Background Geochemistry in Ohio's Major Aquifers

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Ohio EPA,
Division of Drinking
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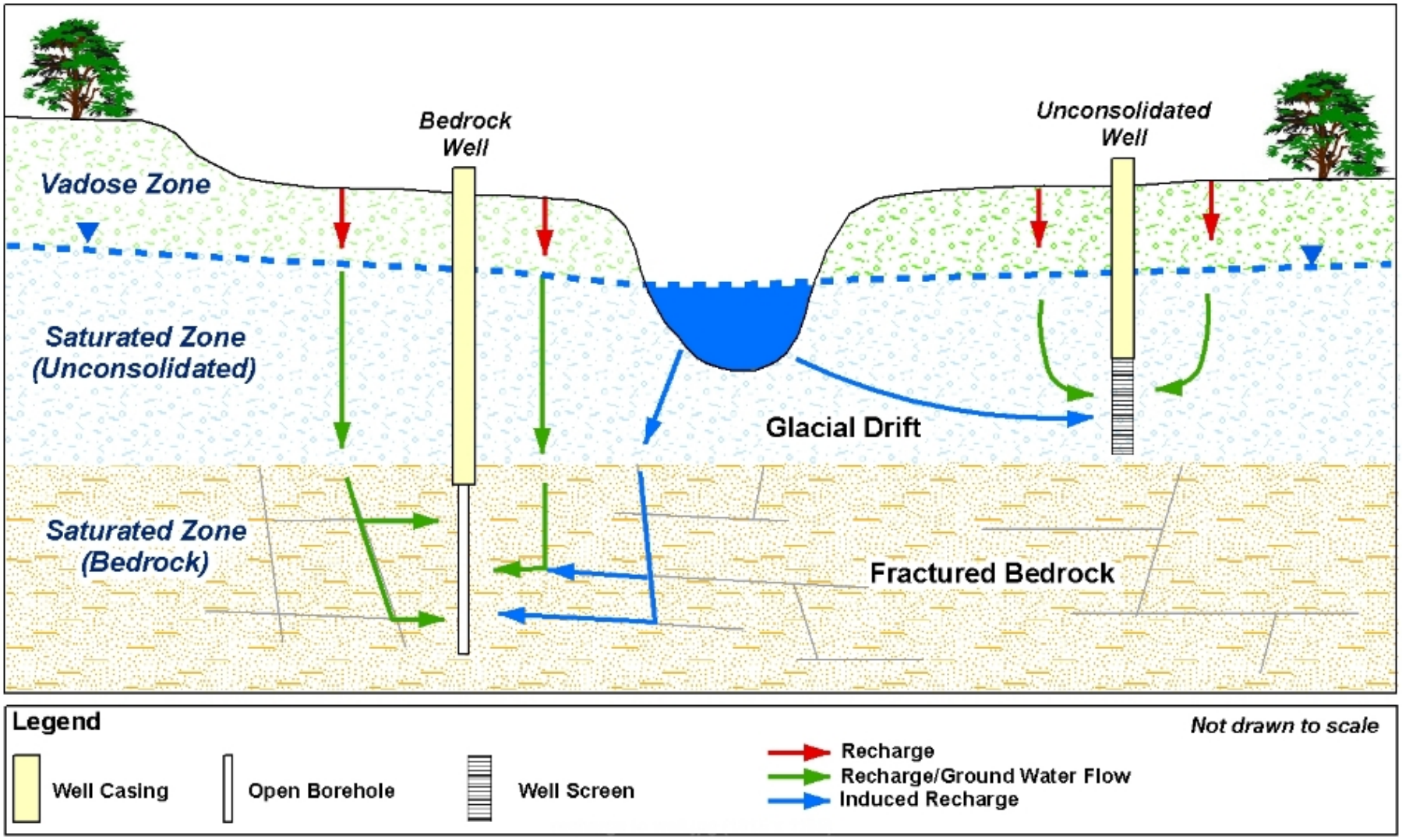
Water Quality

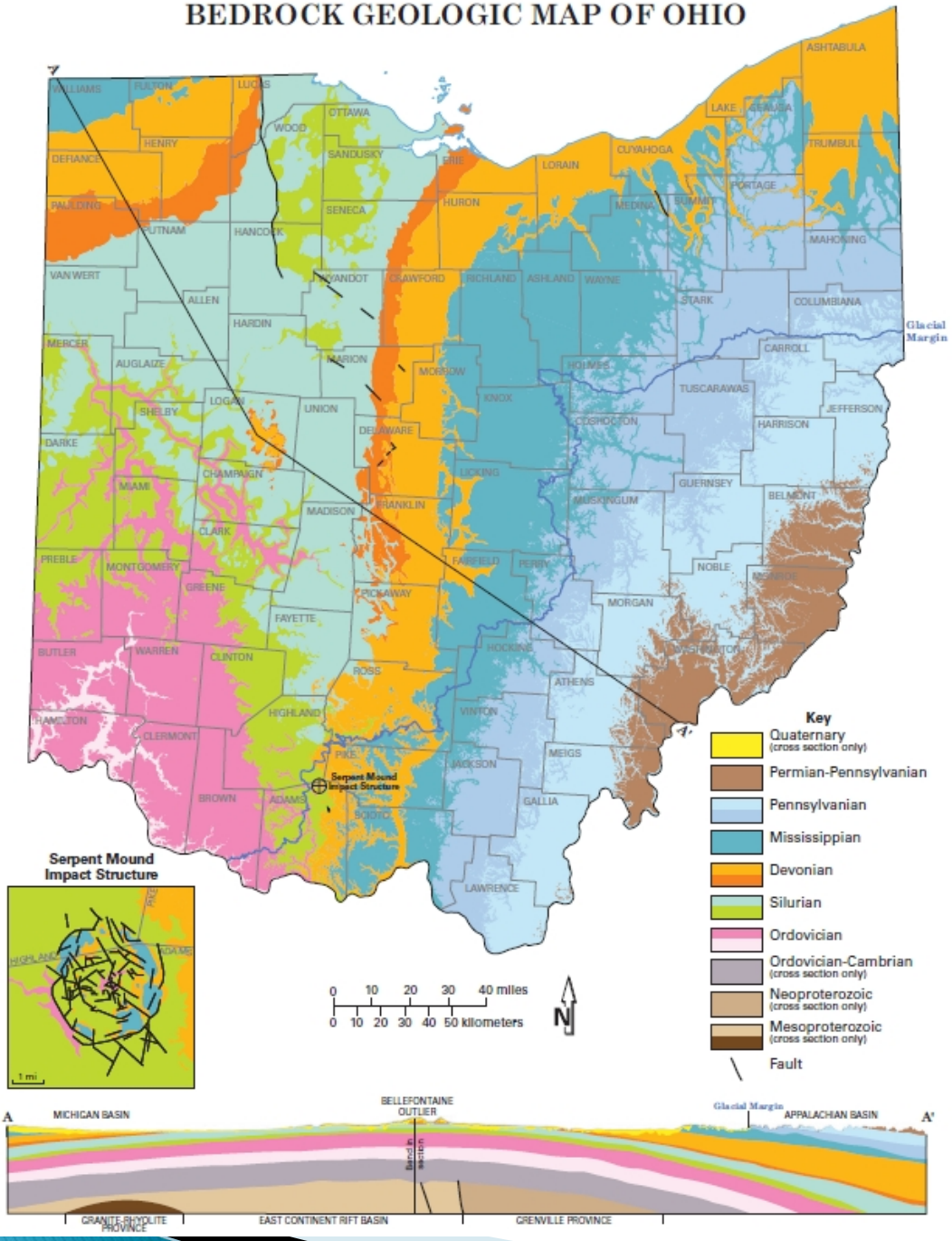
- Water-Rock interactions control the water quality in an aquifer:
  - Along recharge and discharge pathways;
  - Within aquifer
- Controlling factors:
  - Geology;
  - Geochemistry;
  - Aquifer sensitivity and land use.


Bedrock Well
Unconsolidated Well
Vadose Zone
Saturated Zone (Unconsolidated)
Glacial Drift
Saturated Zone (Bedrock)
Fractured Bedrock
Legend
Not drawn to scale
Well Casing
Open Borehole
Well Screen
Recharge
Recharge/Ground Water Flow
Induced Recharge

Outline – Water Quality

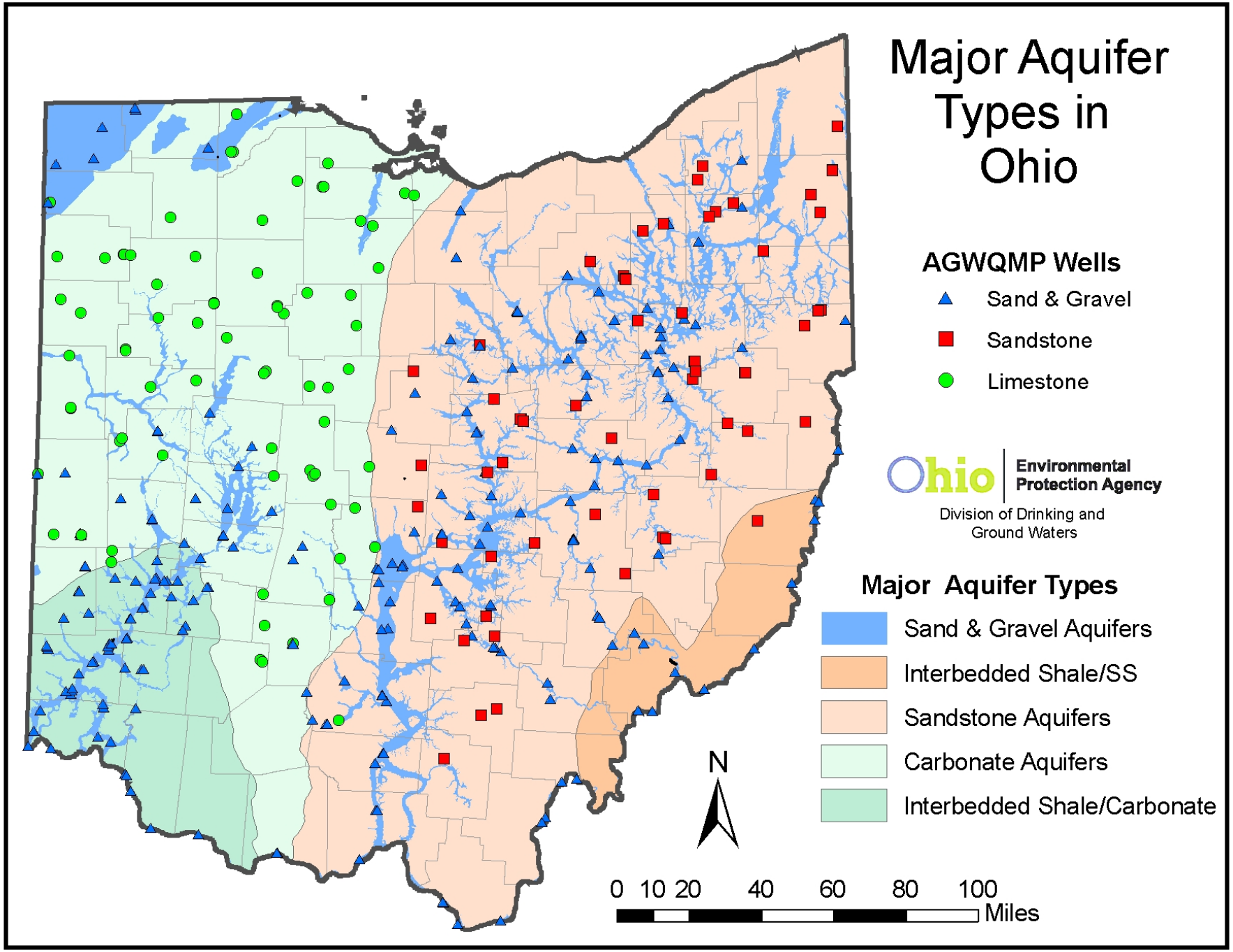
- Ohio Geology
  - Geologic setting
  - Major aquifer types
- Primary controls - natural
  - Geology (dissolution of aquifer material)
    - Regional examples
  - Geochemistry (oxidation-reduction)
    - Local influence
- Local controls – natural and human
  - Well setting and well construction
  - Land use inputs

BEDROCK GEOLOGIC MAP OF OHIO



Major Aquifers in Ohio

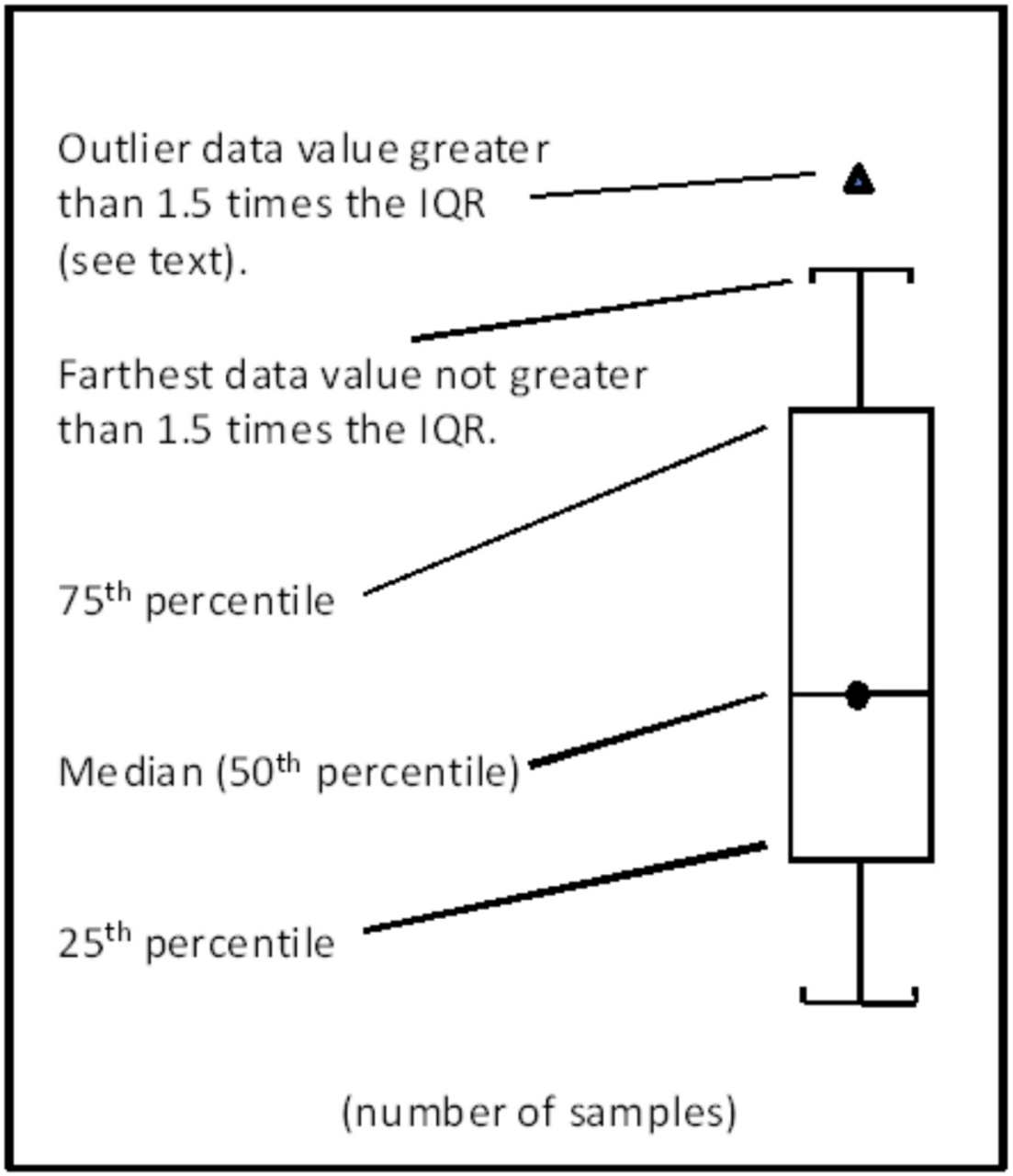
- Carbonate aquifers in western half;
  - Silurian, and Lower Devonian
- Sandstone aquifers in eastern half;
  - Mississippian and Pennsylvanian
- Buried valley aquifers carved into bedrock and backfilled with local bedrock and other glacial debris.
  - Quaternary

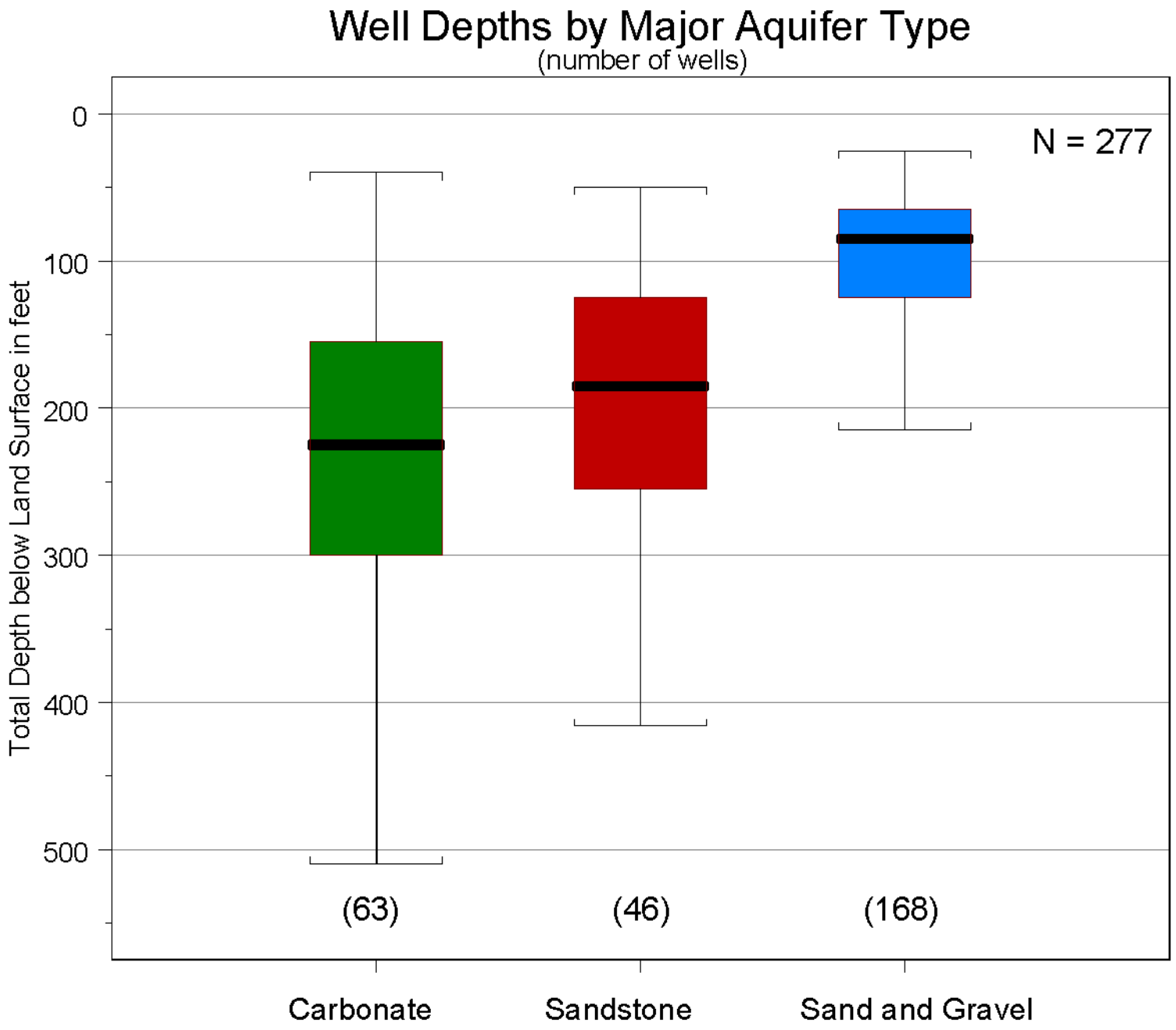

Major Aquifer Types in Ohio
AGWQMP Wells
Sand & Gravel
Sandstone
Limestone
Ohio Environmental Protection Agency
Division of Drinking and Ground Waters
Major Aquifer Types
Sand & Gravel Aquifers
Interbedded Shale/SS
Sandstone Aquifers
Carbonate Aquifers
Interbedded Shale/Carbonate
N
0 10 20 40 60 80 100
Miles

Ambient GW Quality Monitoring Program (AGWQMP)

- Approximately 200 active wells;
- Continuous data for some wells since 1970;
- Analyze raw (untreated) water for 30 inorganic and 61 organic parameters;
  - 85 % of wells are public water system wells;
    - Balance are industrial, commercial, or residential wells
  - Well aquifer types: Sand & Gravel 65%; Sandstone 15%; Carbonate 20%;
  - Primary focus of data collection is to characterize source water for GW based public water systems.

