BIOGEOCHEMICAL PROCESSES AFFECTING GROUNDWATER DISCHARGE IN A CHLOROBENZENE-CONTAMINATED WETLAND

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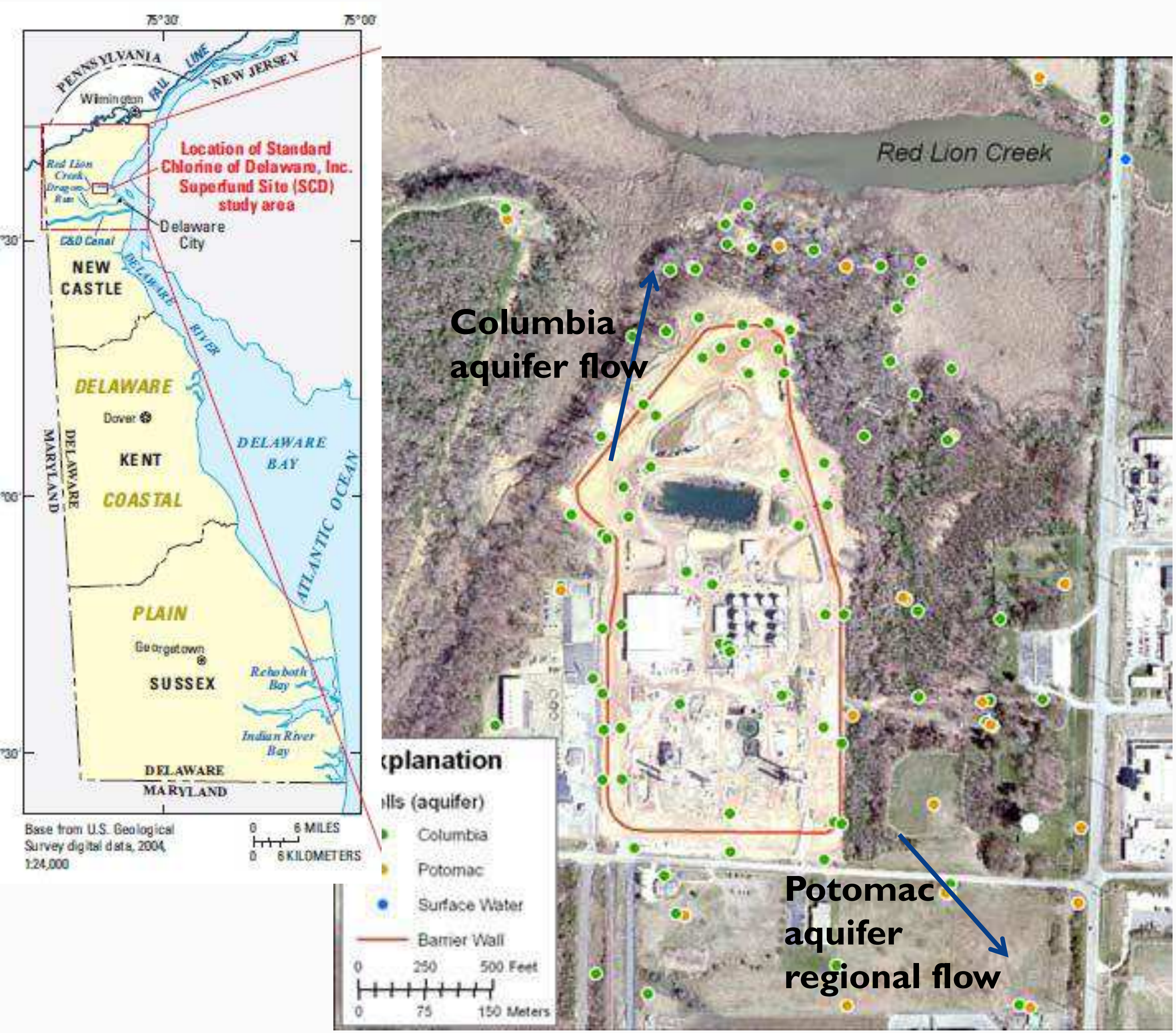
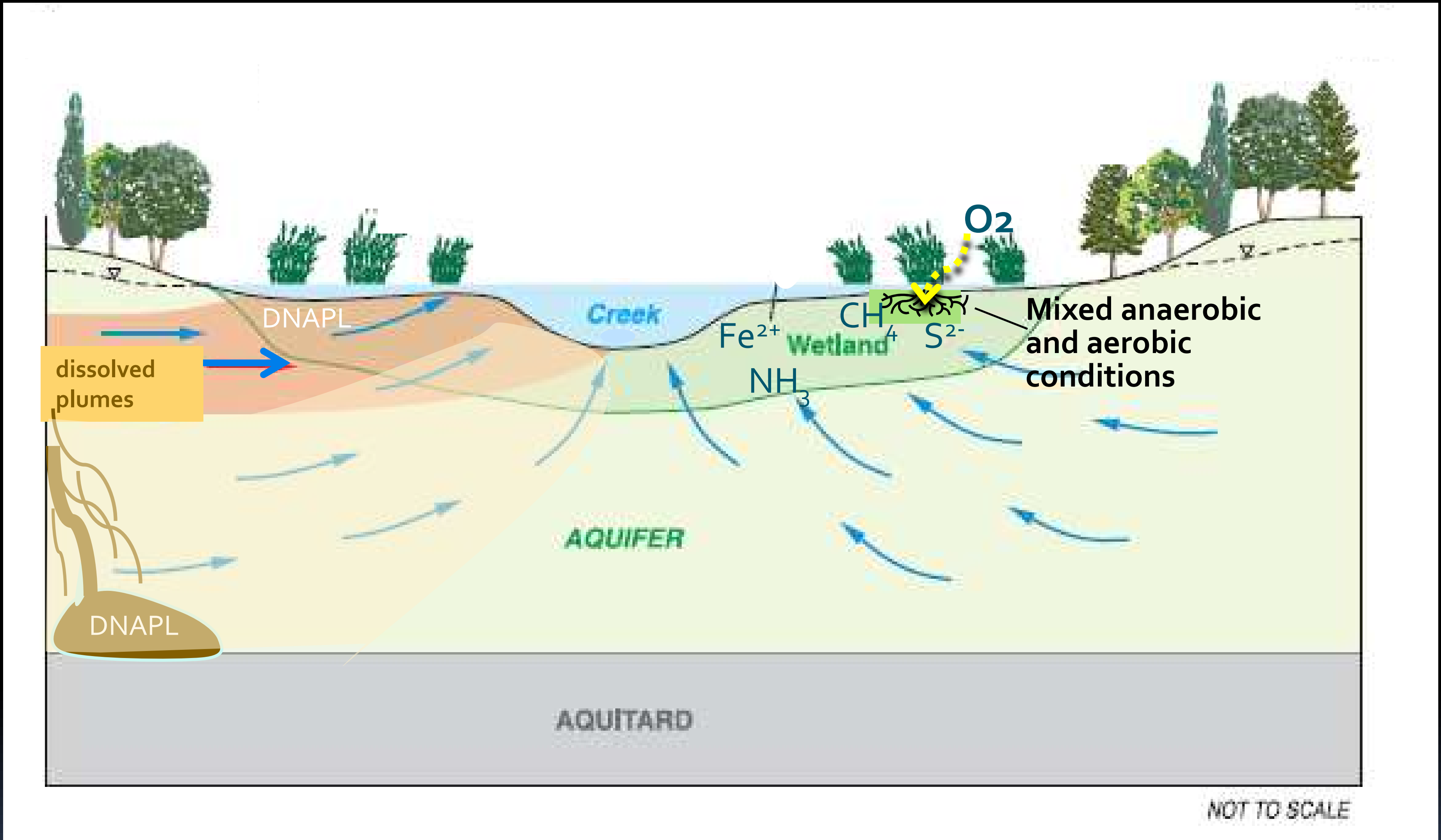
In cooperation with USEPA Region III

