

Measuring Nitrate at the Stream

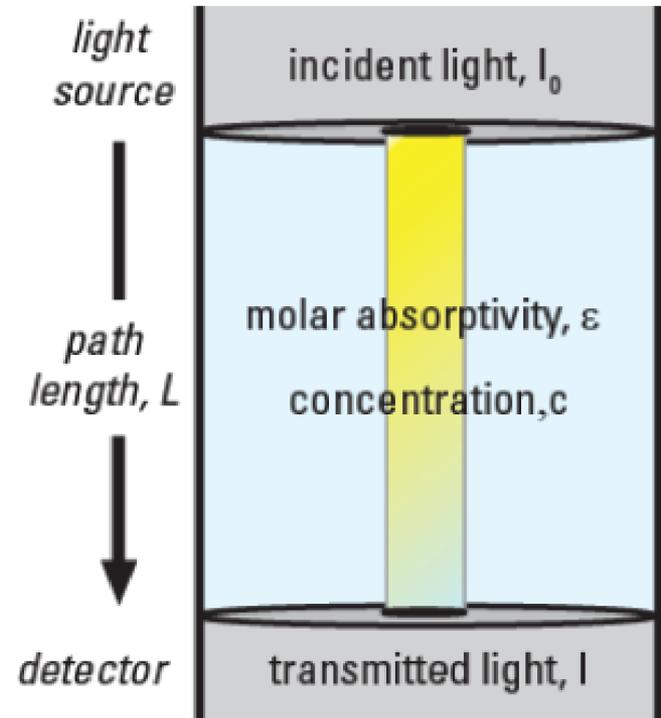


Advantages of instream or streamside NO₃ monitoring

- Permits near-continuous measurement of NO₃
- No need to transport samples back to the laboratory
- Fewer concerns about potential sample contamination
- NO₃ data can be telemetered and observed in real time
- Can provide real-time alerts of water contamination events
- Some NO₃ sensors can also measure other parameters

How optical nitrate sensors work

- Sensors measure amount of light transmitted through the water
- Concentration determined as a function of absorbance, path length, and molar absorptivity of the substance at a given wavelength



Beer's Law

$$A = 2 - \log_{10} \%T$$

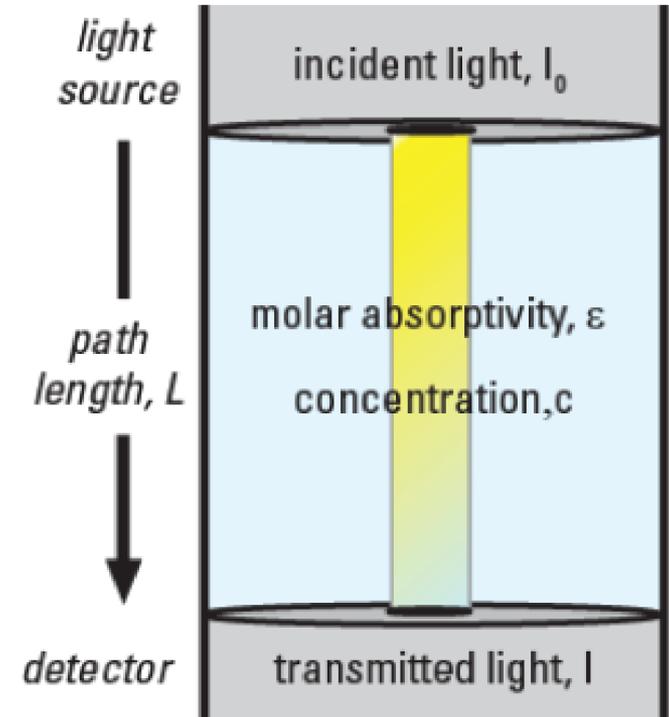
where

A is absorbance, and
 $\%T$ is transmittance as a percentage (that is,
 $100 \times I/I_0$).

