

Experience using the winning sensor from the nutrient sensor challenge (using the WIZ for surface water)

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Low cost nutrient sensor challenge

- Nutrient pollution is associated with harmful algal blooms
- Laboratory methods and sensors for some of the major nutrients (NH_3 , NO_2 , NO_3 , and PO_4) are commercially available
- Problems include:
 - Data comparability between sensors, and laboratory methods
 - Cost of sensors
- These problems were recognized by the community of practice
 - How to overcome these problems



Successful challenges are partnerships

- Alliance for Coastal Technologies
- U.S. EPA, NOAA, USGS, NIST
- Partnership on Technology Innovation and the Environment
- Survey Respondents
 - Environmental Council of States
 - The National Water Quality Monitoring Council
 - Consortium of Universities for the Advancement of Hydrologic Science
 - PTIE Workgroup on Monitoring Nonpoint Source Pollutants
 - Water Keeper Alliance
 - Attendees at NWQMC's 9th National Monitoring Conference
 - Professionals from State, local and Federal governments, academics, non-profit, and corporate interests. (Sensor manufacturers were excluded)

Challenge grant process

- Needs for technological solutions are identified
 - Regulators
 - Researchers
 - Utilities
 - Resource Managers
 - Public Health Authorities
 - Other Stakeholders
- Examine currently available technologies
- Determine gaps
 - Assess whether the gaps represent a commercially viable marketplace
- Issue challenge
- Throughout the process resources are required, and must be obtained from stakeholders

Low cost nutrient sensor challenge

- Multiple vendors participated in a multi location challenge, deploying their sensors in field locations
 - Applications accepted for challengers in 2014
 - Test deployments: Great Lakes, Chesapeake Bay and Hawaii in 2016
- Data were collected and analyzed
- Results were adjudicated by a panel of stakeholders
 - Results were announced at the Association for Sciences of Limnology & Oceanographic Aquatic Sciences (ASLO) meeting March 2017

The winning sensor(s)

- Systea Sp.A. produced the winning sensor
 - This sensor is called the WIZ
 - Configurable for NH_3 , NO_2 , NO_3 , and/or PO_4
 - Uses wet chemistry
- National Oceanography Center also won an award
 - their technology was at an earlier stage of development

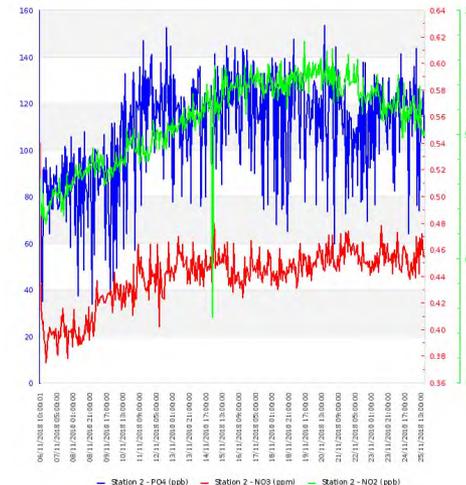


Deploying the nutrient sensor challenge winner

- The Systea WIZ sensor won the Nutrient Sensor Challenge, a challenge grant designed to promote the development of low cost nutrient sensors
- EPA Purchased 2 sensors configured for N as nitrite, N as nitrate, and P as phosphate (ammonia is available but was not chosen)
- One sensor is currently installed at the drinking water treatment plant intake structure on Lake William H. Harsha
 - The second sensor was installed on the Merrimack River in EPA Region 1
- Discussion of the actual deployment details should allow potential sensor users to evaluate the potential value of this sensor in their application