USGS

Standard Chlorine of Delaware, Inc., Superfund Site



- Chemical plant built in 1965 to manufacture chlorinated benzenes
- Two major spills: 1981 (railroad tanker); 1986 (storage tanks- 579,000 gal)
- Superfund site in 1987



Conceptual model for contamination in wetland

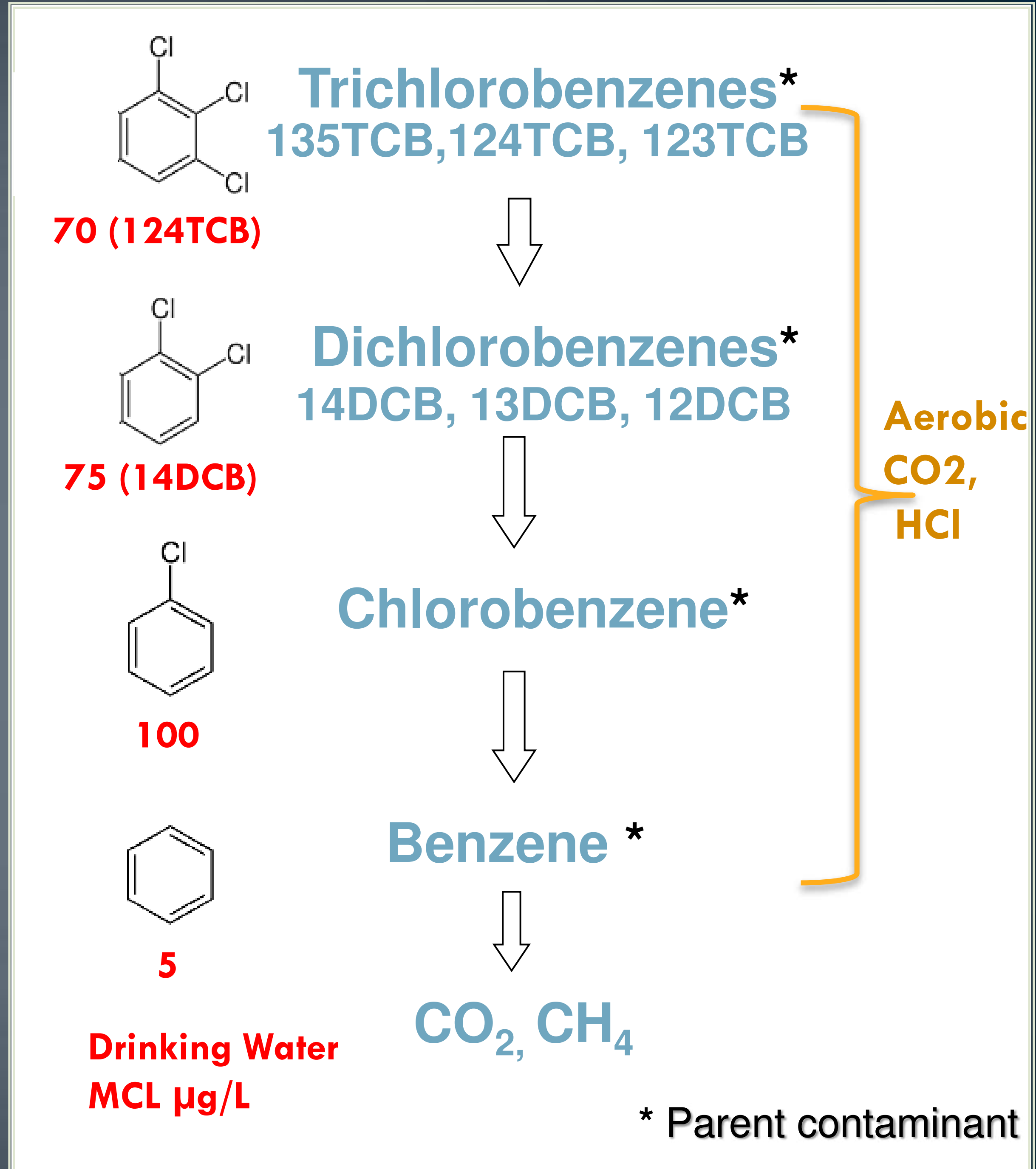
Biodegradation Pathways

Anaerobic (reductive dechlorination)

