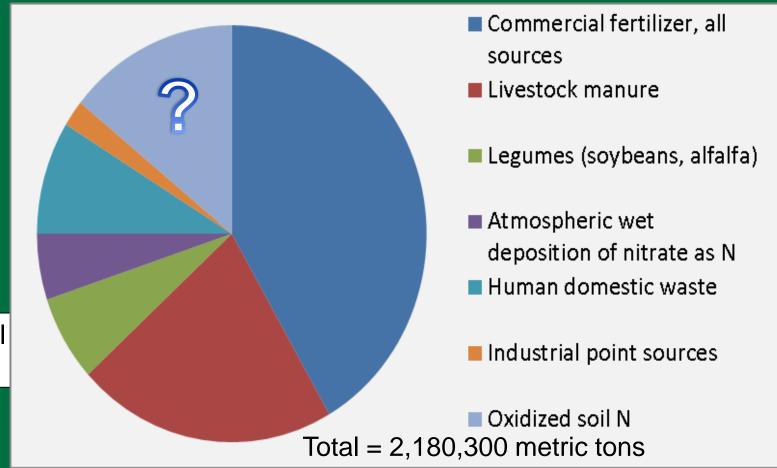


# Real-time Nitrate Monitoring in Streams and Rivers

**Tim Lathrop** 



## What is the source of Nitrogen in our water ways?



Oxidized soil Nitrogen?

Estimates for percent contributions of annual nitrogen for the Ohio River Basin



### Nitrogen and Water

- Nutrients are essential for plant growth
  - Rapid growth, leaf size and quality, hasten crop maturity, promotes fruit and seed development
- Nitrogen is a constituent in amino acids and thereby plays a role in photosynthesis

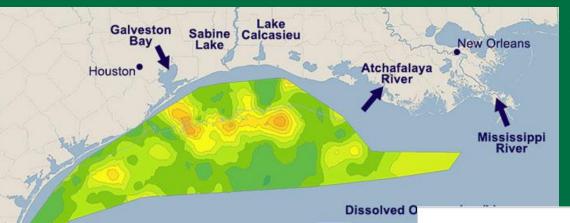
M. Ray Tucker, NCDA, 1999







#### **Gulf of Mexico Hypoxia**



0.0 - 0.5

0.51 - 1.0

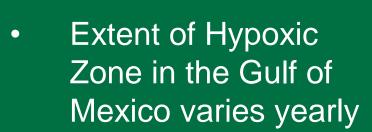
1.01 - 1.5

1.51 - 2.0 2.01 - 2.5

2.51 - 3.0

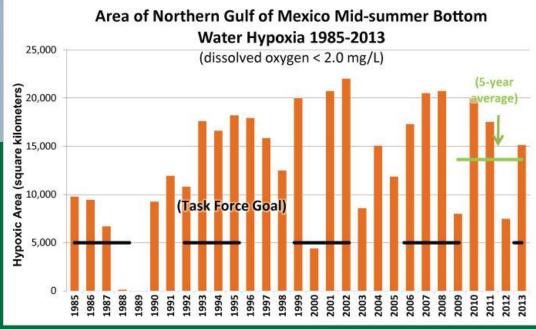
3.01 - 3.5 3.51 - 4.0

- Hypoxia means low oxygen
- Causes: excess nutrients, water body stratification



Brownsville WWW.EPA.gov, 2014

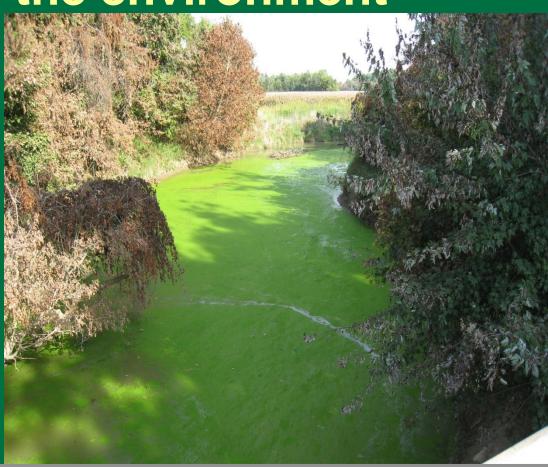




N.N. Rabalais, Louisiana Universities Marine Consortium, R.E. Turner, Louisiana State University, 2013

## Problems with excess levels of nutrients in the environment

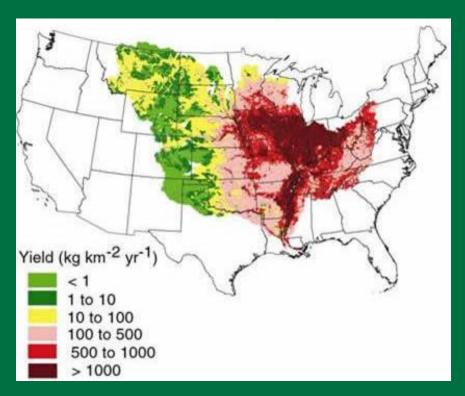
- Eutrophication excessive aquatic plant growth, especially algae
- Clog water intakes, use up DO when decomposing
- Can lead to fish kills, decreased animal and plant diversity
- Negative effects for recreation (boating, fishing, and swimming)
- Health problems
  - Blue baby syndrome
  - Taste and odor



Algae bloom fouls tap water in Indianapolis, Muncie (May 4, 2010 Indianapolis Recorder Newspaper)



