

Diel Cycles in Major and Trace Elements in Streams: Anthropogenic Effects on, and Additions to, Natural Cycles

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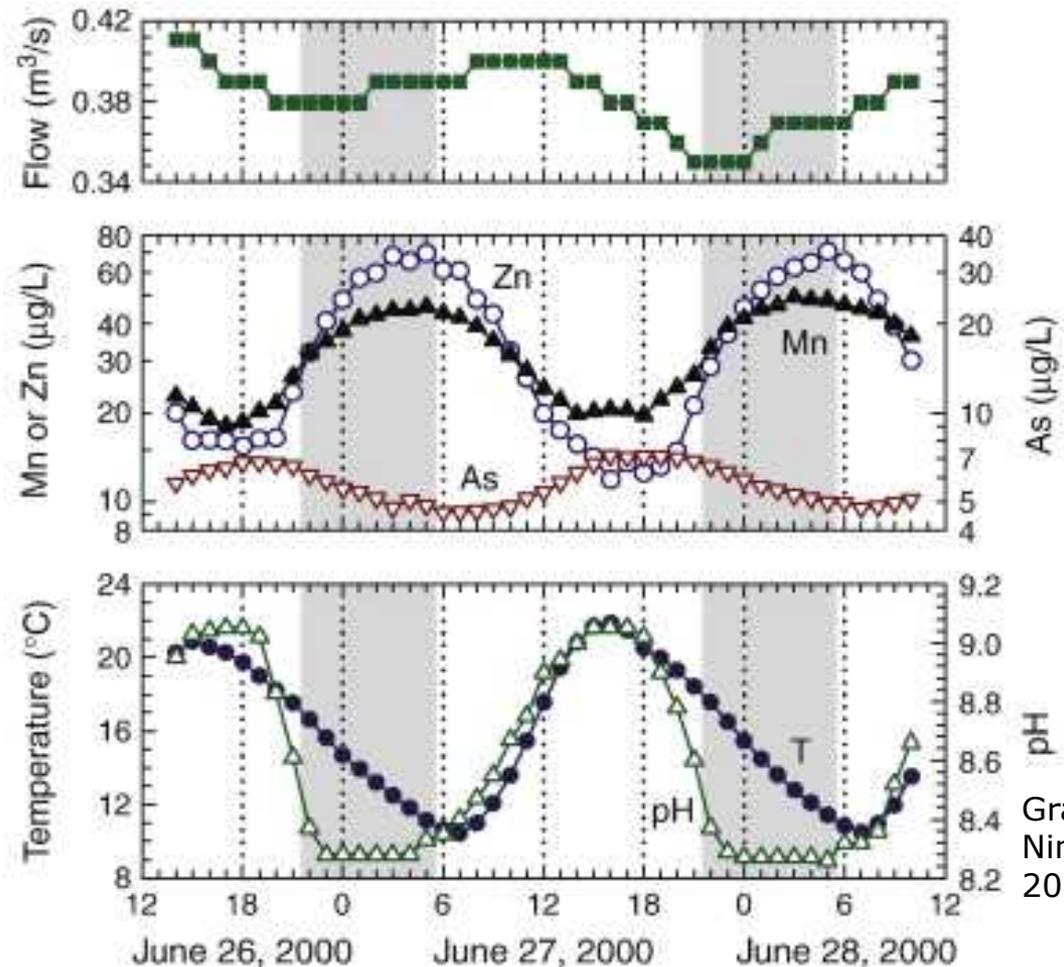


Diel cycles are interrelated one affects many others

- Sunlight – Drives river biology
Photosynthesis $6\text{CO}_2 + 6\text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$
- Streamflow
- Temperature
- pH
- Dissolved gases

Which can affect :