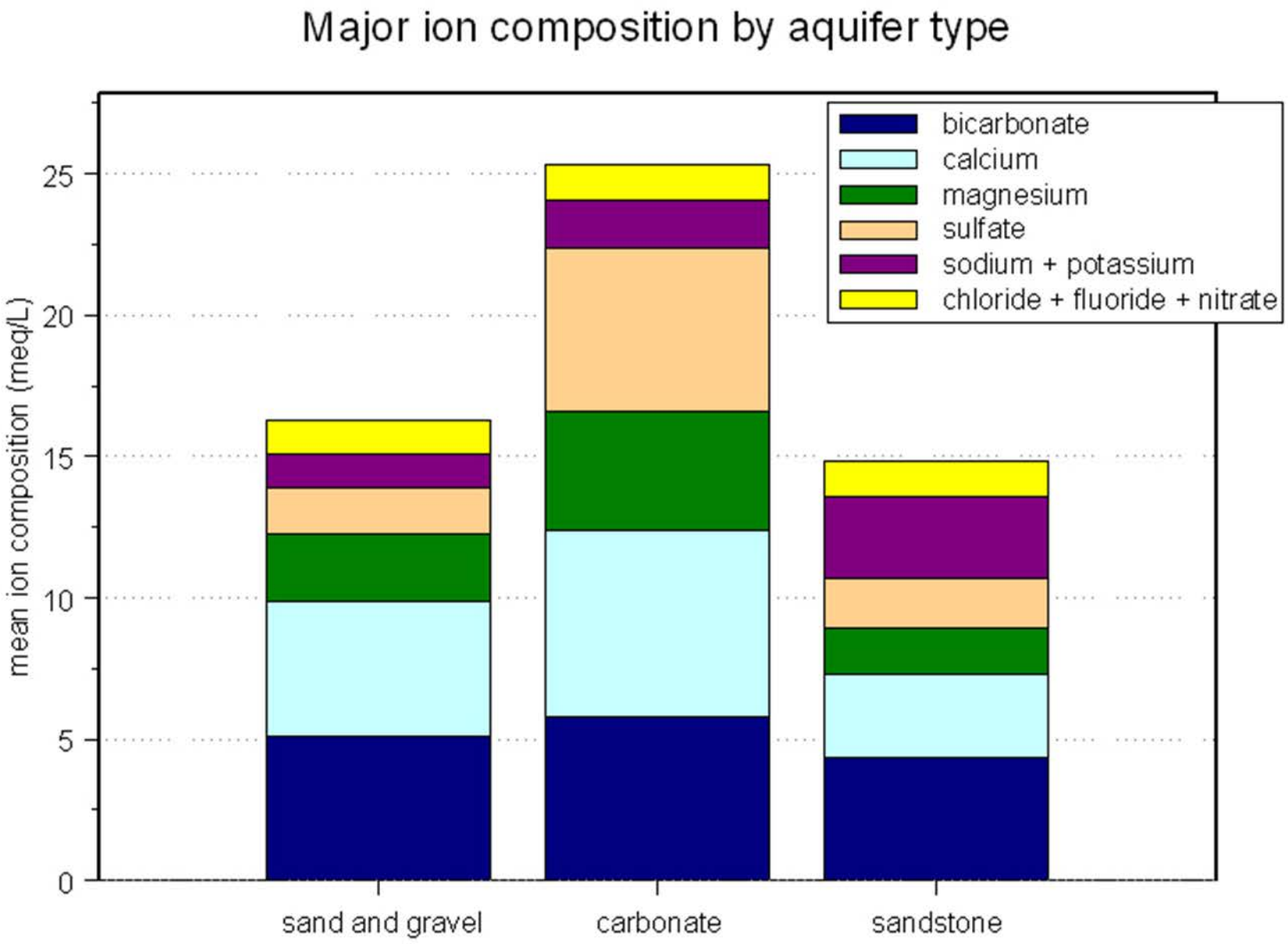
Box Plot Explanation

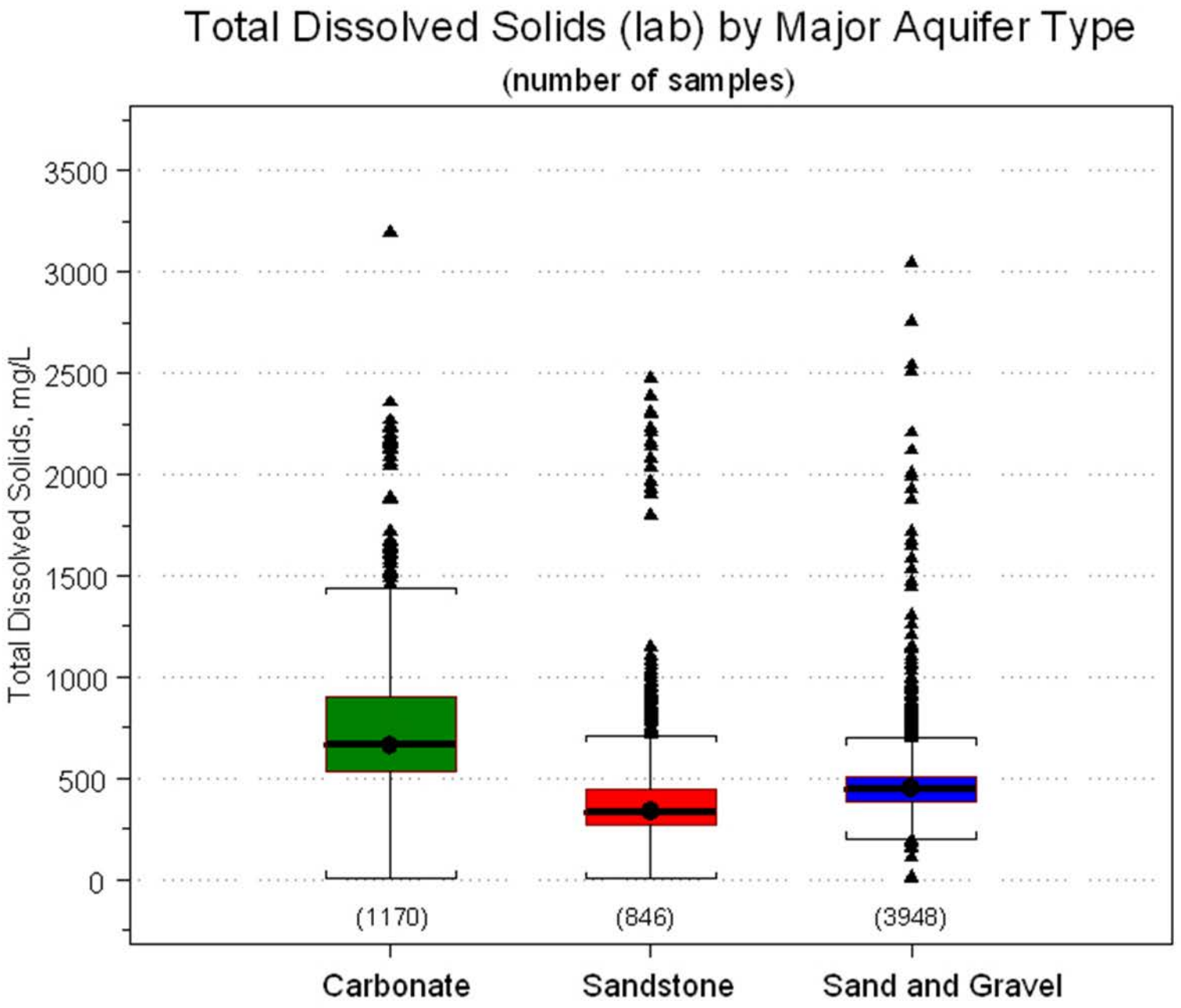


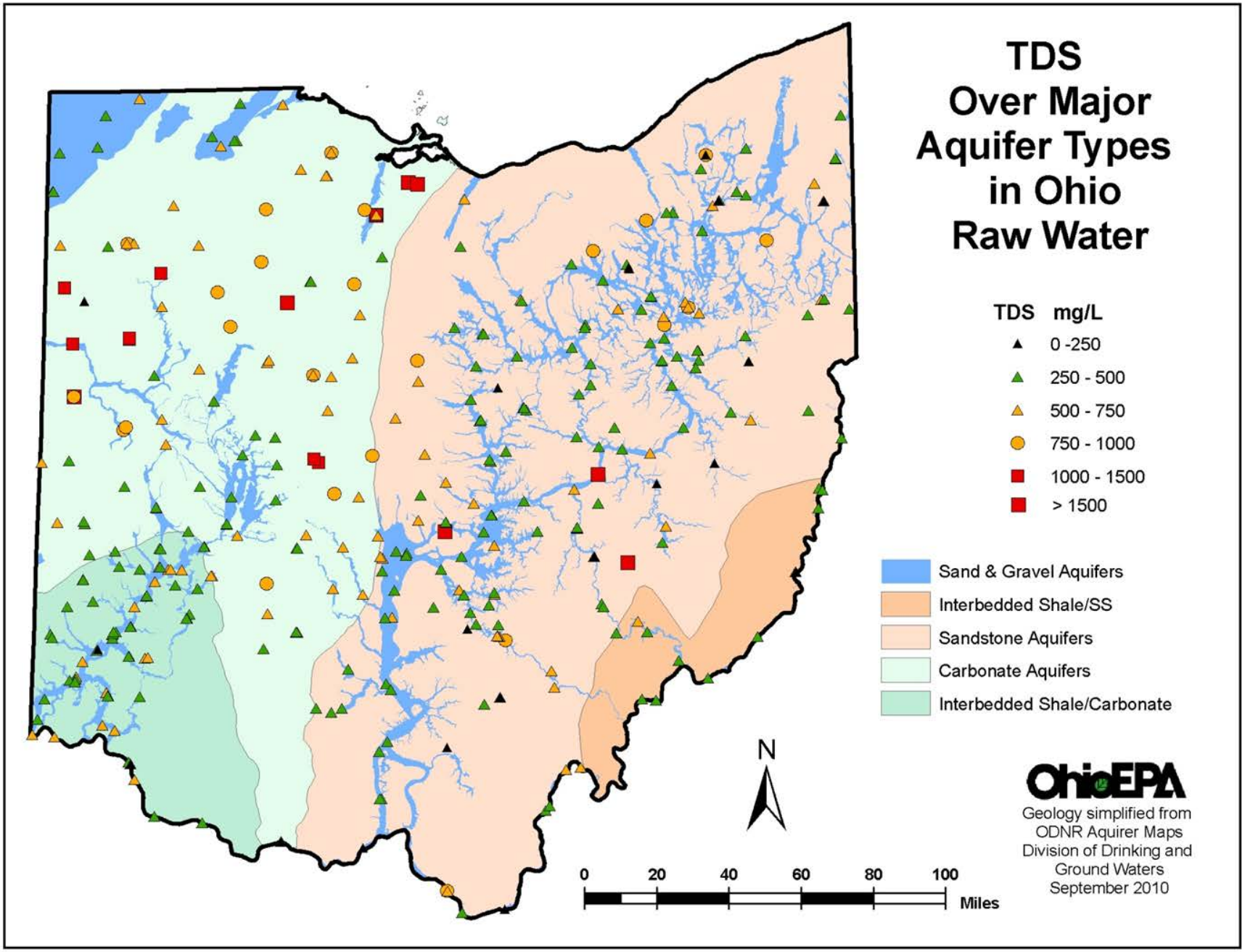

Well Depths by Major Aquifer Type
(number of wells)
N = 277
Total Depth below Land Surface in feet
0
100
200
300
400
500
(63)
(46)
(168)
Carbonate
Sandstone
Sand and Gravel

Water Quality - Regional Variation

- Major Elements
  - Total Dissolved Solids
  - Calcium and Magnesium
  - Sulfate
- Minor Elements
  - Fluoride
  - Strontium


Major ion composition by aquifer type
mean ion composition (meq/L)
0
5
10
15
20
25
sand and gravel
carbonate
sandstone
bicarbonate
calcium
magnesium
sulfate
sodium + potassium
chloride + fluoride + nitrate


Total Dissolved Solids (lab) by Major Aquifer Type
(number of samples)
Total Dissolved Solids, mg/L
3500
3000
2500
2000
1500
1000
500
0
(1170)
(846)
(3948)
Carbonate
Sandstone
Sand and Gravel


TDS
Over Major
Aquifer Types
in Ohio
Raw Water
TDS mg/L
0 -250
250 - 500
500 - 750
750 - 1000
1000 - 1500
> 1500
Sand & Gravel Aquifers
Interbedded Shale/SS
Sandstone Aquifers
Carbonate Aquifers
Interbedded Shale/Carbonate
N
0
20
40
60
80
100
Miles
OhioEPA
Geology simplified from
ODNR Aquirer Maps
Division of Drinking and
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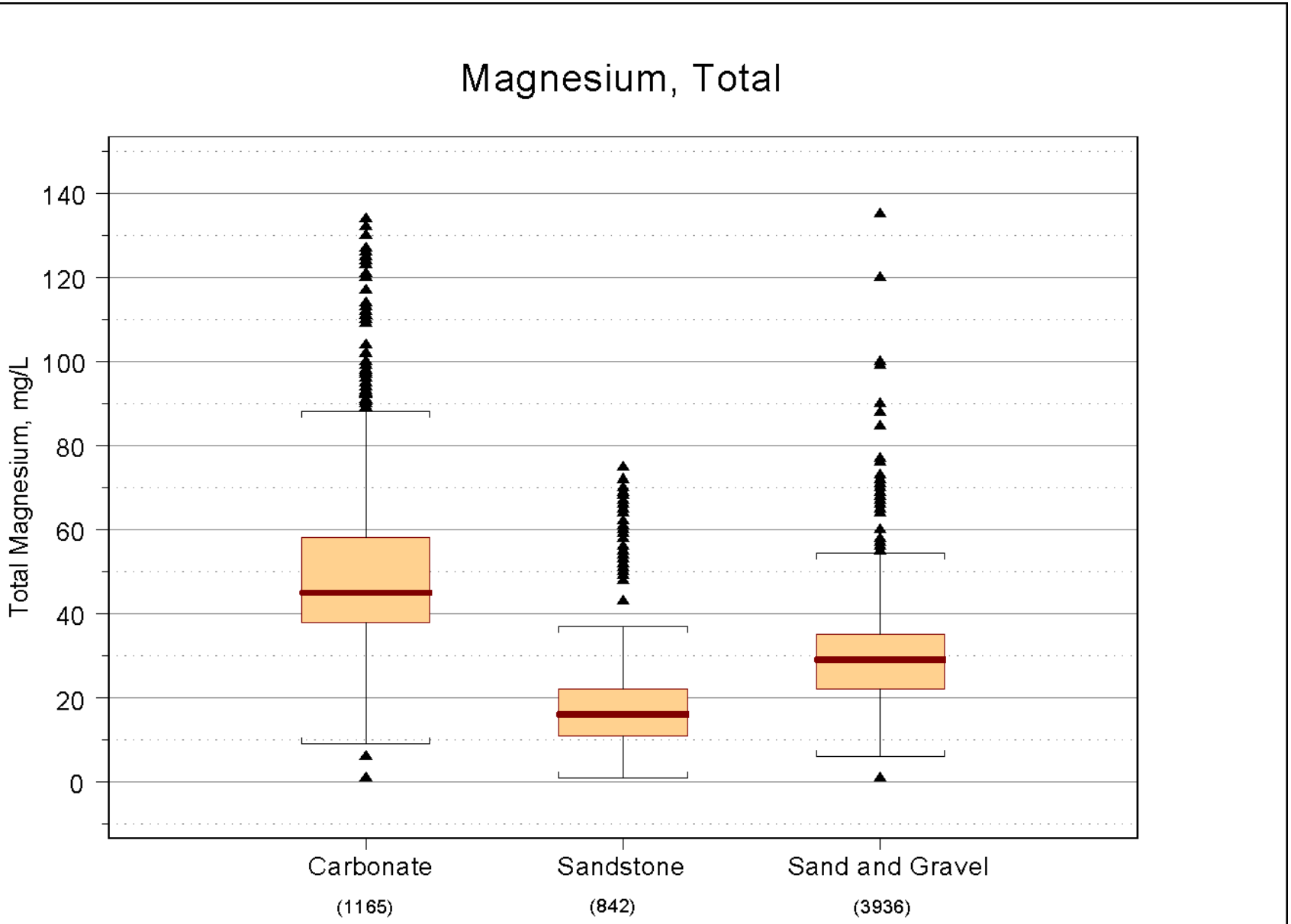
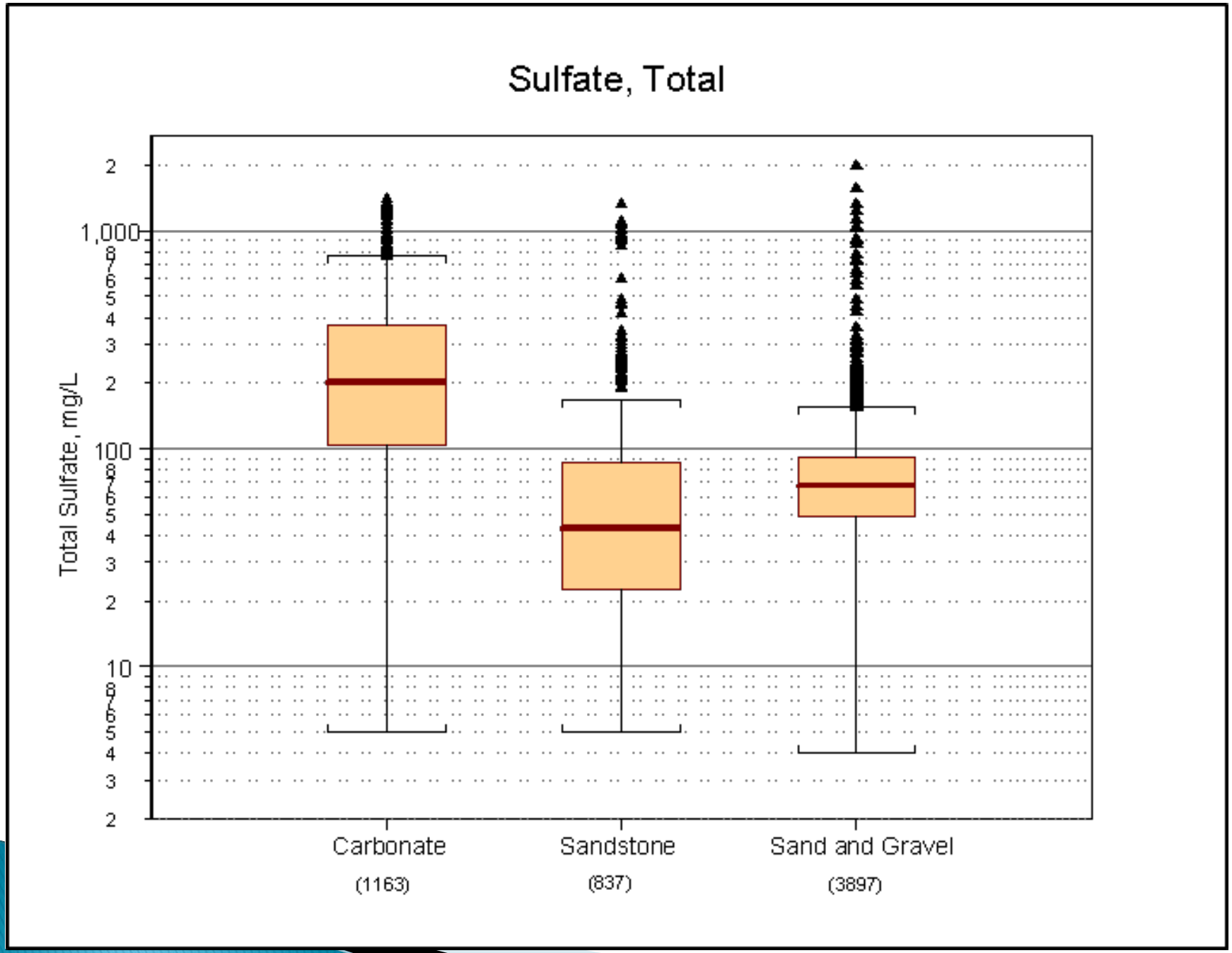
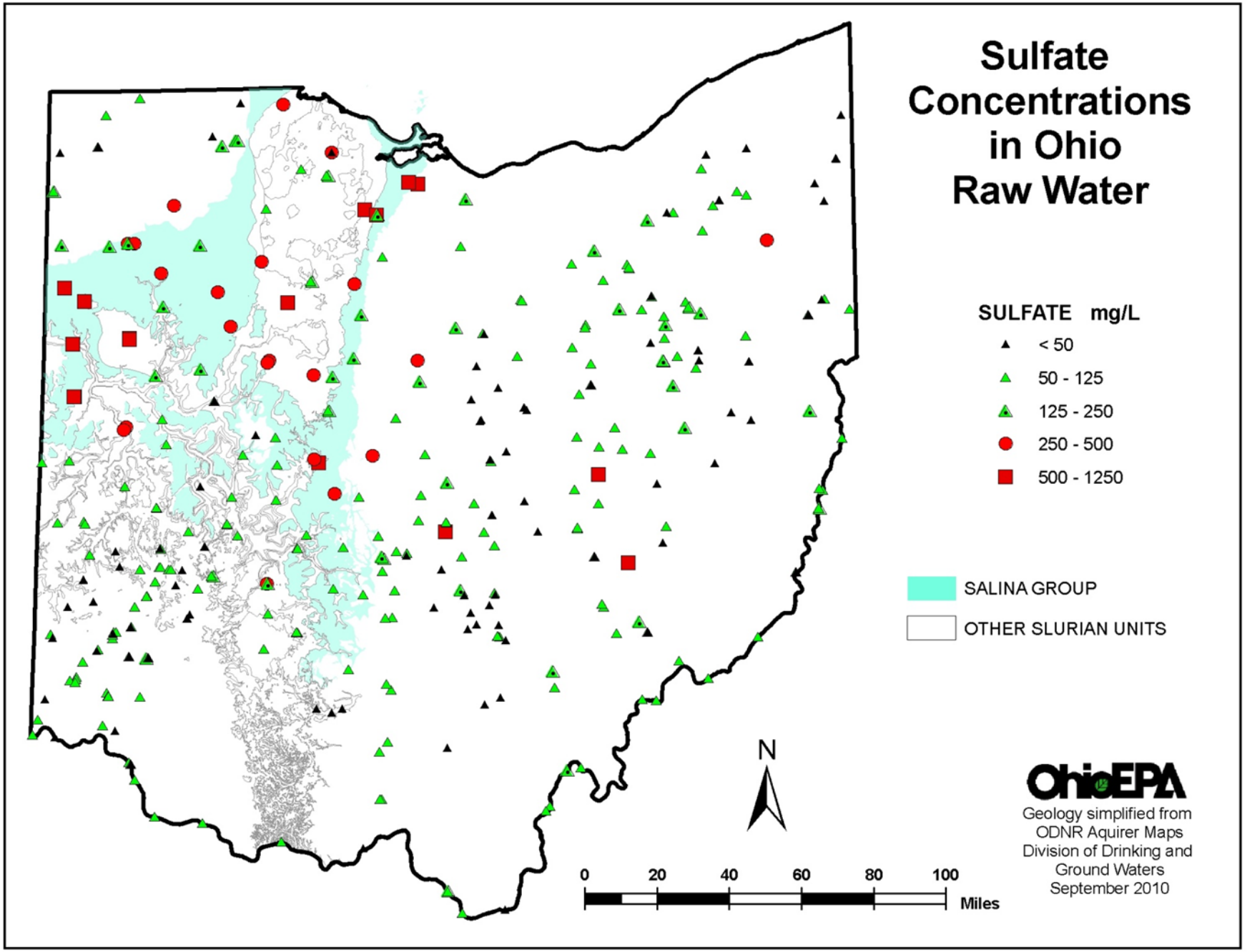
September 2010