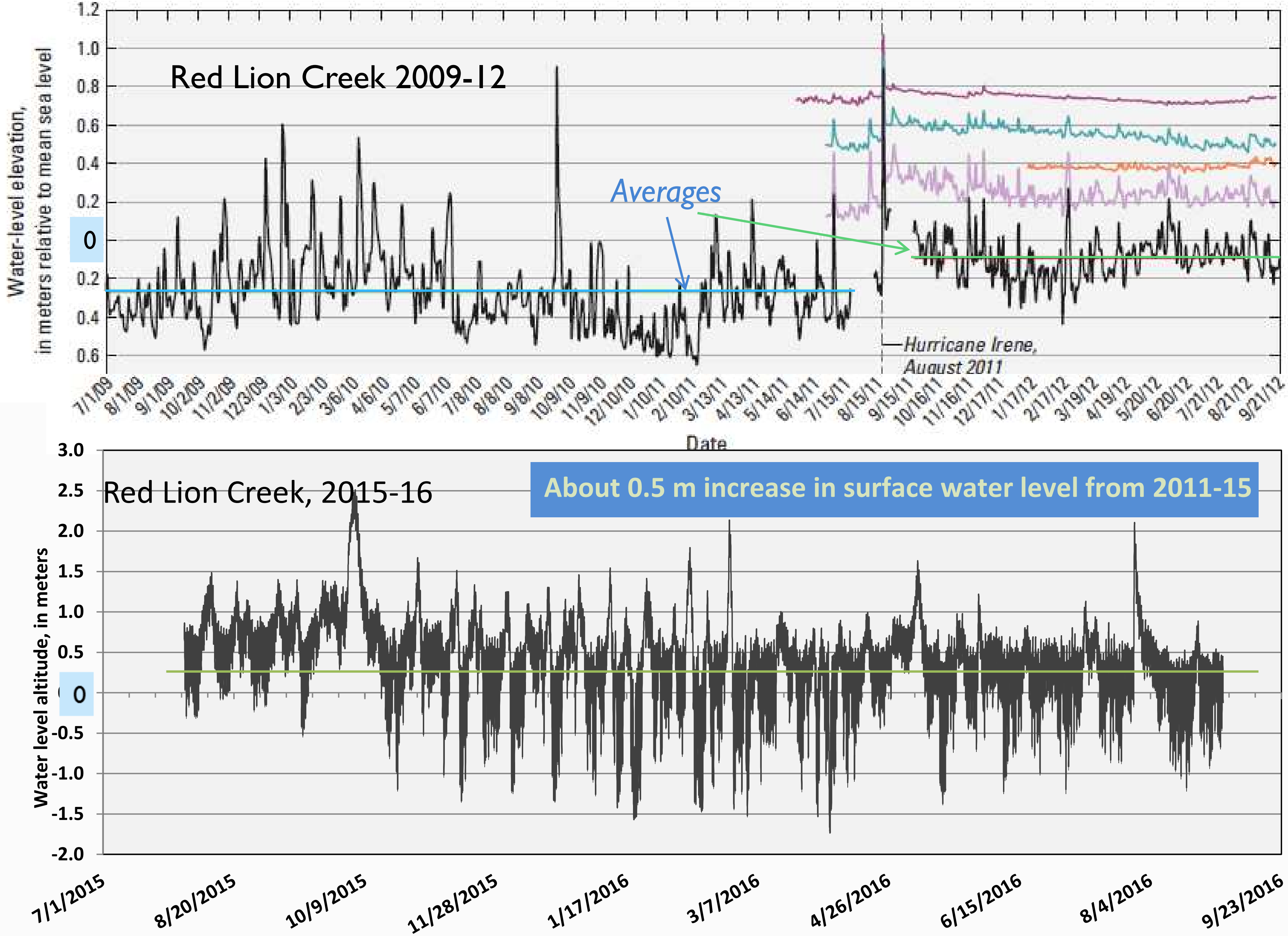
- CB serves as terminal electron acceptor
- Separate e- donor required
- rate decreases with decreasing number Cl

Aerobic (oxidation)

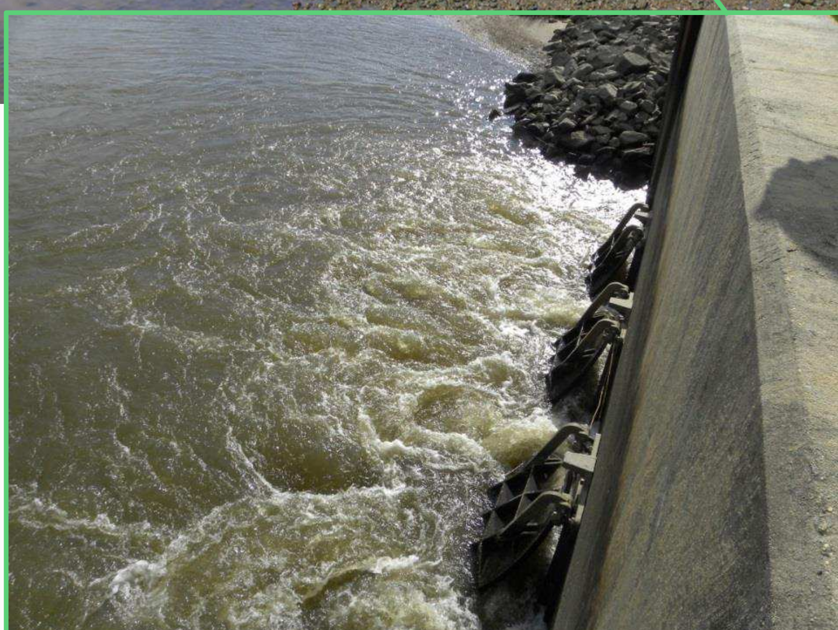
- O_2 required as electron acceptor
- CBs utilized as C and e^- donor
- rate increases with decreasing number Cl
- Short-lived intermediates