- Trace Elements
- Metals
- Nutrients

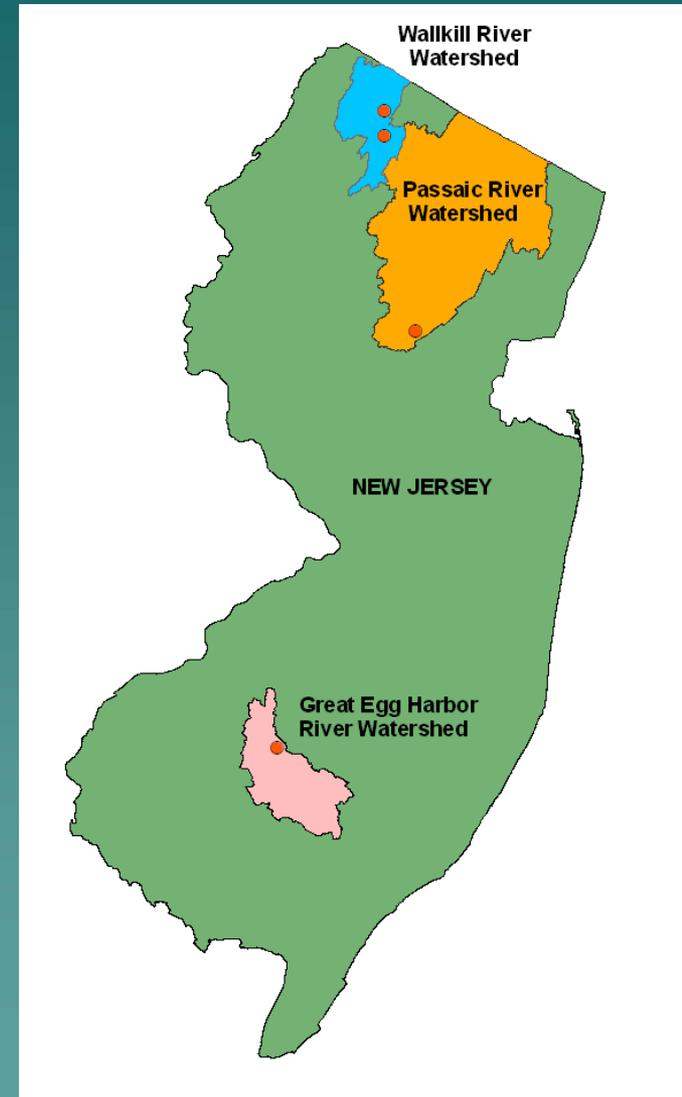


Graph From
Nimick et al,
2011

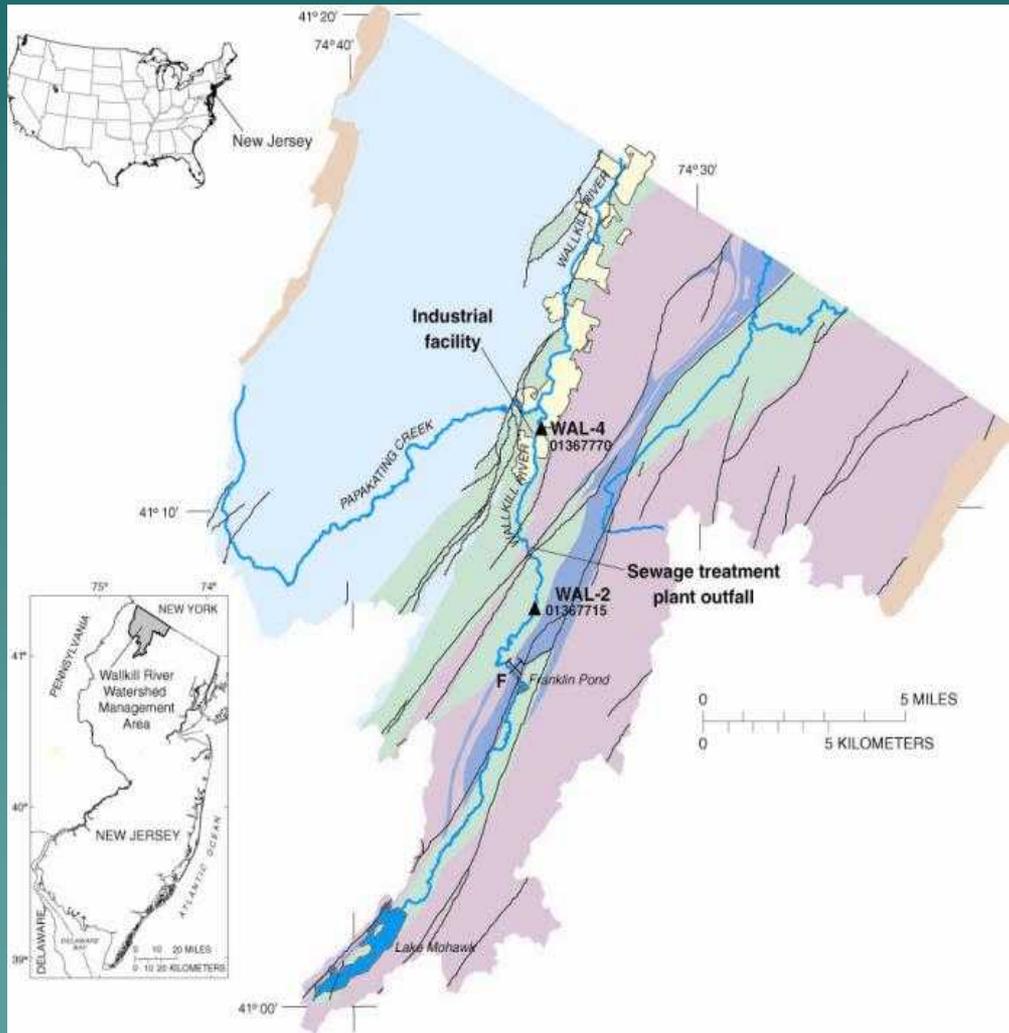
Diel variations in NJ streams

To aid NJDEP in TMDL development three rivers were sampled to determine diel variations in As concentrations:

- ◆ **Wallkill River**
- ◆ **Passaic River**
- ◆ **Great Egg Harbor River**



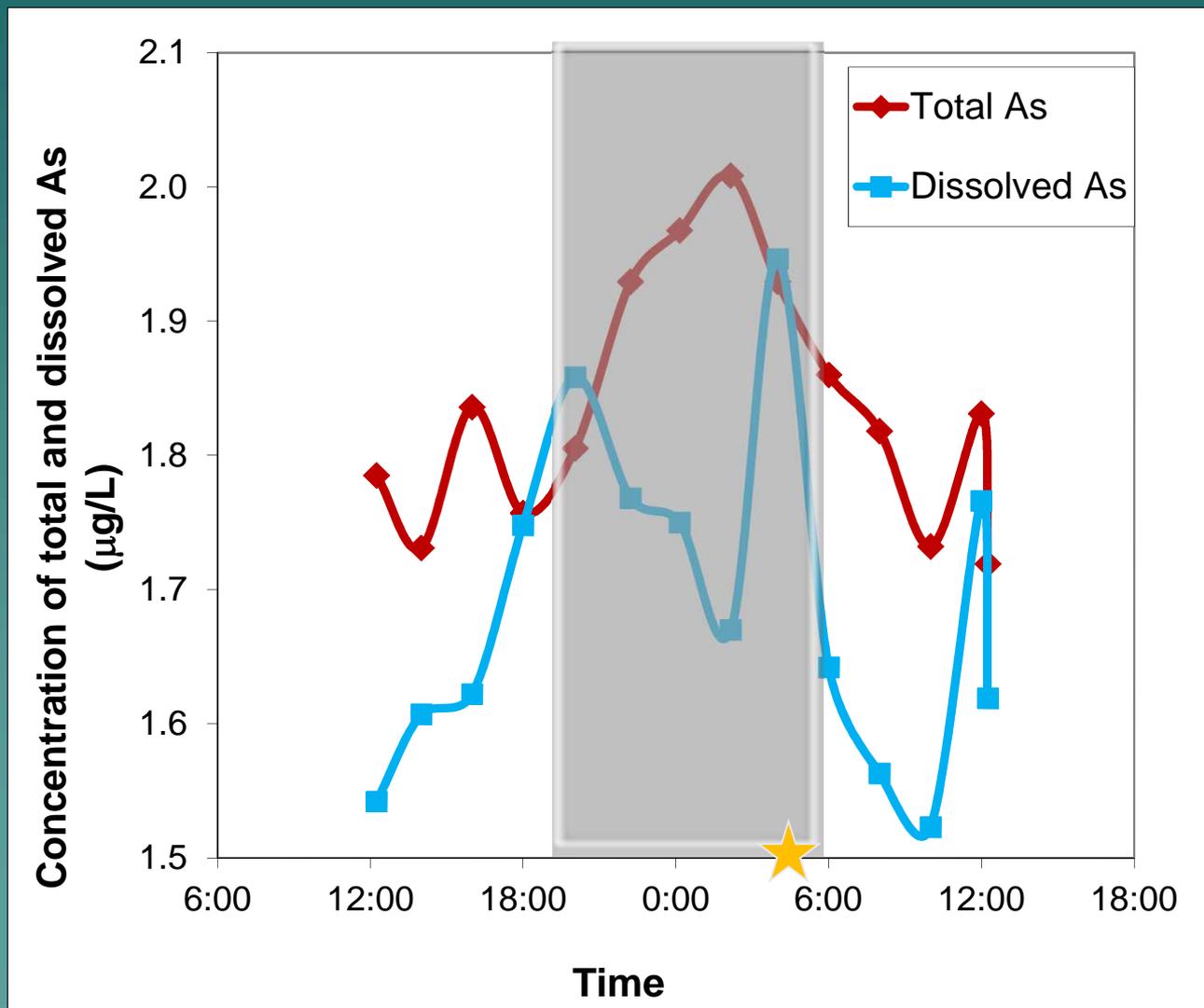
Walkkill River Sampling



- ◆ Franklin Mine upstream of site
- ◆ STP continuously discharging $\sim 0.092 \text{ m}^3/\text{s}$
- ◆ Treated GW discharged to adjacent wetlands
- ◆ Sampled manually using ultraclean techniques