$$c = \frac{A_\lambda}{\epsilon_\lambda * L}$$

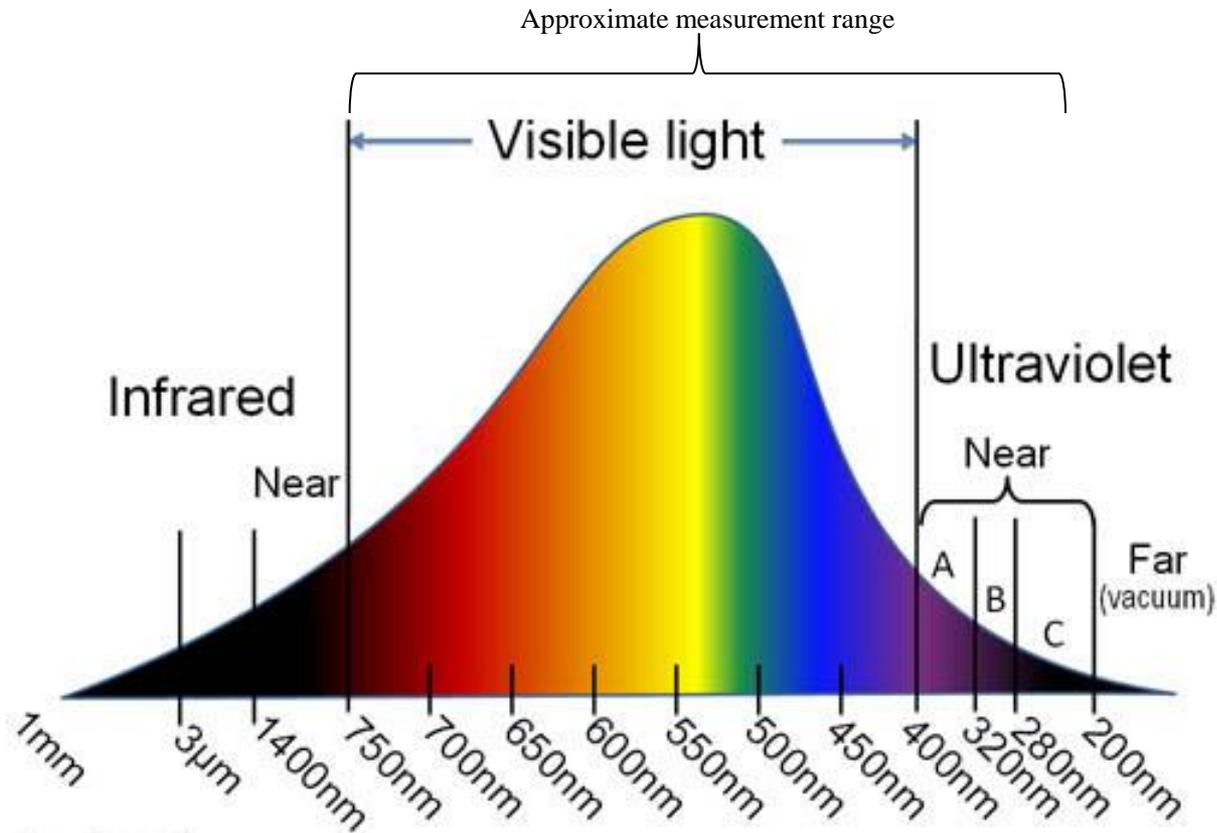
where

c is the concentration of the absorbing
substance,
 A_λ is the absorbance at a specific wavelength (λ),
 ϵ_λ is the molar absorptivity of the absorbing
substance at wavelength λ (a constant), and
 L is the path length.