## Nitrogen contributions to the Gulf of Mexico vary by state

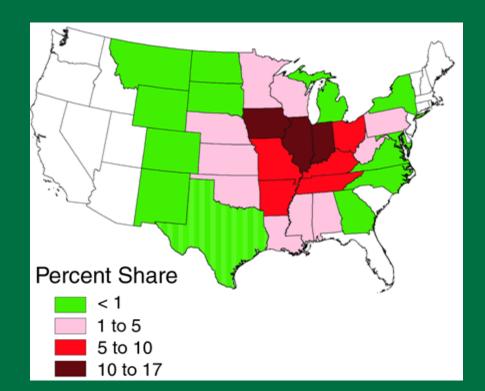


#### Sparrow Model, USGS

http://water.usgs.gov/nawqa/sparrow/

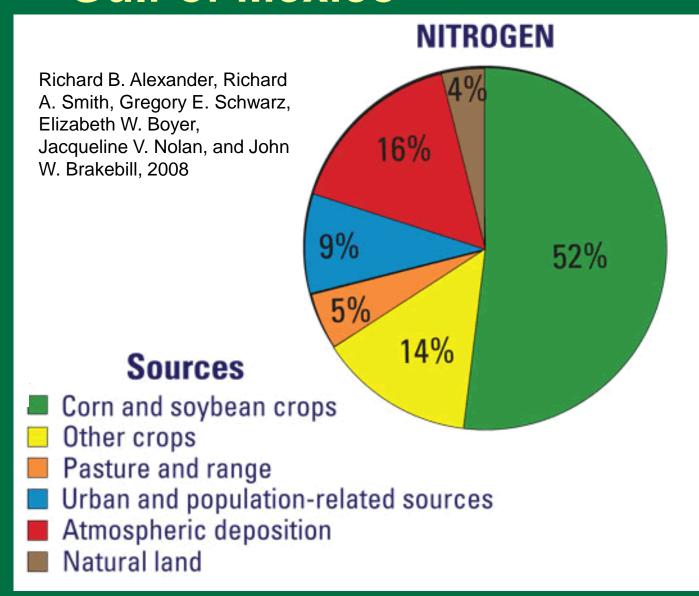


Richard B. Alexander, Richard A. Smith, Gregory E. Schwarz, Elizabeth W. Boyer, Jacqueline V. Nolan, and John W. Brakebill, 2008



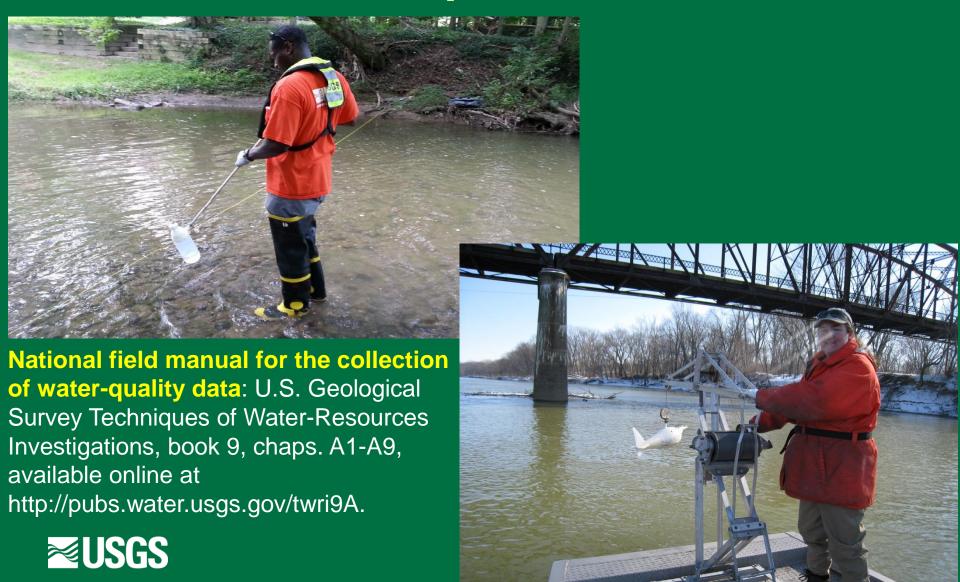
## Sources of nitrogen delivered to the Gulf of Mexico

- 66% of nitrogen originates from cultivated crops
- Atmospheric deposition is an important source



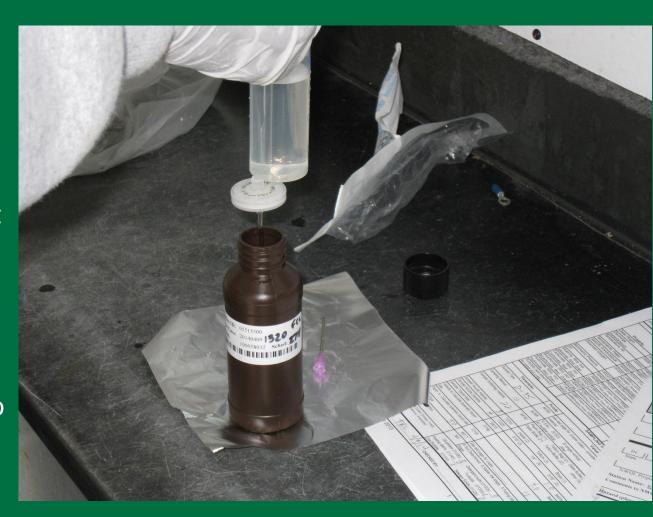


### **USGS Sample Collection**



### Nitrate is a dissolved constituent

- Filter water sample with a 0.45 micron filter.
- USGS samples are typically analyzed at the National Water Quality Laboratory, Denver
- Replicate and Field Blank samples are collected annually to check for bias