September 2005—WALLKILL RIVER

Particulate metals increased at night



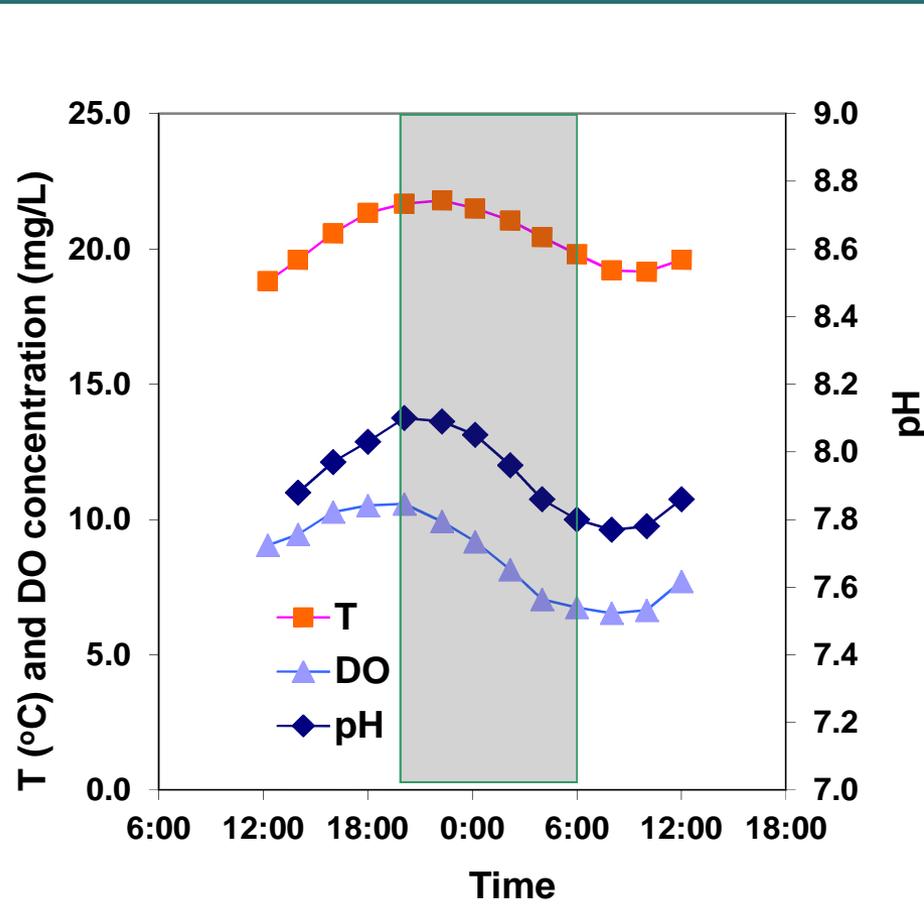
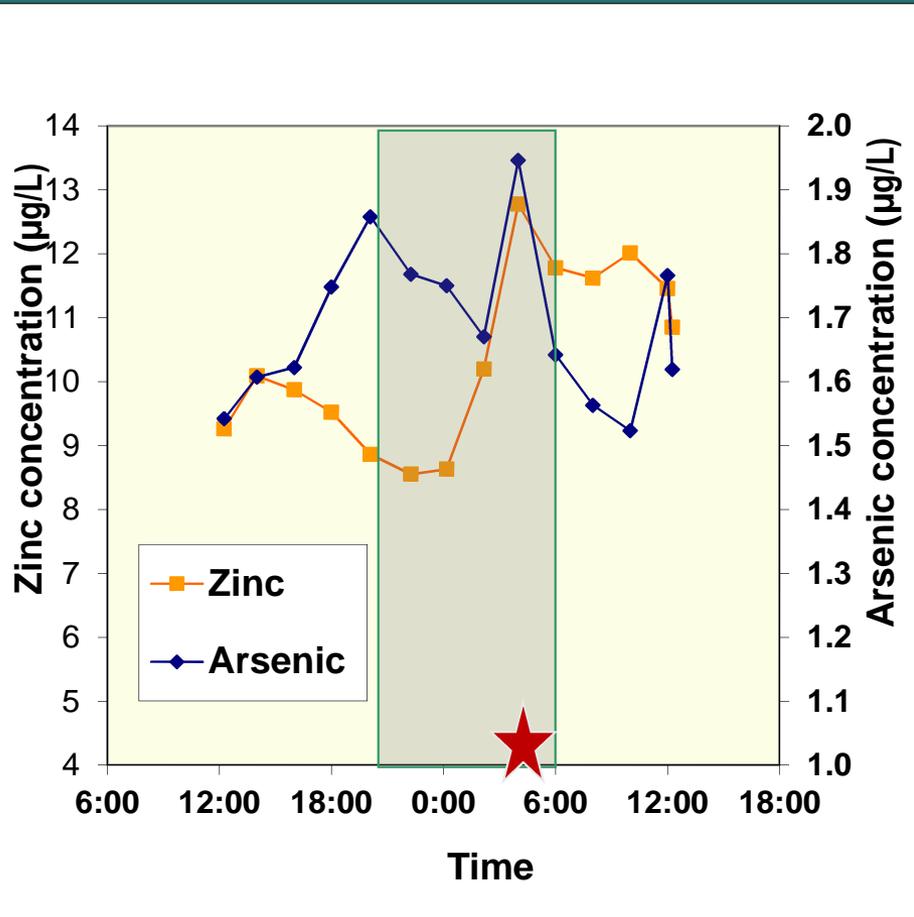
• Nighttime peak of particulate metals are probably from nocturnal sediment stirring by invertebrates.