Magnesium, Total
Total Magnesium, mg/L
140
120
100
80
60
40
20
0
Carbonate
(1165)
Sandstone
(842)
Sand and Gravel
(3936)


Sulfate, Total
Total Sulfate, mg/L
2
1,000
8
6
5
4
3
2
100
8
6
5
4
3
2
10
8
6
5
4
3
2
Carbonate
(1163)
Sandstone
(837)
Sand and Gravel
(3897)


Sulfate Concentrations in Ohio Raw Water
SULFATE mg/L
< 50
50 - 125
125 - 250
250 - 500
500 - 1250
SALINA GROUP
OTHER SLURIAN UNITS
N
0 20 40 60 80 100
Miles
OhioEPA
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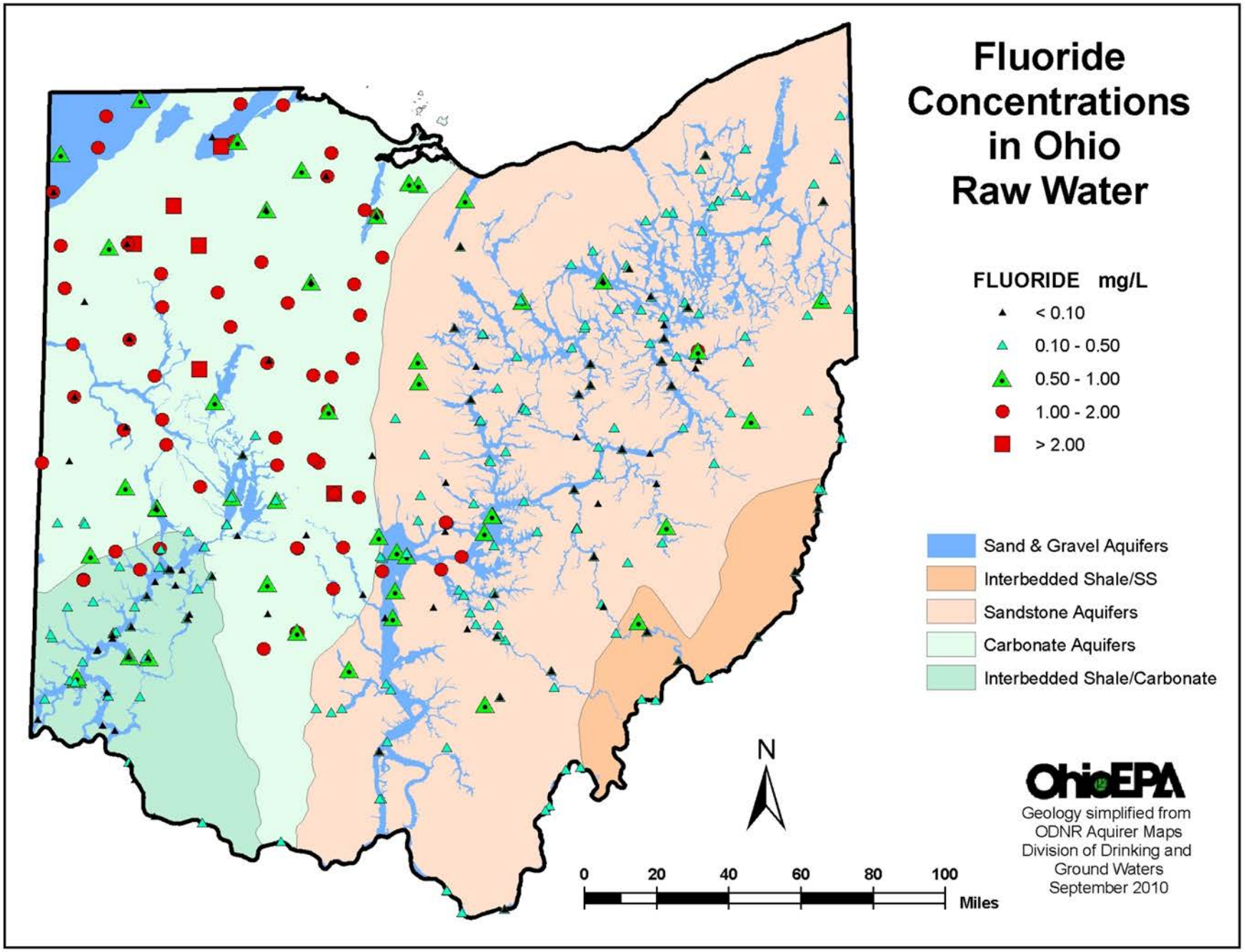
Fluoride Concentrations in Ohio Raw Water
FLUORIDE mg/L
< 0.10
0.10 - 0.50
0.50 - 1.00
1.00 - 2.00
> 2.00
Sand & Gravel Aquifers
Interbedded Shale/SS
Sandstone Aquifers
Carbonate Aquifers
Interbedded Shale/Carbonate
N
0 20 40 60 80 100
Miles
OhioEPA
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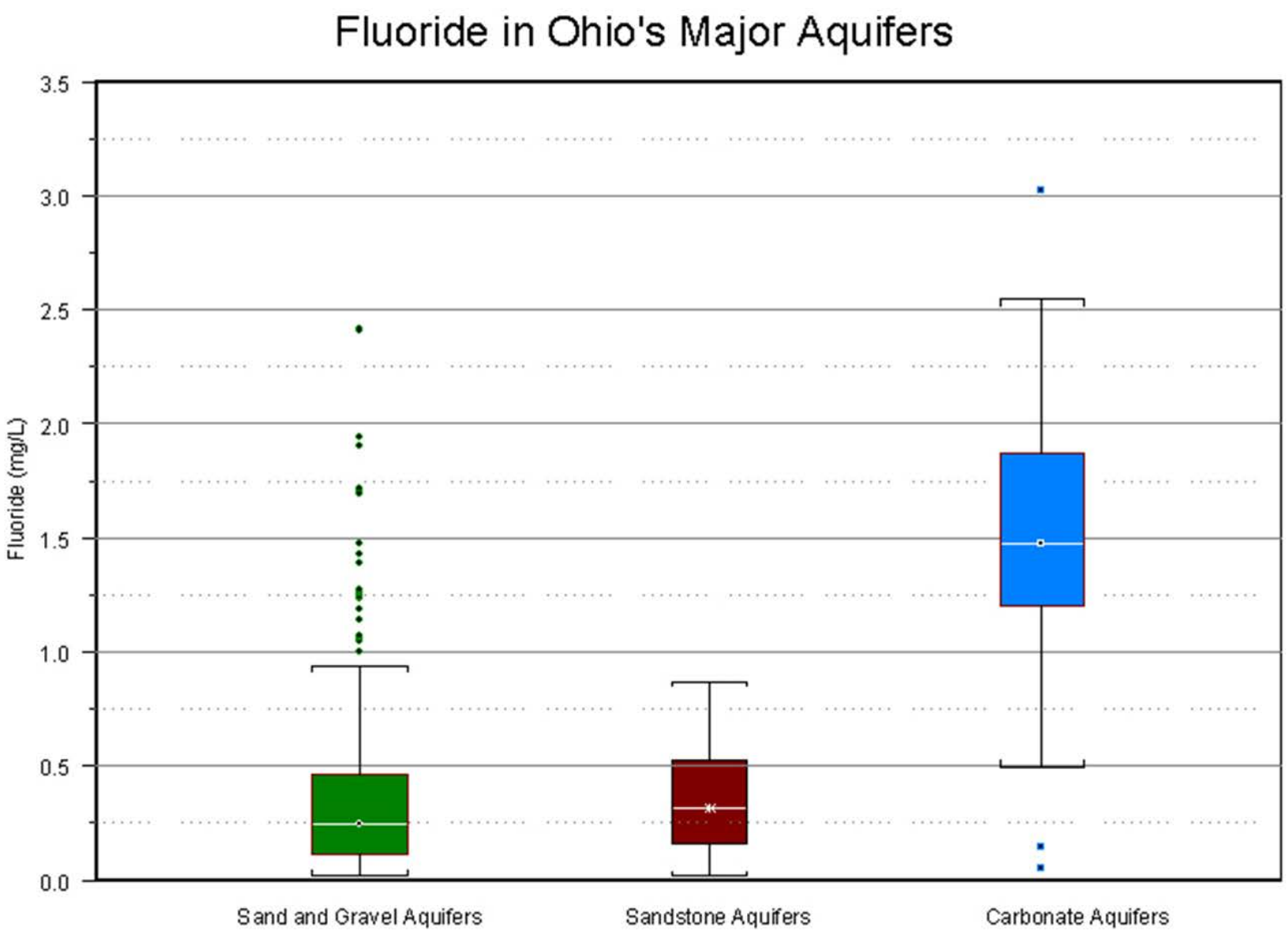
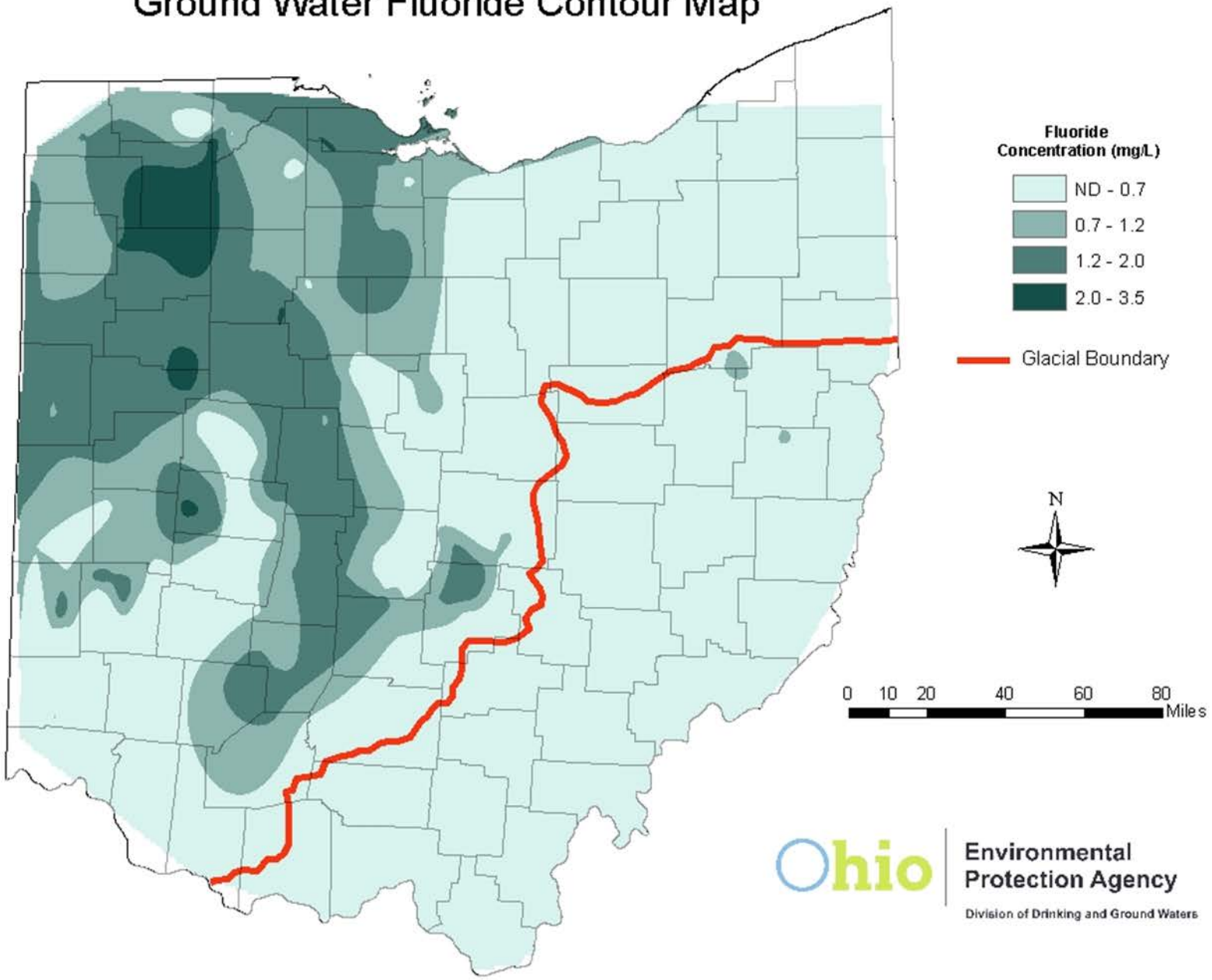

Fluoride in Ohio's Major Aquifers
Fluoride (mg/L)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Sand and Gravel Aquifers
Sandstone Aquifers
Carbonate Aquifers

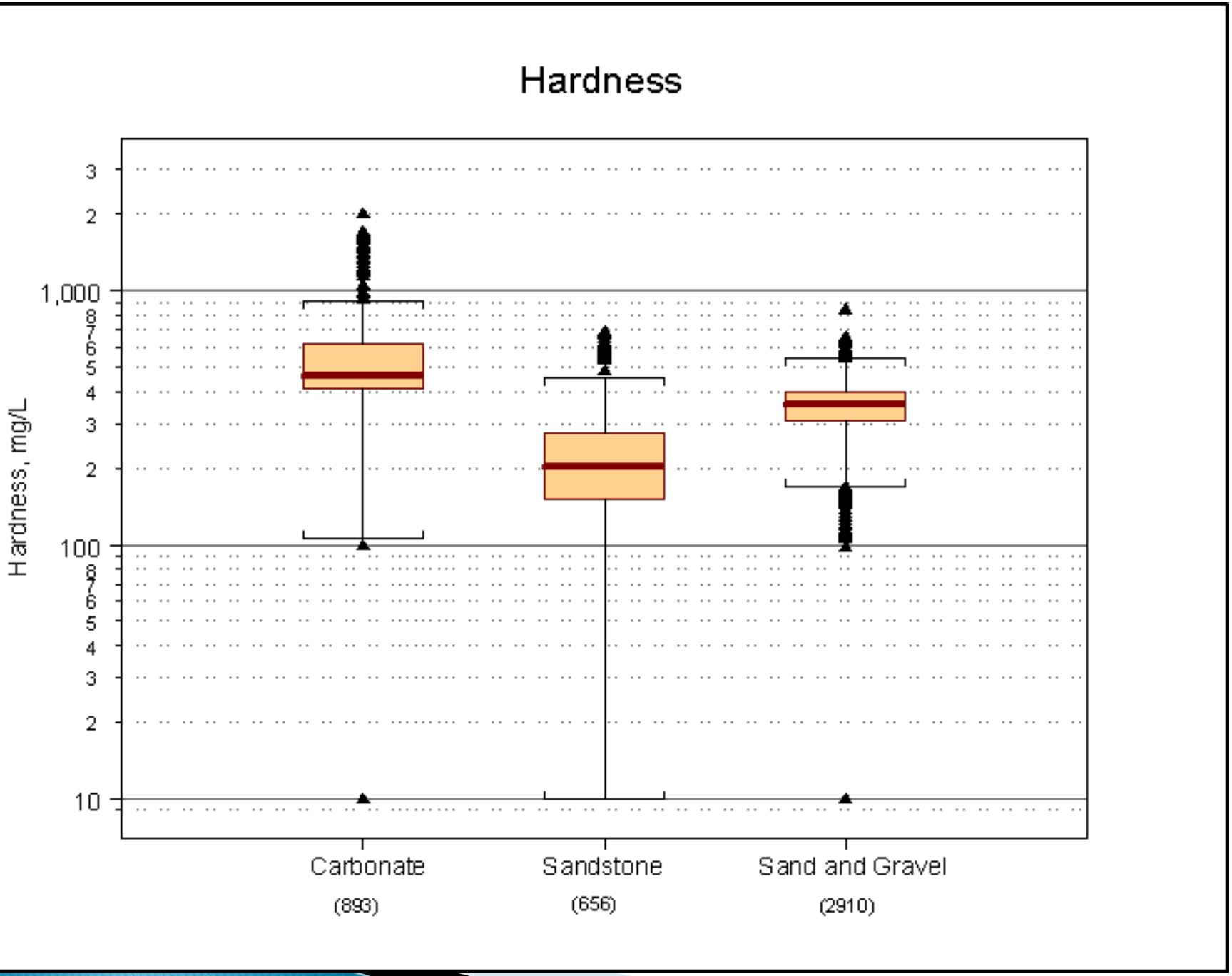
Ground Water Fluoride Contour Map

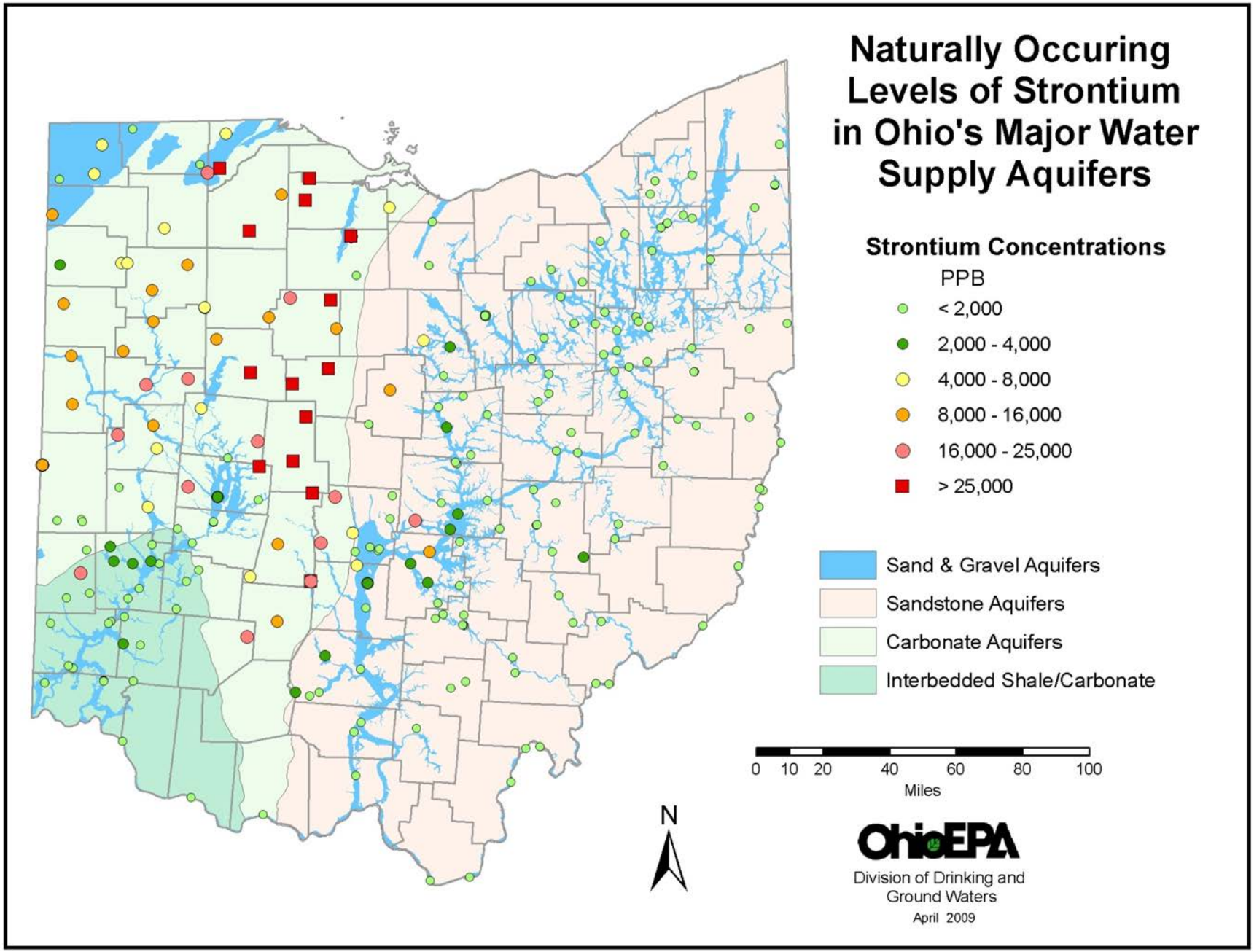


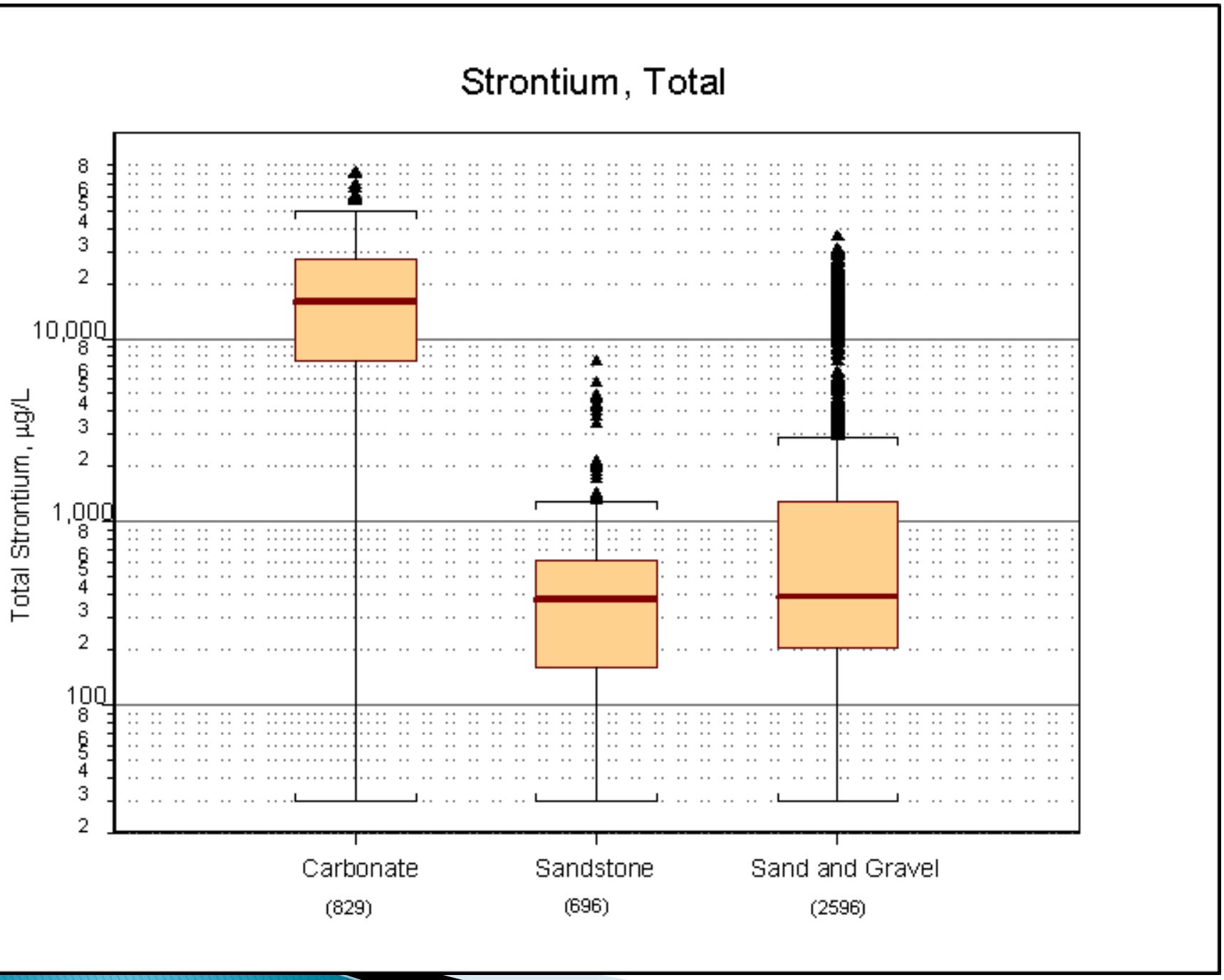
Major Elements

- Carbonate aquifer - consistently higher concentrations than sandstone.
- Sandstone exhibits the lowest concentrations.