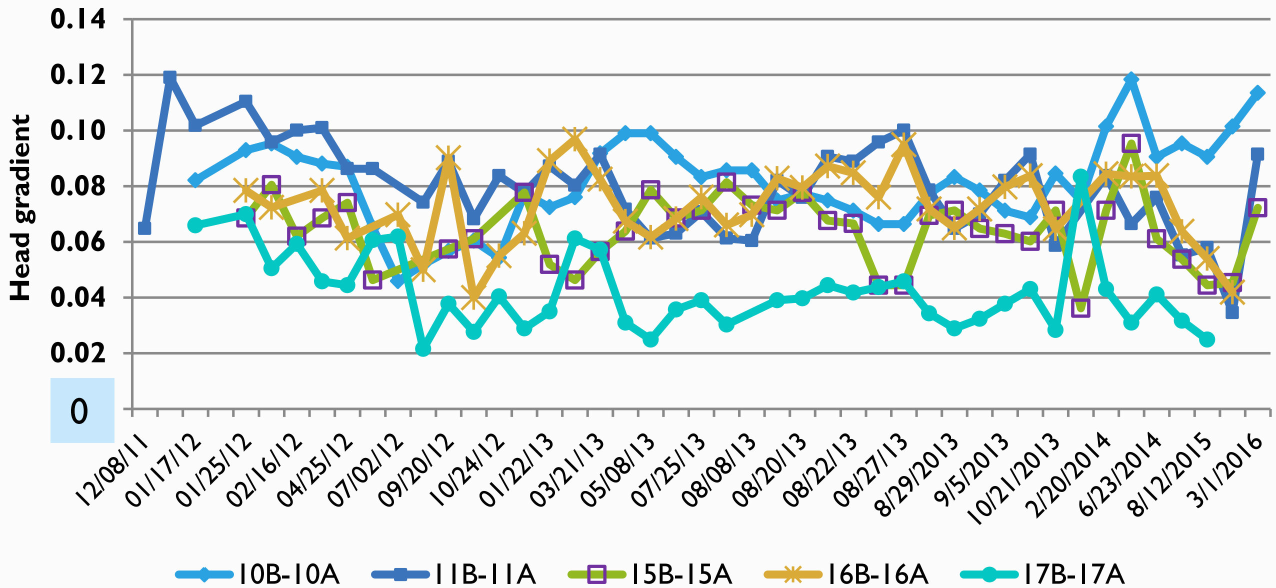
-------Dec 2010-Nov 2011--------



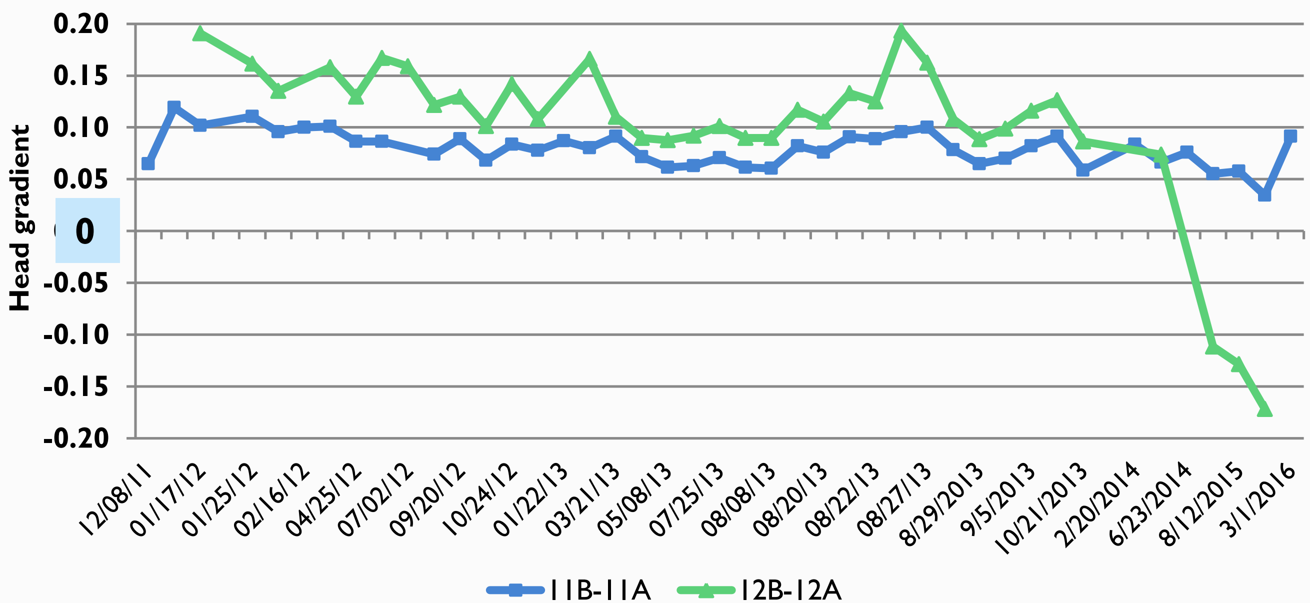
Red Lion Creek tide control structure , from Delaware River, low tide, 2010. *(Photo by Todd Keyser, DNREC.)*



Site 13, view from site 11, low tide, May 2015. *(Photo by Jessica Teunis, USGS.)*

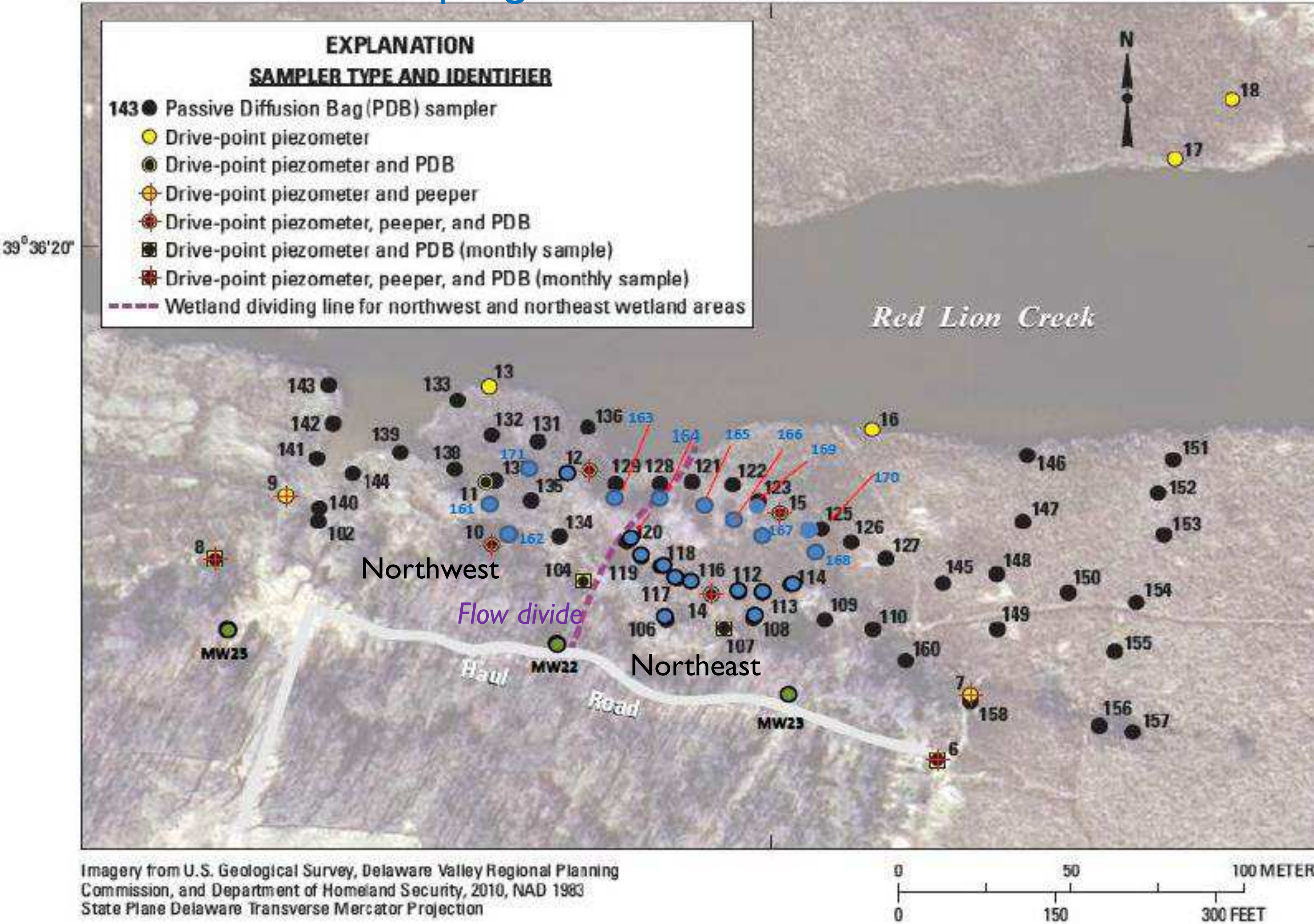


Vertical head gradients in wetland piezometers have remained upward (>0) during 2011-16, despite the rise in creek stage and tidal flooding of wetland…