★ Cause of 4 AM peak unknown

September 2005—WALLKILL RIVER

Dissolved As cycle was roughly opposite to that of dissolved Zn

Temperature, pH and DO peaks occurred later than peaks seen for most other diurnal studies

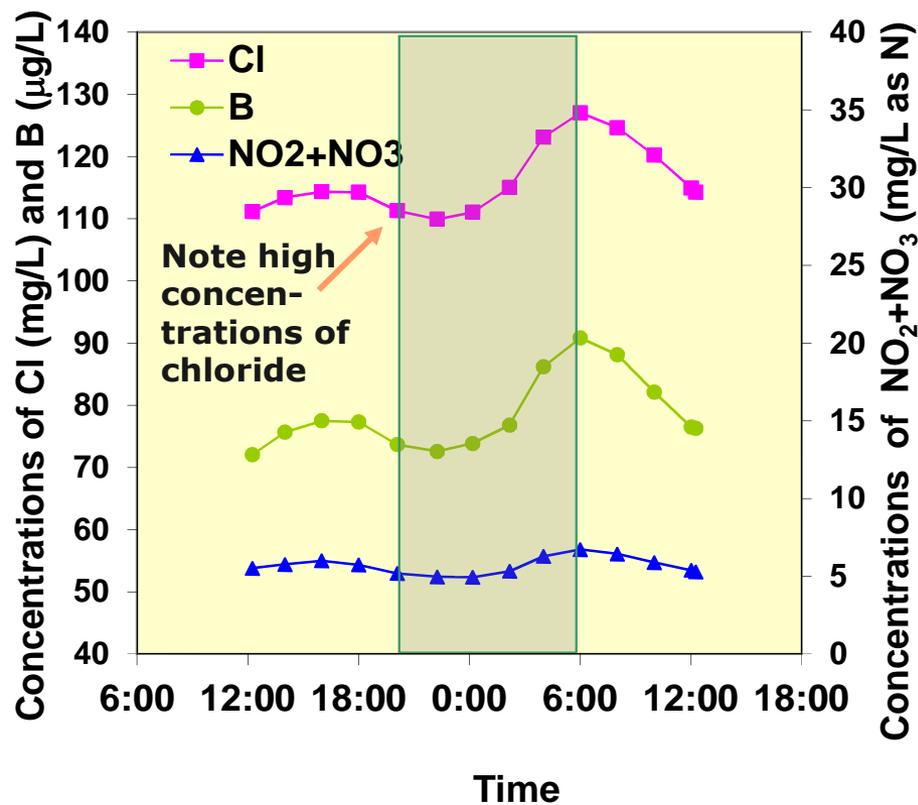
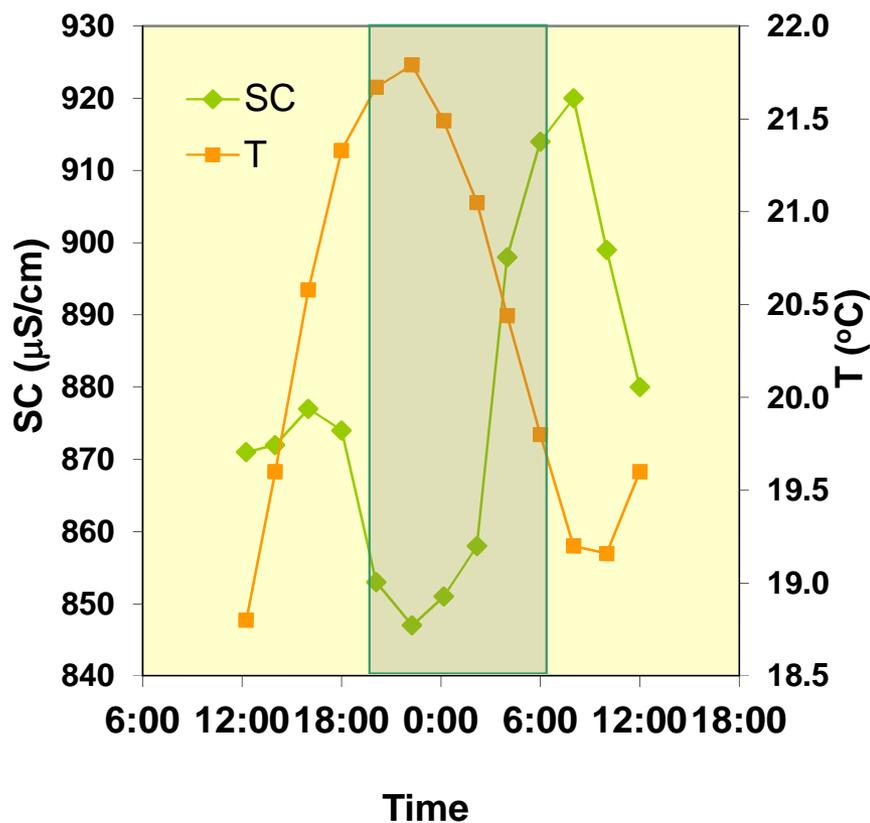


★ Cause of early morning peak unknown

September 2005—WALLKILL RIVER

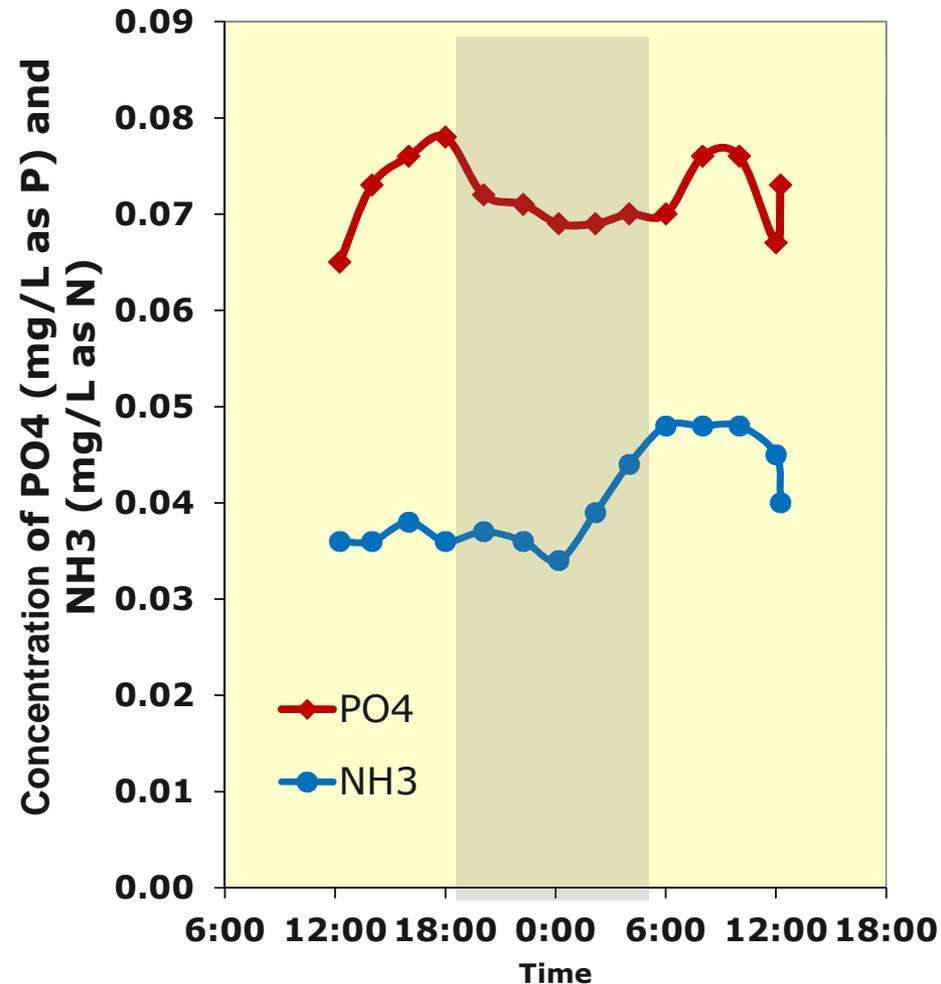


Boron, chloride and nitrite + nitrate concentrations showed two maxima coinciding with a two-maximum diel cycle for specific conductance.