- Why is the water quality in S&G aquifer intermediate between the carbonate and sandstone aquifers?


Hardness
Hardness, mg/L
3
2
1,000
8
7
6
5
4
3
2
100
8
7
6
5
4
3
2
10
Carbonate
(893)
Sandstone
(656)
Sand and Gravel
(2910)


Naturally Occuring Levels of Strontium in Ohio's Major Water Supply Aquifers
Strontium Concentrations
PPB
< 2,000
2,000 - 4,000
4,000 - 8,000
8,000 - 16,000
16,000 - 25,000
> 25,000
Sand & Gravel Aquifers
Sandstone Aquifers
Carbonate Aquifers
Interbedded Shale/Carbonate
0 10 20 40 60 80 100
Miles
N
OhioEPA
Division of Drinking and Ground Waters
April 2009


Strontium, Total
Total Strontium, µg/L
10,000
1,000
100
Carbonate
(829)
Sandstone
(696)
Sand and Gravel
(2596)

Geologic Controls

- Major constituents controlled by lithology of major aquifer;
  - Carbonate is more soluble than sandstone:
  - GW quality in S&G aquifers is intermediate between carbonate and sandstone aquifers;
- Trace elements frequently controlled by secondary mineralization or other variation in composition of geologic strata.

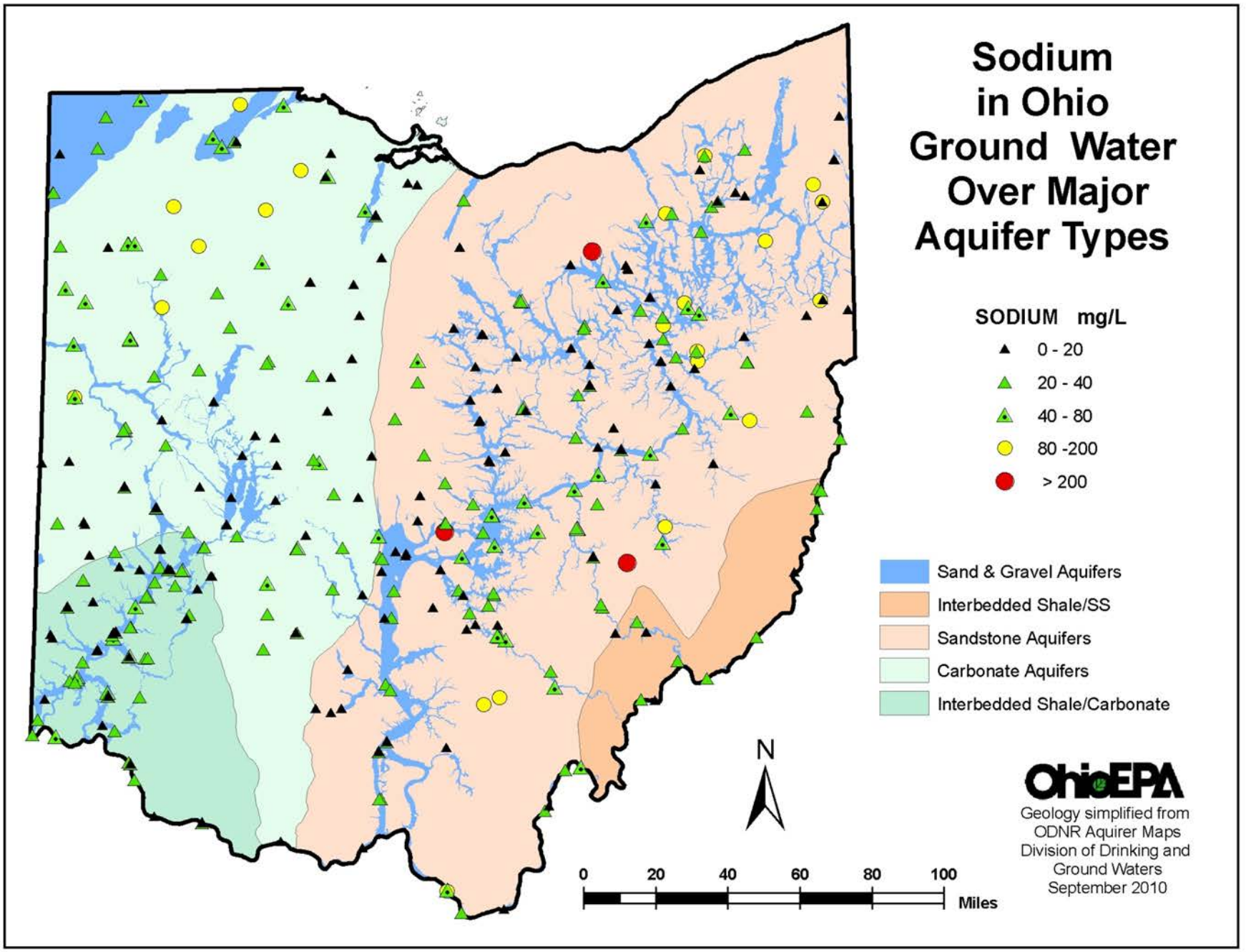
Typical Ranges of Parameters in Ground Water in Ohio Major Aquifers

Parameter	Symbol/ Description	MCL/ SMCL [S]	Sand & Gravel Range	Sandstone Range	Limestone Range	Units *
Alkalinity	Total as $CaCO_3$		80-440	40-400	160-440	ppm
Barium	Dissolved Ba	2000	ND-400	ND-250	ND-200	ppb
Calcium	Total Ca		40-160	10-130	30-230	ppm
Chloride	Cl	250 [S]	ND-80	ND-100	ND-70	ppm
Conductivity	At 25 °C		120-1,000	80-1,200	250-1,500	µmohs/cm
Iron	Dissolved Fe	300 [S]	20-4,000	50-3,000	40-2,500	ppb
Magnesium	Total Mg		10-50	ND- 40	10-90	ppm
Potassium	Total K		ND-4	ND-4	ND-5	ppm
pH	$[H^+]$	7-10.5 [S]	6.5-8.0	6.25-8.25	6.5-7.8	SU
Sodium	Total Na		ND-60	ND-120	ND-90	ppm
Strontium	Sr	HA	ND-3,000	ND-1,200	ND-30,000	ppb
Sulfate	SO_4	250 [S]	ND-150	ND-150	ND-700	ppm
Total Dissolved Solids (TDS)	TDS	500 [S]	200-700	ND-750	ND-1,400	ppm

[S] Indicates secondary MCL

* Units: ppm = parts per million and is equivalent to mg/L; ppb = parts per billion and is equivalent to µg/L; SU = Standard Units

ND = non-detect


Sodium in Ohio Ground Water Over Major Aquifer Types
SODIUM mg/L
0 - 20
20 - 40
40 - 80
80 -200
> 200
Sand & Gravel Aquifers
Interbedded Shale/SS
Sandstone Aquifers
Carbonate Aquifers
Interbedded Shale/Carbonate
N
0 20 40 60 80 100
Miles
OhioEPA
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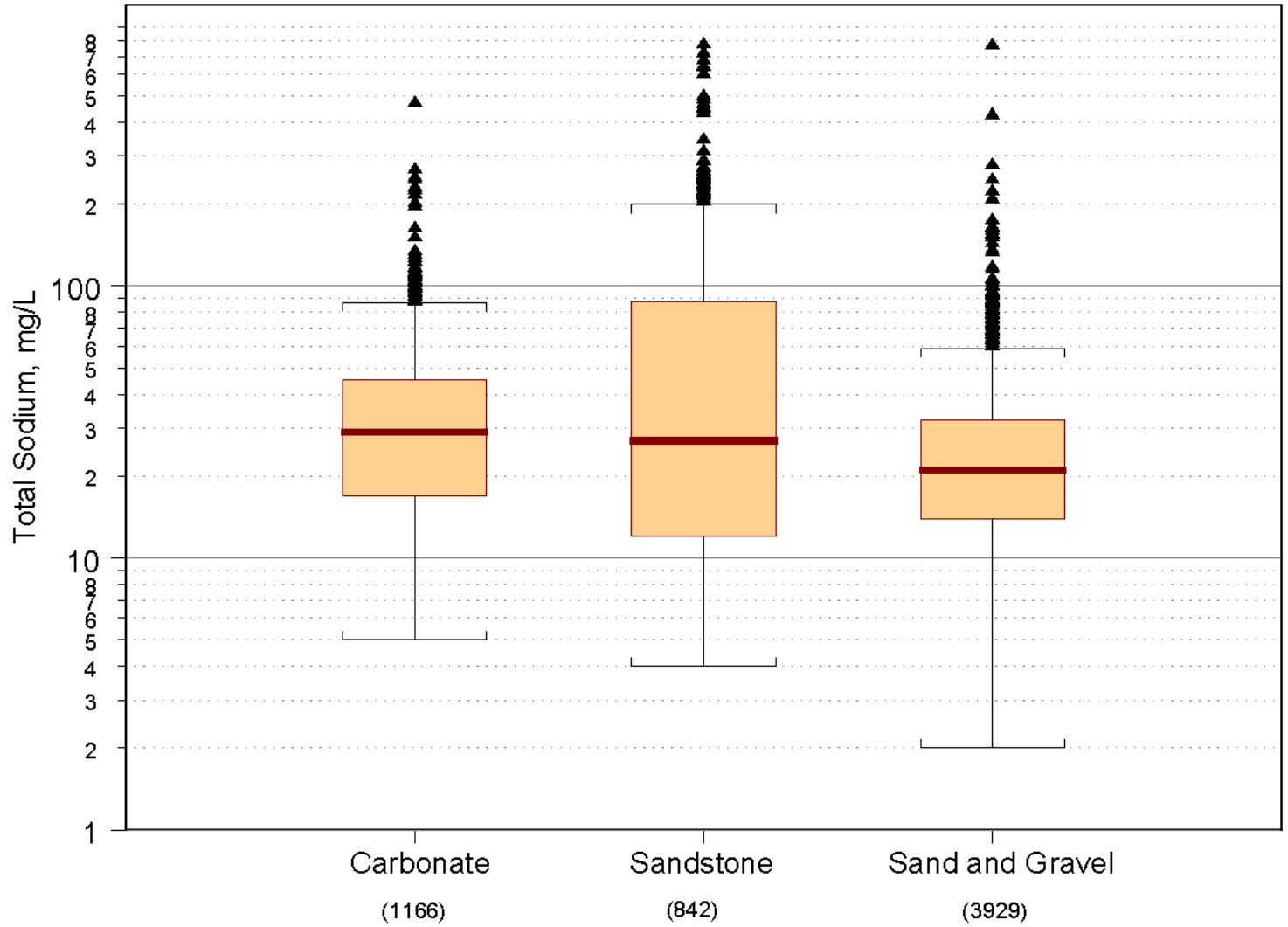
Sodium, Total



Geochemical Controls

- Geochemistry influences the solubility of the earth materials present.
- If a natural contaminant is present in geologic strata, it may become a concern when it is soluble.
- Oxidation-Reduction (Redox) is an important control for dissolution of some natural contaminants.

Oxidation-Reduction in GW

- Controlled by transfer of electrons between electron donors and acceptors
- Process is referred to as terminal electron-acceptor processes (TEAPs)
  - Organic carbon is the electron donor (Oxidized);
  - Electron acceptors are inorganic constituents (Reduced);
  - Reactions mediated by energy for microbial reduction;
  - As GW is reduced, constituents are consumed in order:

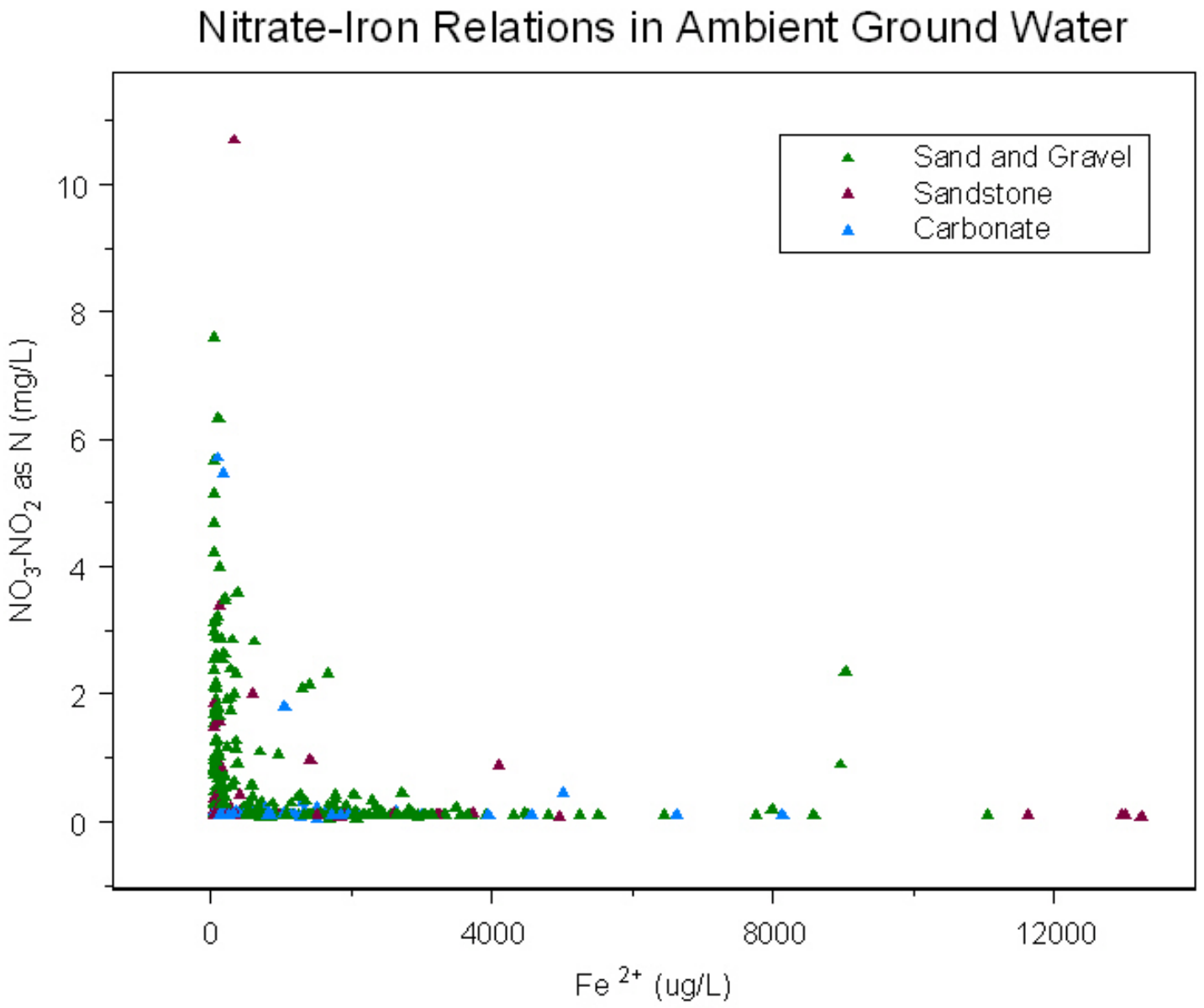
$$O_2 > NO_3 > Mn(IV) > Fe(III) > SO_4^{2-} > CO_2$$

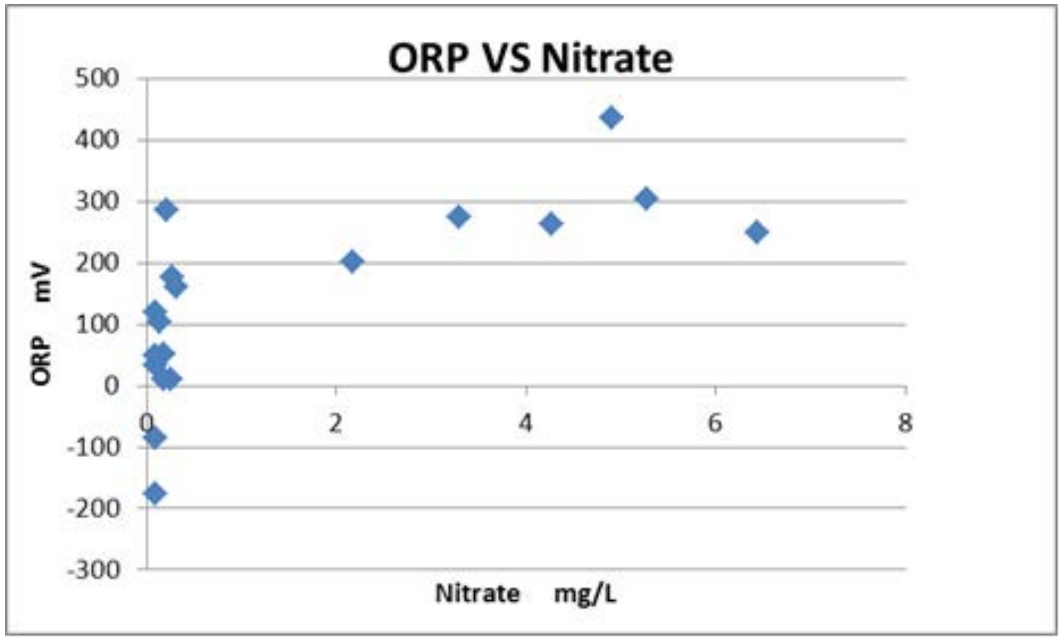
Oxidation-Reduction

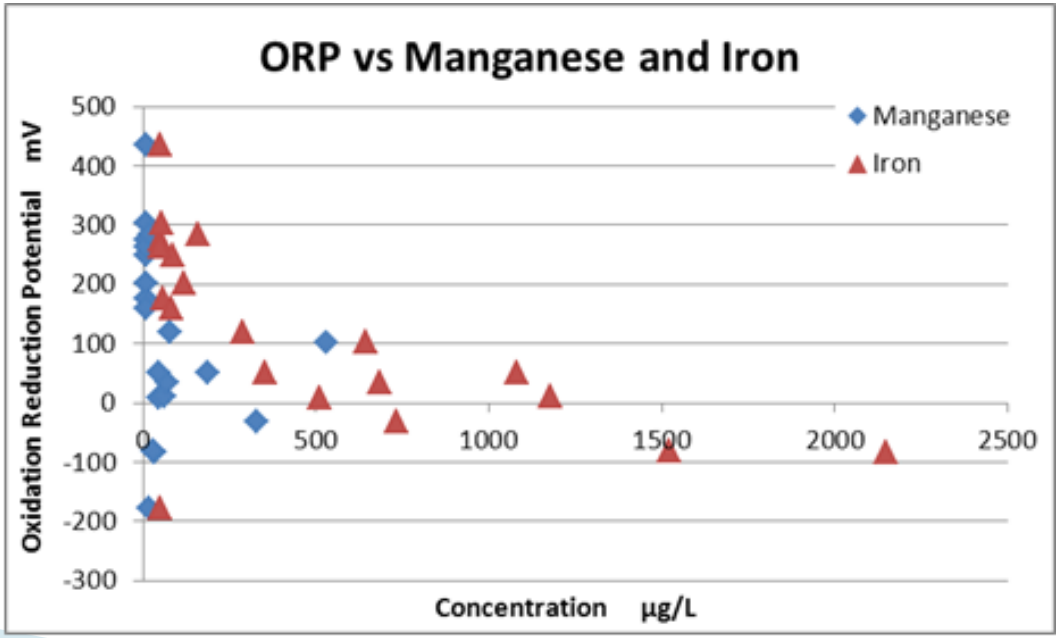
- Microbial metabolism and competition is orderly and the primary control for oxidation-reduction in GW;
- Redox conditions can be deduced by the reactants and products present in GW.

