The DQO/MQO Process: Comparability in Monitoring;

Nitrate as an Example

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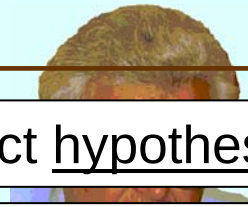
The DQO/MQO process ???



State the project hypotheses

Specify the project DQOs/MQOs

Monitoring

- Select methods
- Collect representative samples
- Complete analysis of samples
- Compile data for project

Check data for consistency with DQOs/MQOs

Interpret data for significance to project hypotheses

The DQO/MQO process

collaborations partnerships

- State the project hypotheses
- Specify the project DQOs/MQOs
- Select methods
- Collect representative samples
- Complete analysis of samples
- Compile data for project
- Check data for consistency with DQOs/MQOs
- Interpret data for significance to project hypotheses

The DQO/MQO process

comparability?

how?

historical data

State the project hypotheses

Specify the project DQOs/MQOs

Select methods

new data

Collect representative samples

Complete analysis of samples

Compile data for project

Check data for consistency with DQOs/MQOs

Interpret data for significance to project hypotheses

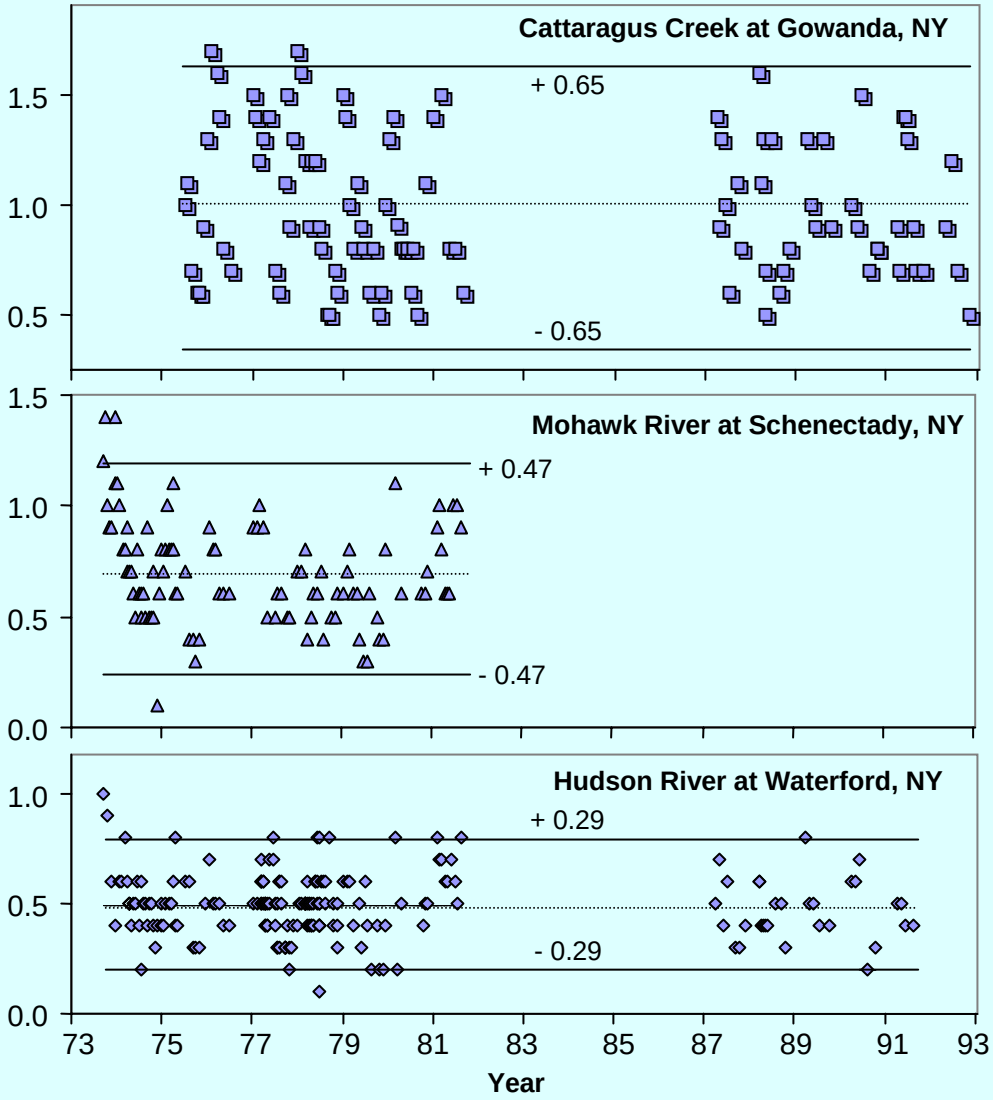
iterative

learning

Historical data - NWIS sites

(waterdata.usgs.gov/nwis)

NWIS historical data - site comparisons

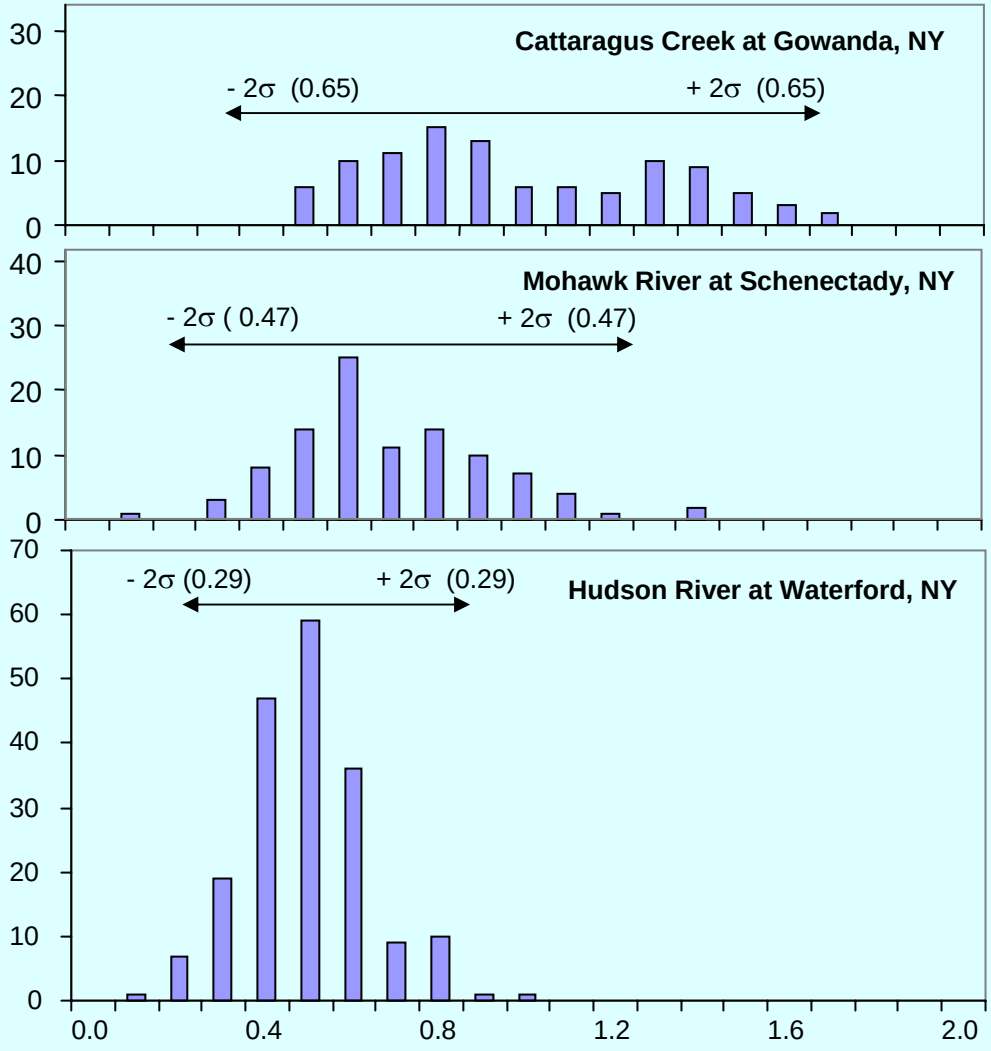


total nitrate-nitrite (mg NO_3-N/L)