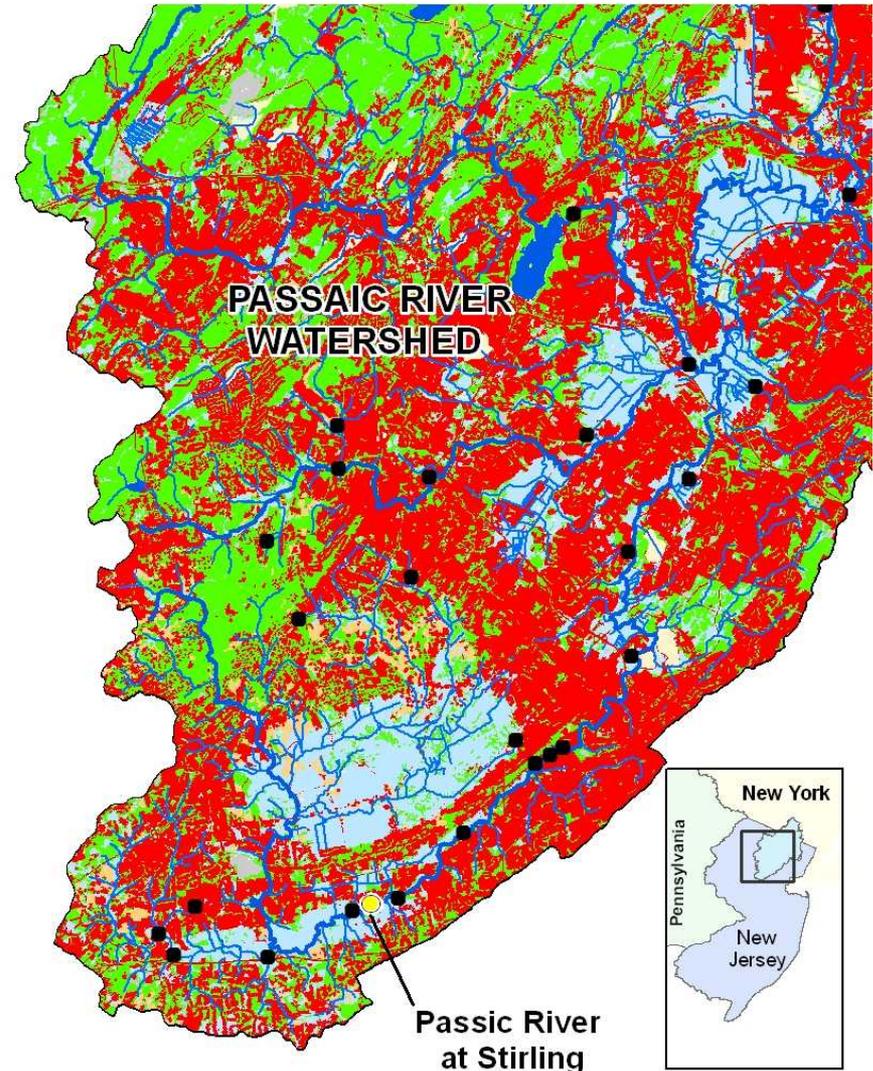
Two Peaked Cycles of constituents

- ◆ The two-peaked nutrient cycles with those of Cl and B is indicative of nearby wastewater inputs to the stream.
- ◆ If cycles were natural, nutrient concentrations (particularly those of NO_3 and PO_4) would likely peak during day.



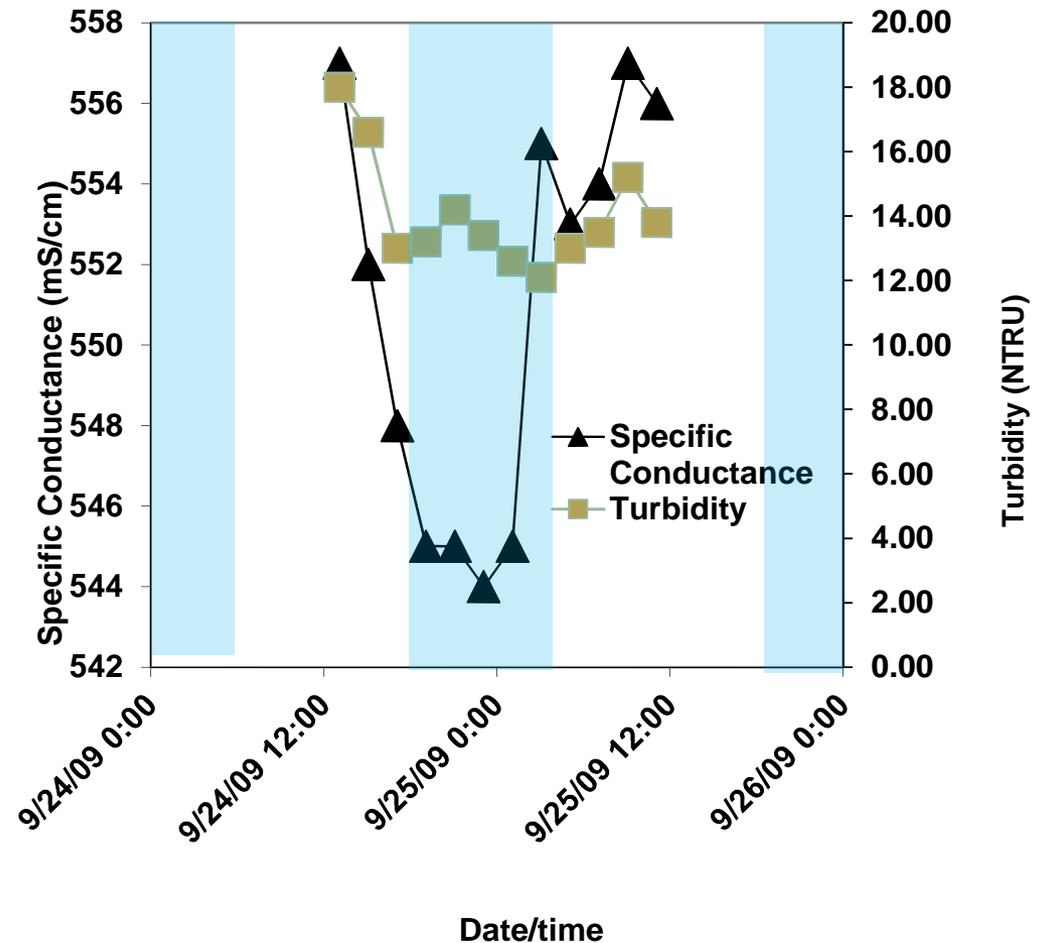
Passaic River Diel Sampling

- Highly urbanized land use
- Numerous effluent inputs upstream of sampling site
- Diel sampling done with automatic sampler in September 2009.