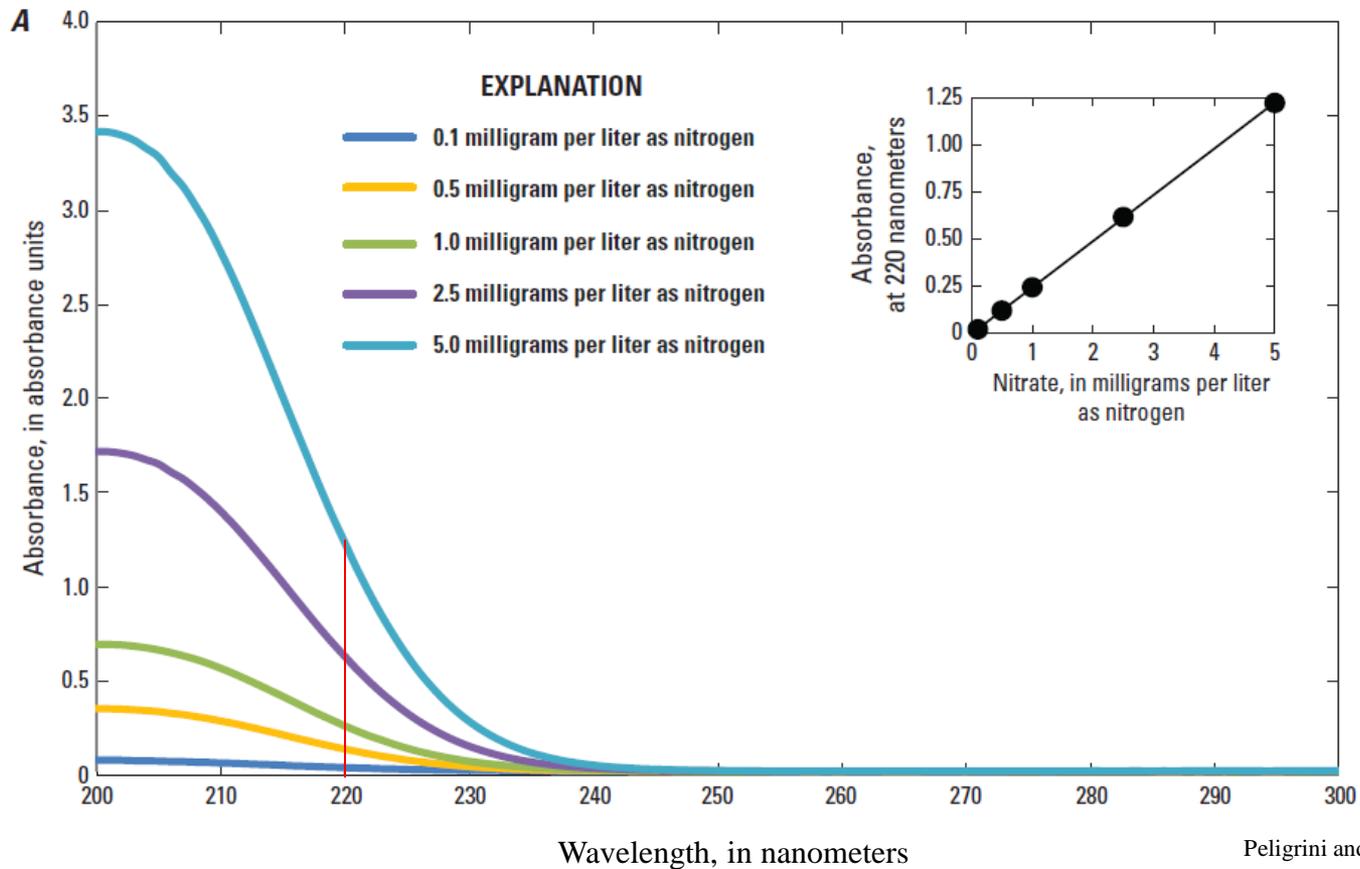


Peligrini and others, 2013

UV-Vis Sensors



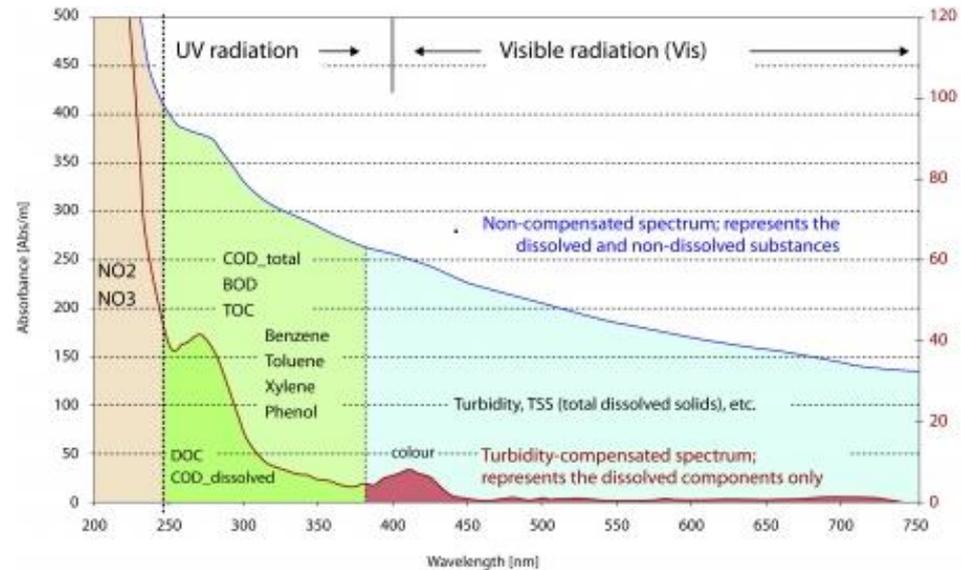
NO₃ absorbance characteristics



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Matrix correction

- To accurately measure NO_3 optically in natural waters, one must account for light-absorbing or light-scattering materials present in the sample (i.e. matrix effects) that interfere with light transmission
- Most instruments use multiple wavelengths to distinguish the absorption due to NO_3 from that due to other substances in the matrix



Several NO₃ sensors on market

Table 2. Ultraviolet (UV) nitrate sensor design and manufacturer-stated data specifications.

[Abbreviations: in, inches; lbs, pounds; m, meters; mg/L as N, milligrams per liter as nitrogen; mm, millimeters; nm, nanometers; sec, seconds; °C, degrees Celsius; %, percent]

Parameter	HACH Nitratax	Satlantic SUNA	S::CAN spectrolyzer	TriOS ProPS
Pathlengths available (mm)	1, 2, 5 (fixed)	5, 10 (fixed)	0.5–100 (semi-fixed)	1–60 (semi-fixed)
Wavelengths measured (nm)	220, 350	190–370	200–750	190–360
Approximate dimensions (in)	13.0 x 3.0	21.0 x 2.3	21.5 x 1.7	20.5 x 2.7
Weight in air (lbs)	7.3–7.9	5.4	7.5	11
Housing materials available	stainless steel	acetal, titanium	stainless steel	stainless steel, titanium
Lamp type	xenon	deuterium	xenon	deuterium
Reference beam	yes	no	yes	No
Windows	quartz	quartz	sapphire, fused silica	fused silica + nano coating
Communications	Modbus (RS485, RS232), USB, RS232, SDI-12, analog	analog	Modbus (RS485, RS232), SDI-12, analog	RS232
Power consumption	24 VDC	8...18 VDC	11...15 VDC	9...36 VDC
Connectors	integrated cables	wet pluggable	integrated cables	wet pluggable
Anti-fouling method	wiper (silicone)	wiper (nylon brush)	wiper or compressed air	compressed air + nano coating
Operating Temperature (°C)	2–40	0–40	0–45	0–40
Maximum operating depth (m)	5	100 ^b	100	500 ^b
Lower detection limit (mg/L as N)	0.1–1.0 ^a	0.007	0.03	0.005–0.3 ^a
Upper detection limit (mg/L as N)	20–100 ^a	28–56 ^a	10–70 ^a	8.3–500 ^a
Accuracy	±3–5% of reading or ±0.5–1.0 mg/L, whichever is greater ^a	±10% of reading or ±0.03–0.06 mg/L, whichever is greater ^a	±2% of reading plus 1/optical path length (in mm; mg/L)	±2% of reading or ±0.155 mg/L, whichever is greater
Precision (mg/L as N)	0.1–0.5 ^a	0.028	0.02–0.1 ^a	0.03
Maximum sampling interval (sec)	60	1	60	120

^aActual specifications dependent on the model used, pathlength, or both.

^bOptions available for deep sea deployments (500 and 2,000 m for SUNA, 6,000 m for TriOS).