WIZ sensor being calibrated in laboratory



WIZ sensor data from deployment

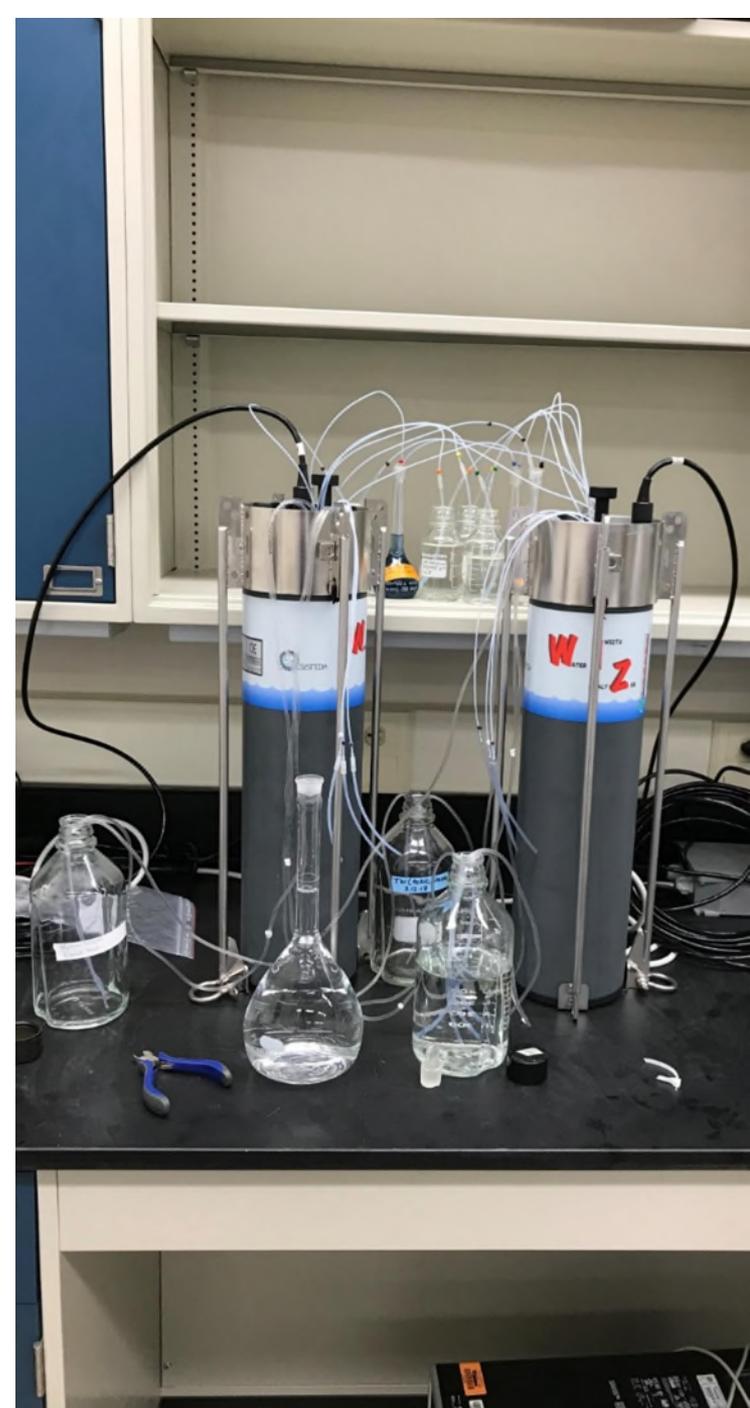
Some EPA methods of chemical analysis for NO_2 , NO_3 , and PO_4