Redox Indicator Pairs

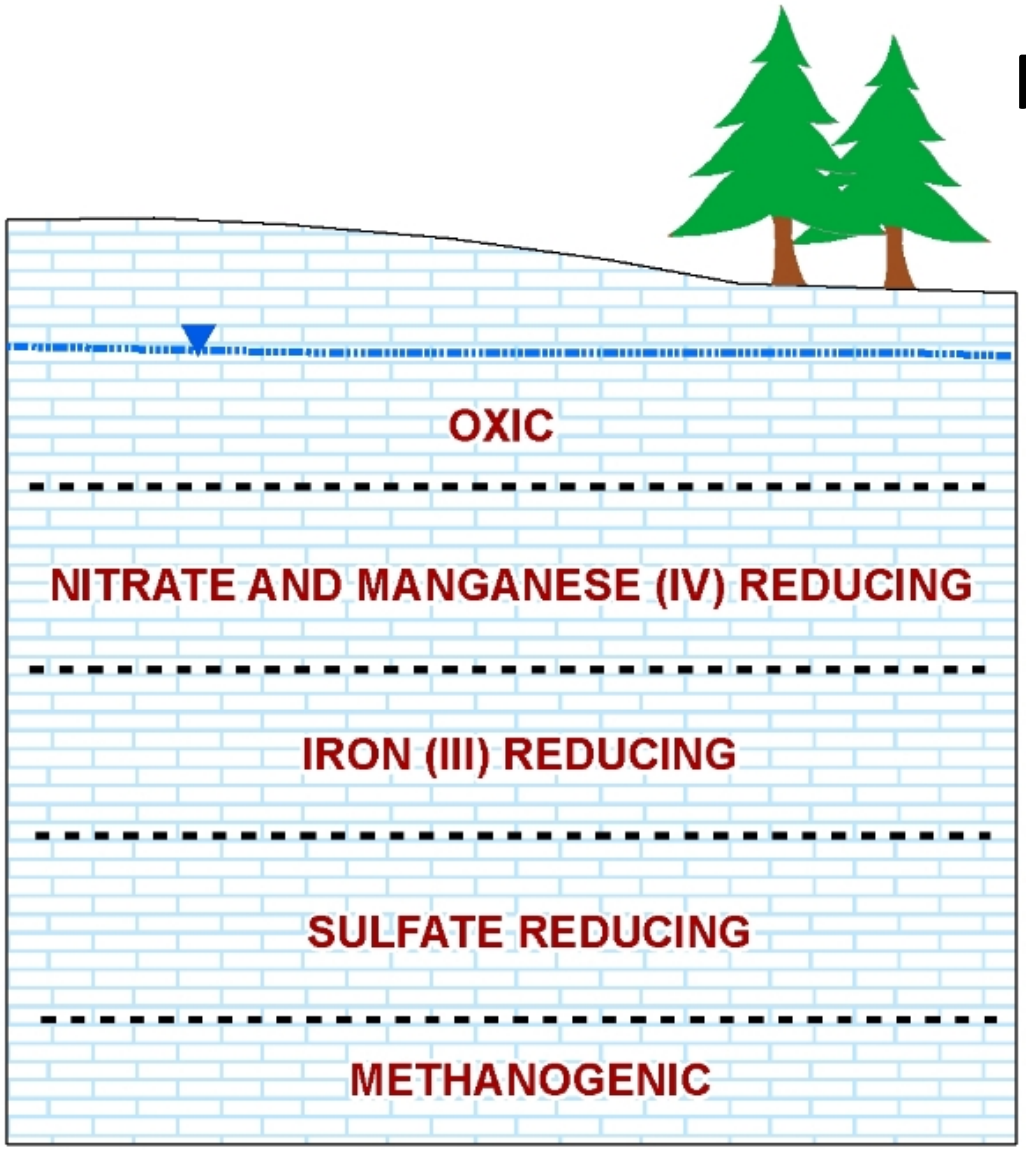
$O_2 : H_20$	Oxic
$NO_3 : N_2$ $MnO_2 : Mn^{2+}$	Sub-Oxic
$Fe(OH)3 : Fe^{2+}$ $SO_4^{2-} : H_2S$	Sulfidic
$CO_2 : CH_4$ $H_2O : H_2$	Methanic


Nitrate-Iron Relations in Ambient Ground Water
Sand and Gravel
Sandstone
Carbonate
NO_3-NO_2 as N (mg/L)
10
8
6
4
2
0
0
4000
8000
12000
Fe 2+ (ug/L)


ORP VS Nitrate
500
400
300
200
100
0
-100
-200
-300
ORP mV
0
2
4
6
8
Nitrate mg/L


ORP vs Manganese and Iron
Manganese
Iron
500
400
300
200
100
0
-100
-200
-300
Oxidation Reduction Potential mV
0
500
1000
1500
2000
2500
Concentration µg/L

Redox Control with Depth



Dissolved O_2

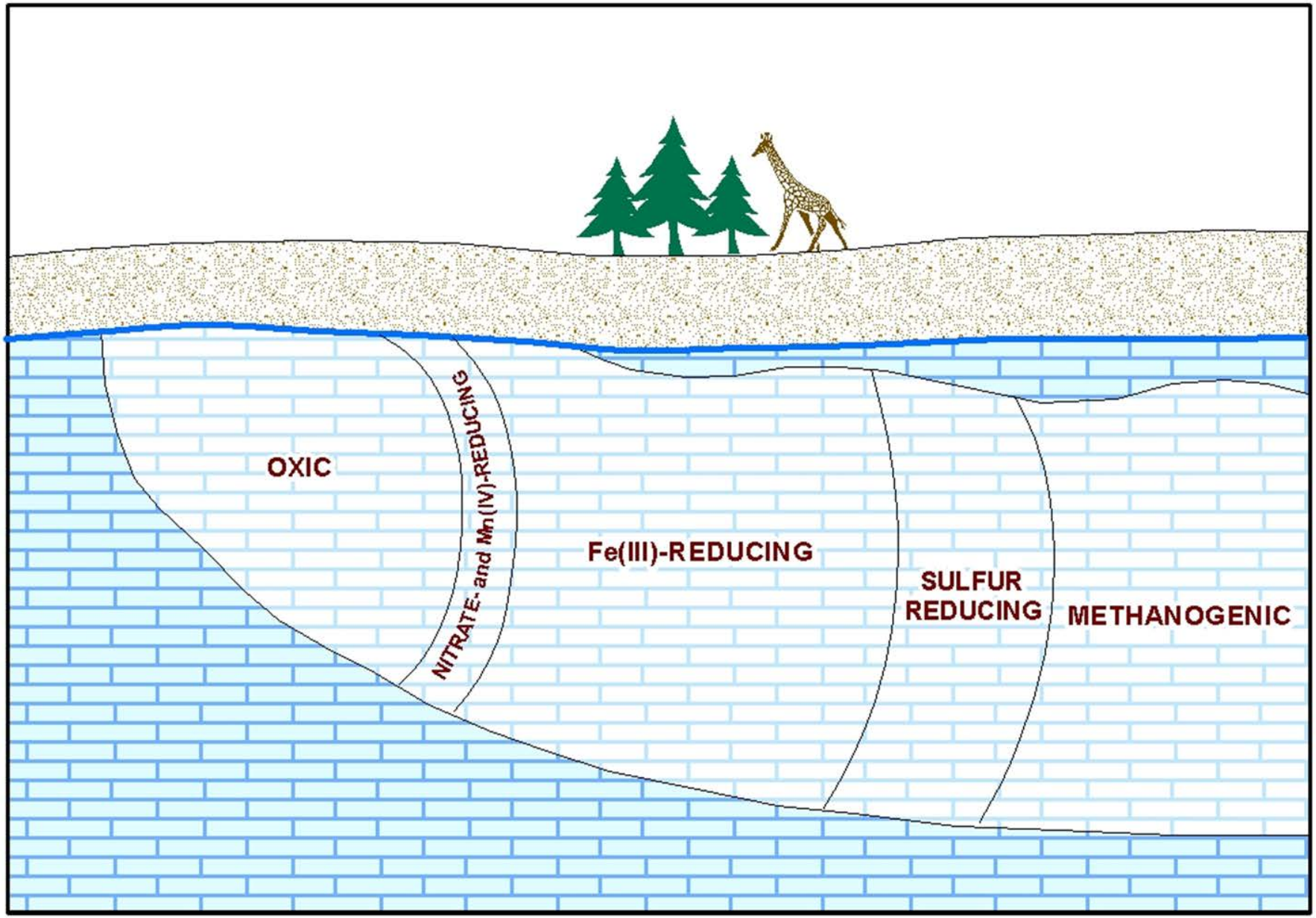
$NO_3 : N_2$

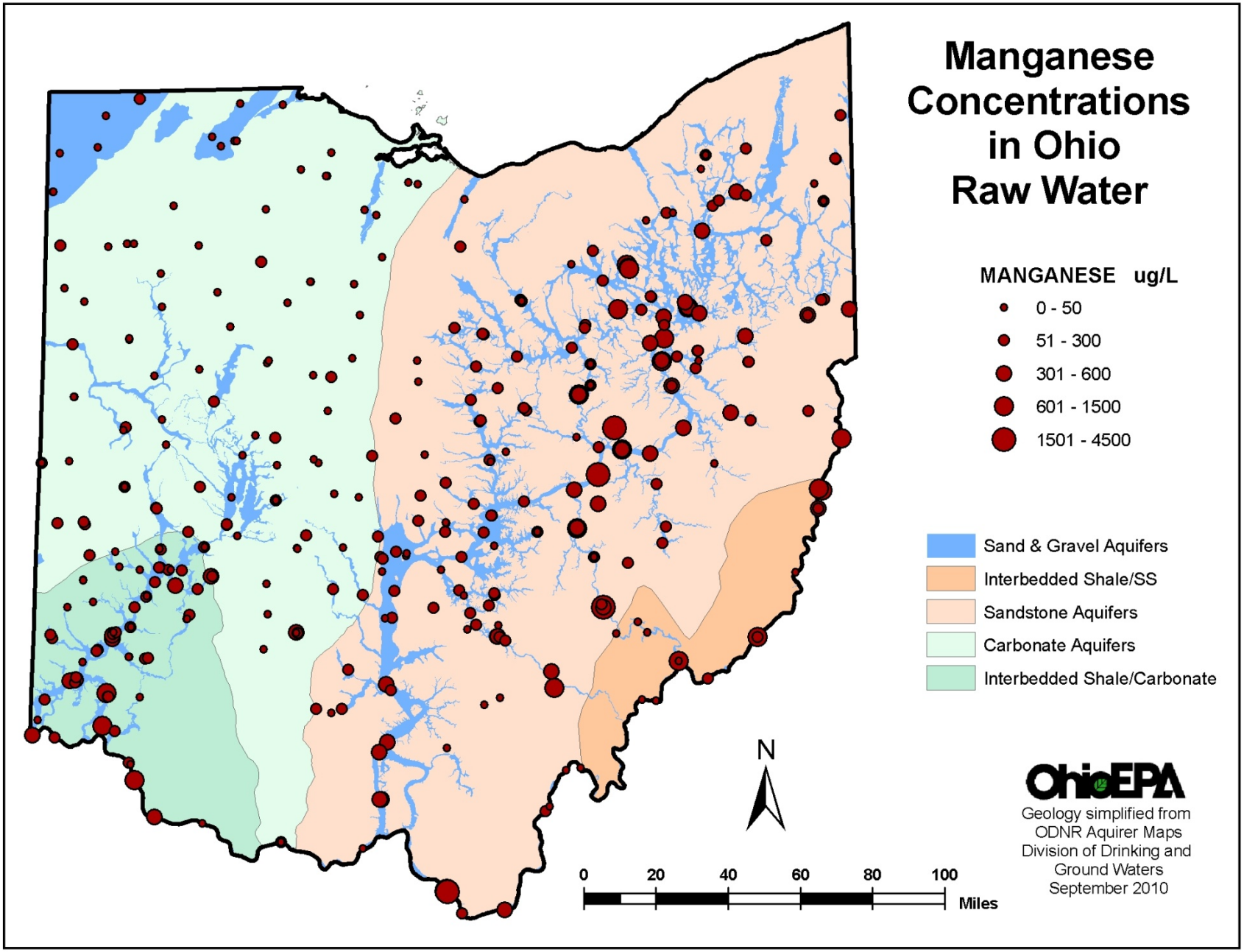
$MnO_2 : Mn^{2+}$

$Fe(OH)_3 : Fe^{2+}$

$SO_4^{2-} : H_2S$

$CO_2 : CH_4$


OXIC
NITRATE- and Mn(IV)-REDUCING
Fe(III)-REDUCING
SULFUR REDUCING
METHANOGENIC


Manganese Concentrations in Ohio Raw Water
MANGANESE ug/L
0 - 50
51 - 300
301 - 600
601 - 1500
1501 - 4500
Sand & Gravel Aquifers
Interbedded Shale/SS
Sandstone Aquifers
Carbonate Aquifers
Interbedded Shale/Carbonate
N
0 20 40 60 80 100
Miles
OhioEPA
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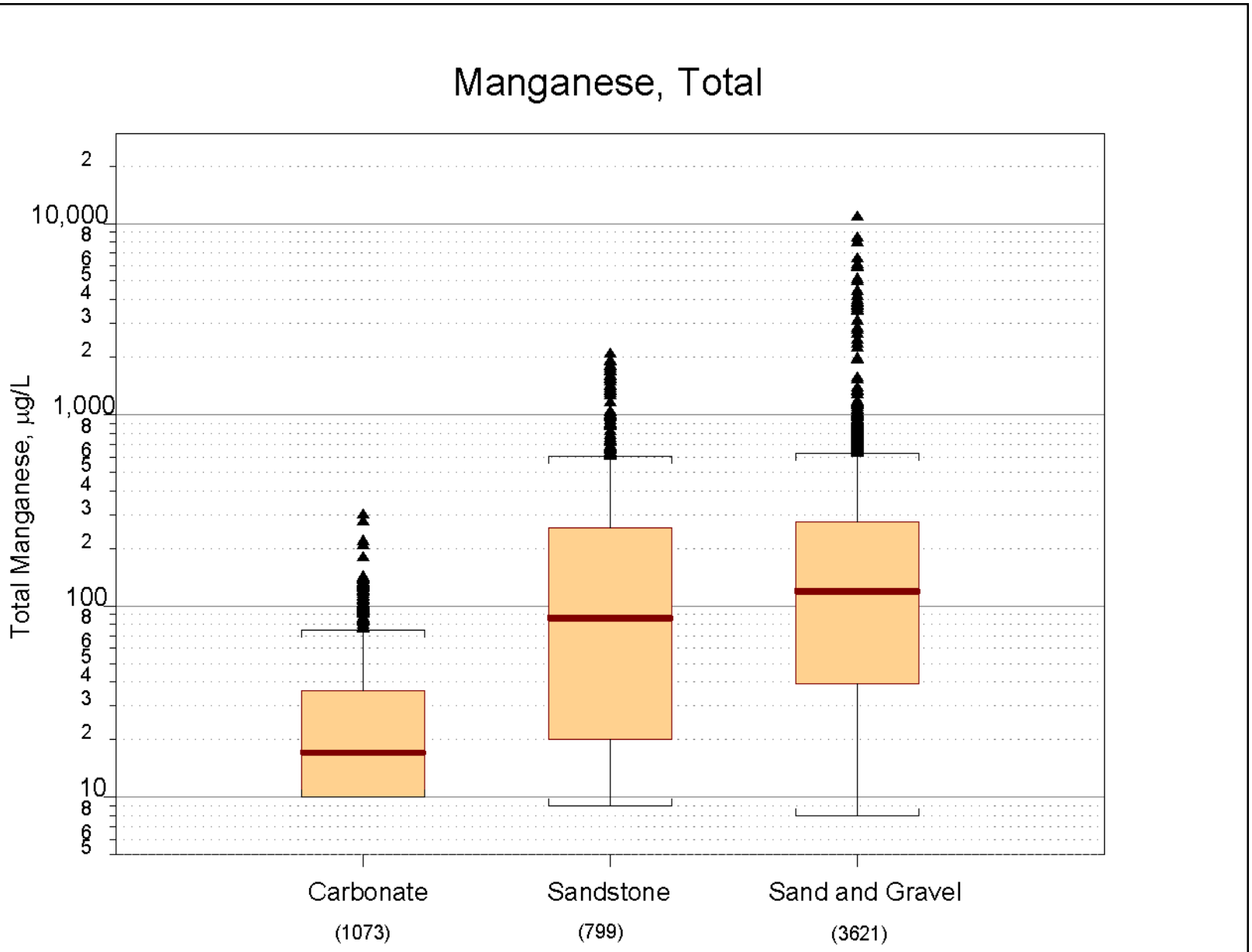
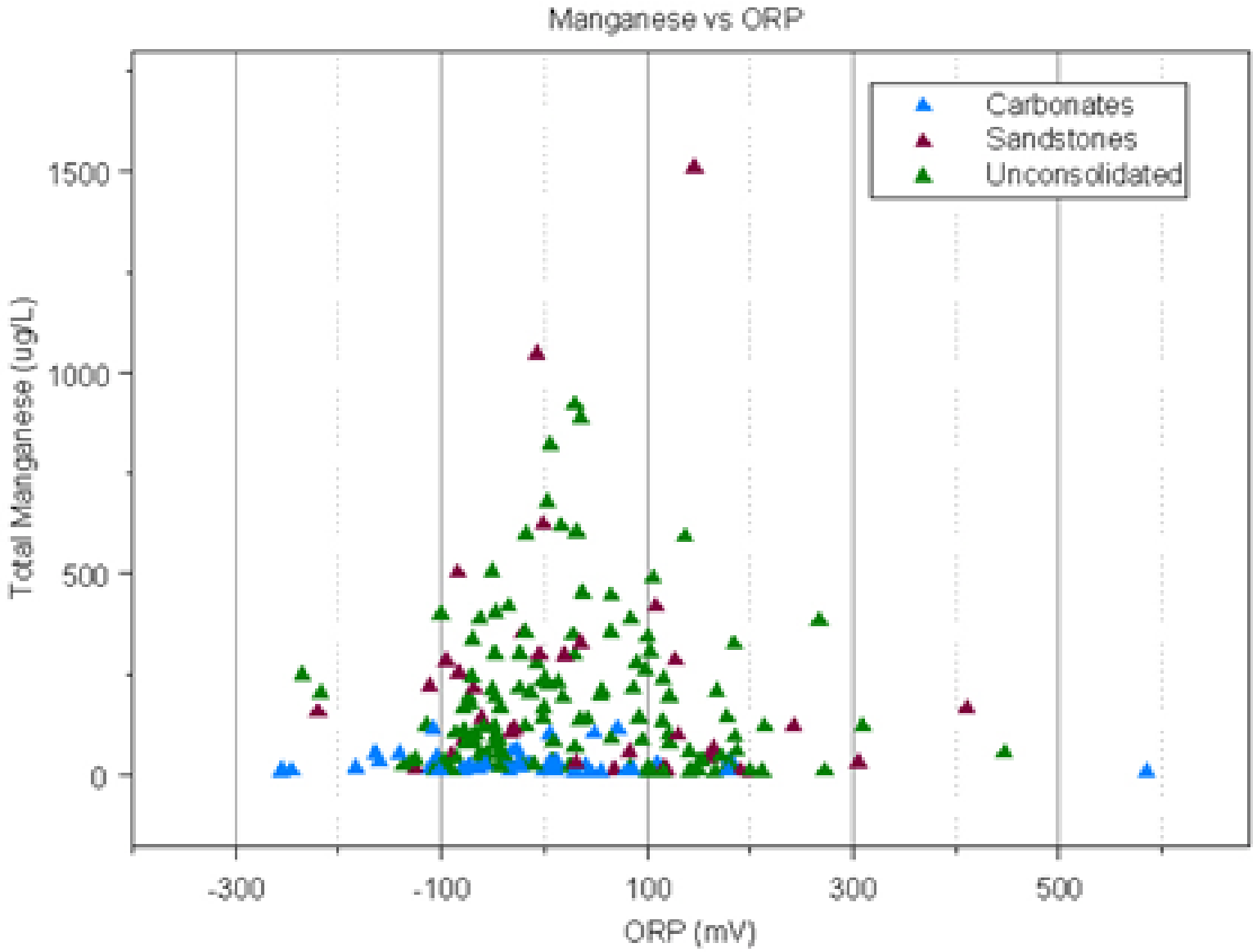
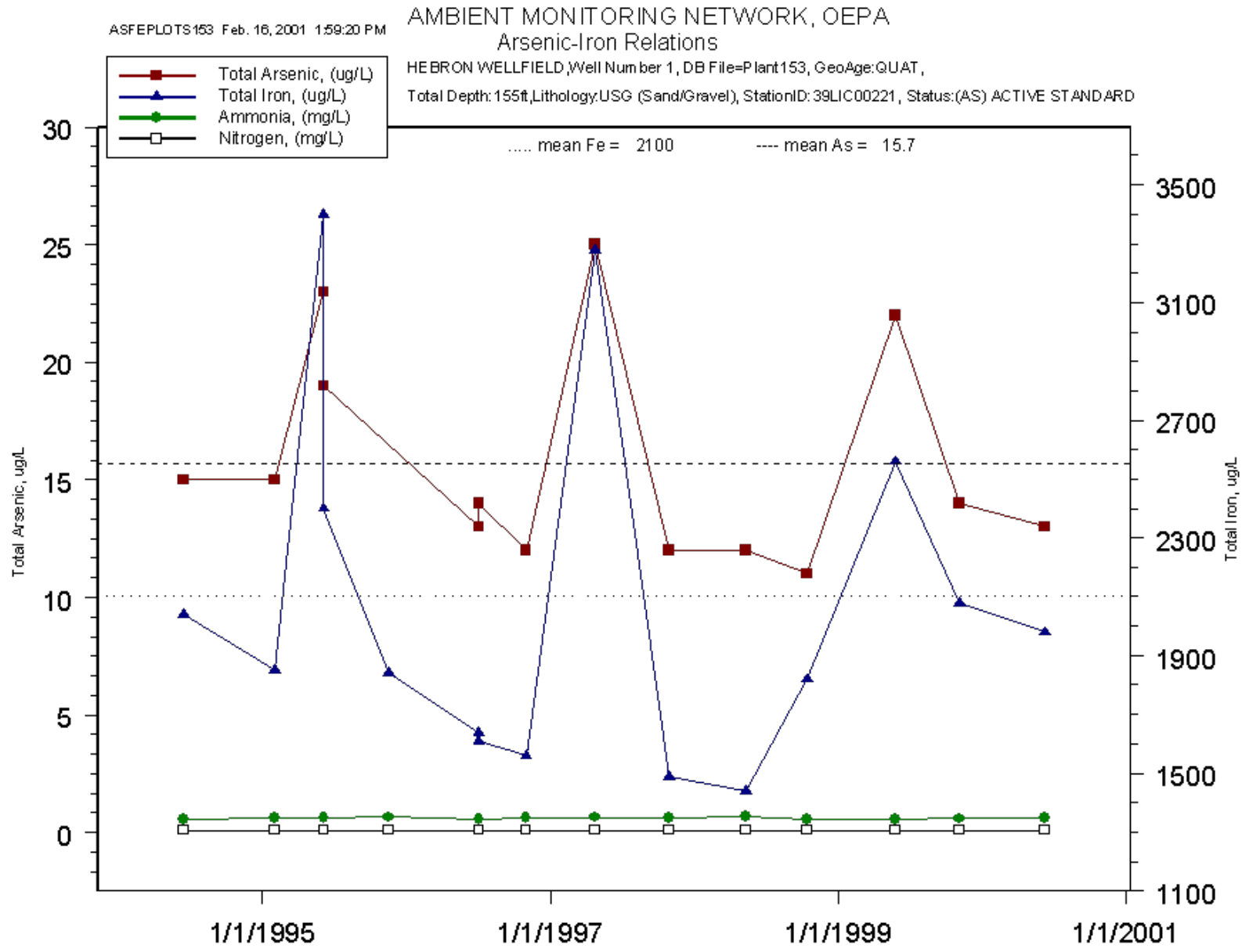
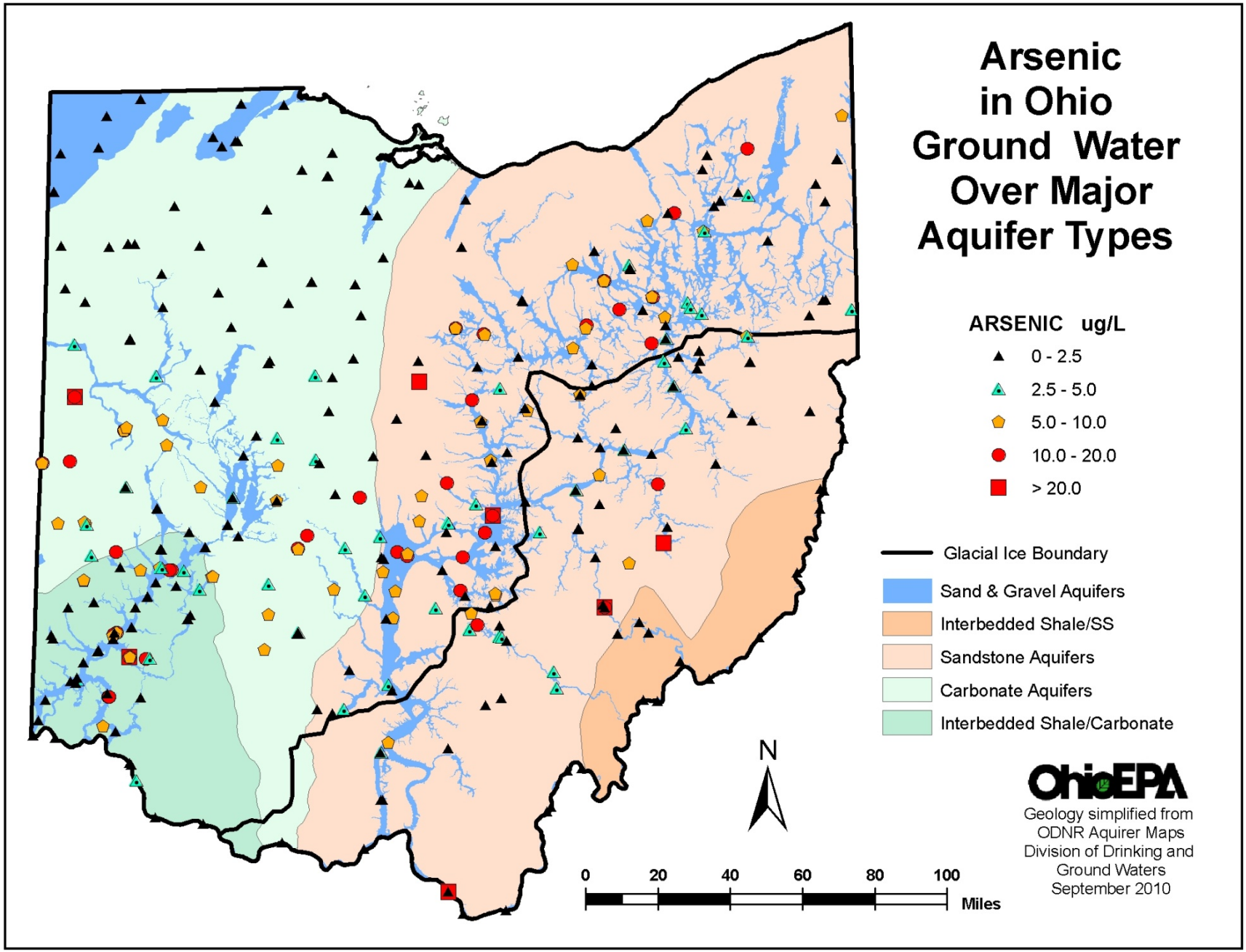