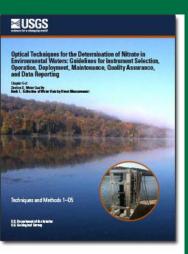


#### Why continuous and real-time?

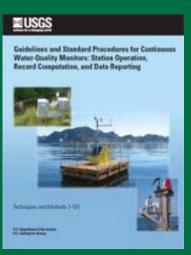
- 1. USGS water-quality data is available in near realtime on the internet
- 2. Time-density improves our knowledge and understanding of the relation between water quality and changes in hydrology, geology, and land use
- 3. Increased data-collection frequency provides an improved understanding of cause/effect relations
- 4. Richer data sets for developing tools and models
- 5. Notification of water resource managers in real time
- 6. Decreases time and costs associated with manual sampling
- 7. Better measures of water quality compared to monthly samples
- 8. Continue to run when you go home and capture hard to anticipate storm events



#### Questions for O&M of continuous sensors?



Pellerin, B.A. Bergamaschi, B.A., Downing, B.D., Saraceno, J.F., Garrett, J.A., and Olsen, L.D., 2013, **Optical techniques** for the determination of nitrate in environmental waters: Guidelines for instrument selection, operation, deployment, maintenance, quality assurance, and data reporting: U.S. Geological Survey Techniques and Methods 1-D5, 37p.



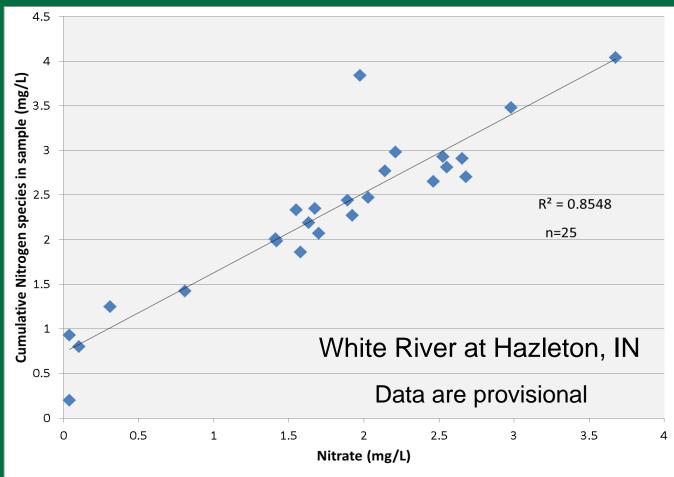
Wagner, R.J., Boulger, R.W., Jr., Oblinger, C.J., and Smith, B.A., 2006, **Guidelines and standard procedures for continuous water-quality monitors – Station operation, record computation, and data reporting**: U.S. Geological Survey Techniques and Methods 1-D3, 51 p. + 8 attachments



Both can be found at *http: pubs.water.usgs.gov* 

## Nitrate is used as a surrogate of Total Nitrogen

- Many forms of nitrogen in typical USGS Total Nitrogen collection
  - Nitrate
  - Organic N
  - Nitrite
  - Ammonia





### **USGS IN field tested - YSI 9600**





Range 0-10mg/L, Accuracy +-5%

Cadmium reduction principle

YSI discontinued production in 2011



#### **USGS IN field tested - HACH Nitratax**





#### **USGS IN field tested - Satlantic SUNA**



Range 0.007–56 mg/L, Accuracy 10% of the reading



### **Manufacturer specifications**

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) analog	, USB, RS232, SDI-12, analog	Modbus (RS485, RS232) SDI-12, analog	), RS232
Power consumption	24 VDC	818 VDC	1115 VDC	936 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 <sup>6</sup>	100	500 <sup>6</sup>
Lower detection limit (mg/L as N)	0.1-1.0*	0.007	0.03	0.005-0.3*
Upper detection limit (mg/L as N)	20-100 <sup>a</sup>	28-56*	10-70°	8.3-500*
Accuracy	±3-5% of reading or	±10% of reading or	±2% of reading plus	±2% of reading or
-	±0.5-1.0 mg/L,	±0.03-0.06 mg/L,	1/optical path length	±0.155 mg/L,
	whichever is greater*	whichever is greater*	(in mm; mg/L)	whichever is greater
Precision (mg/L as N)	0.1-0.5*	0.028	0.02-0.1	0.03
Maximum sampling interval (sec)	60	1	60	120

<sup>&#</sup>x27;Actual specifications dependent on the model used, pathlength, or both.

<sup>\*</sup>Options available for deep sea deployments (500 and 2,000 m for SUNA, 6,000 m for TriOS). Pellerin and others, 2013





#### **Principle of Operation**

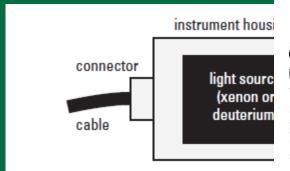
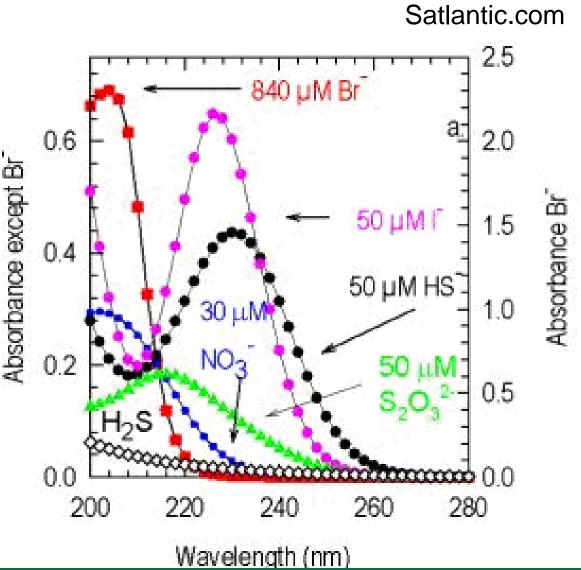


Figure 4. General design and key compothers, 2004).