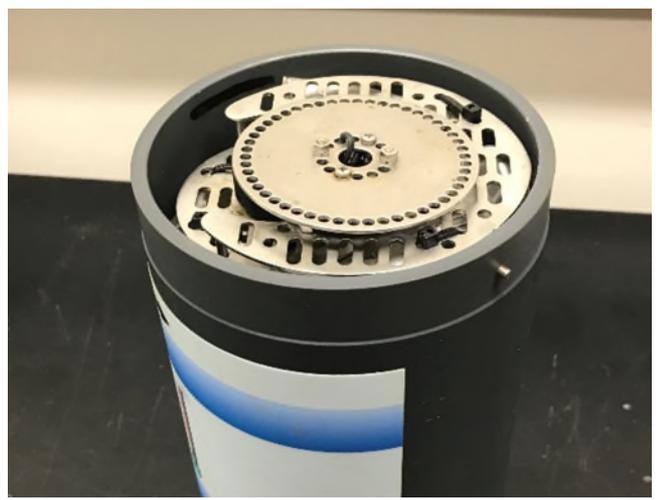
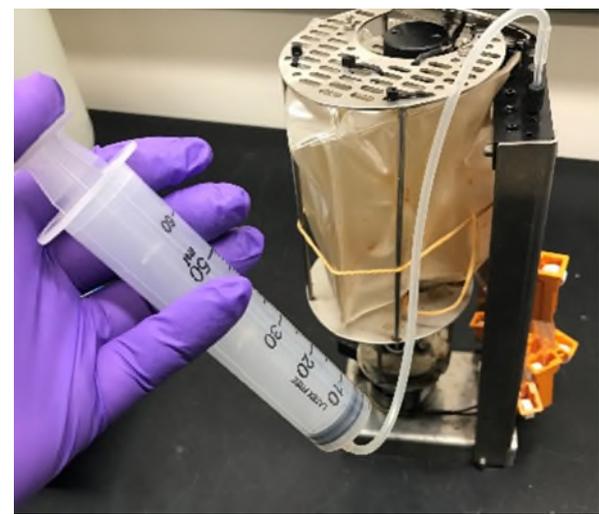
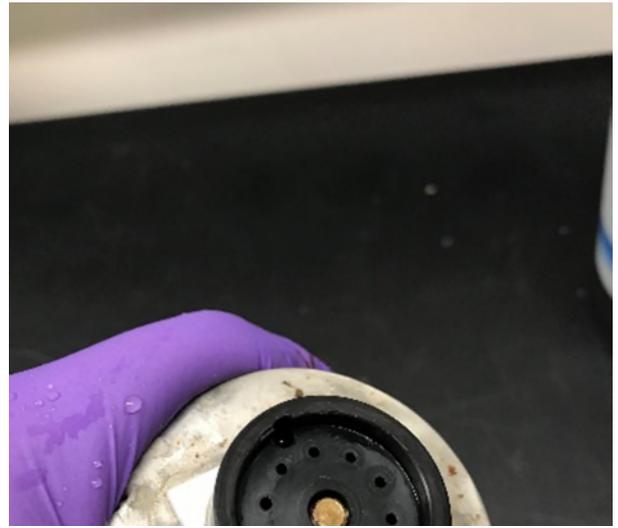
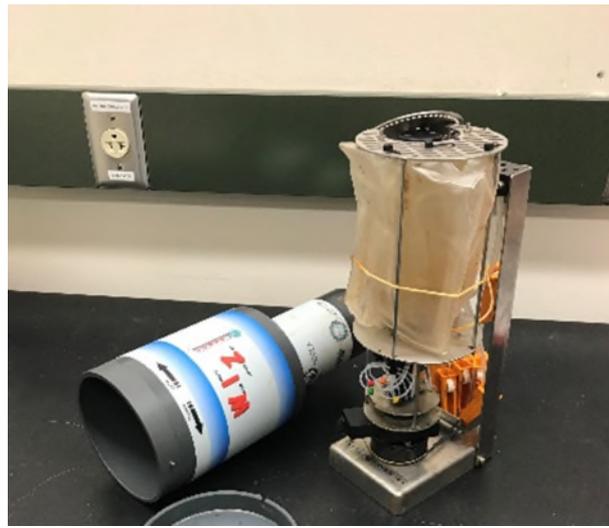
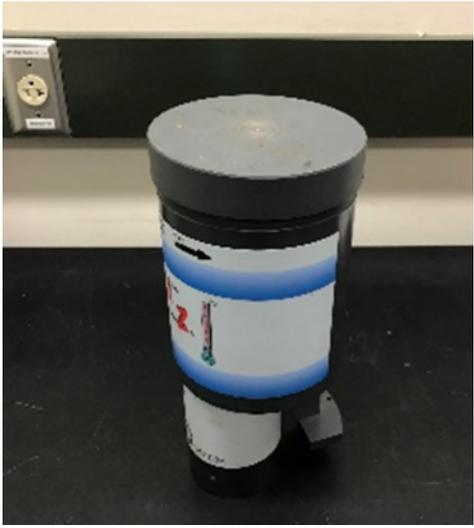
- Nitrate and/or Nitrite:
 - Method 352.1: Nitrogen, Nitrate (Colorimetric, Brucine) by Spectrophotometer
 - Method 353.1: Nitrate-Nitrite by Colorimetry
 - Method 353.2: Determination of Nitrate-Nitrite by Automated Colorimetry
 - Method 353.3: Nitrate-Nitrite by Cadmium Reduction and Colorimetry
 - Method 353.4: Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis
 - Method 354.1: Nitrite by Spectroscopy
 - Method 1685: Nitrate/Nitrite-N in Water and Biosolids by Automated Photometry (Draft)
 - Water Monitoring and Assessment Chapter 5.1 Nitrates
- Phosphorous and/or phosphate
 - Method 365.2: Phosphorous by Colorimetry
 - Method 365.5: Orthophosphate in Estuarine and Coastal Waters by Colorimetry
 - Method 365.1: Phosphorous (all forms) by Semi-Automated Colorimetry

Chemistry of assays in the WIZ

- NO_2 : Nitrites react with sulfanilamide under acidic conditions to provide a diazo compound. With N-(1-Naphthyl) ethylenediamine, this forms a pink complex and a colorimetric measurement made 546 nm.
 - Reported as NO_2 as N, range 0-250 $\mu\text{g/L}$
- NO_3 : The nitrite concentration is read as background using the above chemistry. Nitrate is reduced to nitrite under acidic conditions with the addition of vanadium chloride, and measured as nitrite. The increase following reduction of nitrate is the nitrate concentration
 - Reported as NO_3 as N, range 0-50 mg/L
- PO_4 : Ortho-phosphate is measured by reacting the sample with molybdate in acidic solution to form phosphomolybdate solution. This is reacted with ascorbic acid to form molybdenum blue. The intensity of this dye is measured at 880 nm. Antimony potassium tartrate is used to catalyze the reaction and increase sensitivity.
 - Reported as PO_4 as P, range 2-2000 $\mu\text{g/L}$

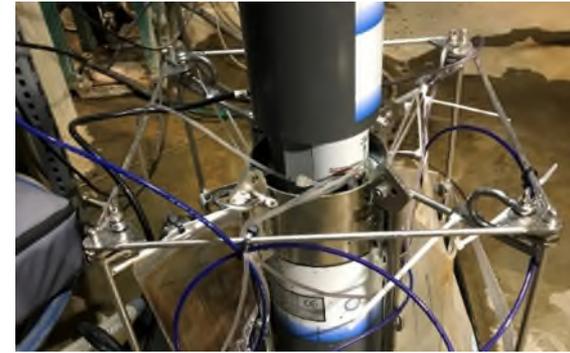


Loading reagents into the reagent canister



The device

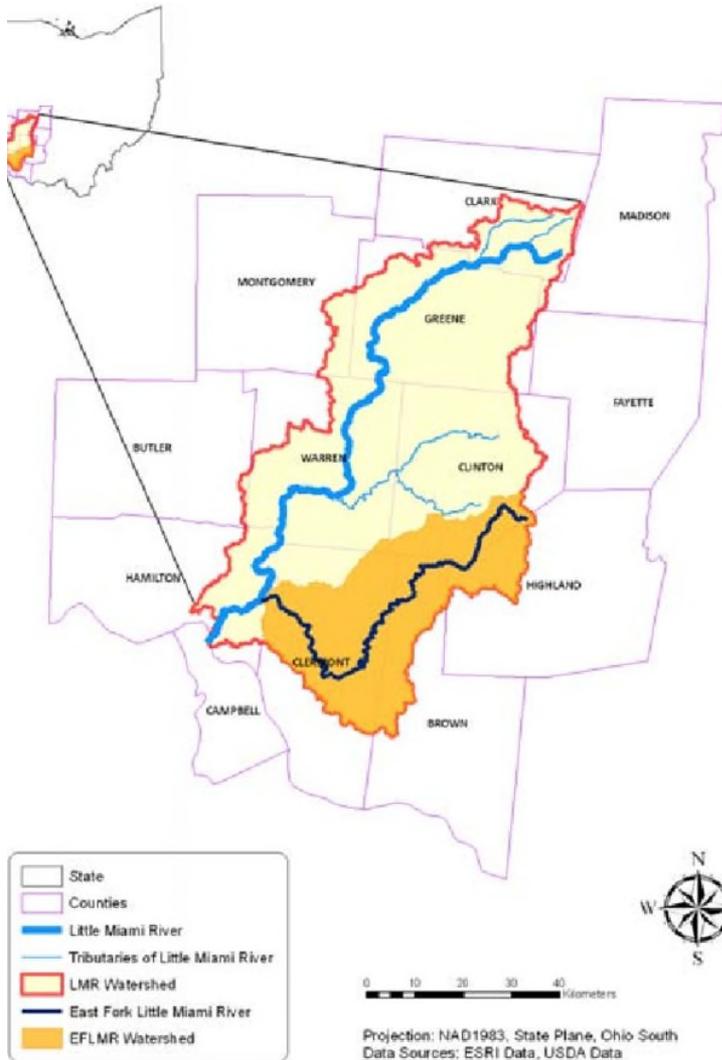
- There are two main structures
 - Electronics package
 - Frame structure
- Electronic package
 - Sealed battery
 - Control electronics
 - Data logger
 - Wireless communications card
- The frame holds
 - Peristaltic pump and valves
 - Hollow fiber ultrafilter
 - Filtered sample reservoir
 - Reaction vessels and LED/colorimeter on probe body
 - Reagent canister attached to probe body
 - Reagent water for flushing
 - Waste receptacles



Lake William H. Harsha (AKA East Fork Lake)

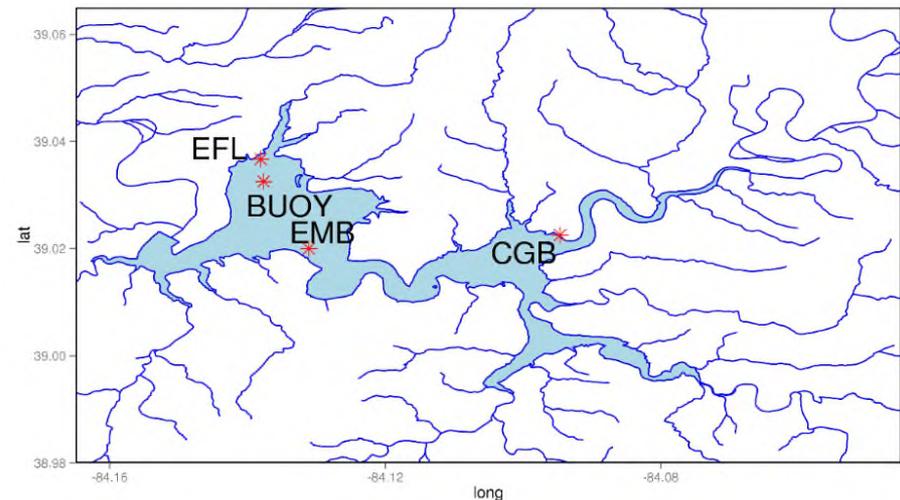
- Located in Clermont County Ohio
- An impoundment of the East Fork of the Little Miami River
- Surrounded by a state park and state wildlife area
- Upstream several towns, and farmland
- Provides water for the Clermont County Water Treatment Plant
- Used in flood control on the Little Miami River
- Supports multiple economically valuable recreational opportunities:
 - Fishing, waterfowl hunting, boating, swimming beaches, open water rowing competitions, multiple boat ramps



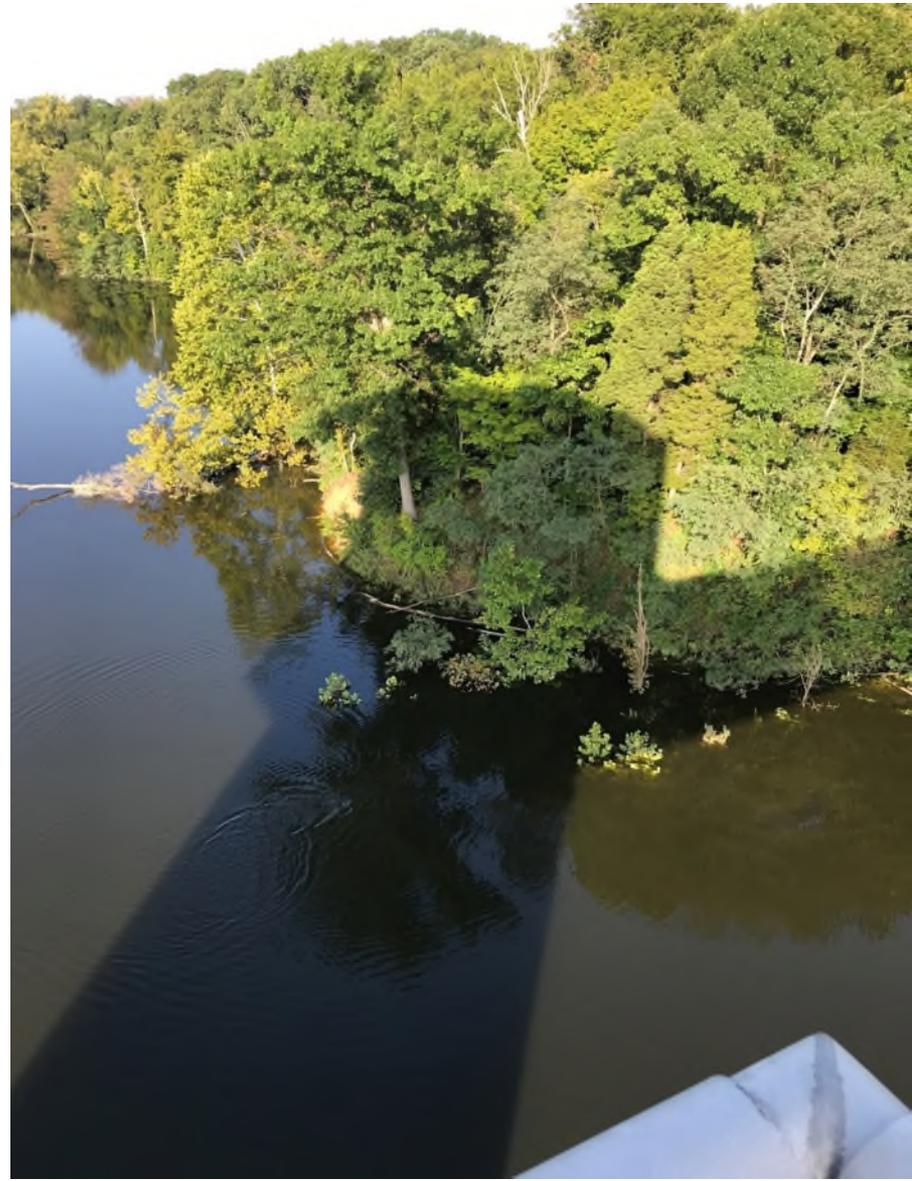


The watershed

- The east fork of the Little Miami River is the southern branch of the Little Miami.
- It runs east to west just north of the Ohio River.



Sampling location



Practical application of the WIZ

- Form factor, functionality, and power requirements of sensor are key considerations for deployment
- Sensor has multiple required components
 - They are all water resistant or water proof
 - Some components are designed for submersion
- Must have ability to access the reagent canister for reagent replacement, and to access liquid handling lines for flushing and calibration
- Calibration requires additional laptop, and power supply to device
- Interior plateau ecoregion targets:
 - TN= 688 ppb
 - TP = 34 ppb
- Lake Harsha is well above these levels most of the time, especially for TP



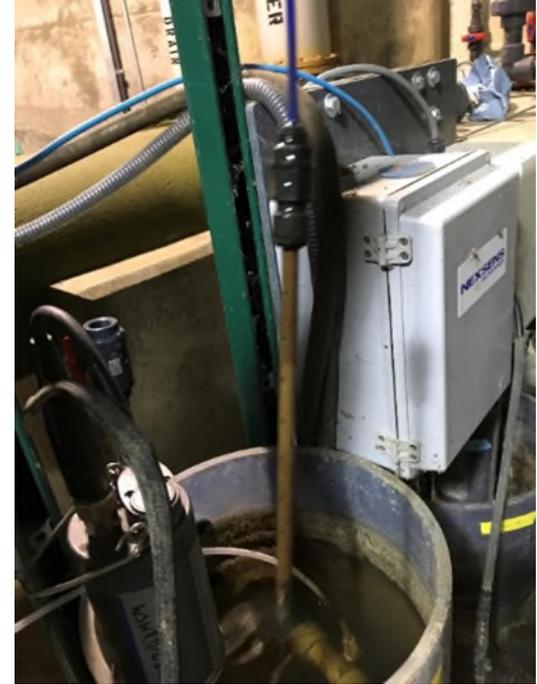
Deployed configuration

- The sampling dip tube is in a reservoir that receives a slip stream
 - There are other monitoring devices using this reservoir
- Uncontaminated waste water is sent directly to the floor drain
- Water reacted with reagents is collected and disposed in the laboratory
 - A spill man will contain any waste spills
- Data communicates via cellular modem
 - A wireless antenna is not evident, but required in this location
- This location has adequate line current which is used instead of the solar panels
 - A solar panel is available as an option
- The connector for the laptop, is evident in this image

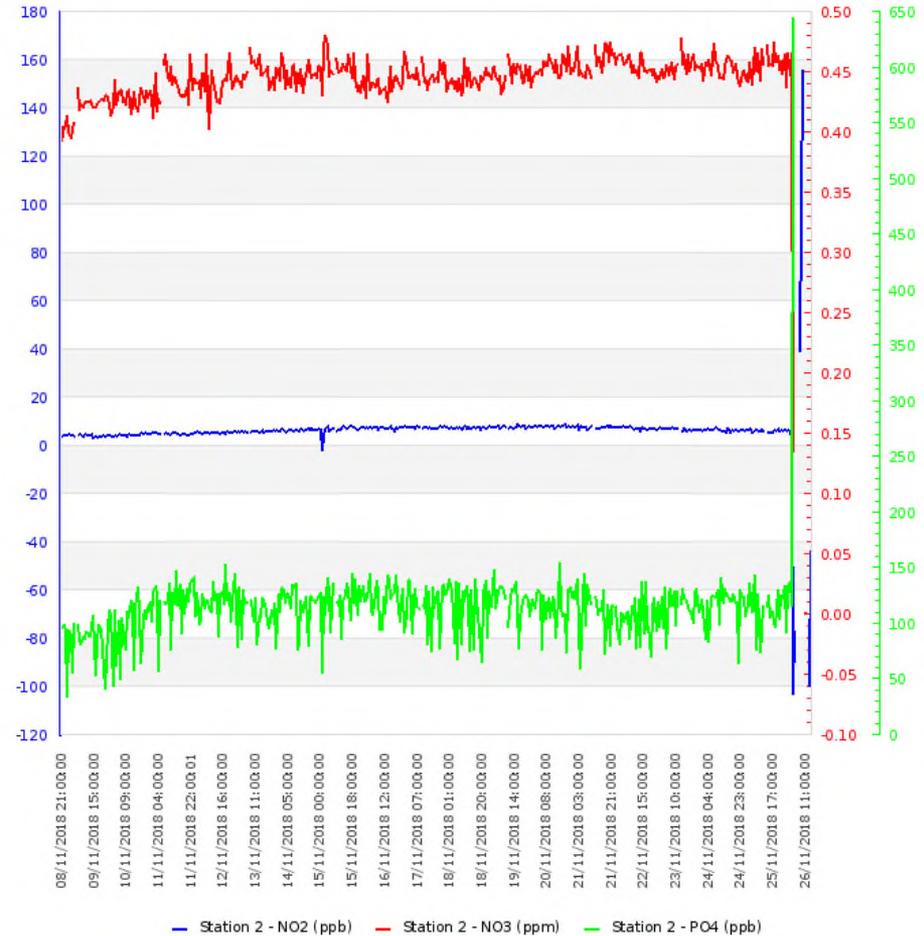


Non-sensor related difficulties

- Sample tube withdrawn from water reservoir
- Water entered the instrument electronics package
- Reagent formulation mistakes (version control of instructions)
- Waste bag detached from frame, fell, leaked
- Wireless antenna fell and broke

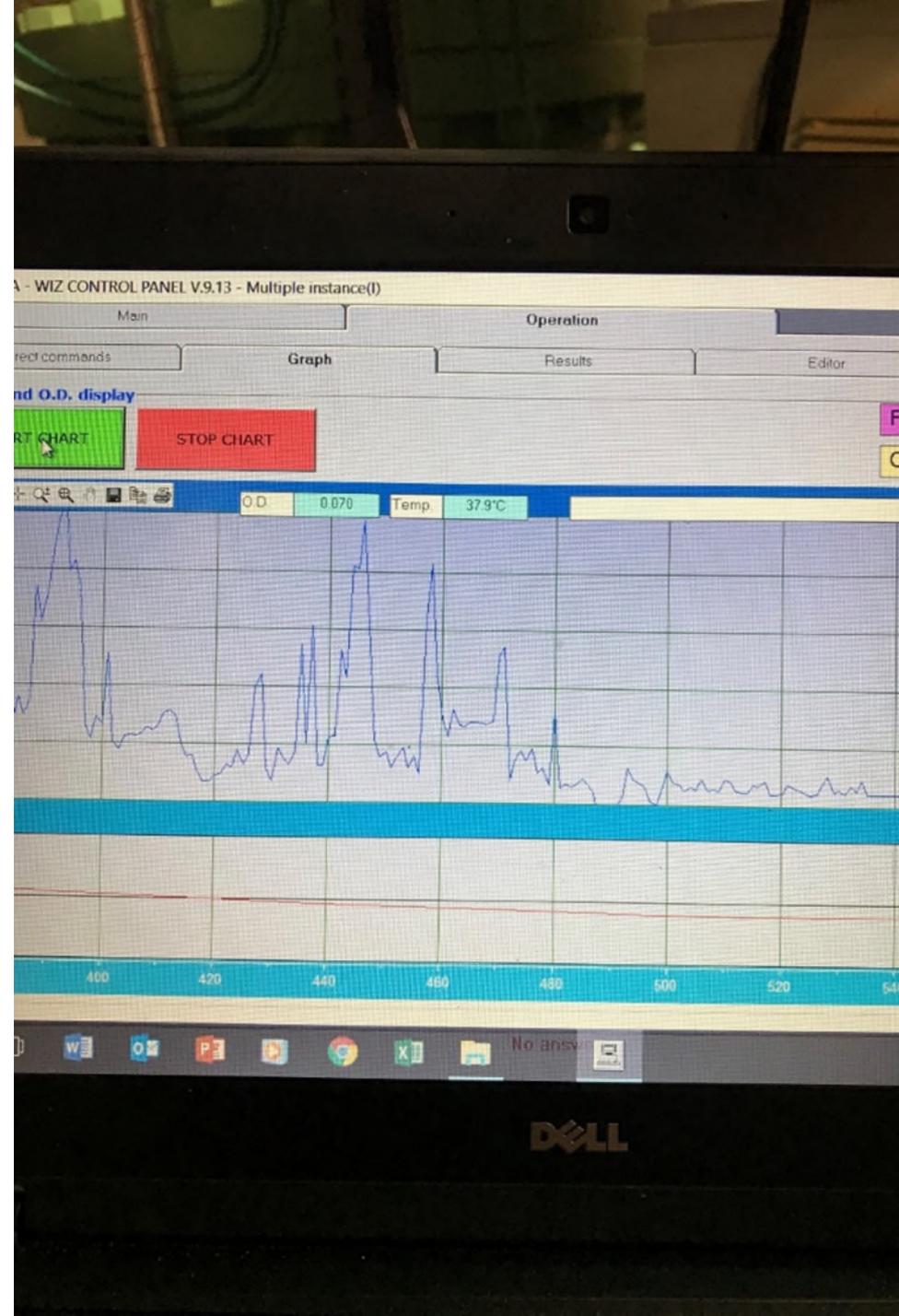


Example data



Regular maintenance and calibration procedures

- Our schedule is monthly based on:
 - Number of assays
 - Reagent capacity of reagent canister
 - Expiration of reagents
 - Duration - approximately 26 minutes minimum for all three assays
- Reagents must be prepared and loaded into reagent canister, soon before field service to preserve expiration
 - Calibrants may be made up the night before, or the morning of the field visit
- On site monthly refresh
 - Clean sample dip tube
 - Remove old/ install new reagent canister
 - Remove/ replace waste and external reagent water
 - Check/ calibrate LED's
 - Bleach, flush and prime reagent lines
 - Calibrate with 3 blanks per analyte and 3 calibrant standards.
 - Check and adjust the calibration values using the data from the blanks and standards.
- Each 3 analytes requires about 26 minutes
- Requires laptop, and perhaps access to electrical supply (15 A 120 V) with hard wired connection to data box



Pros and cons of the WIZ

Pros

- Much greater sampling rate than achievable by grab sampling
- Standardized chemistry measures
- Data may be downloaded in tabular or chart form
 - Hosted by vendor
- Additional testing is underway
- There are plans to move the sensor from Merrimack River to Region 7

Cons

- Minimum data acquisition rate about 26 minutes for 3 analytes
- Long prep time in the laboratory making solutions, cleaning and reloading canister
- Long time (3 to 4 hours) for re-fitting new reagents and calibration
 - Requires long time on station with a power supply, or
 - A long time in the lab if doing a “hot swap”
- Relatively large, heavy.
 - May require two person, lift or mechanical assistance
- Data management solution (vendor hosting)
- Data acquisition versus data reporting lag

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