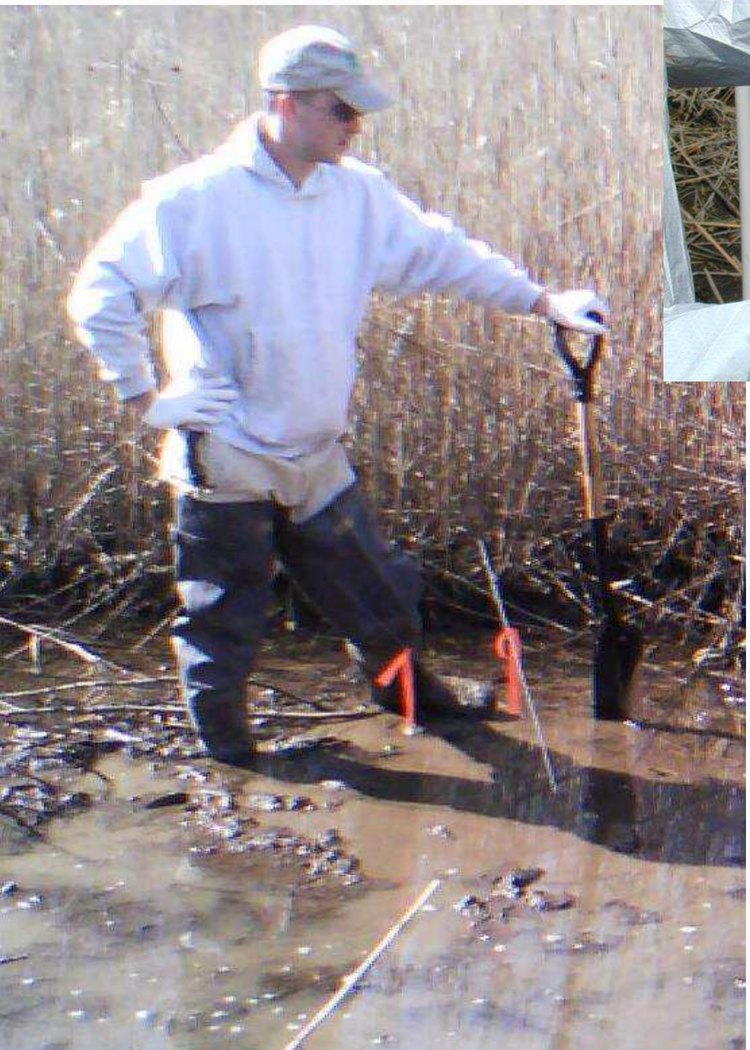
except site 12, now located in creek channel, showed a reversal in gradient 3 years after the broken tide control gates.

Groundwater Sampling Sites, 2010-11 and 2015-16



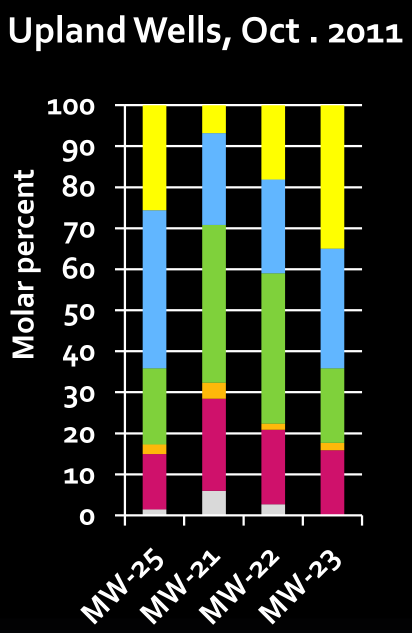
Imagery from U.S. Geological Survey, Delaware Valley Regional Planning Commission, and Department of Homeland Security, 2010, NAD 1983 State Plane Delaware Transverse Mercator Projection