#### Instrument Performance Qualification

- Check the monitor prior to initial deployment
  - 1. Visual inspection
    - Serial numbers
    - Scratches, dents, nicks
    - Optical window
    - Electrical connector
    - Wipers
  - 2. Operational inspection
    - Up to date software
    - Apply power, insure unit is functioning
    - Calibration checks



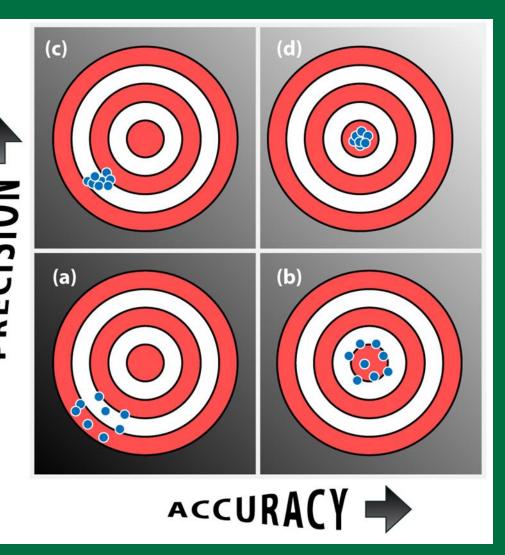
#### **Instrument Performance (cont.)**

- Calibration checks
  - 1. Inorganic-grade b
  - 2. Series of reagentsolutions covering environment

    Accuracy – absolutions measured concentions

    Linearity – least serior

    - **Precision Perfor** the standard devia measured and know
    - **Turbidity checks**





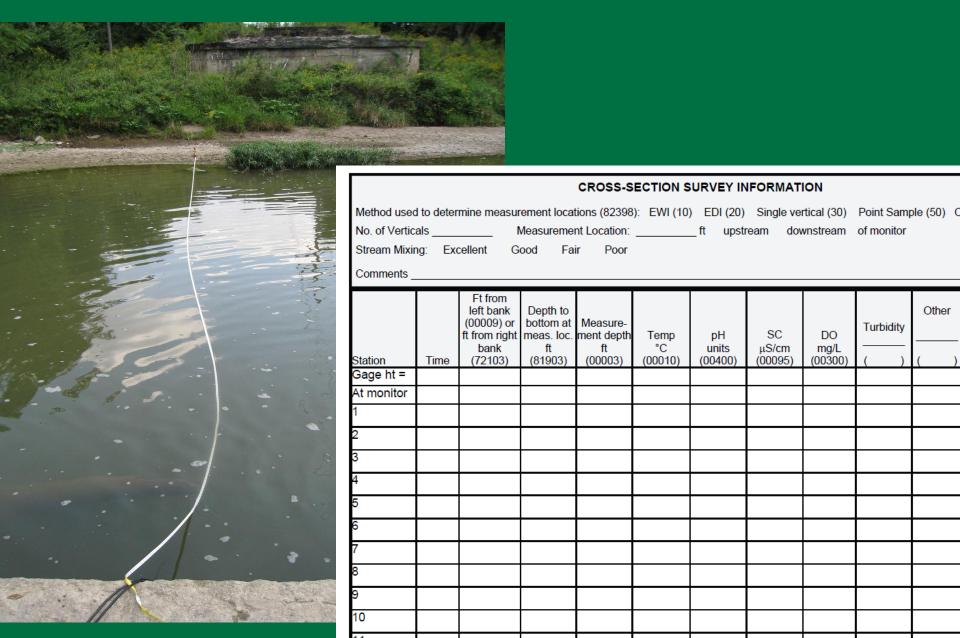
### **Instrument Performance (cont.)**

Calibration checks





#### Site selection



## Nitrate monitors are deployed at USGS Sentry Gages

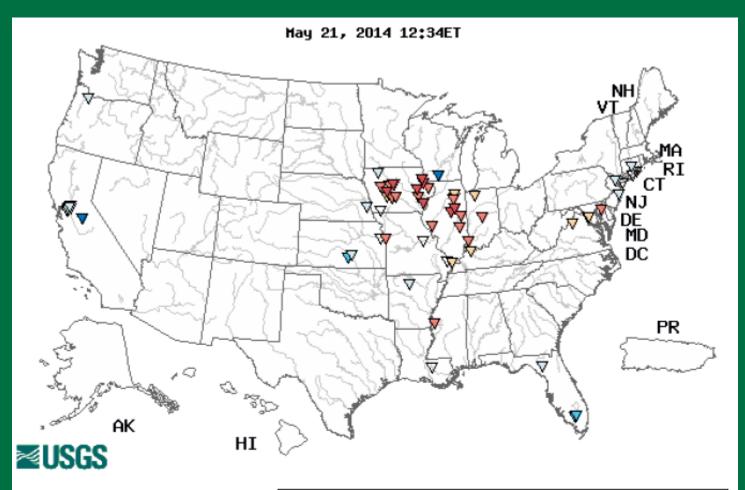
- A USGS streamflow gage that employs several monitoring techniques to understand hydrologic conditions, including:
  - Discharge
  - Continuous water-quality monitoring
    - 5-parameter sondes
    - Nutrient analyzers
  - Representative sampling
  - Surrogate modelling