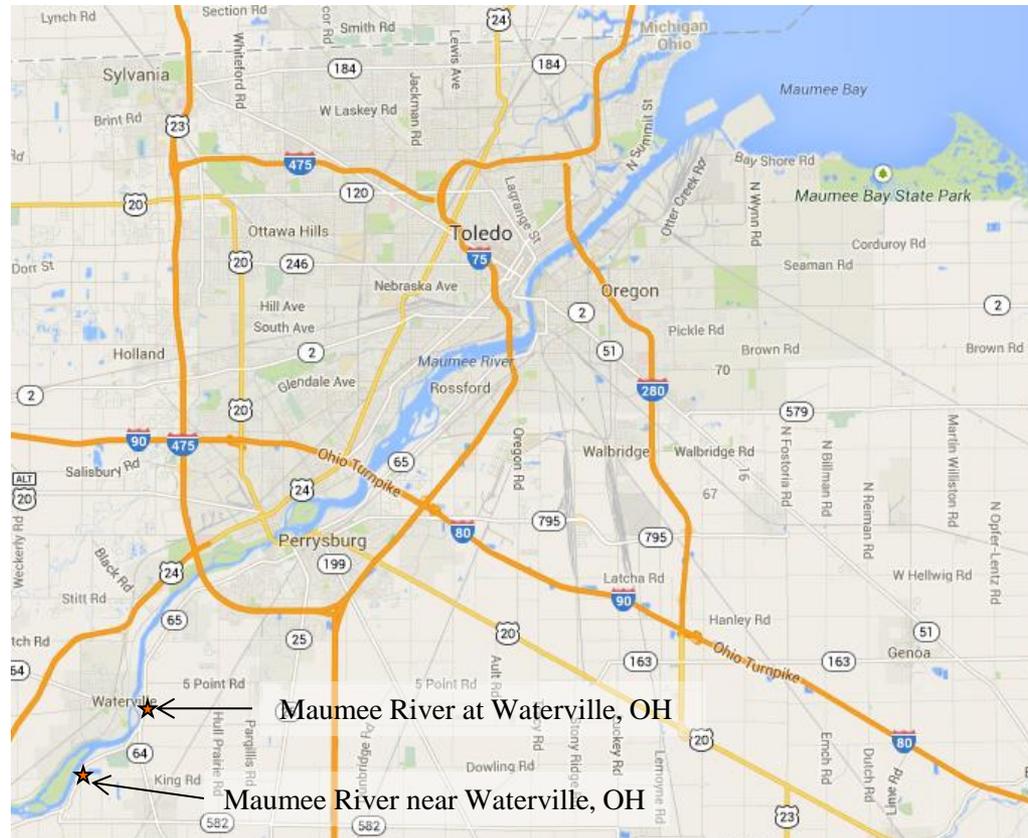
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S::can Spectro::lyser

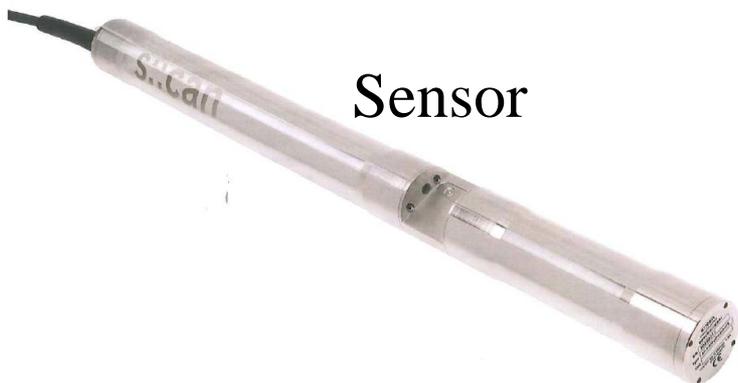
- UV-Vis unit can be configured to measure¹:
 - NO₃-N, NO₂-N
 - Turbidity, TSS
 - COD & BOD
 - TOC, DOC, AOC
 - UV254 (surrogate for natural organic matter in water)
 - color
 - BTX (benzene, toluene, xylene)
 - O₃ (ozone)
 - H₂S



Installation Location



What is installed



Sensor

Con::cube (controller)



Compressor

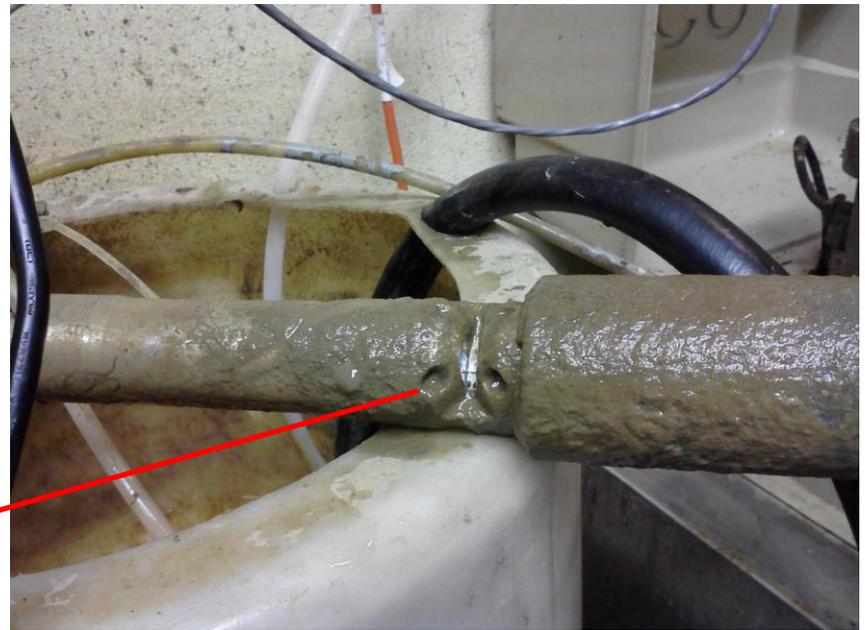


CR1000



Installation configuration

- Sensor is installed in flow-through tank owned by Heidelberg Univ.
- Measurements currently being made at 2 min. intervals