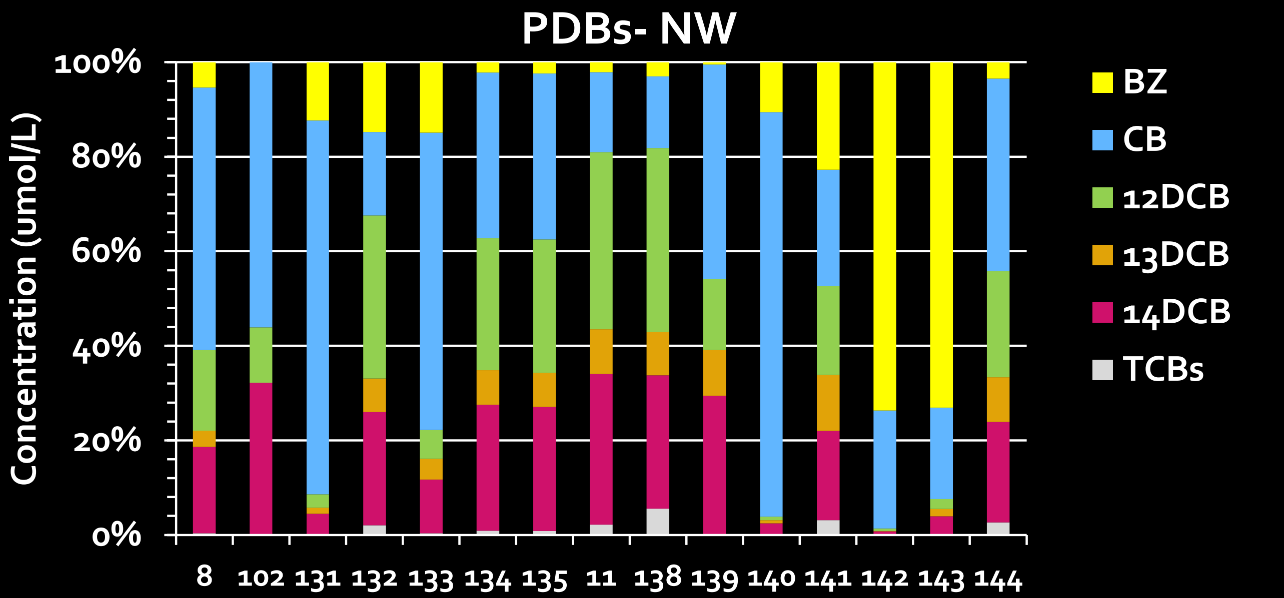
Groundwater Sampling

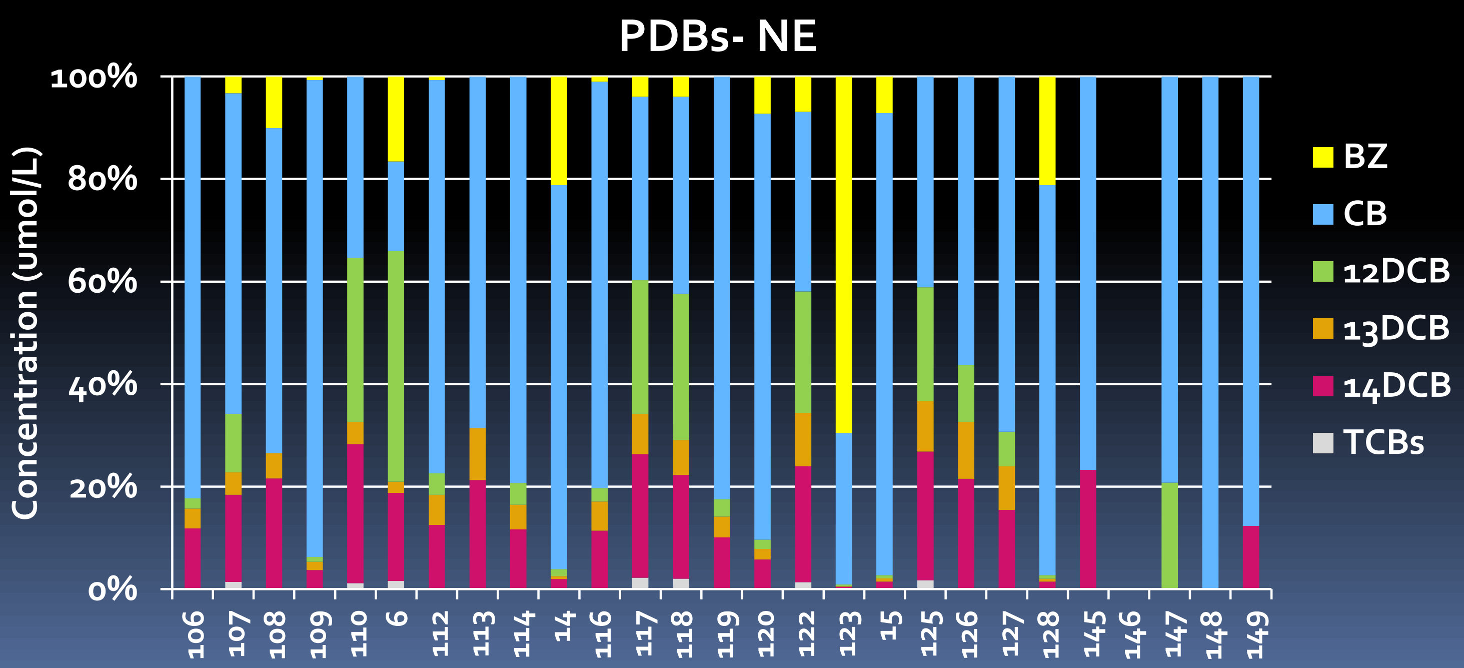


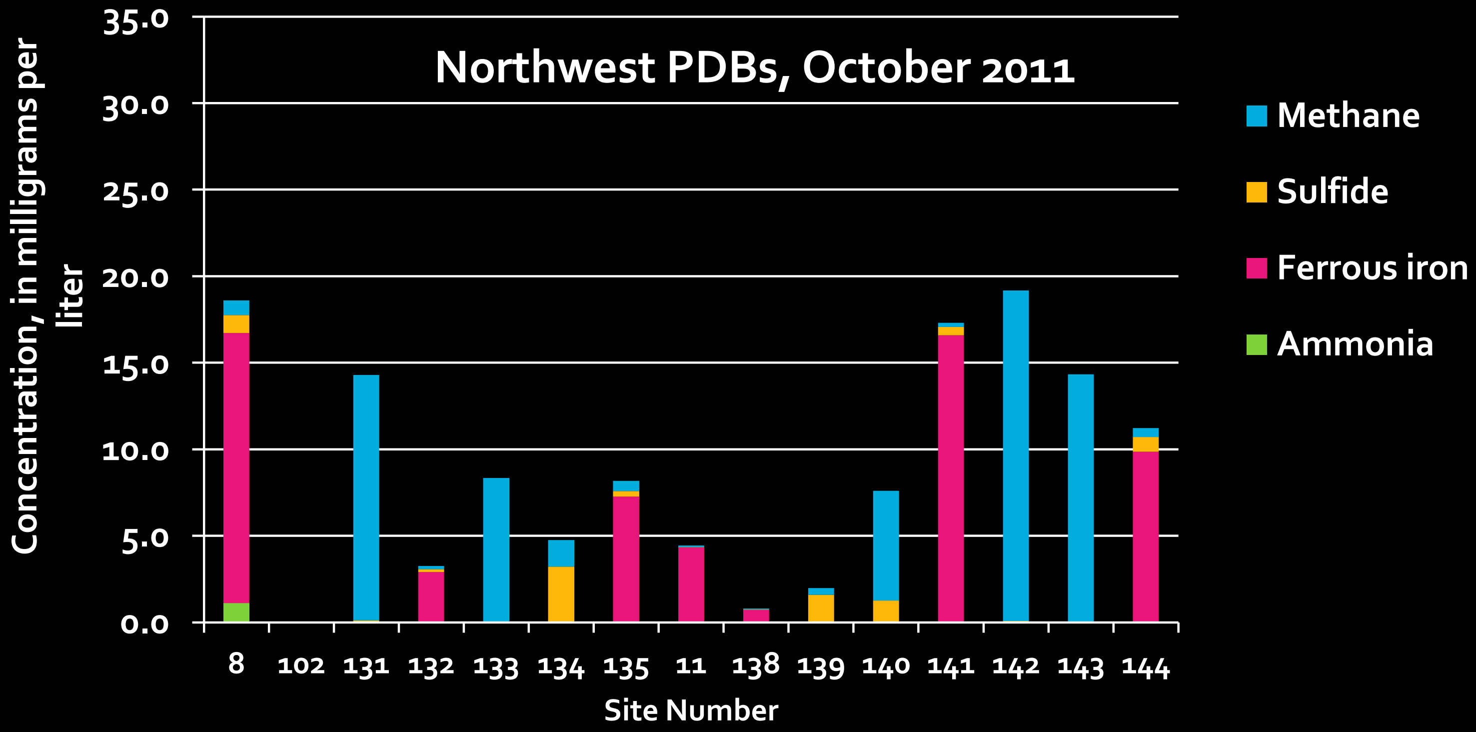
- Passive diffusion bags (PDBs) and dialysis samplers at about 45 sites
- 2 inch drivepoints at 13 sites (plus upland wells)
- 2-ft or 4-ft long porous membrane samplers (peepers)