Manganese, Total
Total Manganese, µg/L
10,000
1,000
100
10
Carbonate
(1073)
Sandstone
(799)
Sand and Gravel
(3621)


Manganese vs ORP
Carbonates
Sandstones
Unconsolidated
Total Manganese (ug/L)
1500
1000
500
0
-300
-100
100
300
500
ORP (mV)

Arsenic Controls

- Arsenic geochemistry is similar to iron;
- Arsenic is adsorbed on to and within iron oxides and hydrodroxides;
- As iron oxides are reduced iron and arsenic are released into solution;
- Thus presence of arsenic in GW is controlled by two factors:
  - presence of Arsenic in the area; (geology) and
  - redox conditions (geochemistry)


ASFEPLOTS153 Feb. 16, 2001 1:59:20 PM
AMBIENT MONITORING NETWORK, OEPA
Arsenic-Iron Relations
HEBRON WELLFIELD,Well Number 1, DB File=Plant153, GeoAge:QUAT,
Total Depth:155ft,Lithology:USG (Sand/Gravel), StationID:39LIC00221, Status:(AS) ACTIVE STANDARD
Total Arsenic, (ug/L)
Total Iron, (ug/L)
Ammonia, (mg/L)
Nitrogen, (mg/L)
..... mean Fe = 2100
---- mean As = 15.7
Total Arsenic, ug/L
Total Iron, ug/L
30
25
20
15
10
5
0
3500
3100
2700
2300
1900
1500
1100
1/1/1995
1/1/1997
1/1/1999
1/1/2001


Arsenic in Ohio Ground Water Over Major Aquifer Types
ARSENIC ug/L
0 - 2.5
2.5 - 5.0
5.0 - 10.0
10.0 - 20.0
> 20.0
Glacial Ice Boundary
Sand & Gravel Aquifers
Interbedded Shale/SS
Sandstone Aquifers
Carbonate Aquifers
Interbedded Shale/Carbonate
N
0 20 40 60 80 100
Miles
OhioEPA
Geology simplified from ODNR Aquirer Maps
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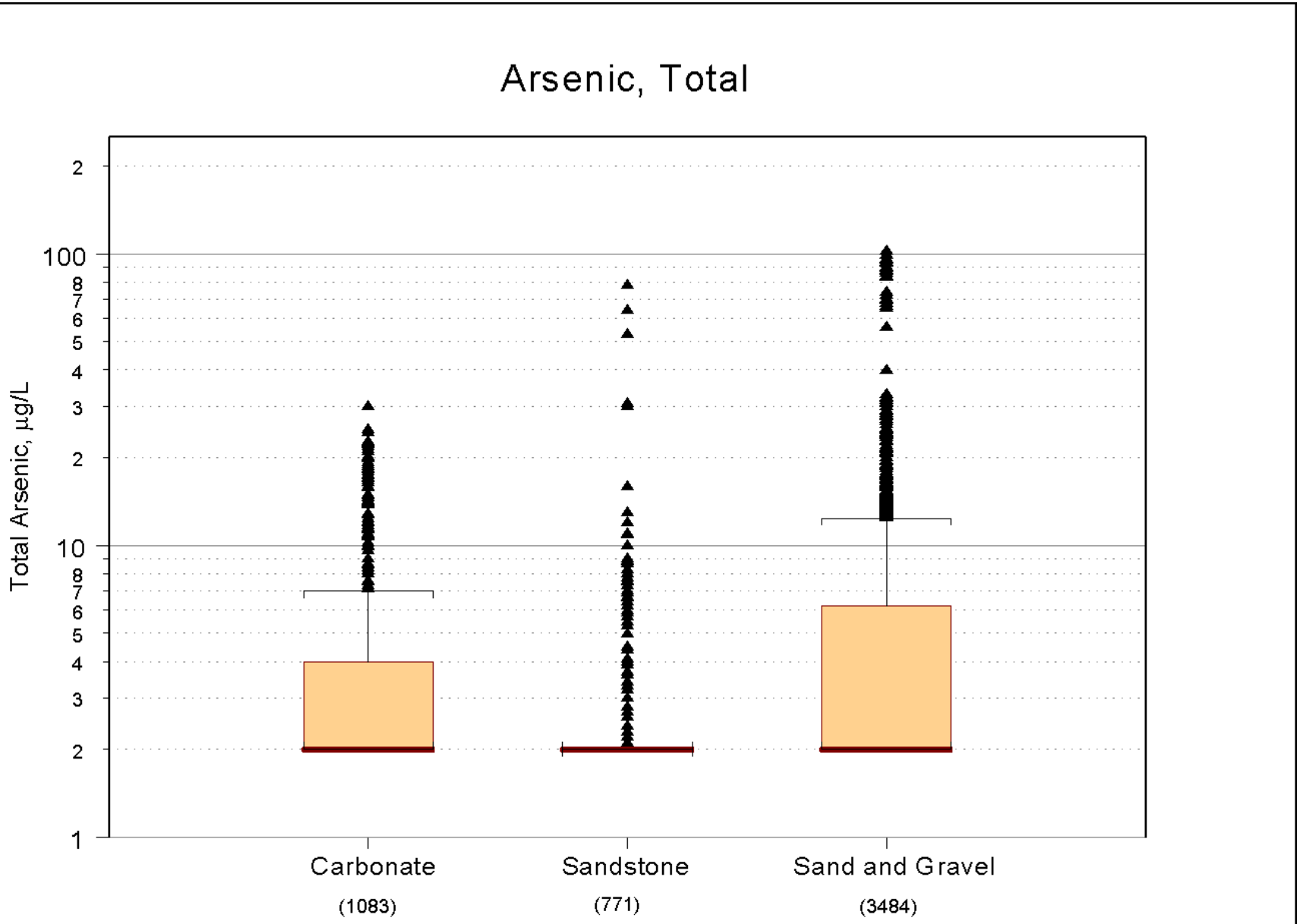
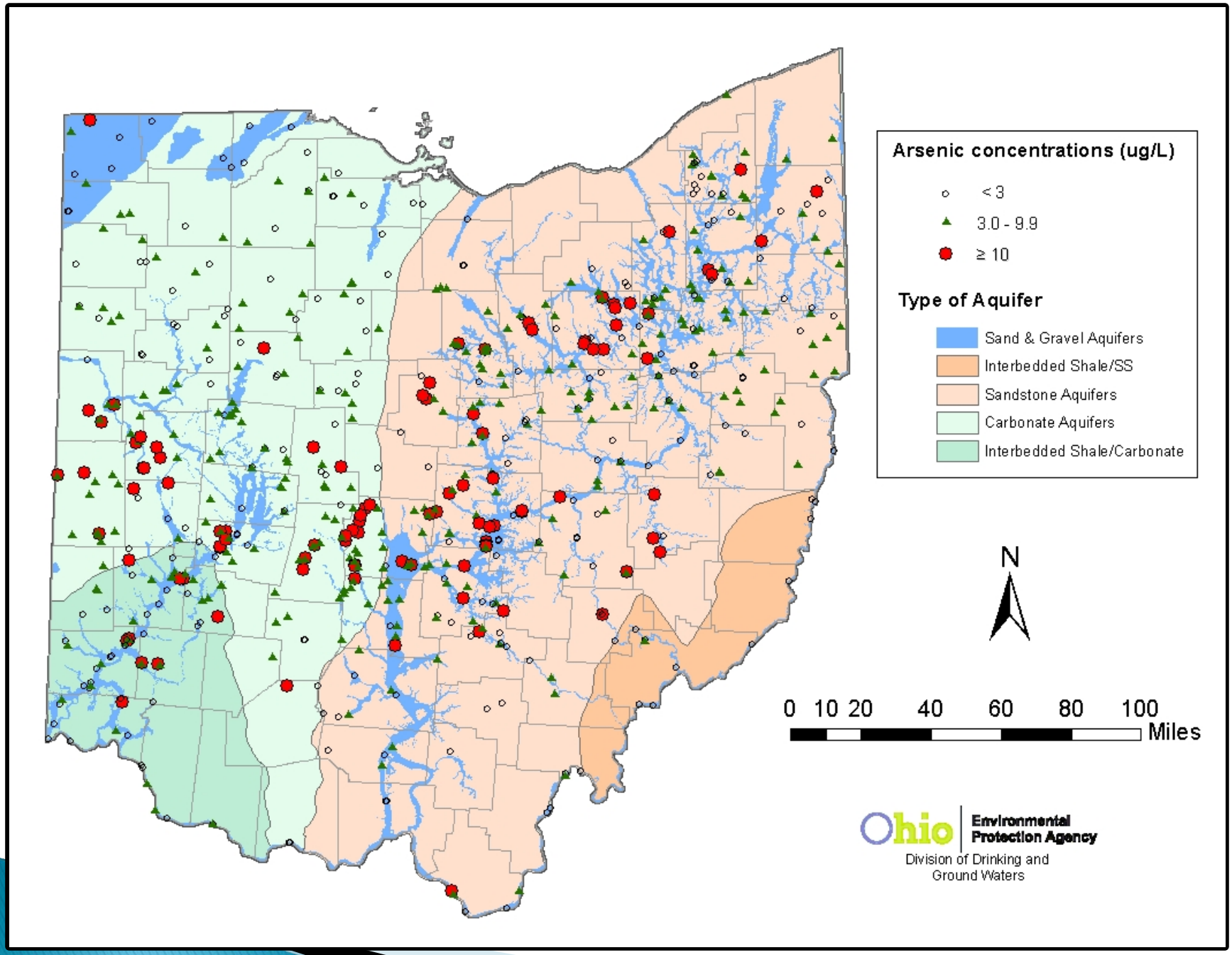
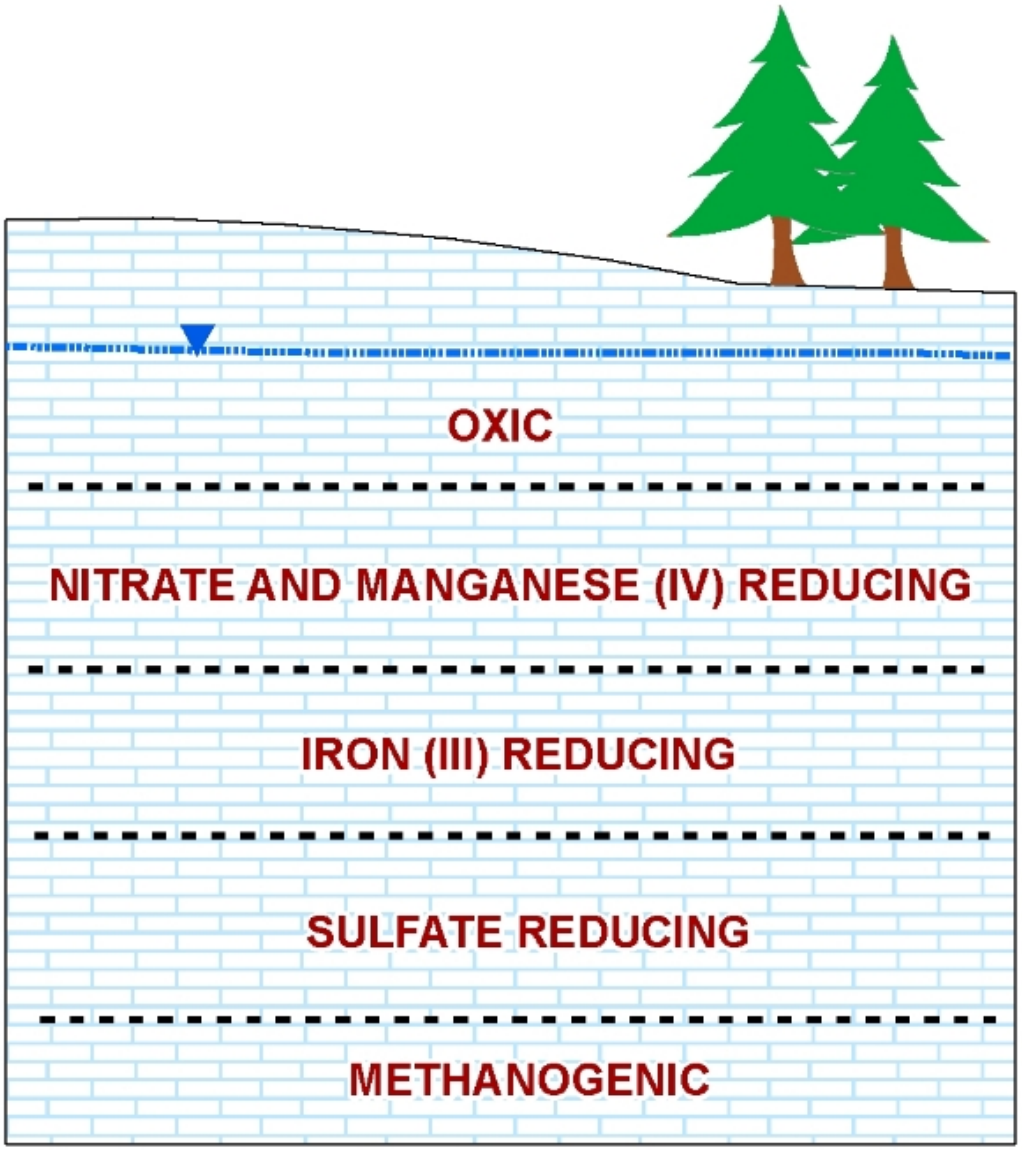

Arsenic, Total
Total Arsenic, µg/L
2
100
8
7
6
5
4
3
2
10
8
7
6
5
4
3
2
1
Carbonate
(1083)
Sandstone
(771)
Sand and Gravel
(3484)


Arsenic concentrations (ug/L)
< 3
3.0 - 9.9
≥ 10
Type of Aquifer
Sand & Gravel Aquifers
Interbedded Shale/SS
Sandstone Aquifers
Carbonate Aquifers
Interbedded Shale/Carbonate
N
0 10 20 40 60 80 100
Miles
Ohio Environmental Protection Agency
Division of Drinking and Ground Waters

Redox Control with Depth



Dissolved O_2

$NO_3 : N_2$

$MnO_2 : Mn^{2+}$

$Fe(OH)_3 : Fe^{2+}$

$SO_4^{2-} : H_2S$

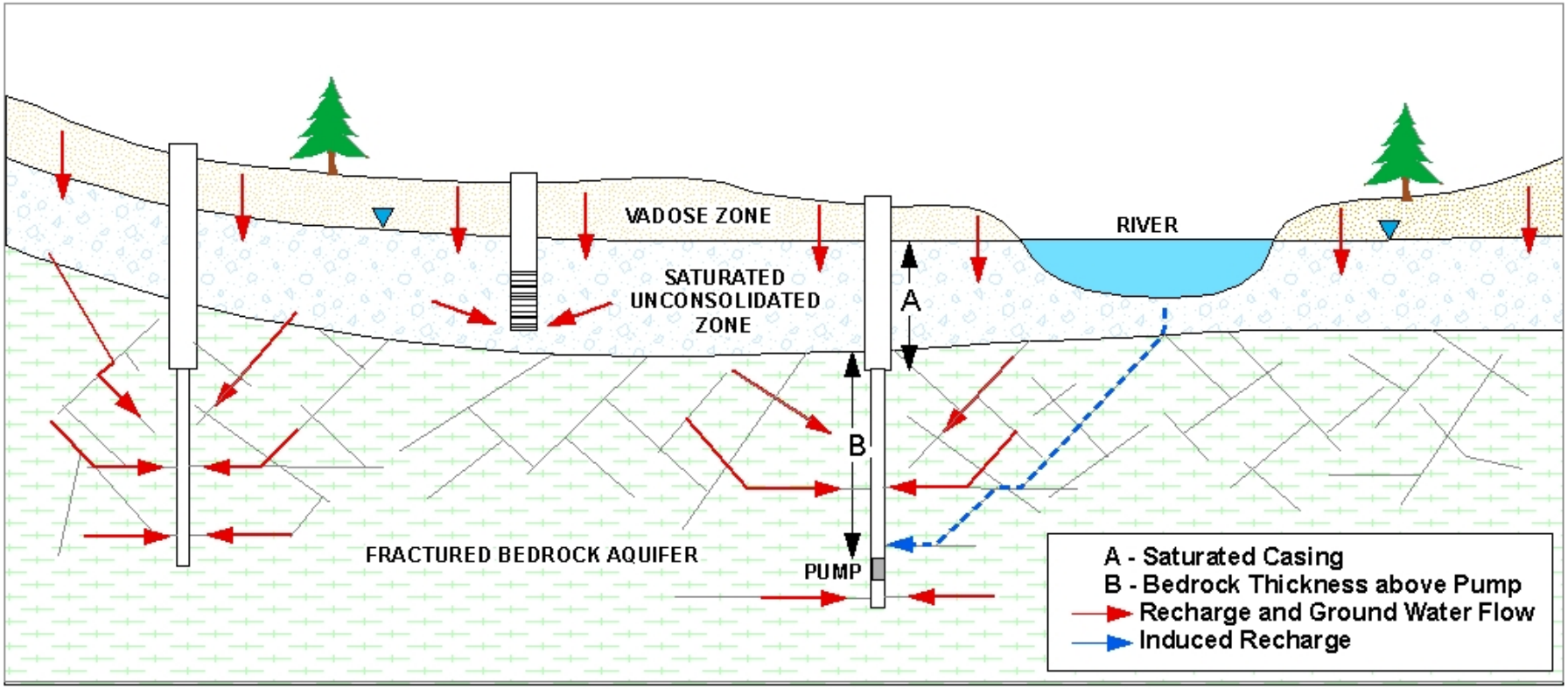
$CO_2 : CH_4$

limestone redox column.jpg (1818 x 1402)

Water Quality Controls

- Geologic
  - Regional to local
- Geochemical
  - Regional to local
- Local
  - Well setting
  - Land use
  - Well construction

Each site is a mystery to sort out with geologic, geochemical and local elements to consider



Not drawn to scale.