$\overline{X}$ ± s	(rsd)	N
0.99 ± 0.33	(33%)	101
0.70 ± 0.23	(34%)	100
0.49 ± 0.15	(30%)	190

NWIS historical data - site comparisons

630 total nitrate-nitrite (mg NO_3-N/L)



range	kurtosis	skewness
1.2	- 0.99	0.36
1.3	0.60	0.54
0.9	0.67	0.38

Hypotheses: comparing data at 3 sites

At a 95 percent level of confidence (α = 0.025)

H_0 (null) NO DIFFERENCE between mean values

H_1(alternate) SIGNIFICANT DIFFERENCE between mean values

t-test of difference between two means $\left|\Delta\overline{X}\right| = \left|\left(\overline{X}_a - \overline{X}_b\right)\right|$

standard deviations not equal $s_a \neq s_b$

number of data points not equal $N_a \neq N_b$

H_0 (null) $\left|\Delta\overline{X}\right| < t\sqrt{V_a + V_b}$

H_1(alternate) $\left|\Delta\overline{X}\right| > t\sqrt{V_a + V_b}$

$$V_a = \frac{s_a^2}{N_a} \qquad V_b = \frac{s_b^2}{N_b} \qquad \text{and} \qquad t \quad @ \quad df = \frac{\left(V_a + V_b\right)^2}{\left(\dfrac{V_a^2}{N_a - 1} + \dfrac{V_b^2}{N_b - 1}\right)}$$

Significant Differences Between Sites

site A	site B	df	P_{eff}	vs	α
Gowanda:Cattaragus R	Schenectady:Mohawk R	181	0.00	<	0.025
Gowanda:Cattaragus R	Waterford:Hudson R	122	0.00	<	0.025
Waterford:Hudson R	Schenectady:Mohawk R	141	0.00	<	0.025

H_1 TRUE: mean values $[NO_3 + NO_2\ (mg/L)]_{total}$ ARE significantly DIFFERENT at the 3 sites

not surprising, because $\dfrac{|\Delta \overline{X}|}{\overline{X}}$ is large { 29 to 51 % }

and df is large in all cases

Hypotheses: comparing different analytes

(for one site at a time)

site	analyte A	analyte B	df	P_{eff} vs α
M R	620 $[NO_3^-]_{total}$	618 $[NO_3^-]_{dissolved}$	81	0.50 > 0.025
M R	630 $[NO_3^- + NO_2^-]_{total}$	631 $[NO_3^- + NO_2^-]_{diss}$	131	0.19 > 0.025
M R	630 $[NO_3^- + NO_2^-]_{total}$	620 $[NO_3^-]_{total}$	72	0.38 > 0.025
M R	630 $[NO_3^- + NO_2^-]_{total}$	620 $[NO_3^-]_{total}$	78	0.51 > 0.025
M R	631 $[NO_3^- + NO_2^-]_{diss}$	618 $[NO_3^-]_{diss}$	7	0.11 > 0.025
paired data				
M R	630 $[NO_3^- + NO_2^-]_{total}$	620 $[NO_3^-]_{total}$	39	0.00 < 0.05

At a 95 percent level of confidence (α = 0.025)

H_o TRUE: NO significant DIFFERENCE between mean concentrations of different analytes at each site

dissolved = total; method selection: no need to filter (USGS 1992)

$[NO_3^-] \approx [NO_3^- + NO_2^-]$ $\left|\Delta\overline{X}\right| / \overline{X}$ < 5% (difference small, insignificant)

New project scenarios (2): hypotheses

Compliance monitoring: *at a particular stream*

[null] $[NO_3^-] \leq 1.5$ mg/L

OR [alternate] $[NO_3^-] > 1.5$ mg/L

with a 95% level of certainty

Ambient monitoring:

A (sites) at *entry of a particular stream into a river*

[null] $[NO_3^-]$ increases by $\leq$ 30%

OR [alternate] $[NO_3^-]$ increases by > 30%

with a 95% level of certainty

B (times) *for a particular stream in consecutive quarters*

[null] $[NO_3^-]$ increases by $\leq$ 50%

OR [alternate] $[NO_3^-]$ increases by > 50%

with a 95% level of confidence

DQOs for two project scenarios

Compliance monitoring:

measure [NO_3^-] in *samples collected quarterly (N = 4) for one year from 50 specified stream locations,*

determine if average annual [NO_3^-] > 1.5 mg/L, with 95% certainty

Ambient monitoring:

measure [NO_3^-] in *samples collected monthly (N = 12) for one year, below consecutive entry points of 15 second-order streams*

determine with 95% certainty if

A (sites) *entry of a particular stream into a river*

[null] [NO_3^-] increases by $\leq$ 30%

OR [alternate] [NO_3^-] increases by > 30%

B (times) *for a particular stream in consecutive quarters*

[null] [NO_3^-] increases by $\leq$ 50%

OR [alternate] [NO_3^-] increases by > 50%

Retrospective: DQOs for two project scenarios

	Compliance	Ambient
Reason for monitoring	comparison to standard	change in water quality (spatial, temporal)
Target analytes	$[NO_3^-]$	$[NO_3^-]$
Locations	50 streams	15 second-order streams, above/below points of entry
Time period	12 mos	12 mos
Sampling frequency	quarterly	monthly

Decisions, actions	stream classification; discharge permits	watershed assessment spatial, temporal
Level of certainty	95 percent	95 percent
False positives	5 percent	5 percent
False negatives	10 percent	10 percent

statistical uncertainty $\pm t \frac{s}{\sqrt{N}}$

MQOs for two project scenarios

	Compliance	Ambient
Target analytes	$[NO_3^-]_{total}$	$[NO_3^-]_{total}$
Matrix	streamwater	streamwater
Quantitation range, mg/L	1.0 to 2.0	0.010 to 2.0
Detection limit, mg/L	≤ 0.5	≤ 0.005
Bias (blanks), mg/L	≤ 0.5	≤ 0.010
Bias (recovery)	≥ 80 %	≥ 80 %
frequency spikes	40 total: one per 20 streams in two different quarters	40 total: one per 10 streams each quarter;
conc. spikes, mg/L	half 1.0, half 1.8	two each, 0.25, 0.50, 0.75, 1.0, 1.5
Precision (replicates, lab)	5% @ 2.0 mg/L 10% @ 1.0 mg/L	2.5% @ 2.0 mg/L 5% @ 0.2 to 1.0 mg/L 25% @ 0.02 mg/L
Reproducibility (field)	≤ 20% RSD	≤ 20% RSD

NO_3^- Method Selection (*www.nemi.gov*)

Method		cost	range (mg/L)	DL (mg/L)	bias (%)	precision (% rsd)
ASTM D6508	CIE-UV	$$	0.10 - 50	0.08	142	8
APHA 4140B	CIE-UV	$$	0.10 - 50	0.08	94	13
APHA 4110C	IC-CD	$$	NR	0.035	103	24
ASTM D4327	IC-CD	$$	NR	0.42	100	10
EPA 300.0	IC-CD	$$	0.40 - 14	0.002	103	2
EPA 300.1	IC-CD	$$	NR	0.008	95	< 1
USGS I-2057	IC-CD	$$	0.05 - 150	0.05	NR	8
USGS I-2058	IC-CD	$$	0.01 - 0.6	0.01	92	8
APHA 4500	RD-VIS	$	0.01 - 1.0	0.01	99	14
EPA 352.1	RD-VIS	$	0.10 - 2.0	0.1	102	14
USGS I-2545	RD-VIS	$	0.05 - 5.0	0.05	97	< 1

NO_3^- method selection

Monitoring scenario	Methods accepted
compliance	all methods ok, meet MQOs
ambient	MQO: DL < 0.005 mg/L NO_3^- EPA method 300.0 DL 0.002 mg/L NO_3^- the *only* method meeting the DL MQO

Comparability of methods and data
for sharing across programs

Data type *supplemental*	Monitoring program (DQOs/MQOs) compliance	ambient
compliance	all data accepted (by definition)	*SOME* compliance data comparable to ambient data, *only if* compliance methods meet ambient DQOs/MQOs
ambient	ALL ambient data comparable to compliance data	all data accepted (by definition)

Final thoughts

Methods and Data COMPARABLE?

INCOMPARABLE?

better than ever?

problem solved!!!