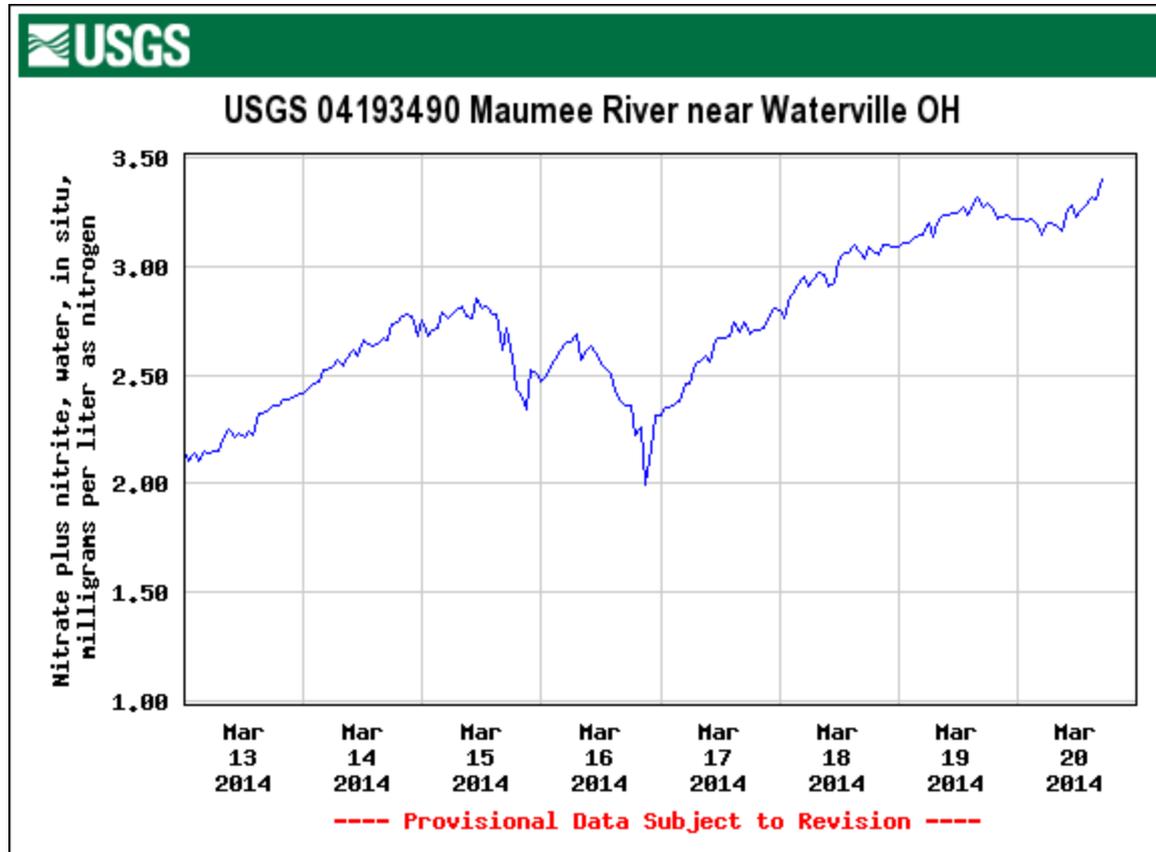
Summer service interval ~2 weeks

Installation configuration

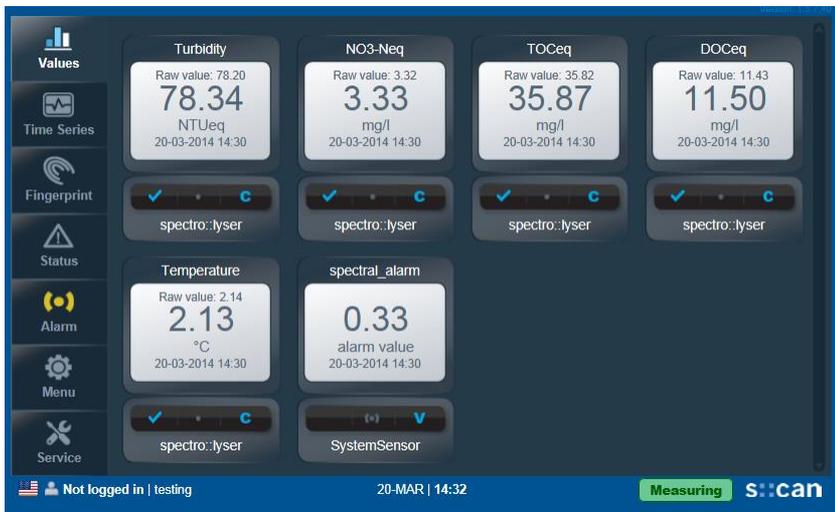
- Con::cube is interfaced via SDI-12 with CR1000
- Con:cube and CR1000 are connected to Internet via cell modem
- Campbell Loggeret software is used to retrieve data hourly
- Retrieved data are automatically loaded into our time-series database and pushed to the Web



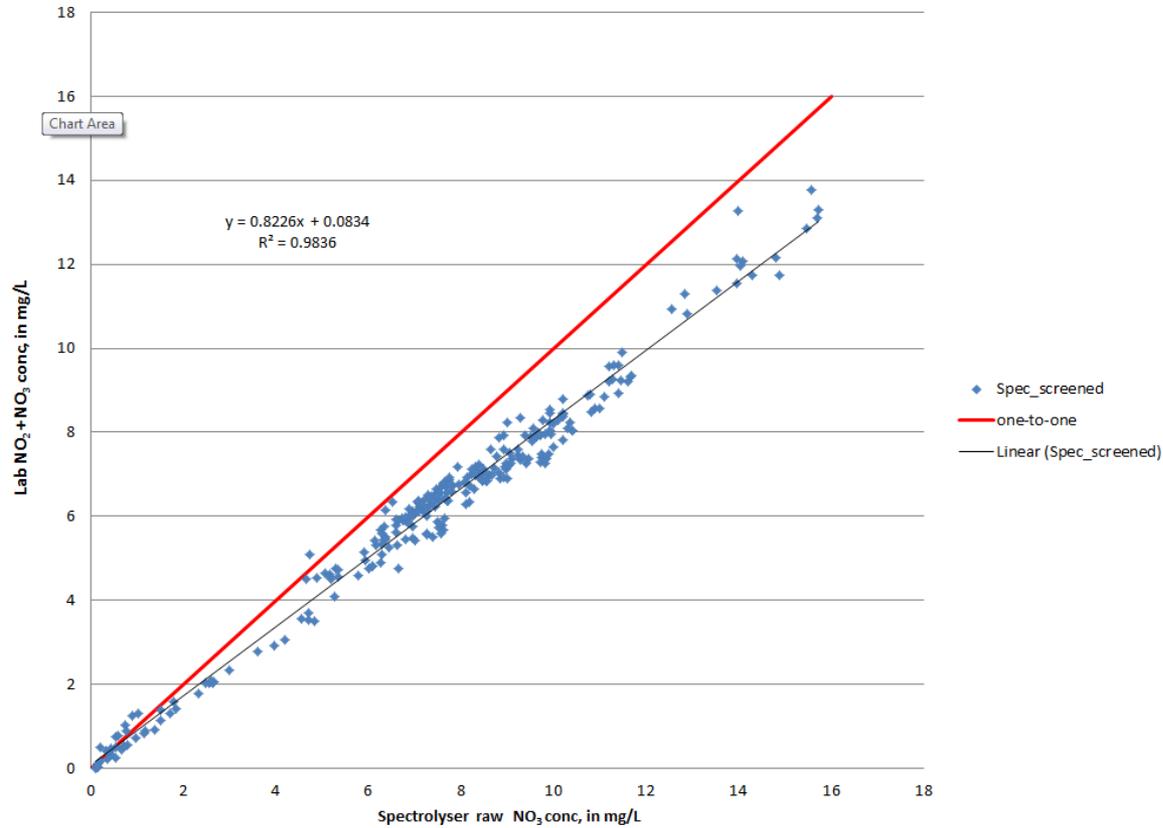
NWISWeb



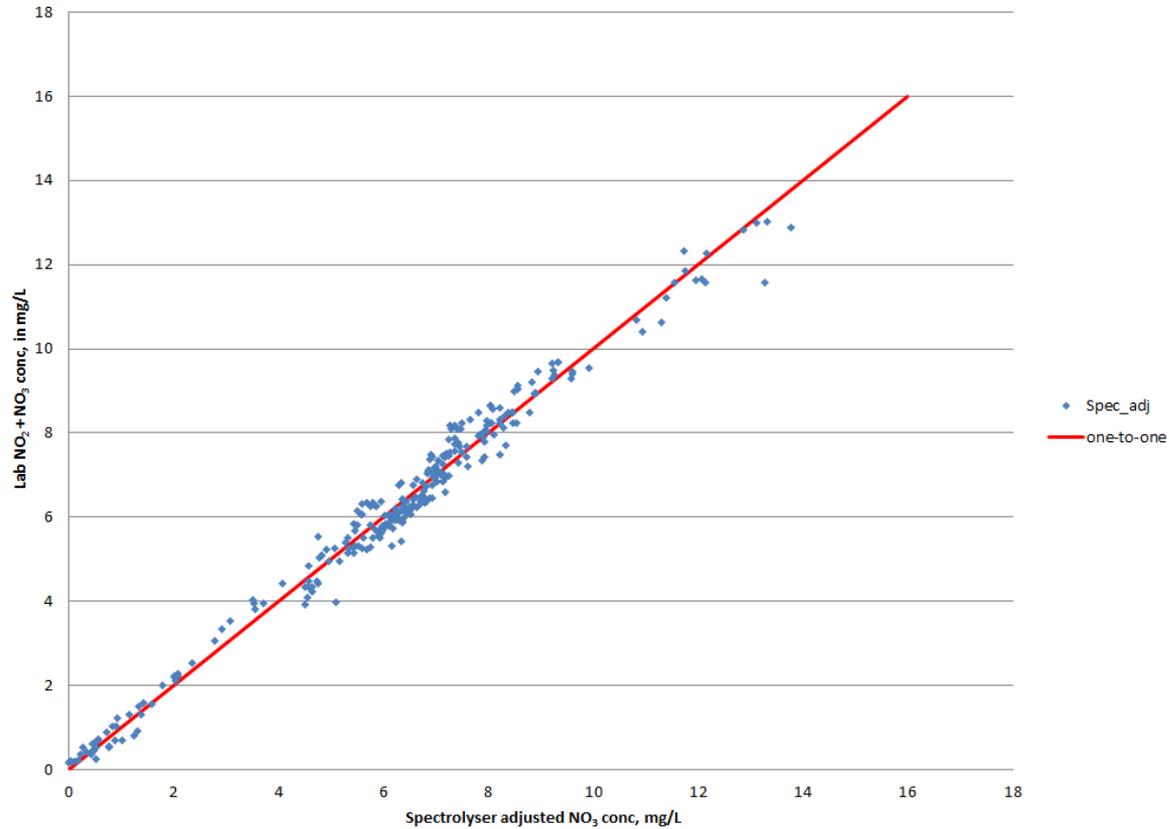
Direct Data Access



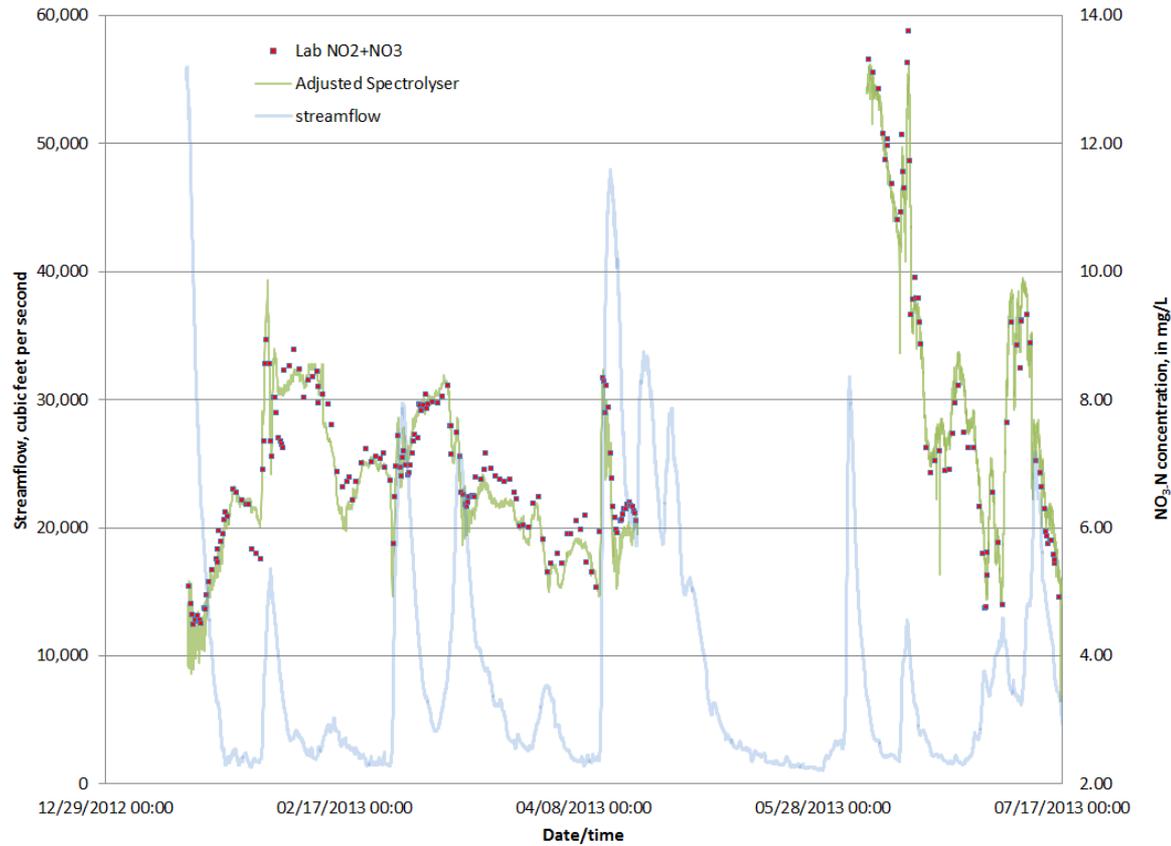
Raw concentration results



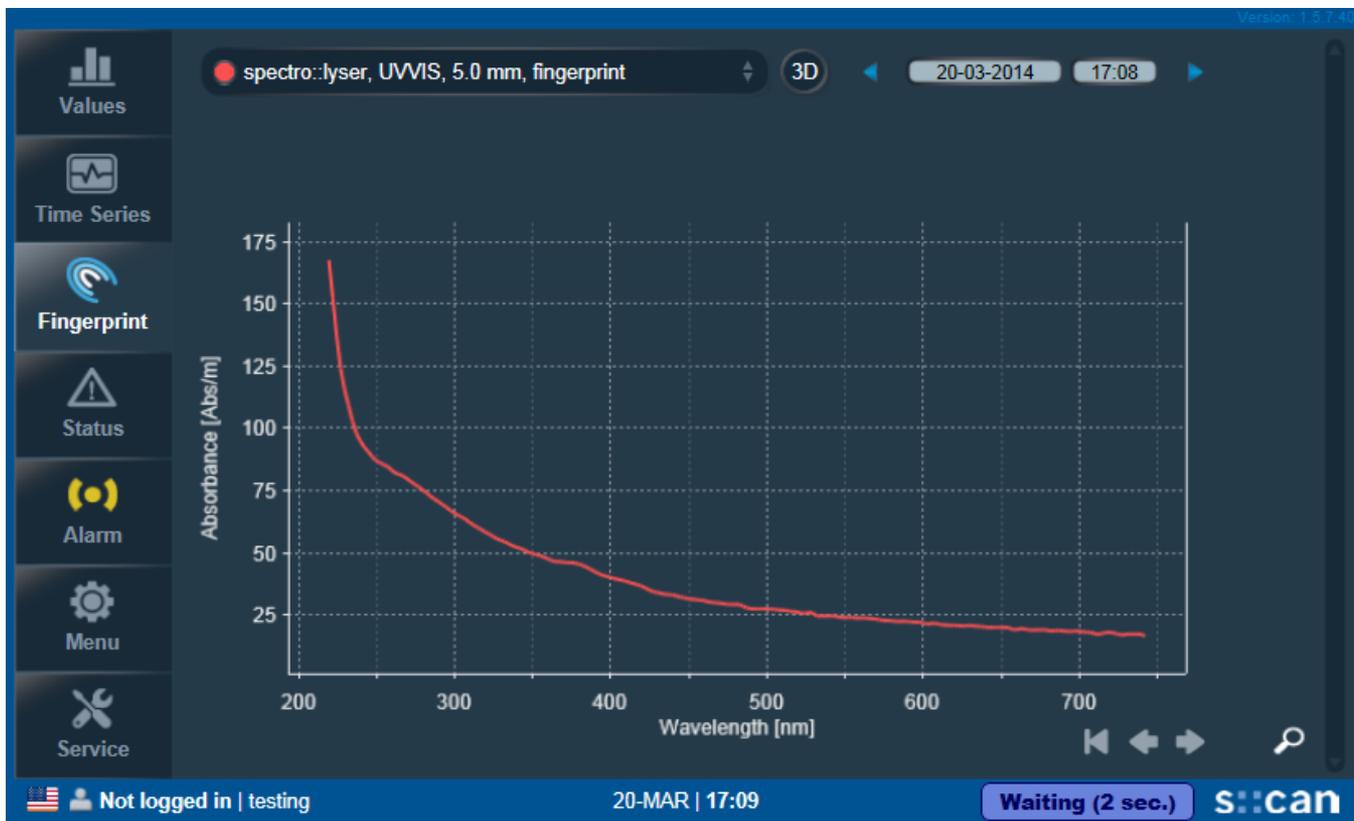
Adjusted concentration results



Time-series comparison

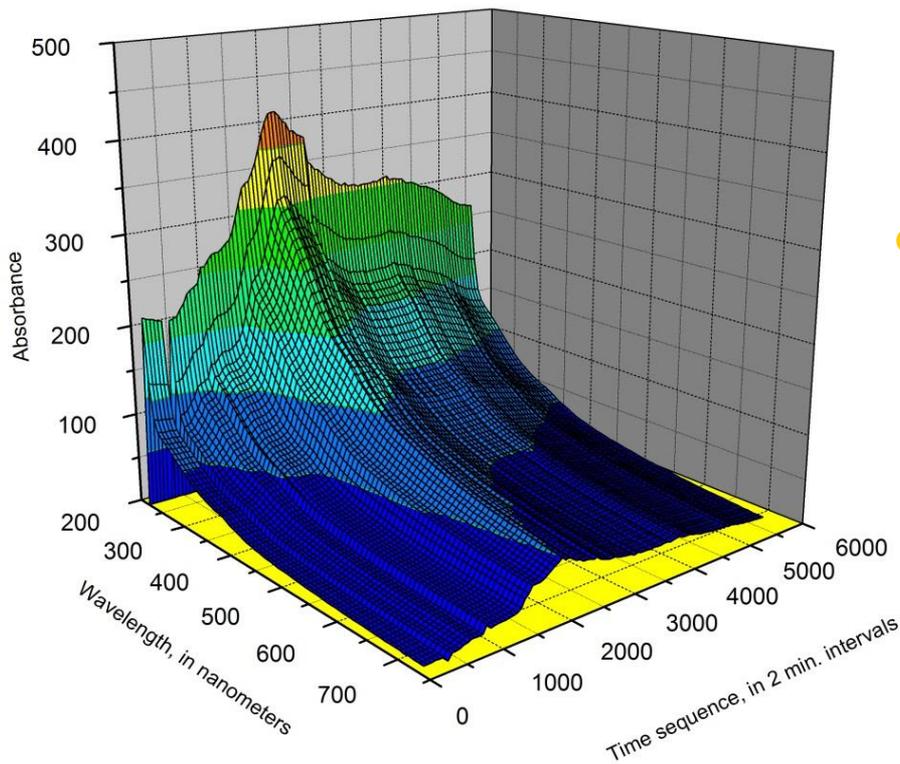


Absorbance Spectra (“Fingerprint”) results



Absorbance Spectra (“Fingerprint”) results

Absorbance spectra time series
03/10/2013 – 03/18/2013



- Can download time series of absorbance spectra
- Absorbance output for wavelengths from 220 to 742.5 nm in 2.5 nm bins

General Impressions



- **Good**

- Spectrolyser has worked well
- Good data quality and excellent data access
- Minimal maintenance

- **Bad**

- High initial price (>\$30K), cheaper version available
- Poor product manuals and customer service

Acknowledgements



- U.S. Army Corps of Engineers
- Heidelberg University National Center for Water Quality Research

For more information ...

Available at:

<http://pubs.usgs.gov/tm/01/d5/>