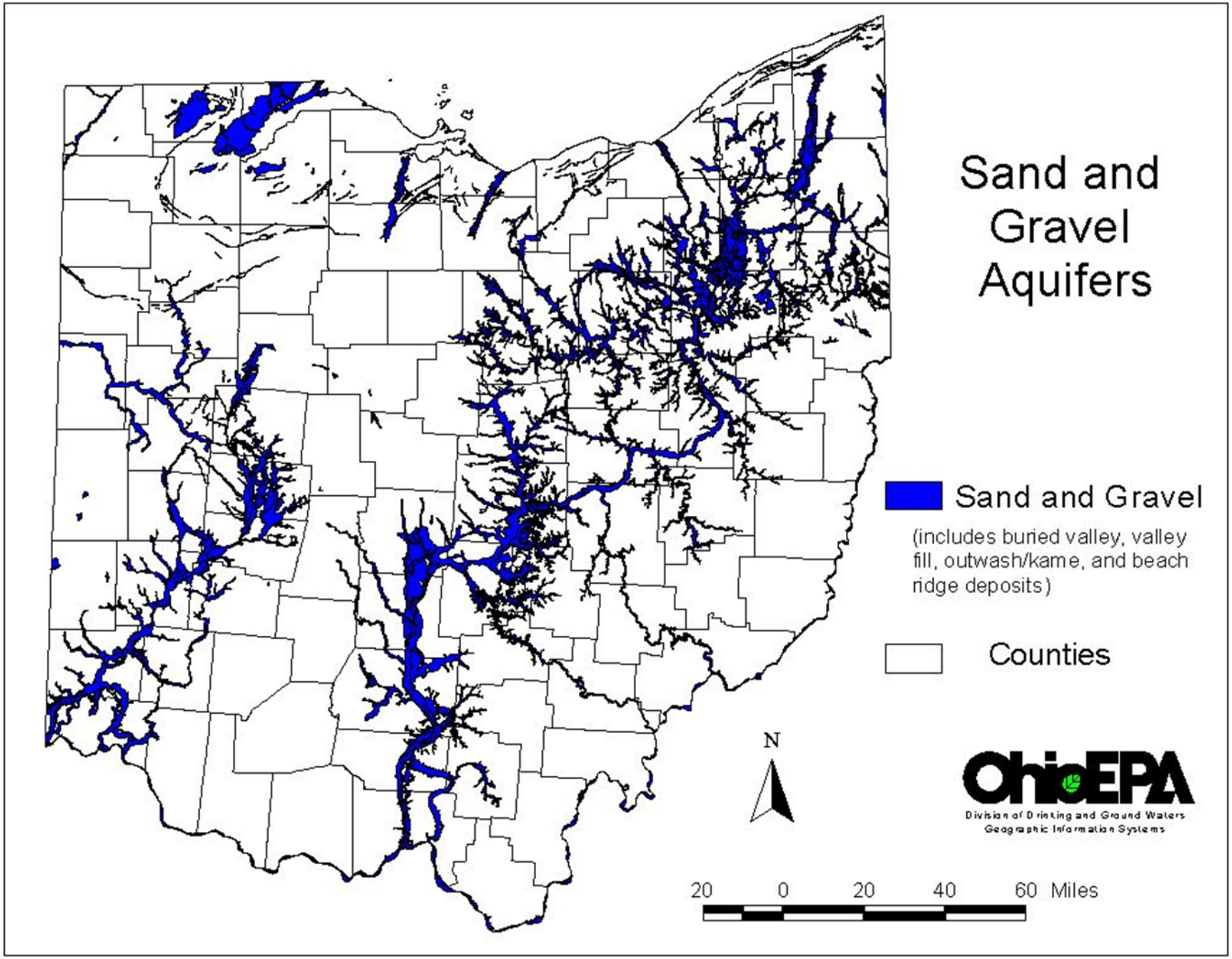
Sensitive Aquifers in Ohio

Buried Valleys

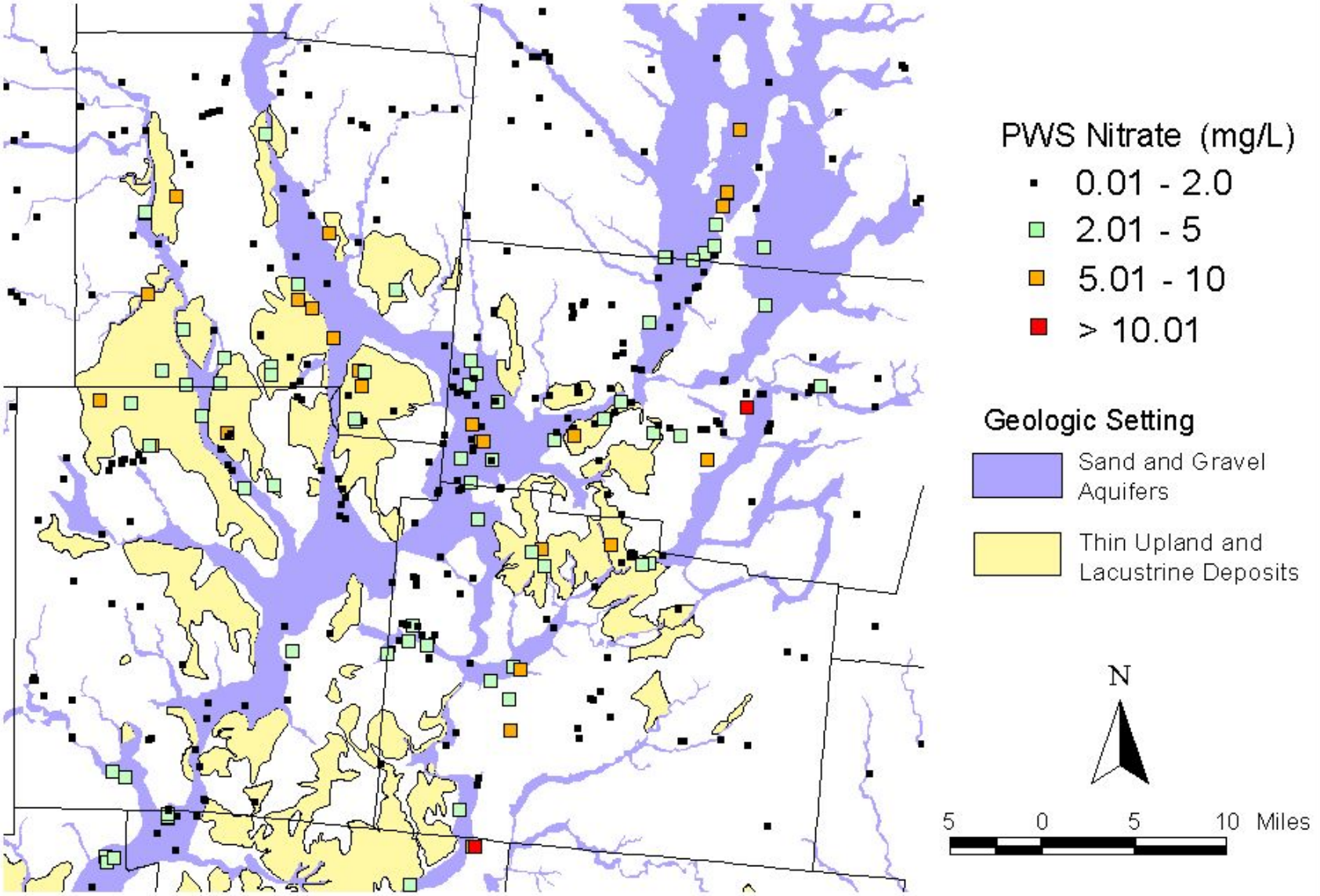
Sand and gravel aquifers are sensitive to dissolved components, but natural filtration may remove particulates like pathogens.

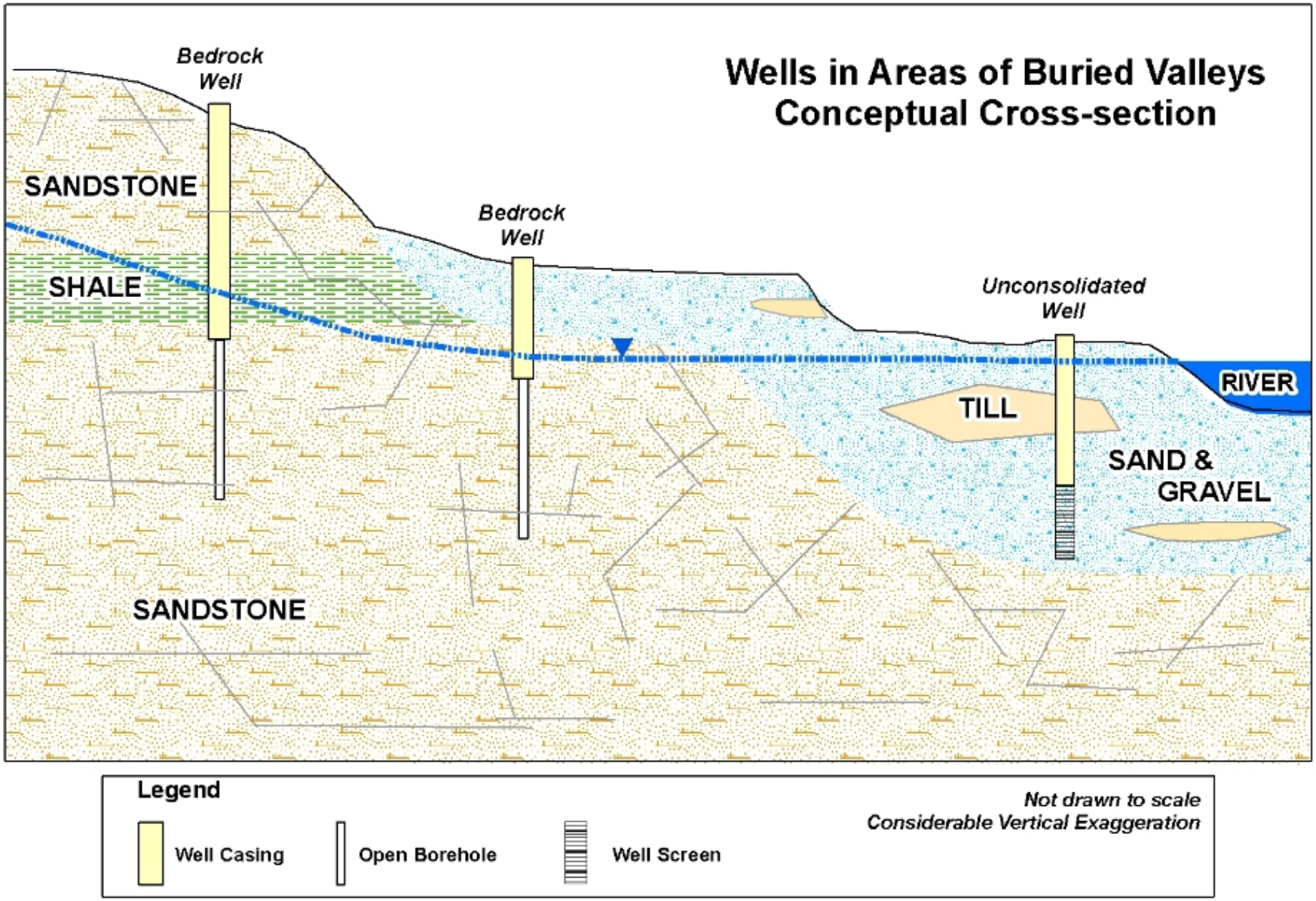
Thin drift over bedrock aquifers

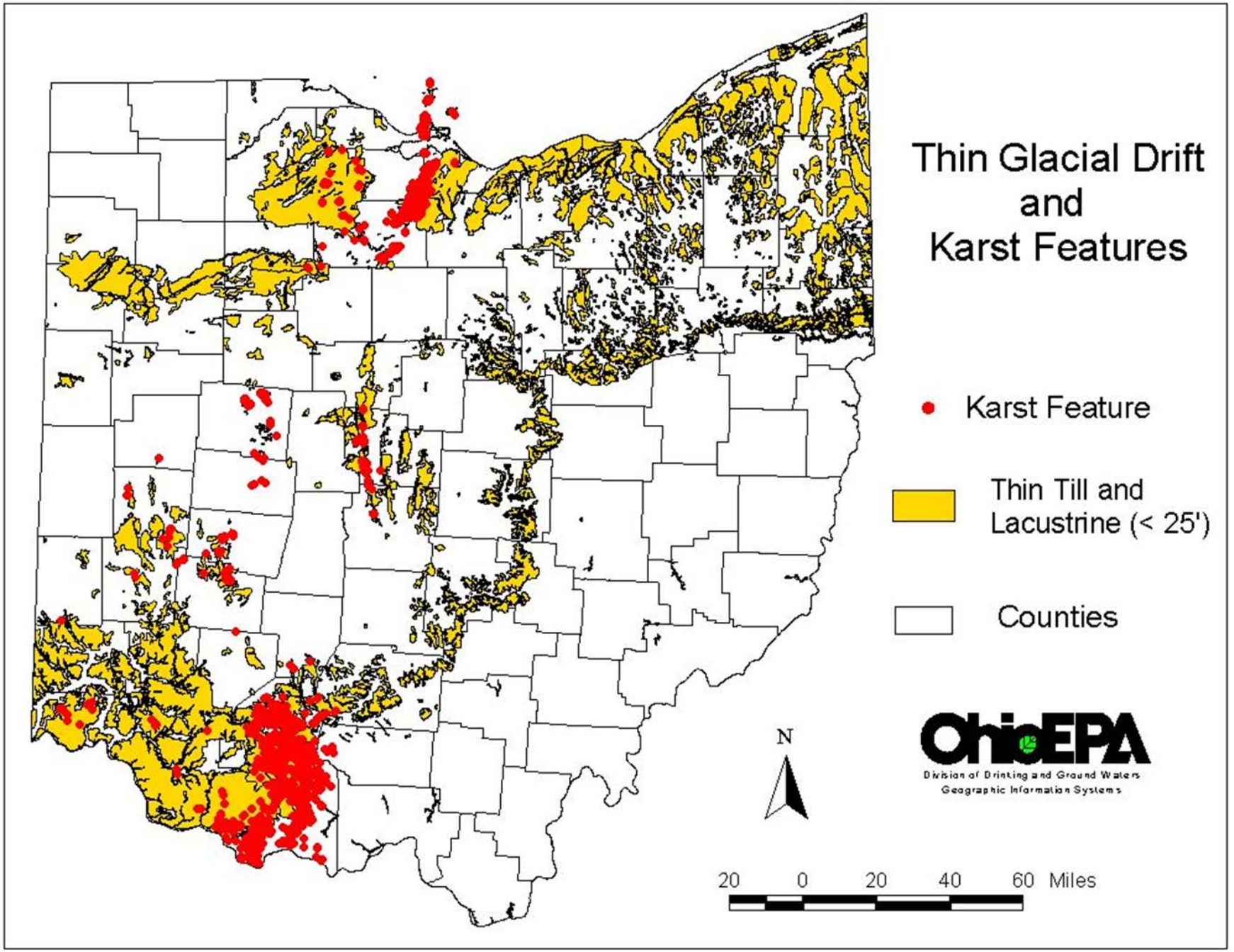
Karst and fractured bedrock are sensitive hydrogeologic settings when unconsolidated cover is thin or absent.

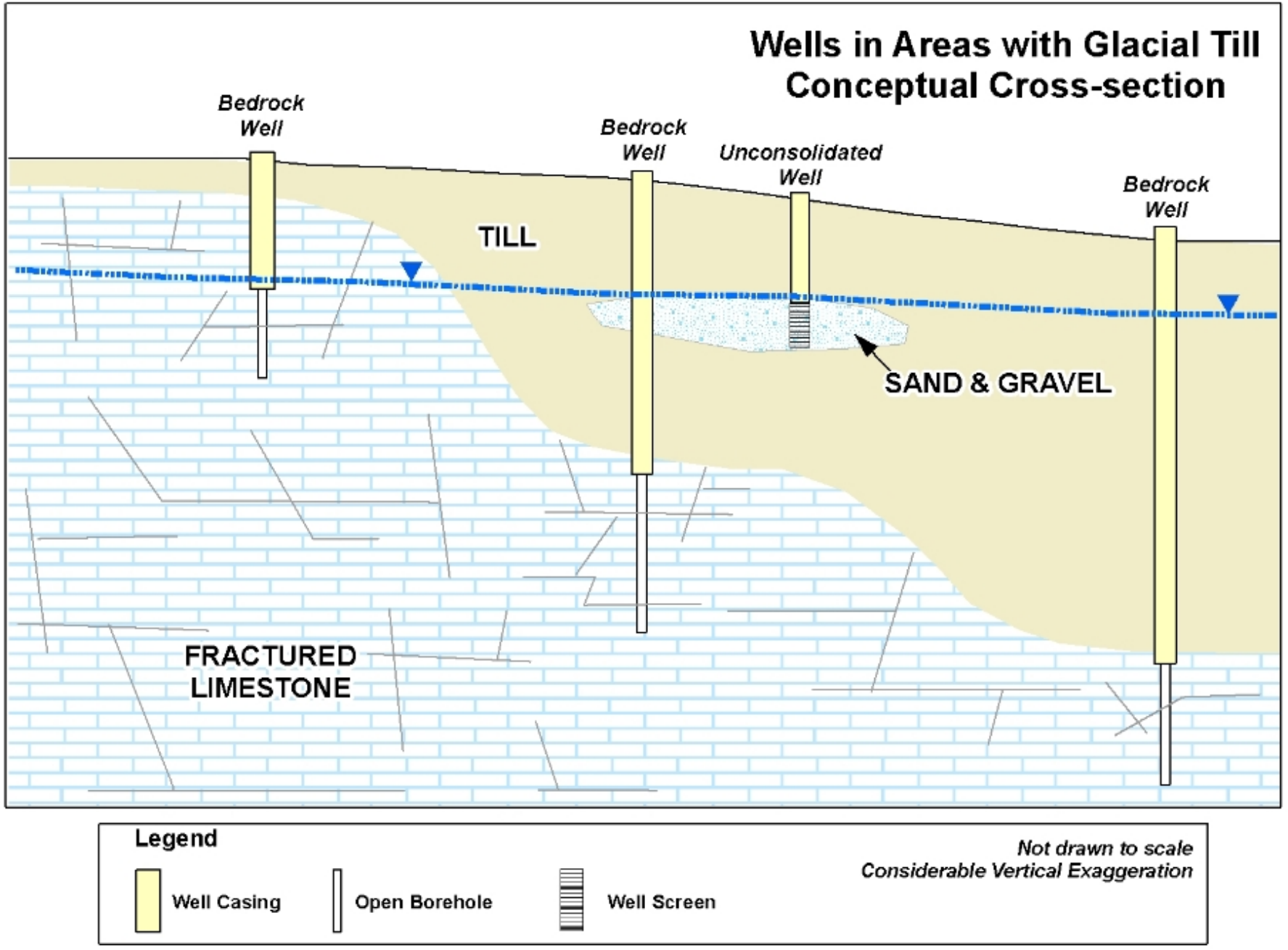

Sand and Gravel Aquifers
Sand and Gravel
(includes buried valley, valley fill, outwash/kame, and beach ridge deposits)
Counties
N
OhioEPA
Division of Drinking and Ground Waters
Geographic Information Systems
20 0 20 40 60 Miles

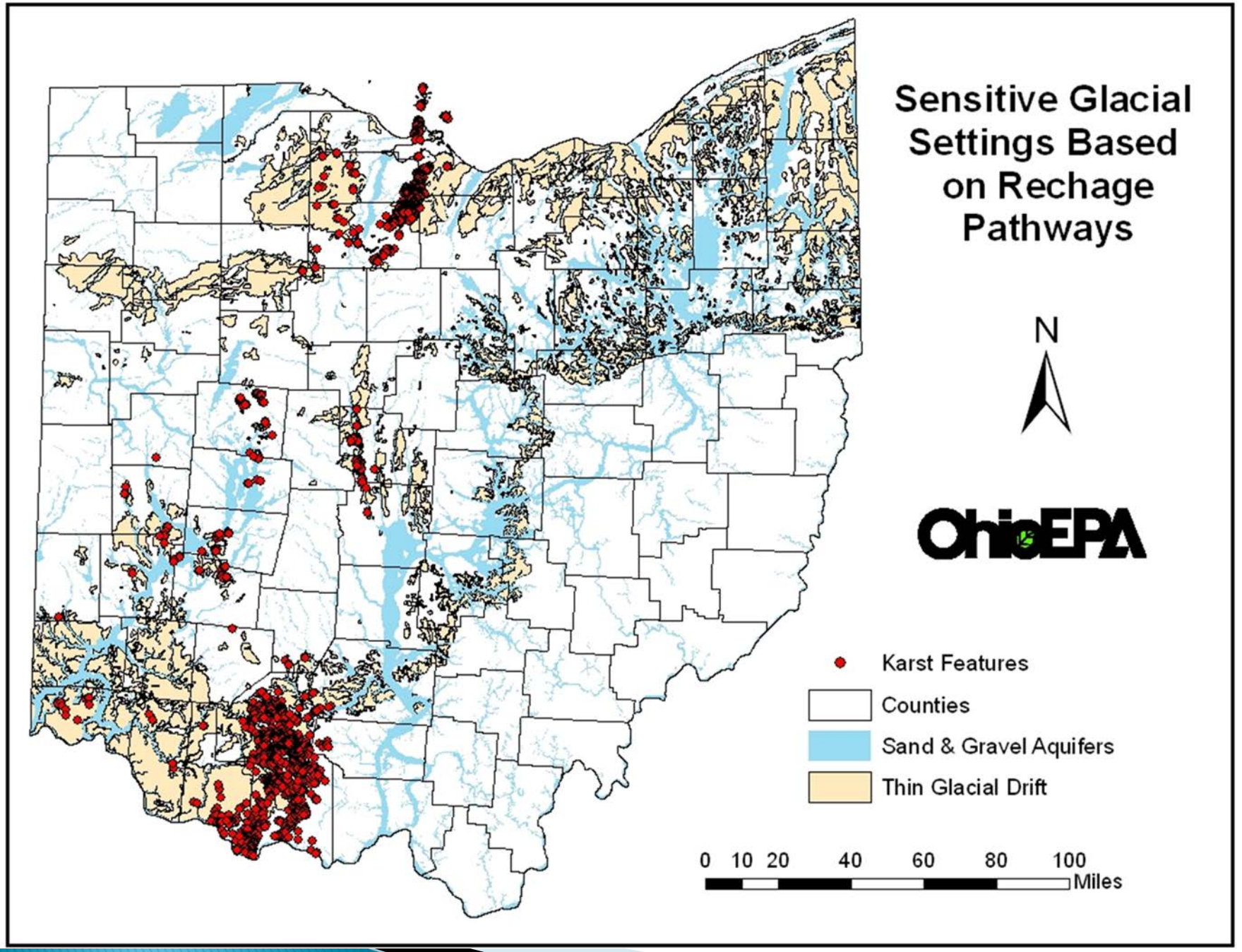
SW Ohio - PWS Nitrate Concentration Associated with Sensitive Glacial Settings