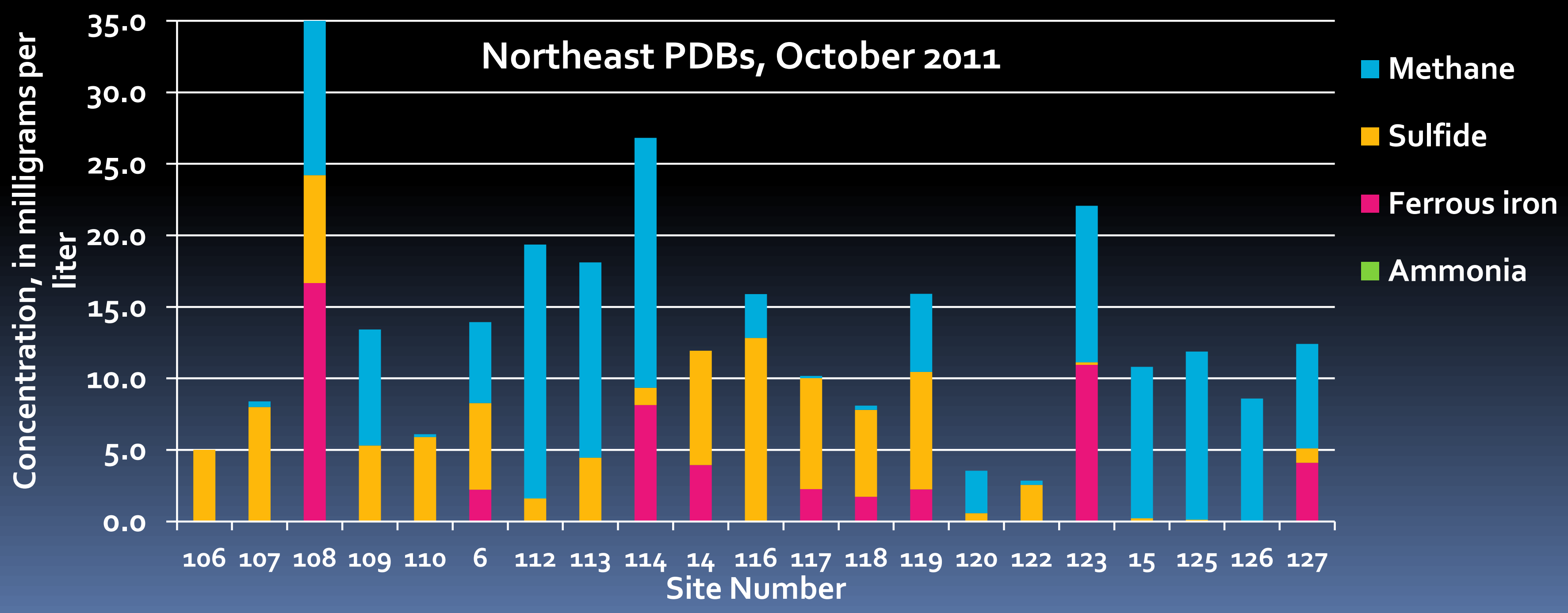
VOCs- PDBs, October 2011



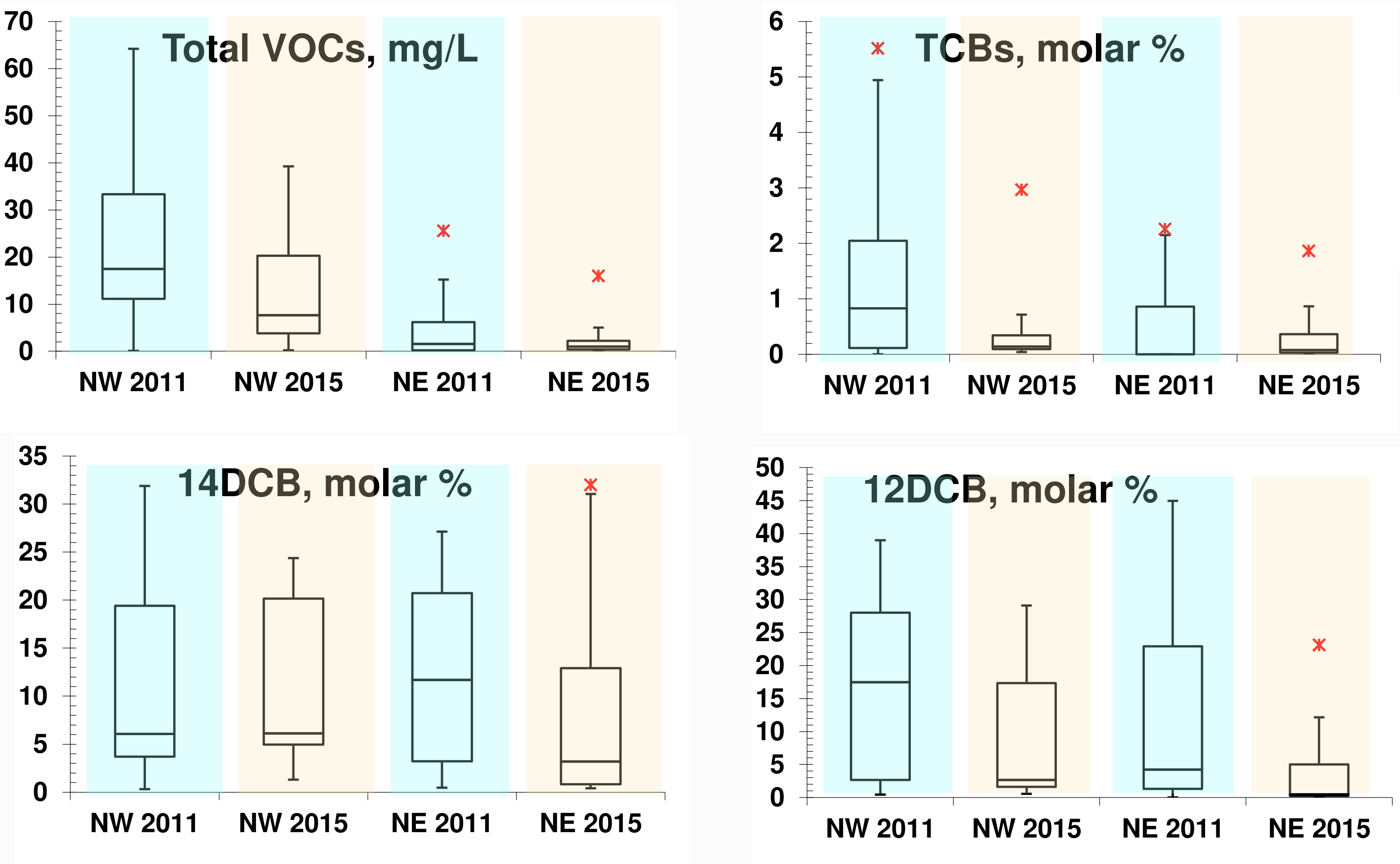





Northwest PDBs, October 2011
Concentration, in milligrams per liter
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
8
102
131
132
133
134
135
11
138
139
140
141
142
143
144
Site Number
Methane
Sulfide
Ferrous iron
Ammonia