### **Location of Sentry Gages**



### **USGS** Real-time Nitrate Monitoring





http://waterwatch.usgs.gov

Explanation							
$\overline{}$		$\nabla$	$\nabla$	$\overline{}$	$\overline{}$	$\overline{}$	$\nabla^*$
<.1	.129	.399	1-2.99	3-9.99	10-29.9	>30	No Data

### Nitrate sensor deployment





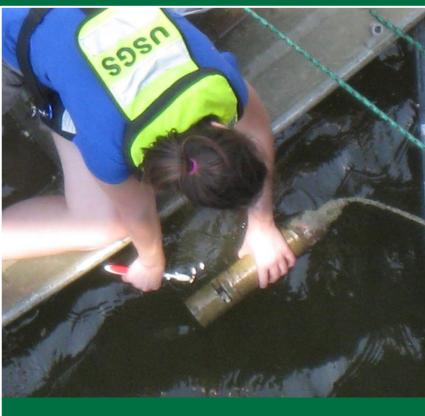


#### Field maintenance

- Deploy a field meter. Collect before cleaning readings.
- 2. Remove the monitor from the stream and clean it.

  Clean the inside of the monitor housing if necessary.





### Field maintenance (cont.)

3. Return the monitor to the stream. Let the monitor

equilibrate





#### Field maintenance (cont.)

- 5. Remove the monitor from the stream and begin calibration checks
- 6. Check the monitor with Inorganic Blank Water and then a standard(s) which brackets the expected range





November 1	-	CONTINU				AL SURVEY TY MONITOR						
Station No.					Station	Name						
Monitor Inspected By Date Watch Time Time Datum												
	(Risin										— I	
Monitor Mak						Monitor	Serial N	No			— I	
	Make/Model id Cool Warm Hot										— I	
Comments:		Ham hist Sieet	SHOW	numic	bry Cloudy	Priciousy Overc	tast Crea	windy Gusty I	sreeze	Cam	I	
											- 1	
											=	
			M	ONITO	OR FOULING		_		- 01-		-	
				Before Cleaning Time			$\dashv$	Atti Tin		aning	-	
				Recorded/ Field Meter		ter	Recorded/		Field Meter			
Parameter					ve Monitor Reading	Reading	g	Live Monitor Reading		Reading		
Temp (°C)			-		. washing	+	$\rightarrow$	rveaunig	$\dashv$		$\dashv$	
pH (units)			-	_		_	$\rightarrow$		+		-	
DO (mg/L)							$\rightarrow$		$\dashv$			
SC (µS/cm	1		-			_	$\rightarrow$		$\dashv$		-	
-	FNU NTU NTRU FNMU	FNRU FAU FBU	AU )			_	$\rightarrow$		$\dashv$		-	
	Meth					1	- 1		- 1		- 1	
Other							$\neg$		$\dashv$		$\neg$	
				<u> </u>			_		_		_	
			CAL	IBR/	ATION DRII	FT CHECKS			_		_	
				ecorded/Live Field Meter nitor Reading Reading			Field Meter		Field Meter			
	ermometers; ± 0.2 °C			me Time		.	2-pt check Date		5-pt check Date			
				_	-		-		+		$\neg$	
Comments:											-	
Comments.												
SPECIFIC CONDUCTANCE				Calibration Check				Recalibration				
Calibration Criteria: ± 5 percent for SC ≤ 100 μS/cm or ± 3 percent for SC >100 μS/cm			m or	Time				1	ime_	·—		
Standard	Standard	Standard	Expira	tion	Standard	sc	Error	Standard		sc	Error	
Value	Lot No.	Type KCI; NaCI	Dat	e	Temp 'C	Reading µS/cm	%	Temp 'C	R	eading µS/cm	%	
				$\neg$							М	
											П	
Cell	Reading in air =			$\neg$							П	
range =	(should be zero)										щ	
Comments:												
					- 1					or form ver	_	

### Field maintenance (cont.)

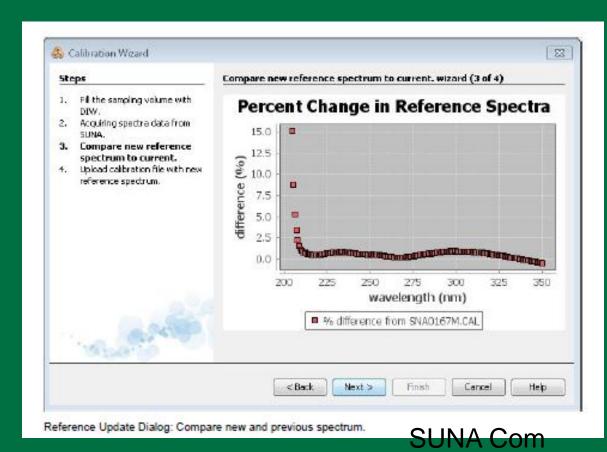
- 7. Recalibrate the monitor if necessary
- 8. Return the monitor to the stream and collect final readings prior to departure

Pellerin and others, 2013

Table 5. Calibration criteria for inorganic blank water checks of the ultraviolet (UV) nitrate sensors based on manufacturer stated accuracy in a zero milligram per liter (mg/L) as nitrogen (N) solution for different sensor models (Hach) or wavelengths (Satlantic, s::can, TriOS).

[Only the wavelengths commonly used for natural waters are shown for the s::can. Abbreviations: mg/L as N, milligram per liter as nitrogen; mm, millimeter; %, percent]

Pathlengths	Stated accuracy	Calibration criteria in inorganic-free blank water (mg/L as N)						
Hach Nitratax								
1, 2, 5	±3-5% of reading or	-0.5 to +0.5 (plus, clear)						
	0.5–1.0 mg/L, whichever is greater	-1.0 to +1.0 (eco)						
Satlantic SUNA								
5, 10	±10% of reading or	-0.03 to +0.03 (10 mm)						
	0.03-0.06 mg/L, whichever is greater	-0.06 to +0.06 (5 mm)						
S::CAN spectrolyzer								
0.5-100	±2% of reading plus	-0.03 to +0.03 (35 mm)						
	l/optical path length (in mm; mg/L)	-0.2 to +0.2 (5 mm)						
	(m mm, mg/L)	-0.5 to +0.5 (2 mm)						
TriOS ProPS								
1-60	±2% of reading or ±0.155 mg/L, whichever is greater	-0.155 to +0.155						



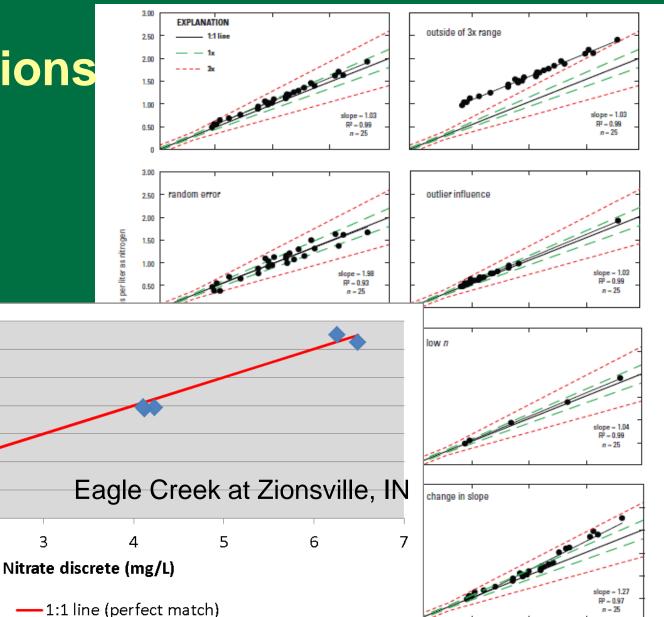
#### **Bias Corrections**

Problem: The presence of dissolved organic matter, bromide or suspended particles in the matrix water can result in systematic errors or bias. To correct:

- 1. Data corrections based on continuous in situ measurements of interfering substances
- 2. Corrections based on the correlation of continuous measurements with nitrate concentrations from discrete water-quality samples analyzed in a laboratory



## Bias Corrections (cont.)





0

Nitrate continuous (mg/L)

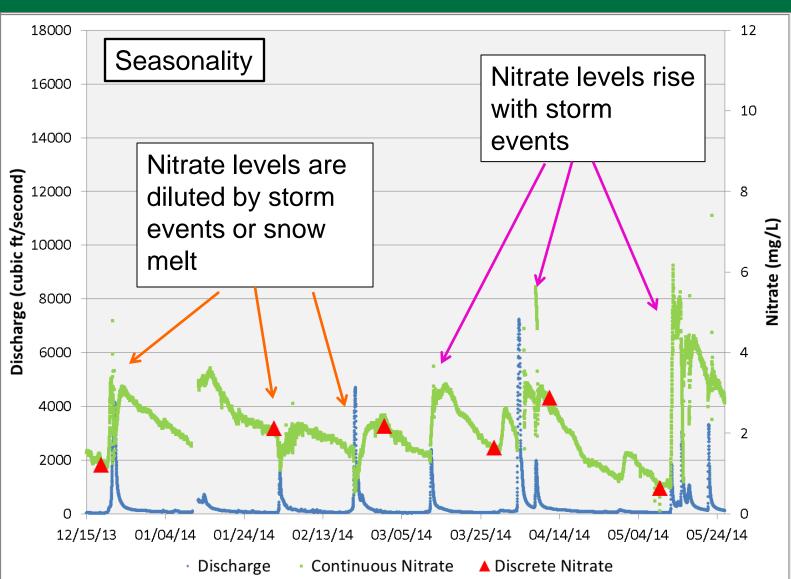
Lab nitrate, in milligrams per liter as nitrogen