Wells in Areas of Buried Valleys
Conceptual Cross-section
Bedrock Well
Bedrock Well
Unconsolidated Well
SANDSTONE
SHALE
RIVER
TILL
SAND & GRAVEL
SANDSTONE
Legend
Well Casing
Open Borehole
Well Screen
Not drawn to scale
Considerable Vertical Exaggeration

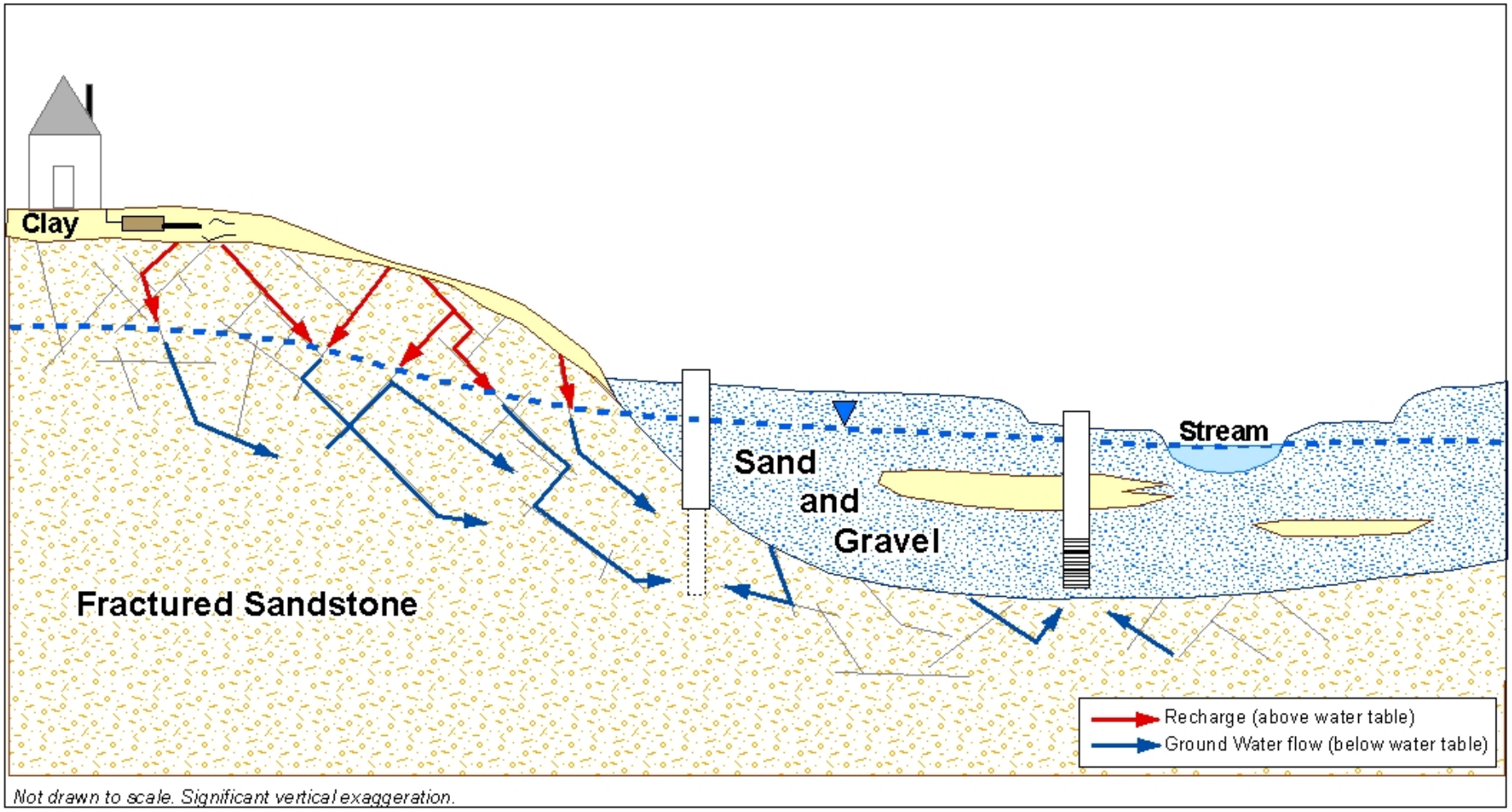

Thin Glacial Drift
and
Karst Features
Karst Feature
Thin Till and
Lacustrine (< 25')
Counties
N
OhioEPA
Division of Drinking and Ground Waters
Geographic Information Systems
20 0 20 40 60 Miles


Wells in Areas with Glacial Till
Conceptual Cross-section
Bedrock Well
Bedrock Well
Unconsolidated Well
Bedrock Well
TILL
SAND & GRAVEL
FRACTURED LIMESTONE
Legend
Well Casing
Open Borehole
Well Screen
Not drawn to scale
Considerable Vertical Exaggeration


Sensitive Glacial Settings Based on Rechage Pathways
N
OhioEPA
Karst Features
Counties
Sand & Gravel Aquifers
Thin Glacial Drift
0 10 20 40 60 80 100
Miles

Site Specific Consideration

- **Natural Factors**
  - Major lithology of aquifer
  - Geochemical control
  - Geologic setting – sensitive aquifer?
  - Recharge pathways
- **Anthropogenic Factors**
  - Well construction
  - Land use


Clay
Sand
and
Gravel
Stream
Fractured Sandstone
Recharge (above water table)
Ground Water flow (below water table)
Not drawn to scale. Significant vertical exaggeration.

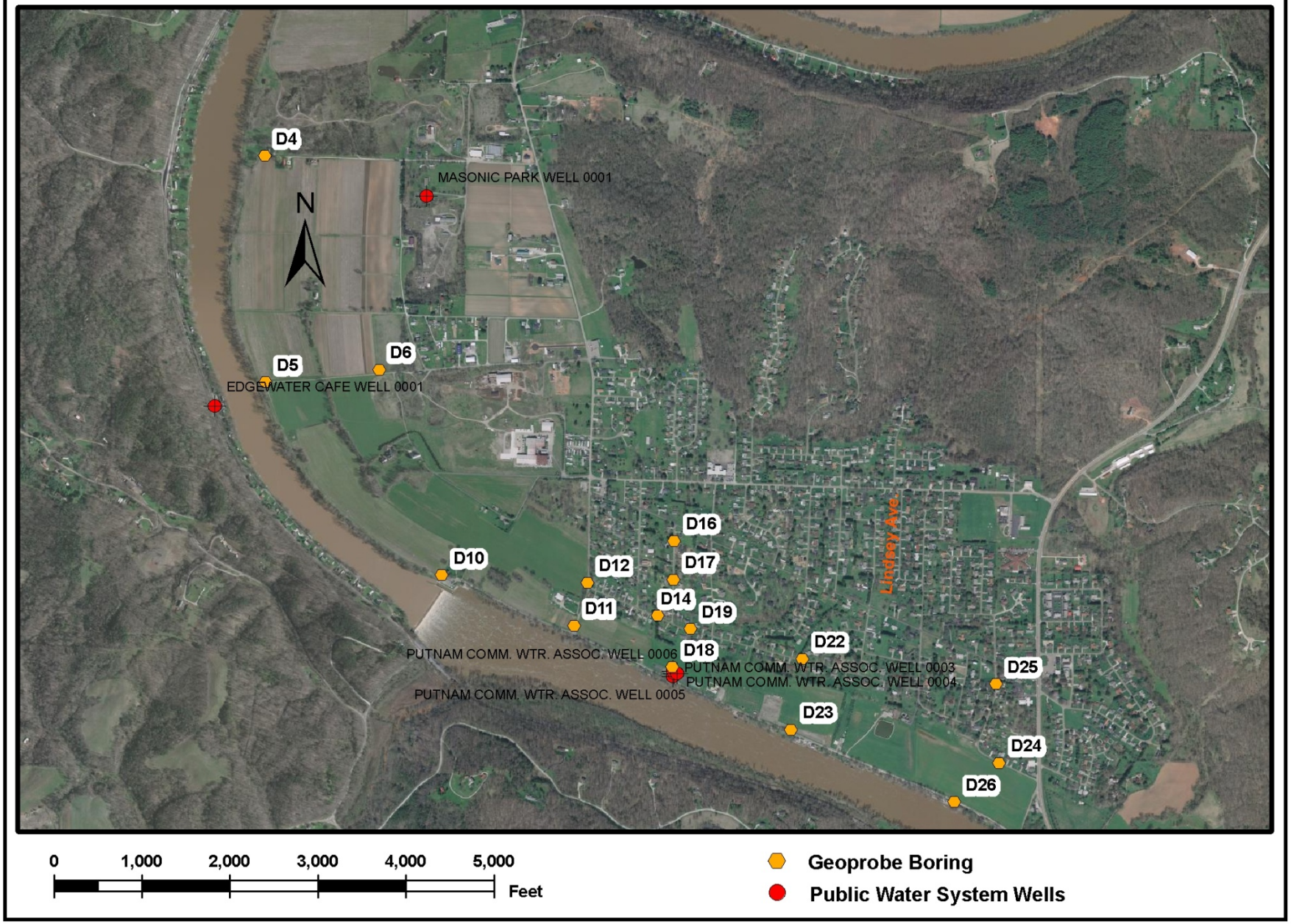
Acknowledgments

Mike Slattery and Linda Slattery
Ohio EPA staff
PWS operators
ODNR Map Products

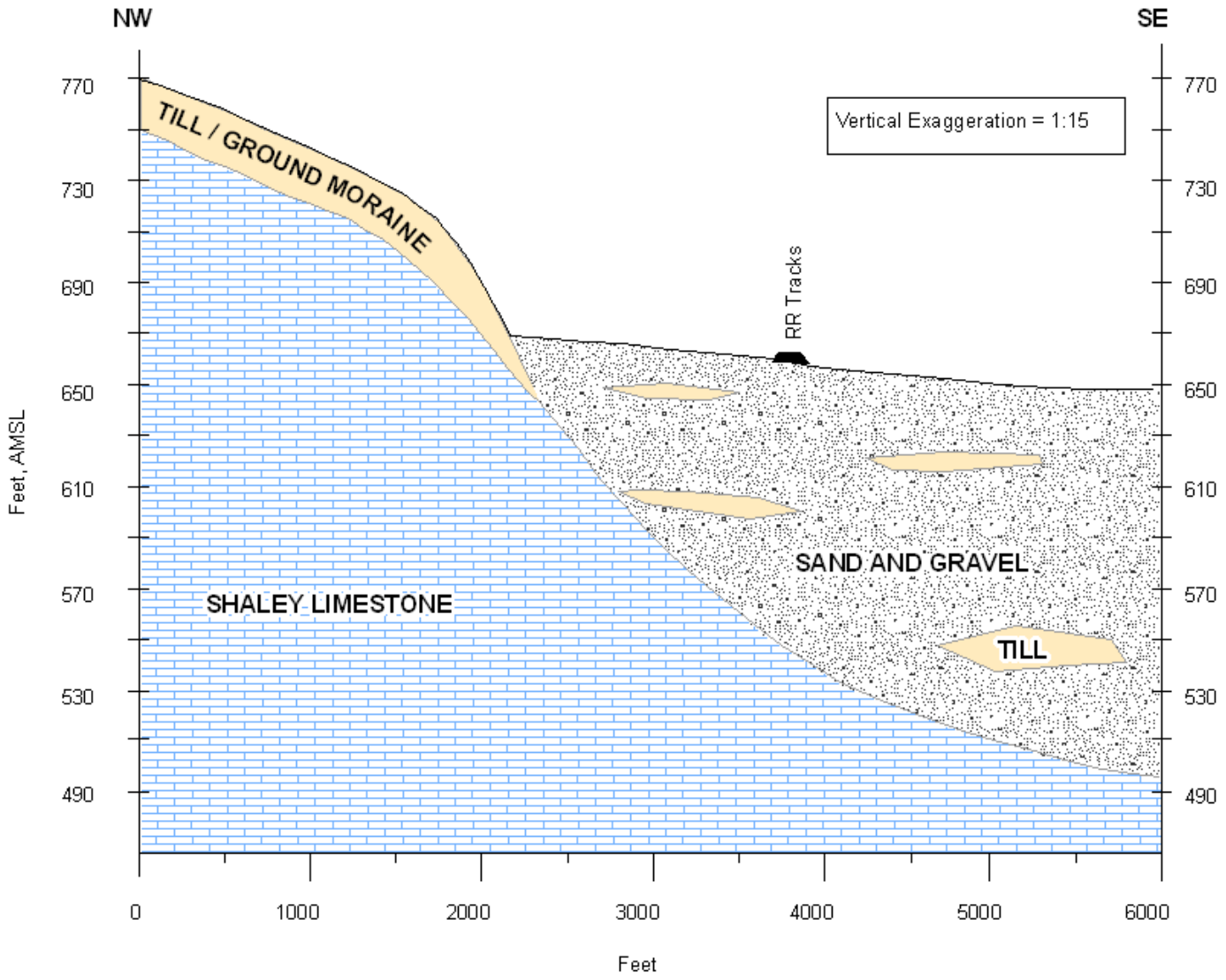
Additional Information

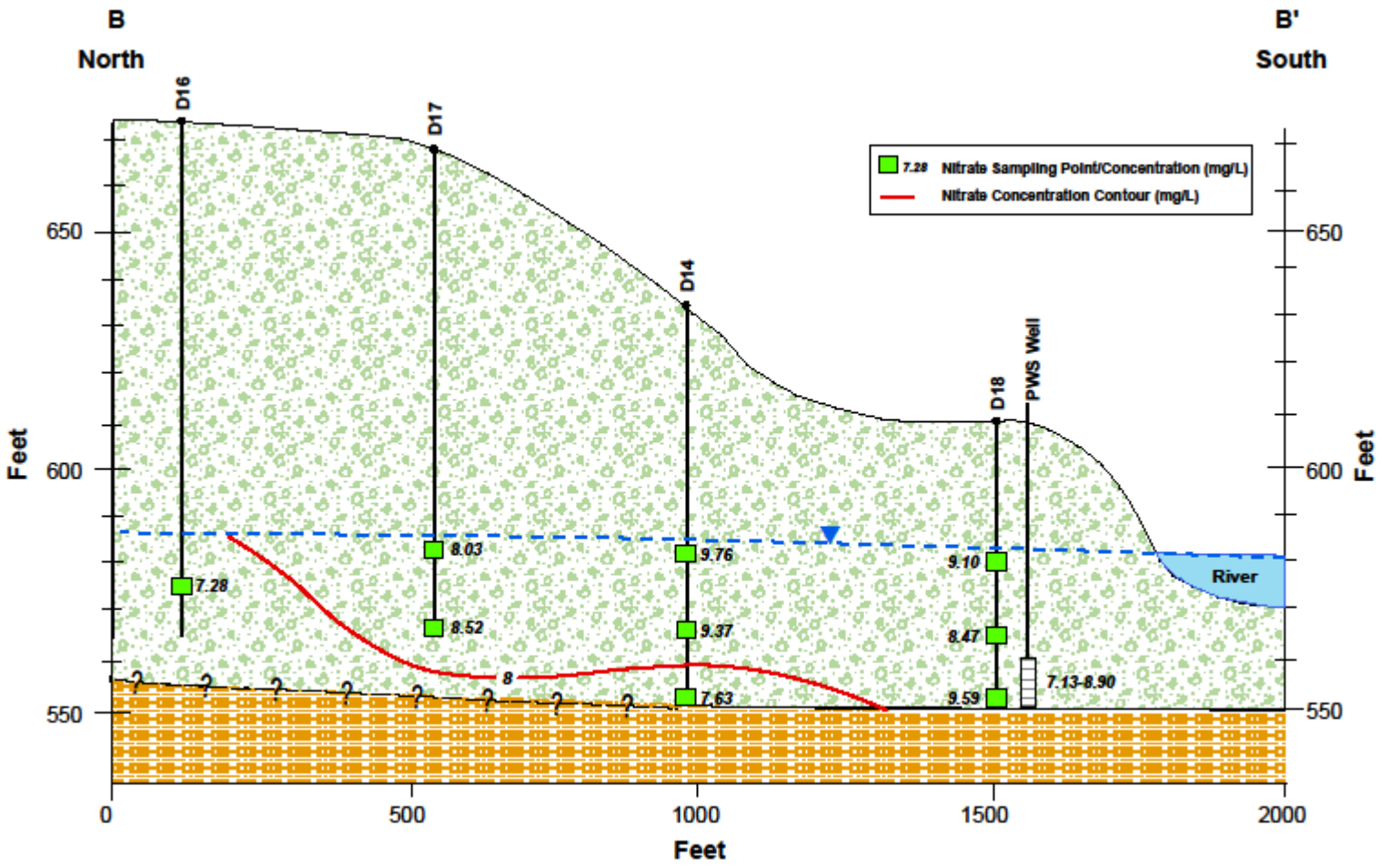
- Web address:
  http://www.epa.ohio.gov/ddagw/gwqcp.aspx
- Chris Kenah: 614/644-2903
  christopher.kenah@epa.state.oh.us

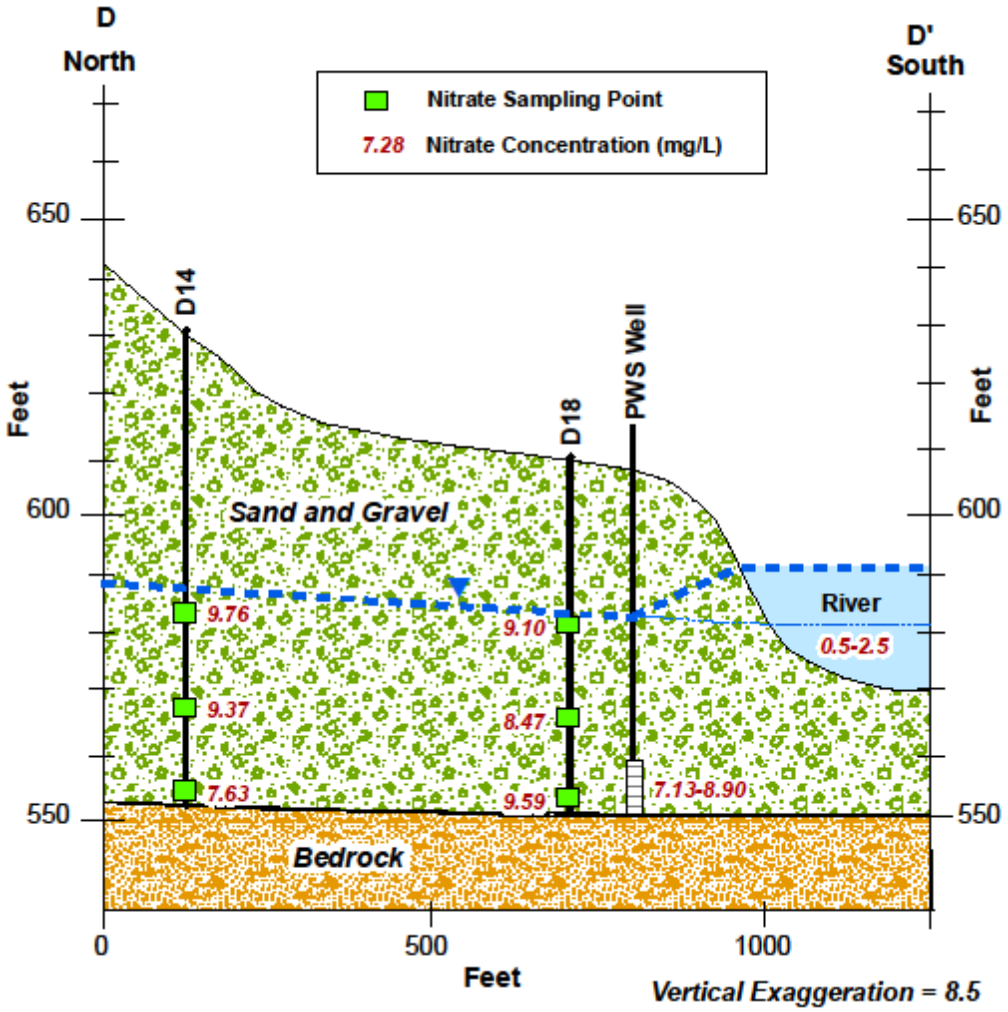
Devola Area


D4
MASONIC PARK WELL 0001
N
D5
D6
EDGEWATER CAFE WELL 0001
D16
D10
D12
D17
D14
D11
D19
Lindsey Ave.
D22
D18
PUTNAM COMM. WTR. ASSOC. WELL 0006
PUTNAM COMM. WTR. ASSOC. WELL 0003
PUTNAM COMM. WTR. ASSOC. WELL 0004
D25
PUTNAM COMM. WTR. ASSOC. WELL 0005
D23
D24
D26
0
1,000
2,000
3,000
4,000
5,000
Feet
Geoprobe Boring
Public Water System Wells

Conceptual Cross-section




B
North
B'
South
D16
D17
D14
D18
PWS Well
7.28 Nitrate Sampling Point/Concentration (mg/L)
Nitrate Concentration Contour (mg/L)
650
600
550
Feet
7.28
8.03
8.52
8
9.76
9.37
7.63
9.10
8.47
9.59
7.13-8.90
River
0
500
1000
1500
2000
Feet


D
North
D'
South
Nitrate Sampling Point
7.28 Nitrate Concentration (mg/L)
650
600
550
Feet
D14
D18
PWS Well
Sand and Gravel
River
0.5-2.5
9.76
9.37
7.63
9.10
8.47
9.59
7.13-8.90
Bedrock
0
500
1000
Feet
Vertical Exaggeration = 8.5