date, been reported for other rivers. These cycles had two maxima, and coincided with a two-maximum diurnal cycle for specific conductance.

Note high concentrations

Variations in concentrations of chloride (Cl), nitrite + nitrate (NO$_2$+NO$_3$), and boron (B) over a 24-hour period, Wallkill River at WAL-4, September 2005
Concentrations of phosphate (PO$_4$) and ammonia (NH$_3$), to a lesser degree, also showed a two-peaked cycle.

- If cycles are natural, nutrient concentrations (particularly those of NO$_3$ and PO$_4$) would be expected to peak at night.
- The coincidence of the two-peaked nutrient cycles with those of Cl and B is indicative of nearby (?) wastewater inputs to the stream.
Conclusions:

Cycles in filterable (dissolved) As, Mn, and Zn appear to result from adsorption/desorption reactions driven by pH (and T) changes.

The cause of the particulate metals cycles is not known, but, because of the timing, the cycles appear related to biological activity.

Wastewater inputs may account for the unusual two-peaked cycles observed for nutrients and some anions.

Inputs of treated ground water from a nearby industrial facility may account for the late timing of T, pH and DO peaks and increase in streamflow.
Material shown in this presentation is published in the following journals and reports:


