Overview

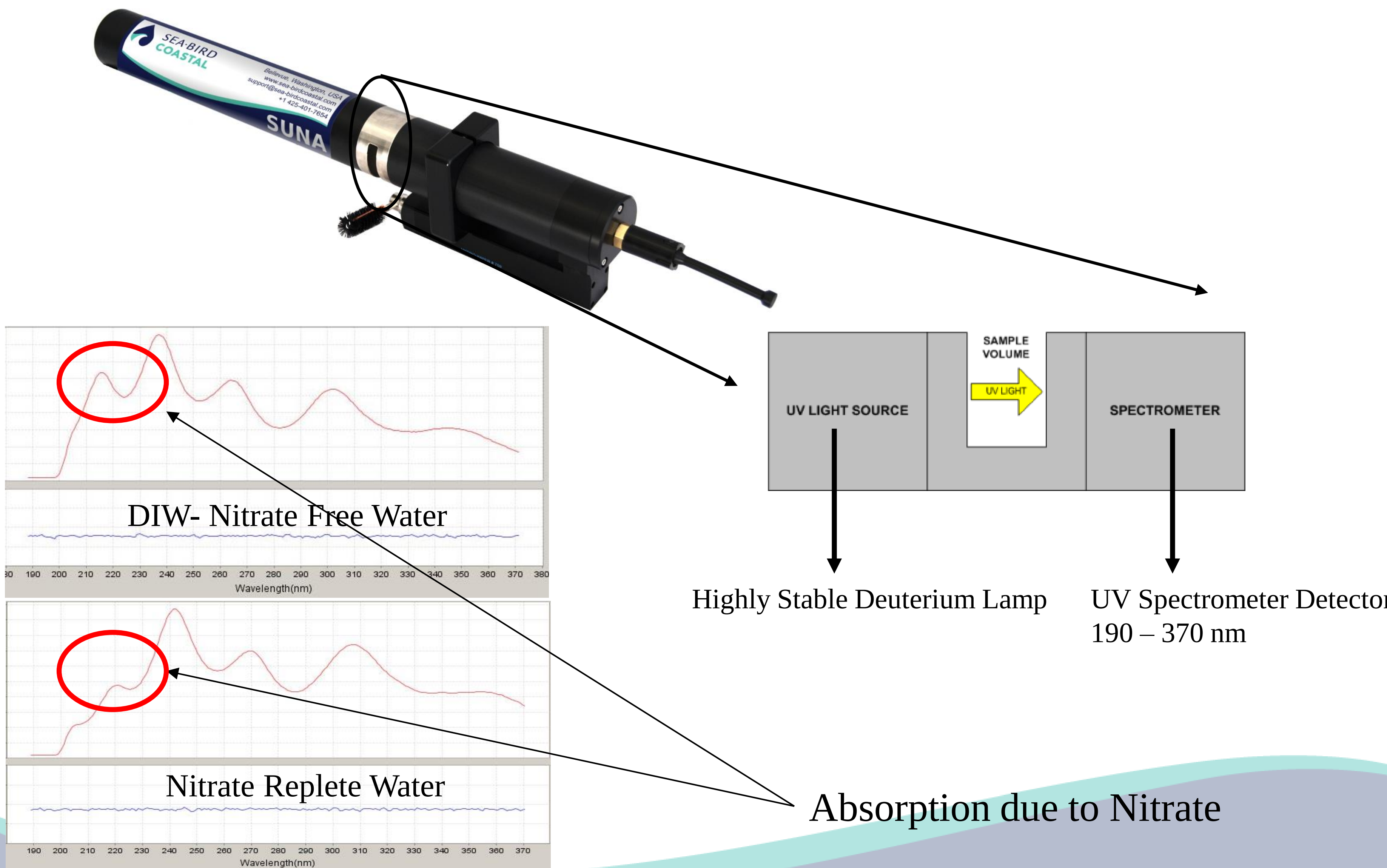
of Sea-Bird

Nutrient Sensors

Overview

- Sensors
  - SUNA Nitrate Sensor
  - Cycle-P Phosphate Sensor
  - Prototype Cycle-NH4
- Western Lake Erie HABs
- Yaquina Bay Inter-annual variability

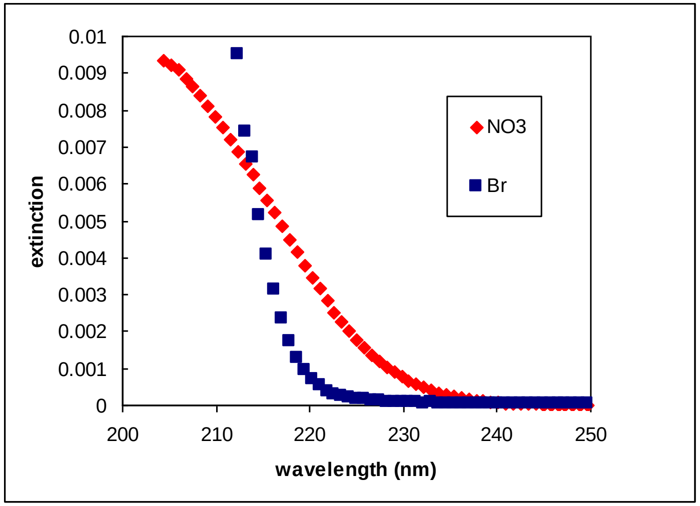
SUNA/ISUS Nitrate Sensor



SUNA Features

- Multivariate calibration for Bromide compensation (MBARI method), NTU compensation, and wider dynamic range
- Detection: 0.007 – 56 mg/L (0.5 to 4000 uM)
  - 5mm path length Increased CDOM & NTU handling capabilities.
  - 10mm path length Higher accuracy
- Accuracy: +/- 0.028 mg/L (2 uM) or 10% of reading (10 mm)

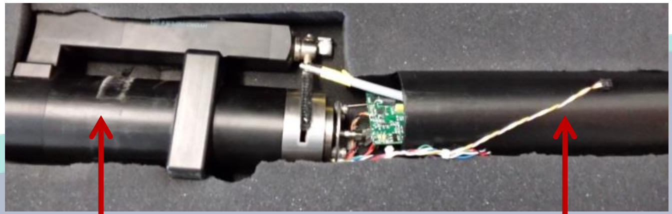
  +/- 0.056 mg/L (4 um) or 10% of reading (5 mm)



- Turbidity Range: 625 NTU (10 mm), 1250 NTU (5 mm)
- Long term drift: < 0.003 mg/L per hour of lamp time
- Depth rating: 100 m (with wiper), 500 m (without)
- Integrated antifouling wiper: 90° sweep with slip ring
- Adaptive sampling increase spectrometer integration for better S/N at low light levels
- ~650 mA needed for sampling, 20 mA standby

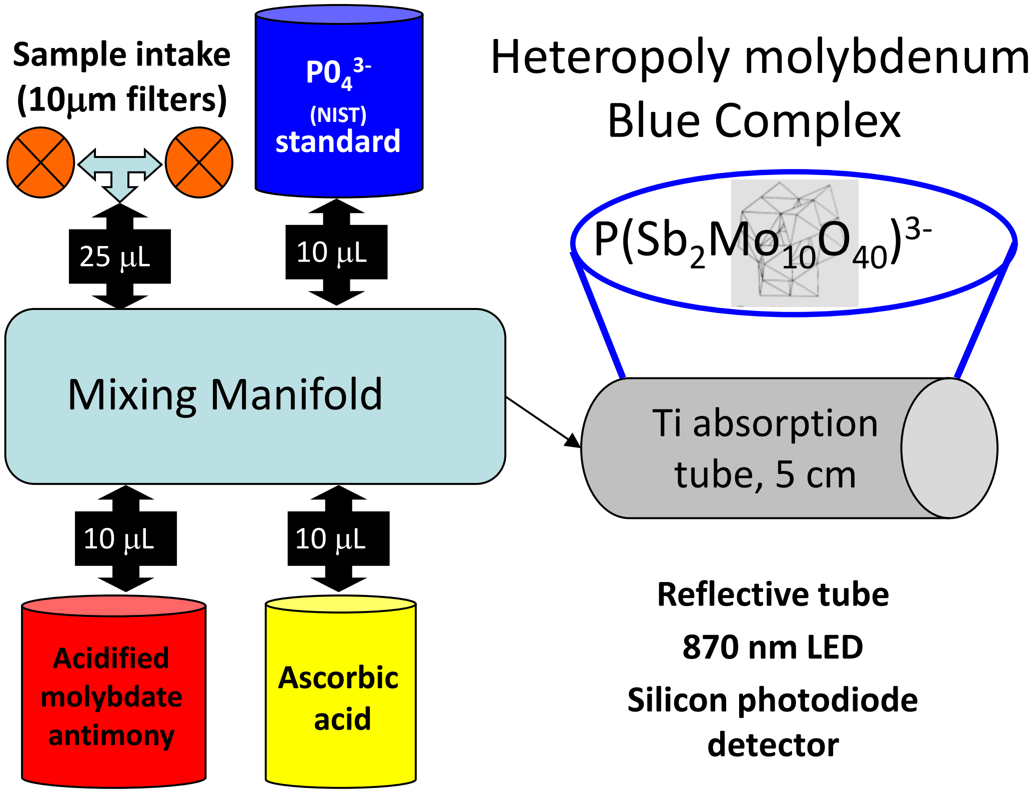
SUNA practical considerations

- All about the optics
  - Regularly (weeks to months) clean windows
  - Reference updates account for drift
  - Wiper can be key in sediment and fouling environs
    - Wiper can be moved, but care not to bend the wiper arm or knock it during deployment. If the wiper becomes mis-aligned it will not wiper properly.
  - CDOM/NTU are interferents
    - SUNA outputs quality meta data
      - RMSE on algorithm fit, avg. spec counts, A254 & A350
  - Mounting at two fixed points critical to minimize humidity ingress
    - Quality upgrade may be available for SUNAV2s with high humidity
  - Cables often need annual replacement in high fouling coastal zones
  - Annual service, and calibration recommended
  - Lamp lasts ~1000 hours



Mounting point *Flow force*

Cycle-P In-situ Phosphate Sensor



Based on:

-Murphy, J.; Riley J.P. Anal. Chim. Acta. (1962)

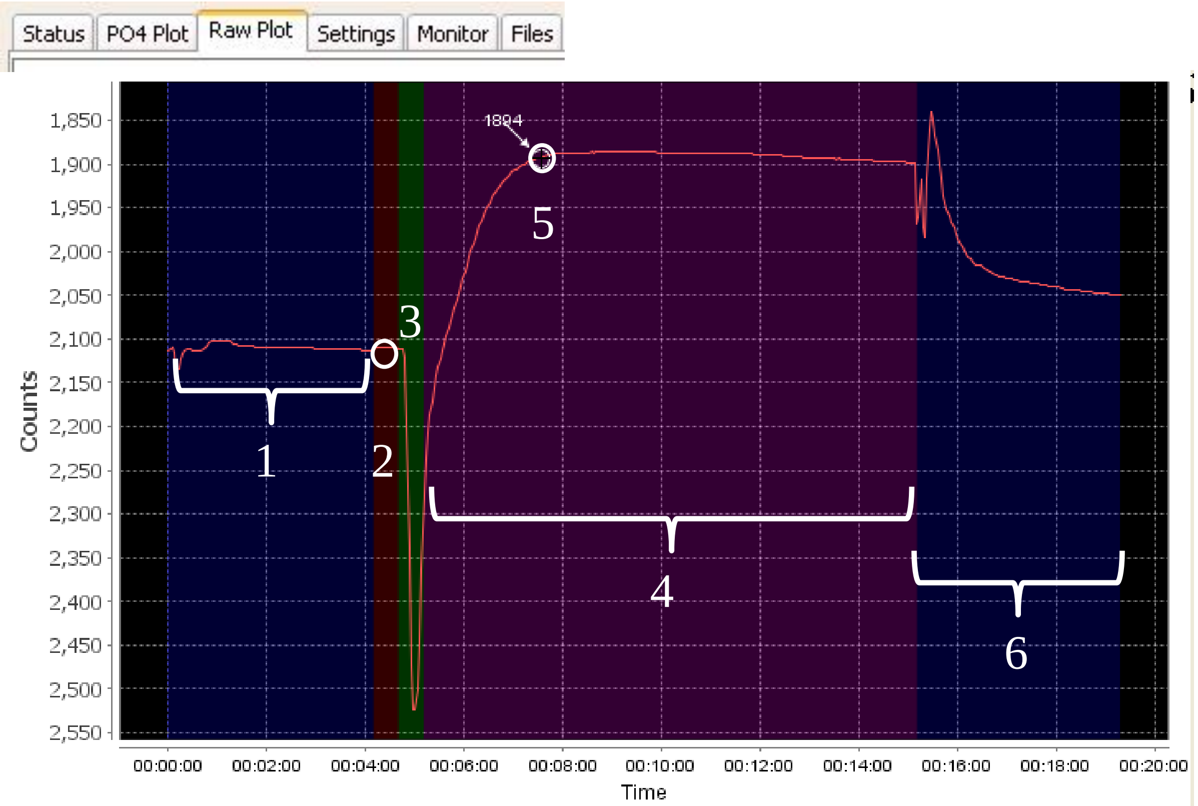
-US EPA method 365.5

SEA·BIRD COASTAL

Cycle-PO4 features

- On board reagent cartridges and NIST standard addition (keyed, leak-free, and color-coded)
- Over 1000 samples and optimized chemistry for deployments of three months
- Dual intake filters 10 µm stainless steel (to exclude particles)
- Copper mesh screens on intake filters prevent fouling on intake
- Titanium optical cell collects scattered light
- Calibrated output with User Definable units
- Pressure compensation for internal pumps to 200m
- ~ Soluble reactive ortho-phosphate
- LOD, IDL: $3*\sigma \leq 0.0023$ mgP/L (75 nM PO_4)
- LOQ: $10*\sigma \leq 0.0077$ mgP/L (250 nM PO_4)
- Range: 0-0.3 mgP/L (0-10 µM PO4)
- Maximum 2-4 samples per hour
- Up to 2A needed (~120 mA average)

Analysis of a Sample



1. Ambient sample flush/rinse
2. Baseline (ambient) measurement
3. Mixing: reagents added, pumps sample to optical cell

Concentration PO4 ∝ absorption

4. Sample reaction: product formation
5. Reaction completed, slope inflection point identified
6. Flush and rinse with ambient

~ 20 minutes per sample

Cycle-PO4 practical considerations

- Proper setup key to good deployment data
  - Fluidics and optics don't like bubbles
  - Vacuum prime sensor after cartridge install
  - Filter lifetime can vary in high sediment and bloom conditions—clogging generates bubbles
  - Pressure compensation upgrade may be needed if >30m depth
  - Windows stain, a bleach or surfactant clean is needed every ~1000 samples
  - Quality meta data: flush1 and VAPO4
  - Reagent stability

0 Months	3 Months	3-6 Months	6-12 Months
> 35^0 C	5^0 C - 35^0 C	~ 21^0 C	~ 3^0 C

SEA·BIRD COASTAL

The CYCLE-NH4

Freshwater (FW) and Saltwater (SW) versions

Current Figures of Merit

- LOD, IDL: 3*$\sigma \leq$ 0.25 µM
- σ of 5 µM (lab standard)
  - ≤ 75, 150 nM (FW, SW)
- Range
  - 0-10 µM Estuary
  - 0-25 µM freshwater
- > 1000 samples
- 3 samples per hour
- Reagent cartridges (~1 mo stability)
- On-board standard (currently FW)
  - Saltwater buffer needed
- GUI-based software

Target Specifications

- *LOD: 0.1 µM*
- σ of 5 µM ≤ 50 nM FW & SW
- *Range:*
  - *0 to >25 FW & SW*
- ✓
- ✓
- *Reagent cartridges (3 mo stability)*
- On-board standard (Salt and Freshwater)
- ✓

18 cm

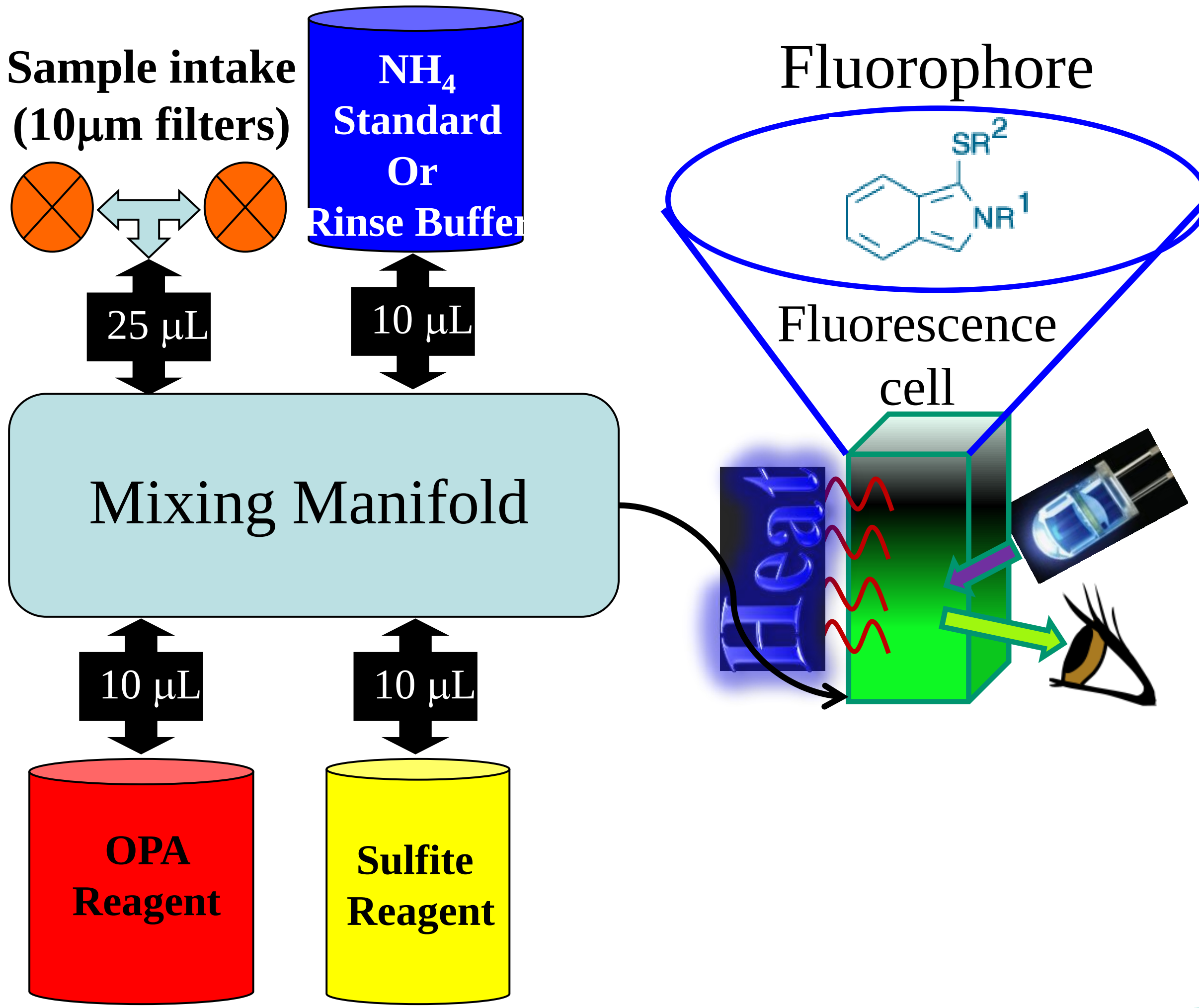
56 cm

6.8 kg

Alliance of Coastal Technologies report No. ACT-06-08

Priority Nutrients	Desired Precision	Desired Limit of Detection
Ammonium (NH_4^+)	0.1 µM	1 µM

Instrument and Chemistry



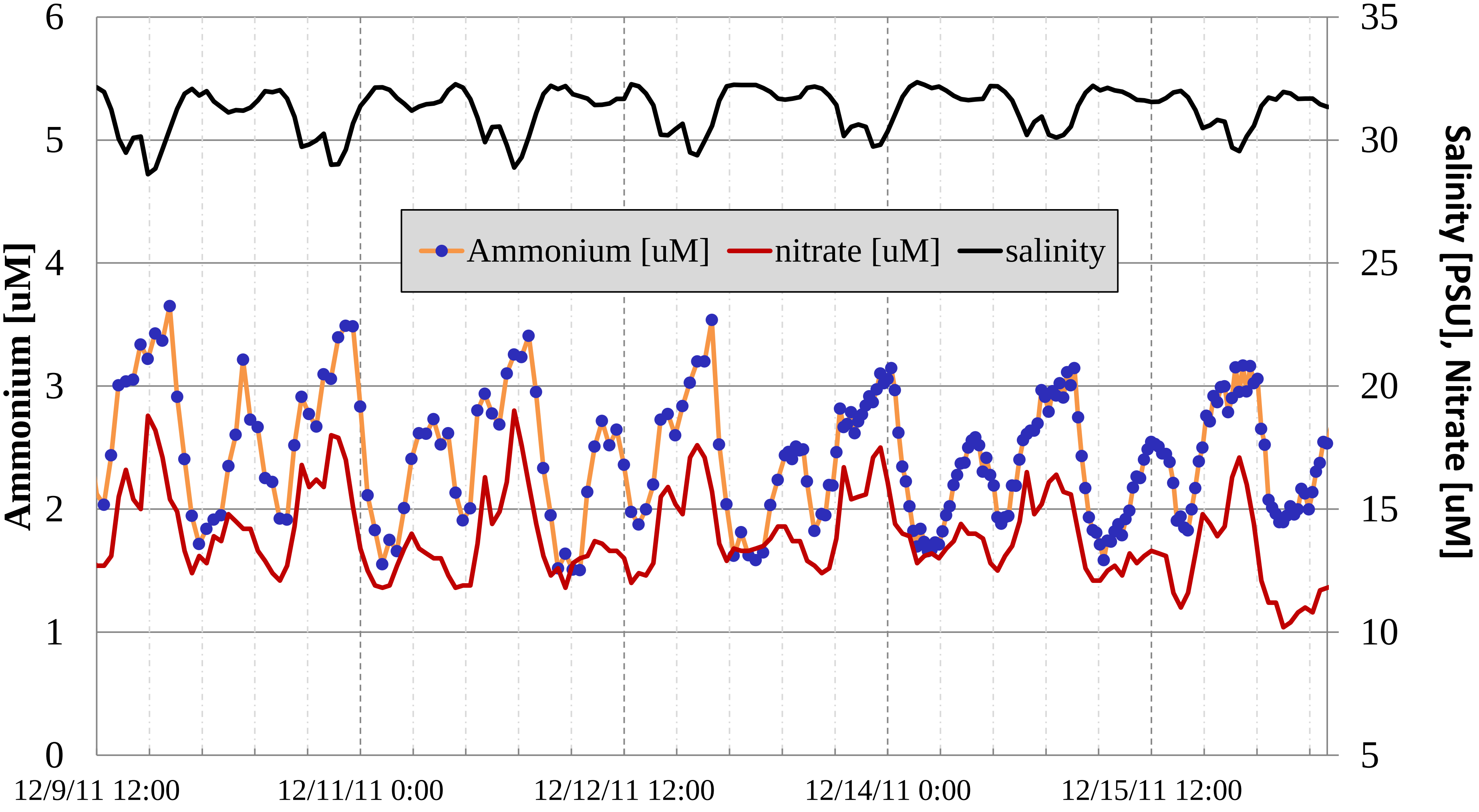
Heated, thermostated reaction chamber

LEDs

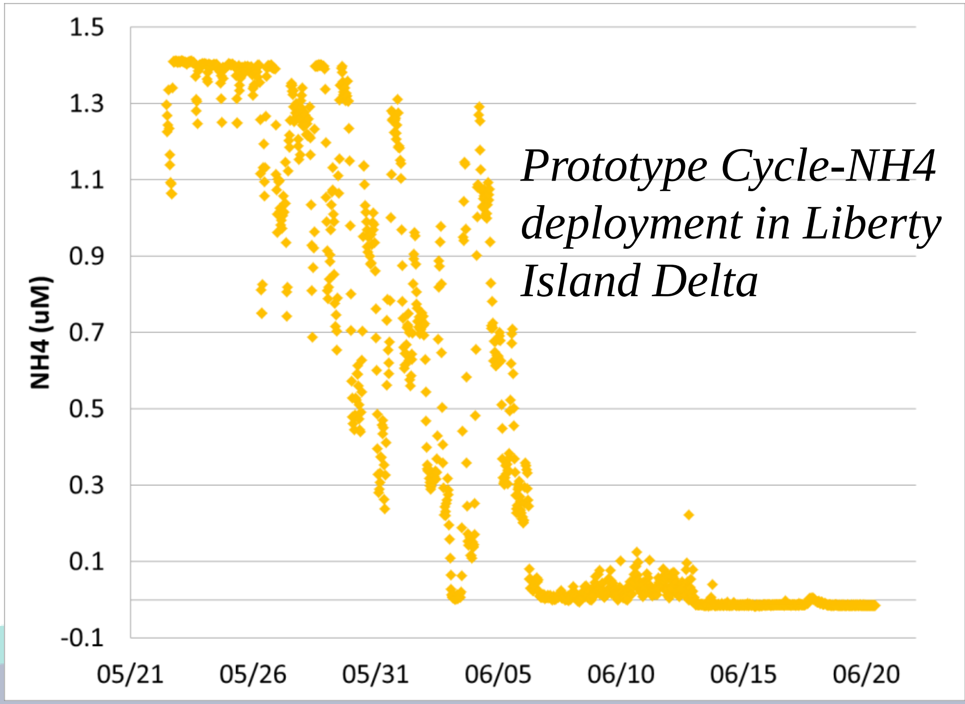
Interference filters

Silicon photodiode detector

Alpha testing Yaquina Bay Deployment



- More development needed into reagent stability
- Need to understand stability over time and temperature to characterize drift
- Better methods needed to supply reagents to minimize decay time
- Interference of CDOM and NTU needs to be characterized



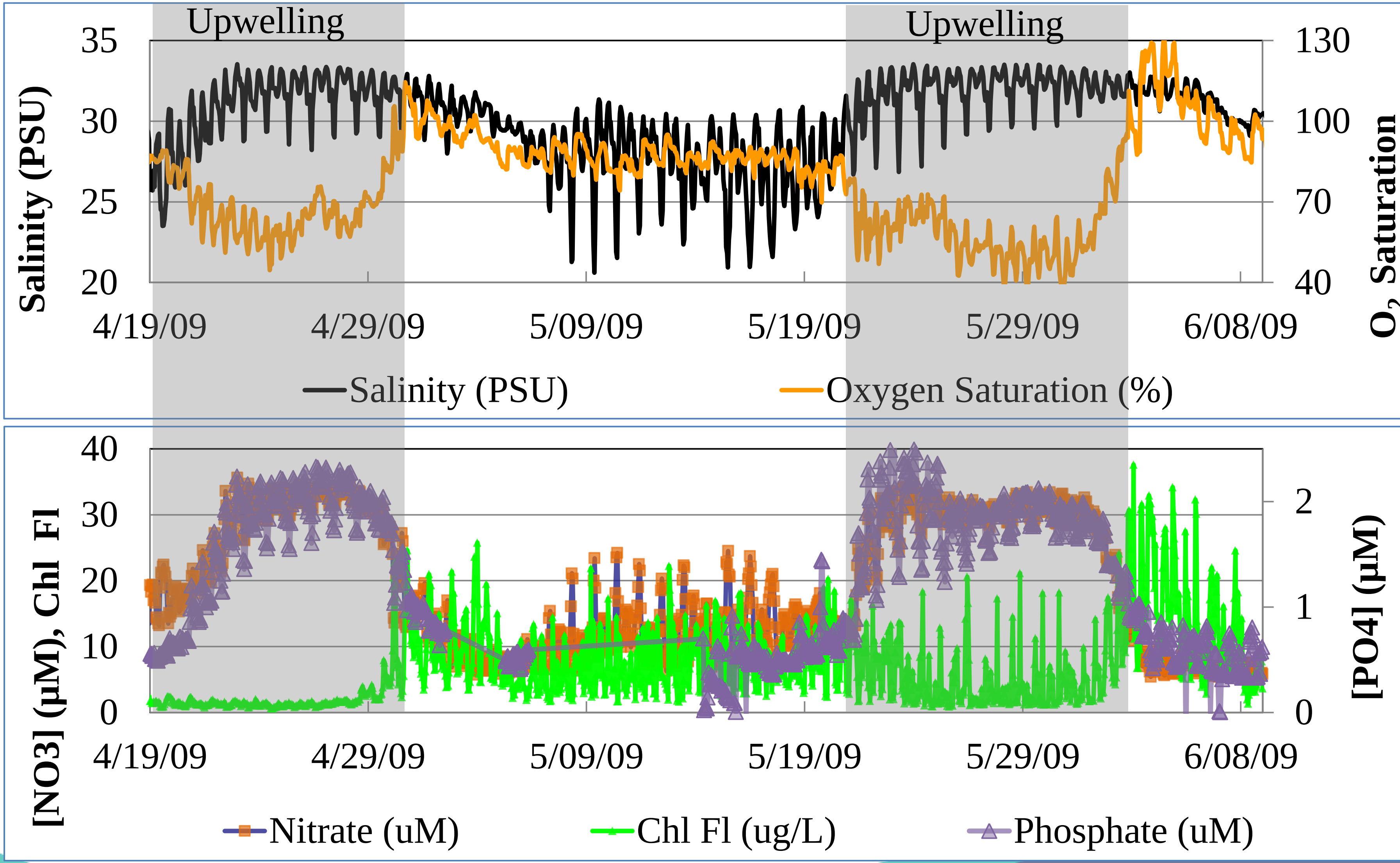
Yaquina Bay Productivity

•Mesotidal, drowned river estuary affected by seasonal upwellings
•Watershed: 655 km^2, ~93% forested (~15% N-fixing red alder), 1 waste treatment plant, ~80% precipitation from Nov. to April
(Brown & Ozretich; Sigleo & Frick)

•Hourly observations 2009-2013
- •LOBO (data control, management, power)
- •SUNA (optical nitrate sensor)
- •Cycle-P (wet chemical phosphate)
- •WQM (Salinity, Temperature, DO, Pressure)
  - •ECO (CDOM Fluorescence, Turbidity, Chlorophyll Fluorescence)

•Serviced every 6-12 weeks

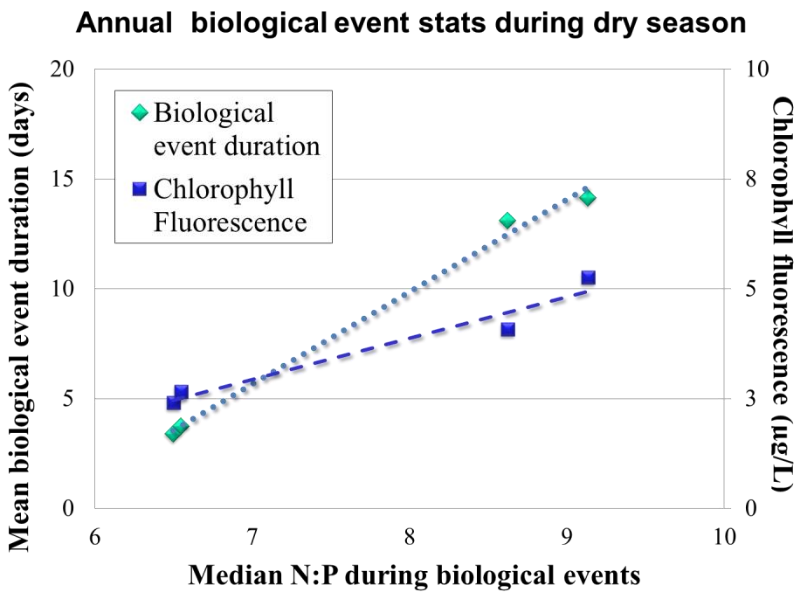
Yaquina Bay Upwelling Response

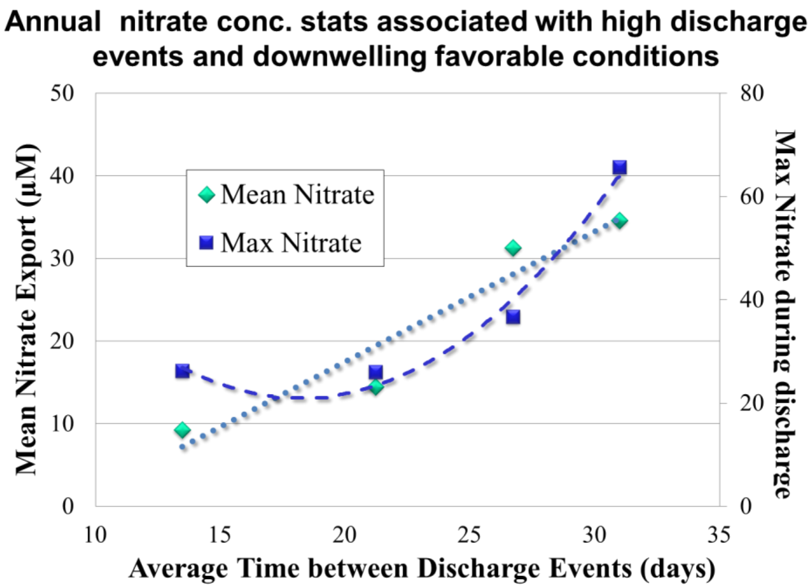


- NO3:PO4 axis16:1; upwelled nutrients in Redfield ratios drive blooms

Yaquina Bay Inter-annual variability

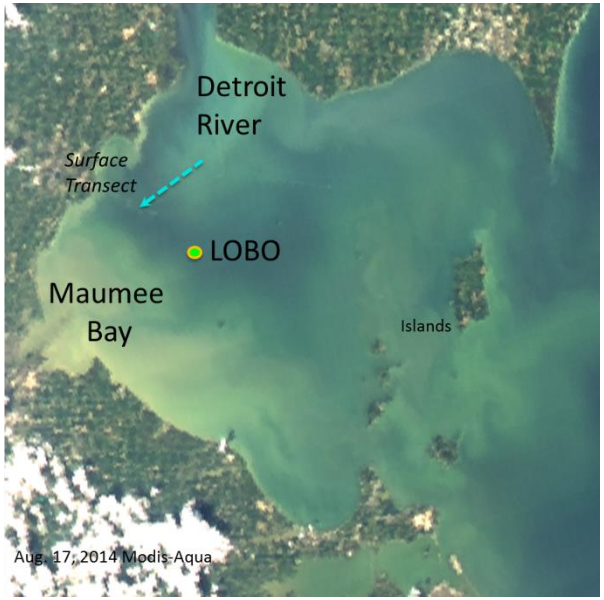
• Aggregate hourly data (2009-2013) powerful tool to describe system dynamics





- **N:P ratio correlated with bloom duration and mean Chlorophyll**
- **Time between discharge events controls NO_3^- export**

Western Lake Erie Harmful Algae



- Widespread Microcystis blooms in late summer to early fall
- Produce toxins that severely impact fisheries, recreation, and drinking water sources
- Suite of in-situ sensors was deployed to continuously monitor water quality, nutrients, and algal blooms.
    - Optimize statistical ecological niche models to develop predictive models

NOAA GLERL

Timothy Moore (UNH), Mike Twardowski (Sea-Bird), Corey Koch (Sea-Bird), NOAA GLERL

Western Lake Erie Harmful Algae

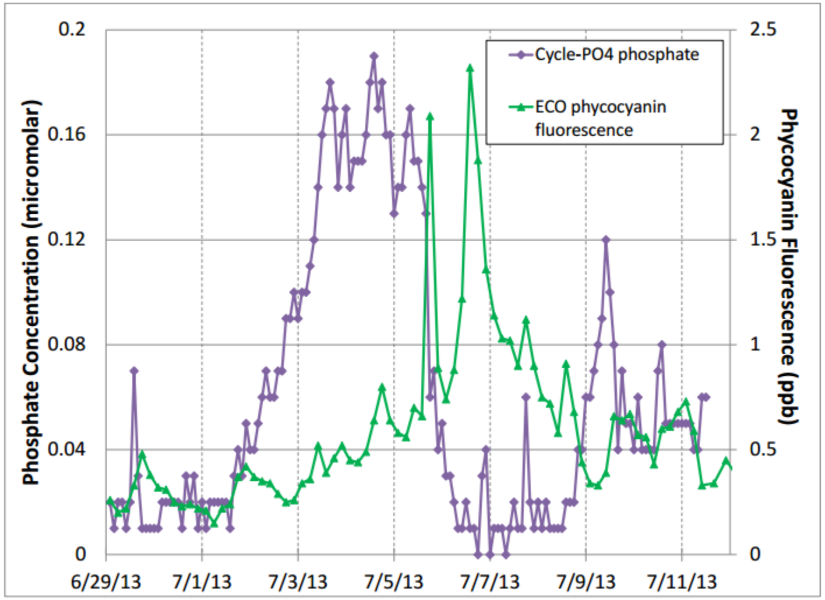
- LOBO is seasonally located next to the Toledo Light #2,
  - hot spot for cyanobacterial blooms
  - Blooms fueled by nutrients brought to the surface by wind mixing
  - spring nutrient input from the Maumee pre-determins overall nutrient levels.
- Conductivity, temperature, dissolved oxygen, chlorophyll fluorescence (WQM), phycocyanin fluorescence (ECO), turbidity, and phosphate (Cycle-PO4)

Results

•Summer of 2013 monitored surface phosphate pulses thought to come from wind mixing in WLE

•Conductivity and CDOM often correlate with phosphate, suggesting Maumee or, wind driven, resuspension sources. Detroit River may dilute apparent concentrations.

•As phosphorus was consumed, phycocyanin fluorescence spiked in conjunction with blooms observed from ships transects and satellite imagery.



Challenges

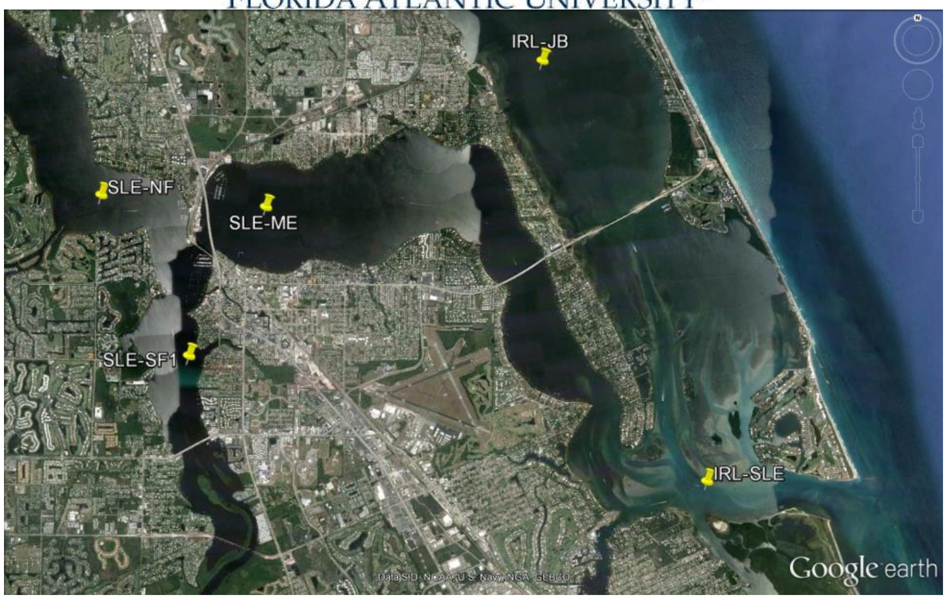
•PO_4 gets less precise as the bloom progresses – likely due to filter impaction. Limited ability to understand response to PO_4 once bloom was large due to low levels and eroded precision.

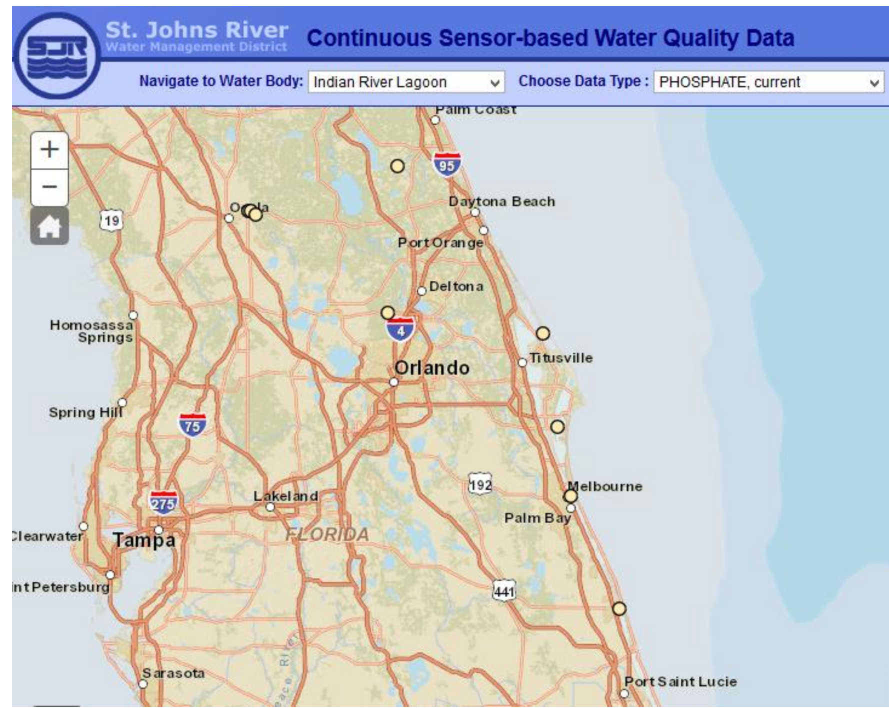
•PO_4 is often near the detection limit except for quickly consumed pulses into the system.

Indian River Lagoon

- Trying to understand Ag discharges, HABs, and die-offs in the lagoon

HARBOR BRANCH
FLORIDA ATLANTIC UNIVERSITY





- ~10 nutrient buoys, ~10 opportunity moorings