September 2009—Passaic River

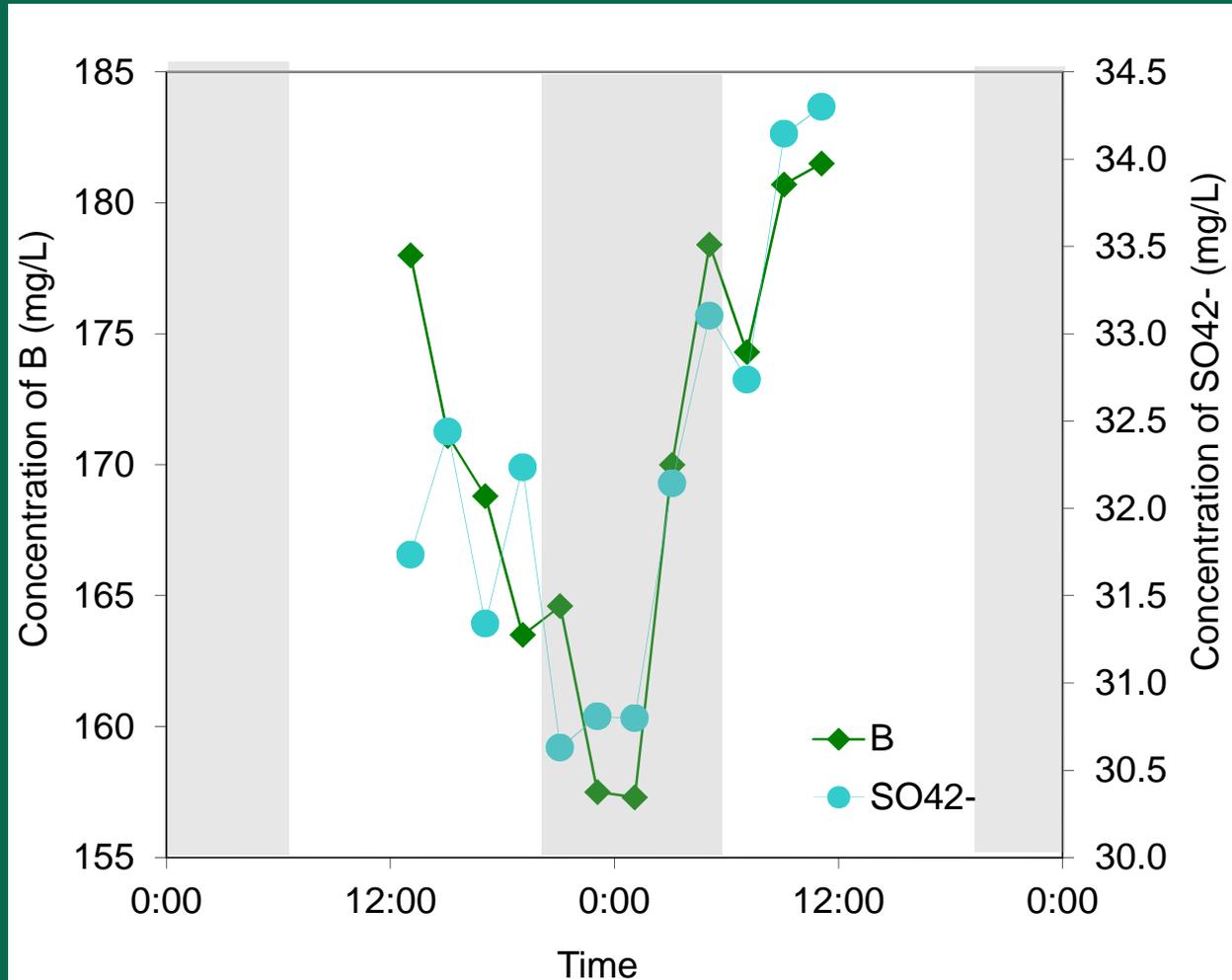
- Fluctuations in specific conductance point to mainly daytime inputs of effluent.
- Turbidity fluctuations during the night may be due to nocturnal benthic activity?