Series1

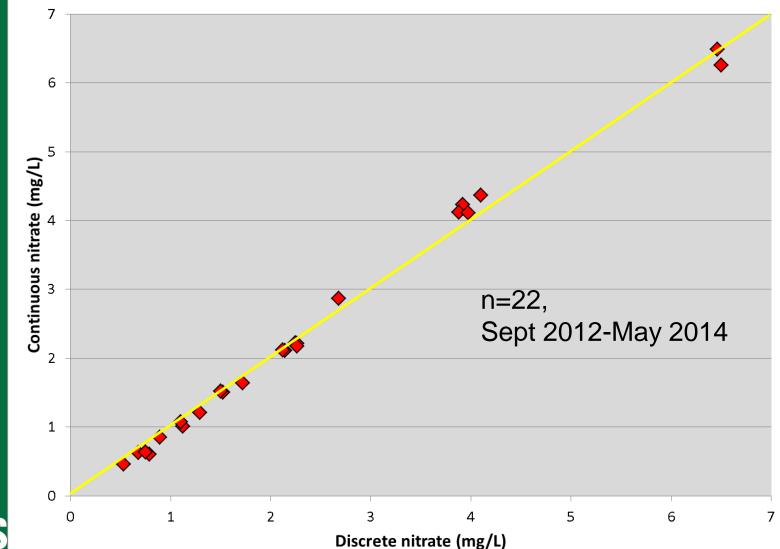
#### Eagle Creek at Zionsville, IN

Nitrate – Discrete Continuous





#### Zionsville – Continuous vs. Discrete

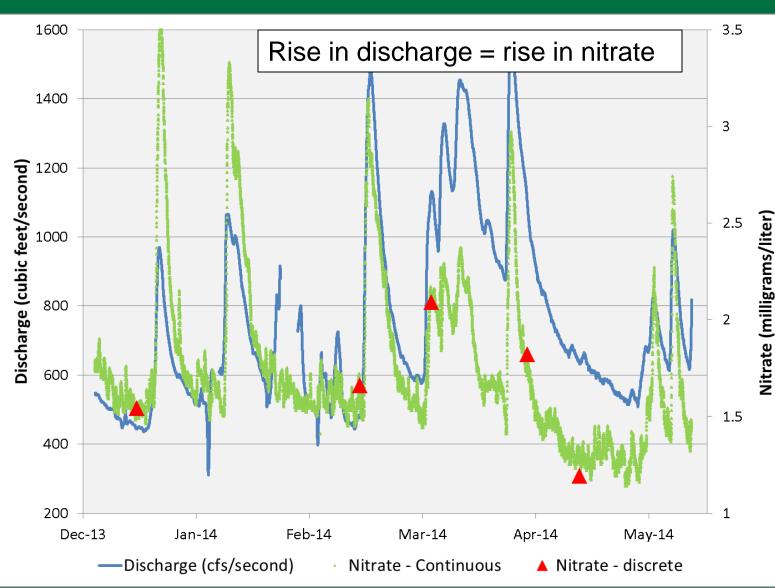




#### Kankakee River at Davis, IN

Nitrate –
Discrete
Continuous

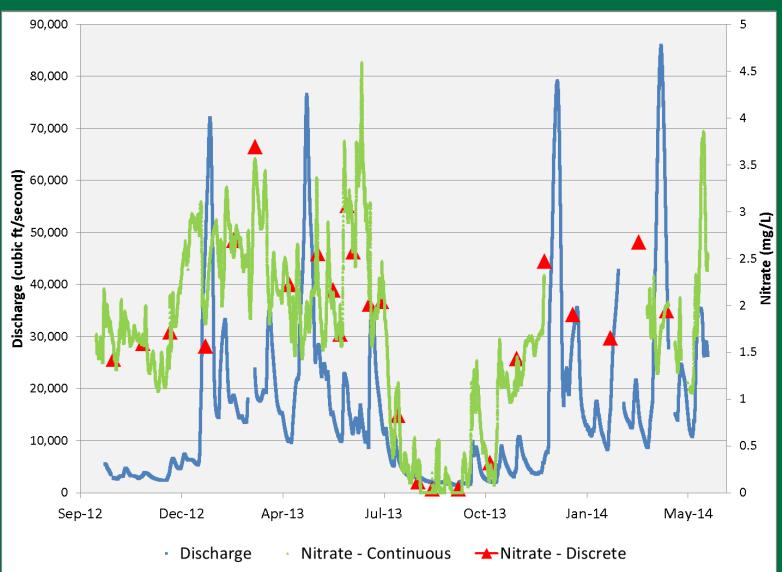




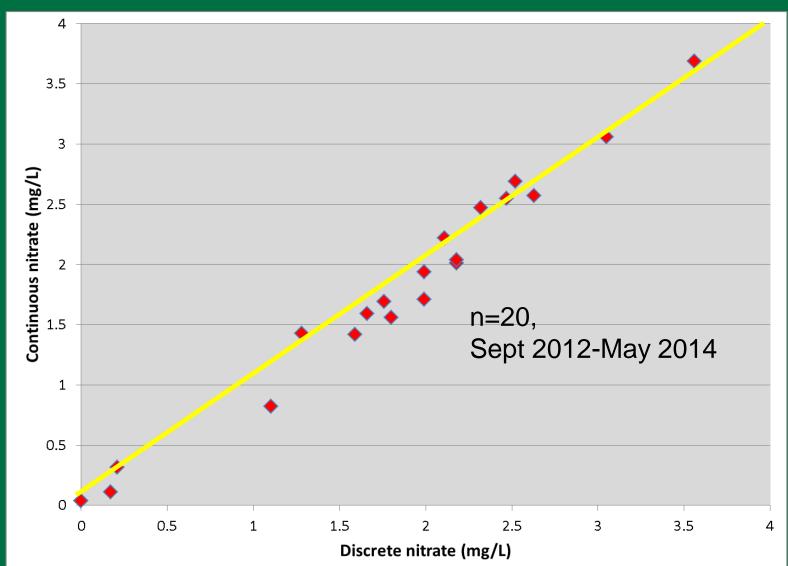
#### White River at Hazleton, IN

Nitrate – Discrete Continuous





### Hazleton – Continuous vs. Discrete





### Rating the data

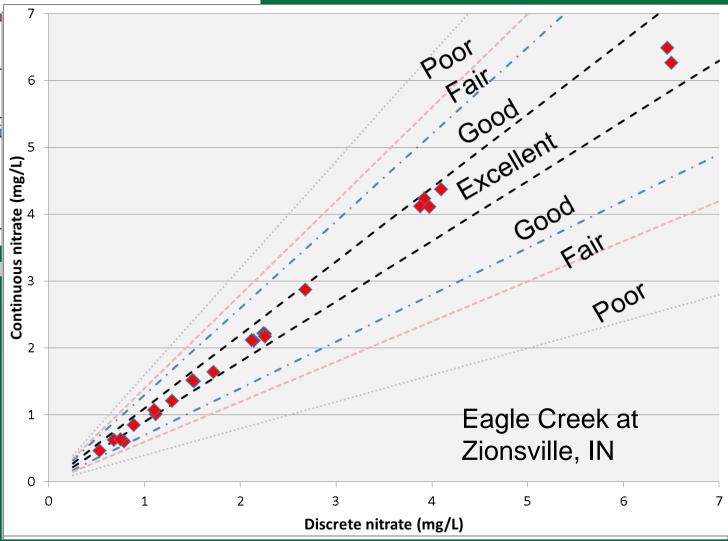
**Table 10.** Accuracy ratings based on the absolute sums of the combined fouling, drift, and bias corrections to discrete samples for continuous ultraviolet nitrate measurements.

[The sensor accuracy used can be n calculated values.]

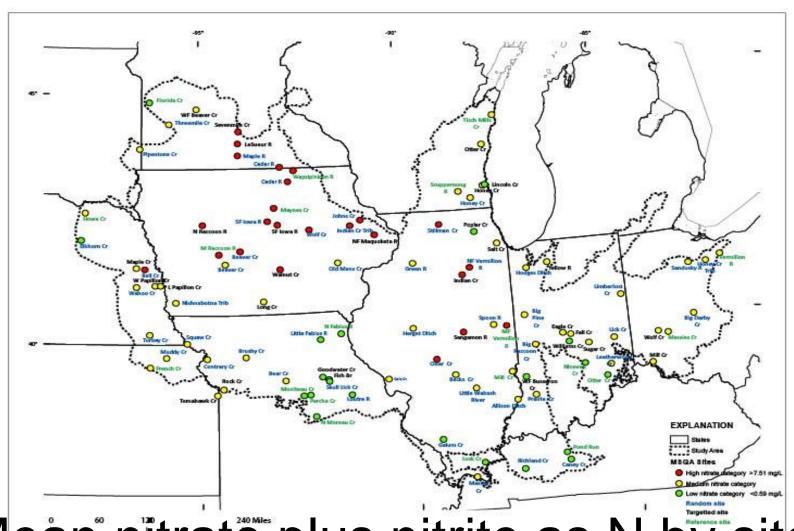
Accuracy rating	
Excellent	Withi
Good	±1-3
Fair	±3-4
Poor	±46

Table 10 (Pelle





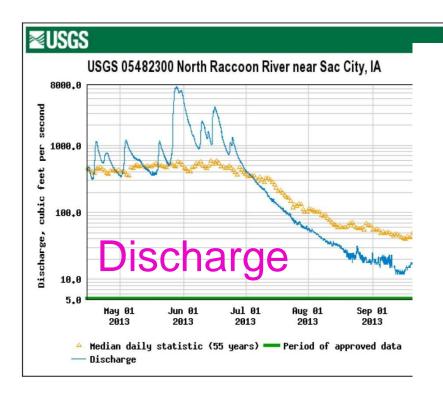
## USGS Midwestern Stream Quality Assessment 2013



Mean nitrate plus nitrite as N by site

## Continuous nitrate comparison data - lowa

Page 1 of 1



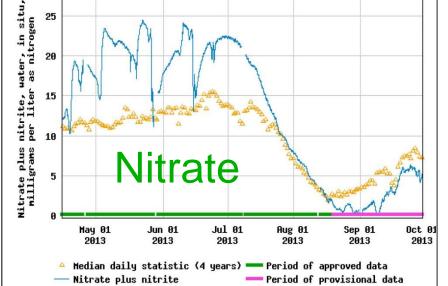
http://137.227.241.66/nwisweb/data/img/USGS.05482300.01.00060..20130415...

Data are provisional





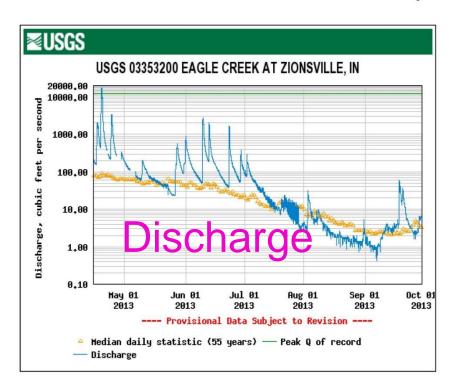
Page 1 of 1



http://137.227.241.66/nwisweb/data/img/USGS.05482300.16.99133..20130415... 11/19/2013

## Continuous nitrate comparison data - Indiana

Page 1 of 1

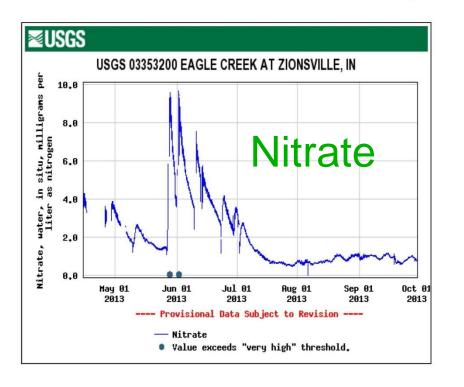


http://137.227.241.66/nwisweb/data/img/USGS.03353200.01.00060..20130415... 10/24/20130415...

#### **≥USGS**

#### Data are provisional

Page 1 of 1



http://137.227.241.66/nwisweb/data/img/USGS.03353200.18.99137..20130415... 10/24/2013





Tim Lathrop triathro@usgs.gov

http://in.water.usgs.pov