September 2009—Passaic River

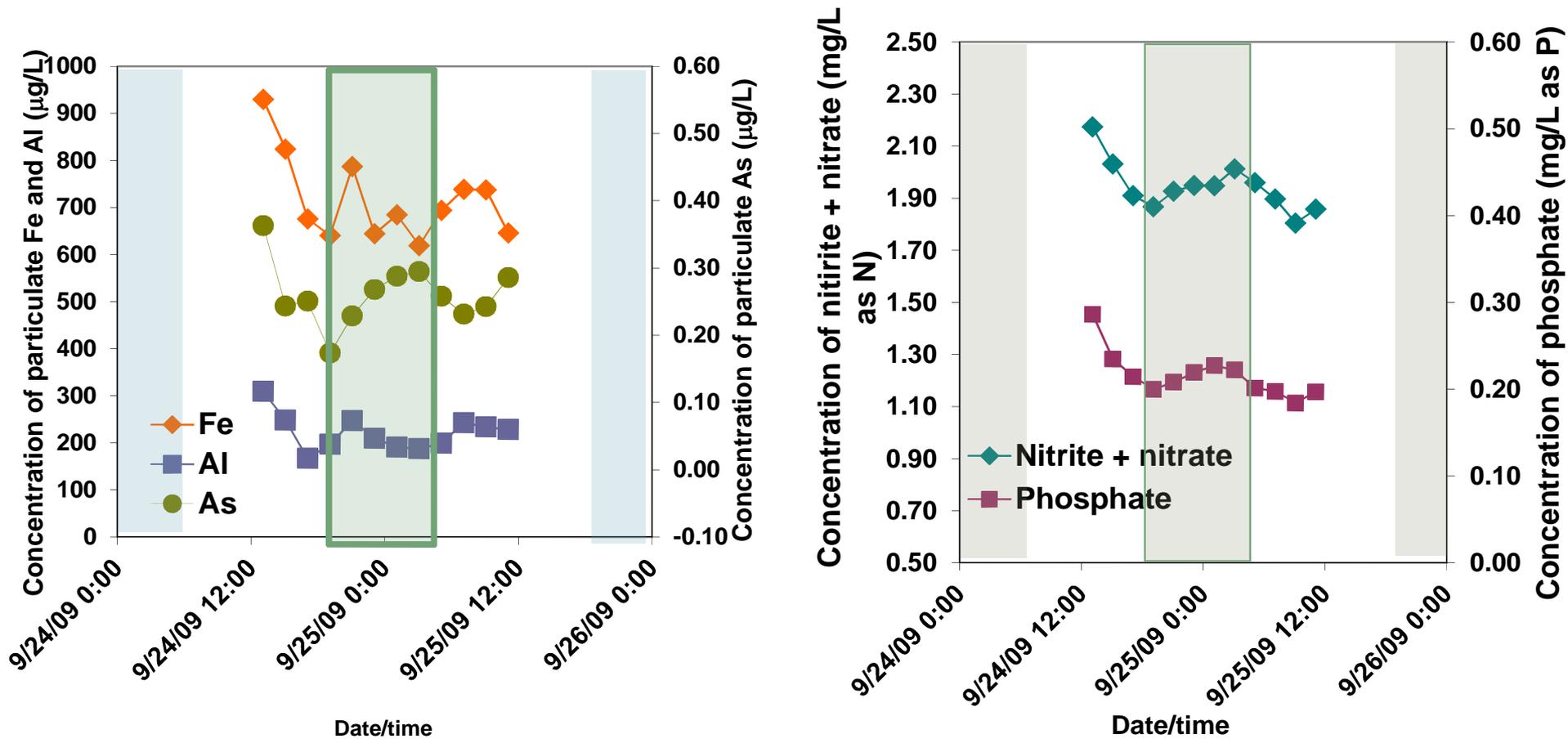
Downstream from a Sewage treatment plant (STP)

● Boron (B) and sulfate (SO₄) concentrations decreased at night, probably reflecting variations in effluent inputs from the STP.



September 2009—Passaic River

Concentrations of particulate iron and aluminum were high during daytime, but also showed a nighttime peak. Fluctuations in particulate As coincided with those of phosphate and nitrite + nitrate.



August 2006--Great Egg Harbor River

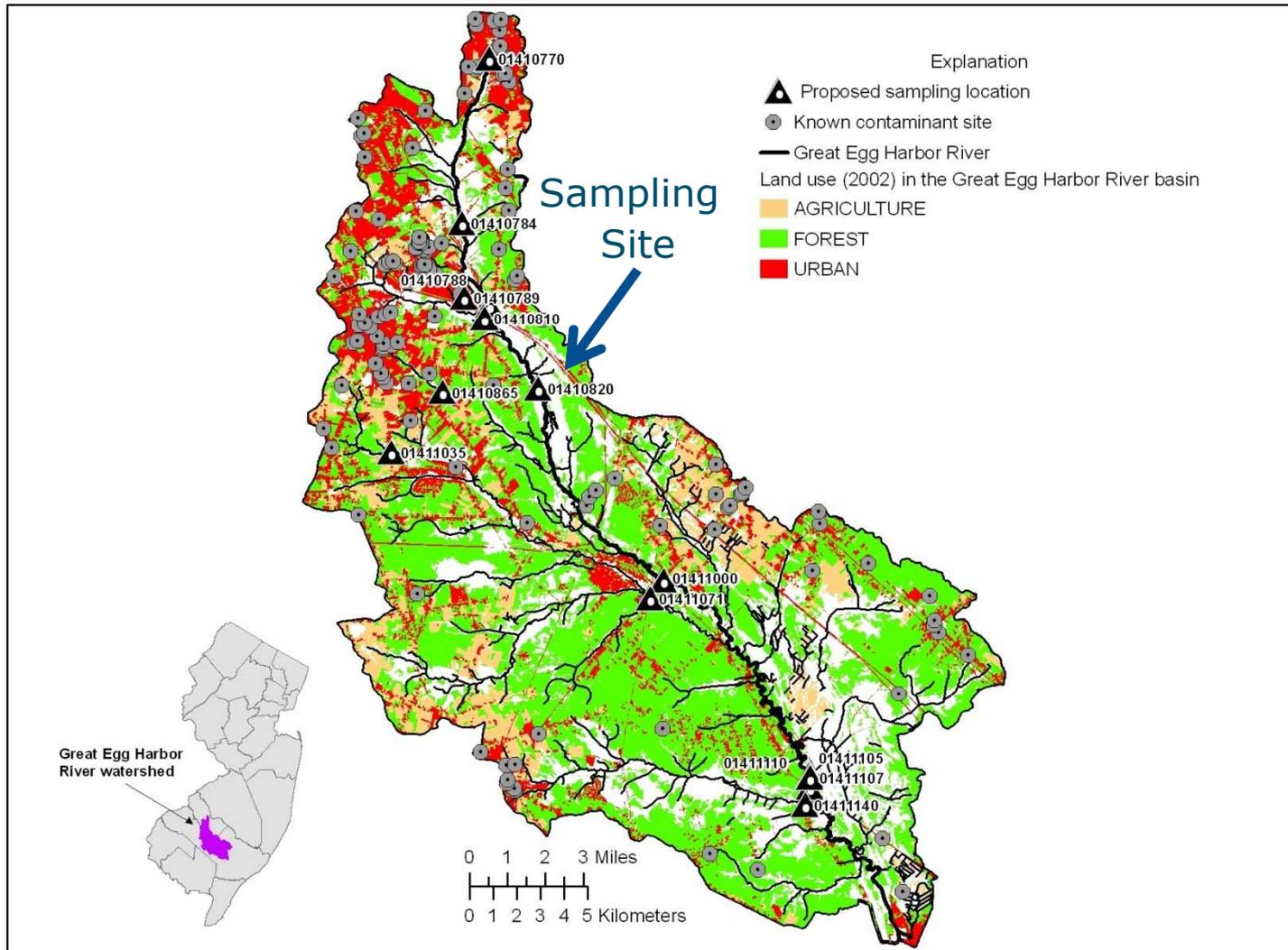
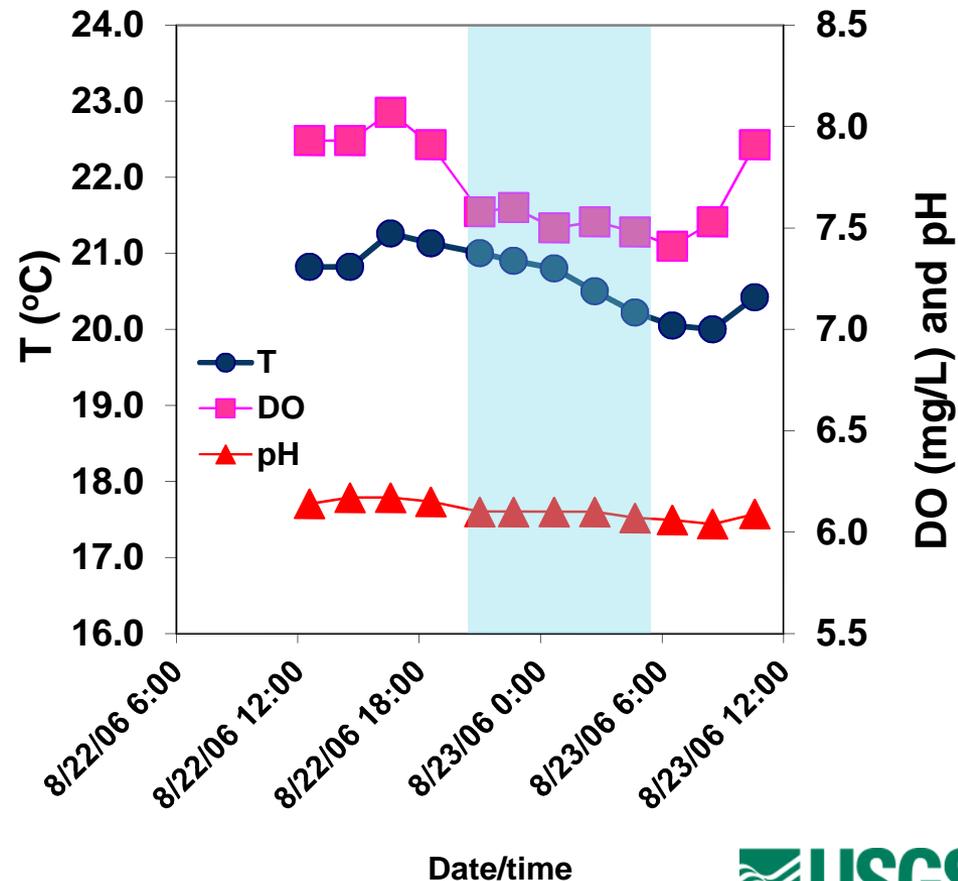


Figure 1. Great Egg Harbor River watershed, southern New Jersey, showing 2002 land use and the locations of known contaminant sites and proposed sampling sites

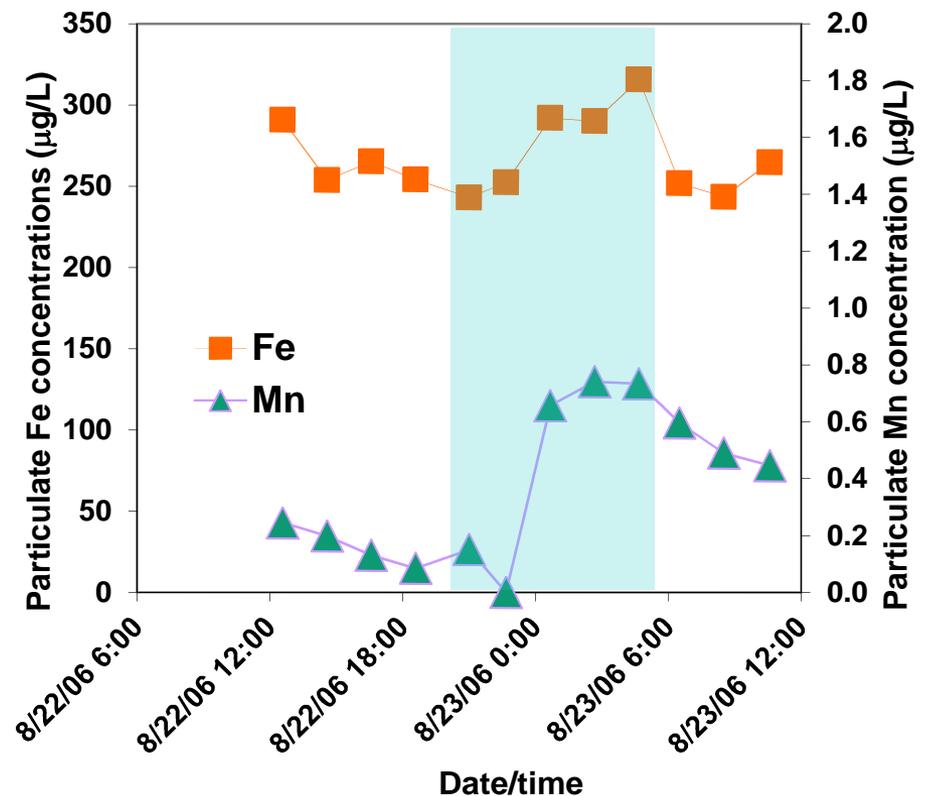
August 2006--Great Egg Harbor River

- Fluctuations in temperature (T) and dissolved oxygen (DO) were driven by irradiance, photosynthesis and respiration.
- There was little variation in pH.
- pH was sufficiently acidic that no desorption reactions for As occurred and thus no diel cycling was observed



August 2006—Great Egg Harbor River

- The only recognizable diel cycles observed for metals were in concentrations of particulate Fe and Mn.
- Stirring of sandy bottom sediments by invertebrate nocturnal activities is a likely cause of these cycles



Summary:

- ◆ The Wallkill River shows that cycles in dissolved As, Mn, and Zn apparently result from adsorption/desorption reactions driven by pH (and T) changes which were influenced by stream inputs.
- ◆ Particulate metals cycles (as shown for the all three basins)— may be related to nocturnal biological activity in the bed sediments.
- ◆ In the Passaic River nighttime nutrient peaks also coincided with the particulate As peak; benthic activity or organic matter releases could account for the nighttime peaks.

CONCLUSIONS

- ◆ At the Wallkill River, wastewater inputs may account for two-peaked cycles observed for nutrients, B and Cl. We are still unsure about the the 4 AM spike in dissolved concentrations???
- ◆ Inputs of treated wastewater in the Passaic River induce different cycles for many constituents based on timing of releases.
- ◆ The adsorption/desorption cycles for metals seen in alkaline streams are not seen in acidic streams such as the Great Egg Harbor River.
- ◆ Particulate metals cycles may be seen wherever bottom sediments can be stirred by nocturnal biological activity.

TAKE-HOME MESSAGE

- ◆ Because natural diel cycles and human-induced cycles exist in streamwater for a variety of constituents, timing of sample collection can substantially affect results.
- ◆ Whenever possible, investigate the chemistry of a stream before planning a sample-collection effort!