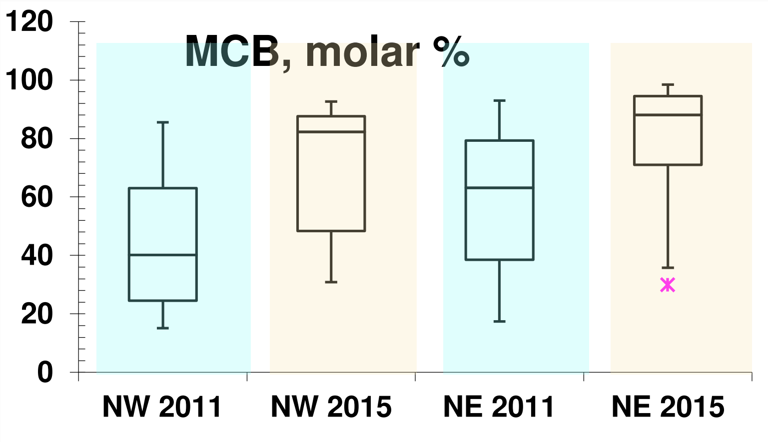

Northeast PDBs, October 2011
Concentration, in milligrams per liter
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
106
107
108
109
110
6
112
113
114
14
116
117
118
119
120
122
123
15
125
126
127
Site Number
Methane
Sulfide
Ferrous iron
Ammonia

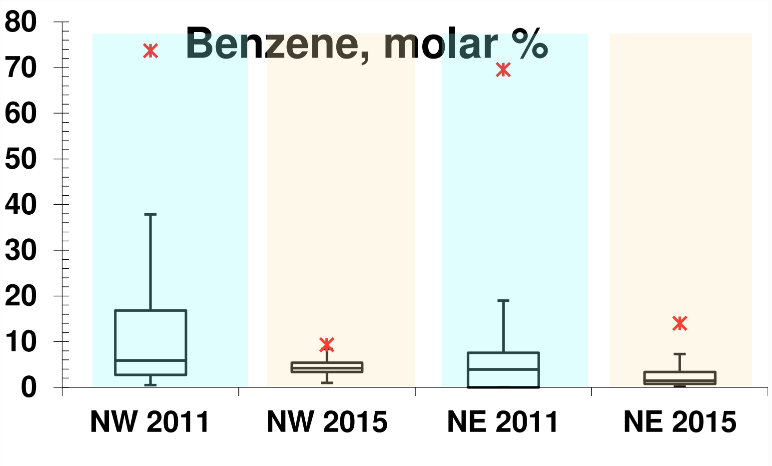
PDBs, Shallow Wetland Groundwater (20-30 cm depth)

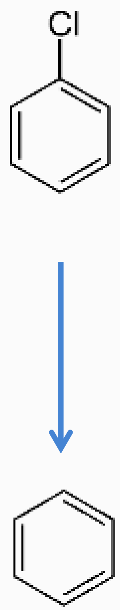


In 2015, total VOC concentrations decreased, and VOC composition showed lower percent TCBs and DCBs.

PDBs, Shallow Wetland Groundwater (30-45 cm depth)

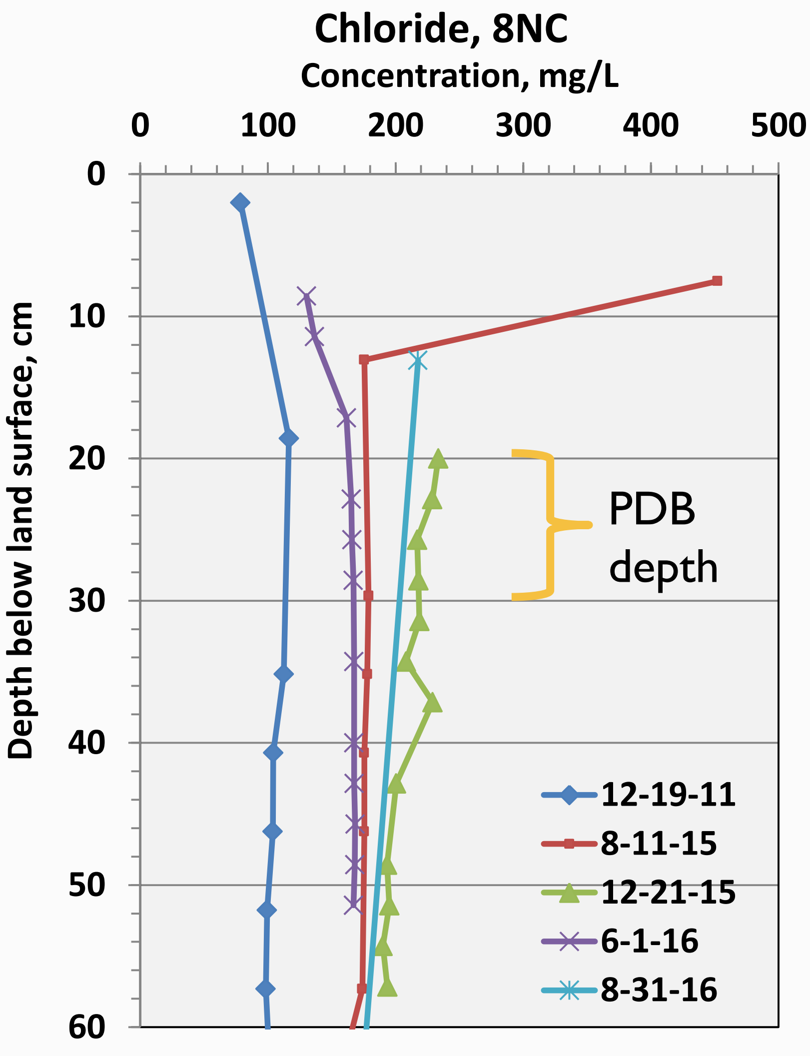


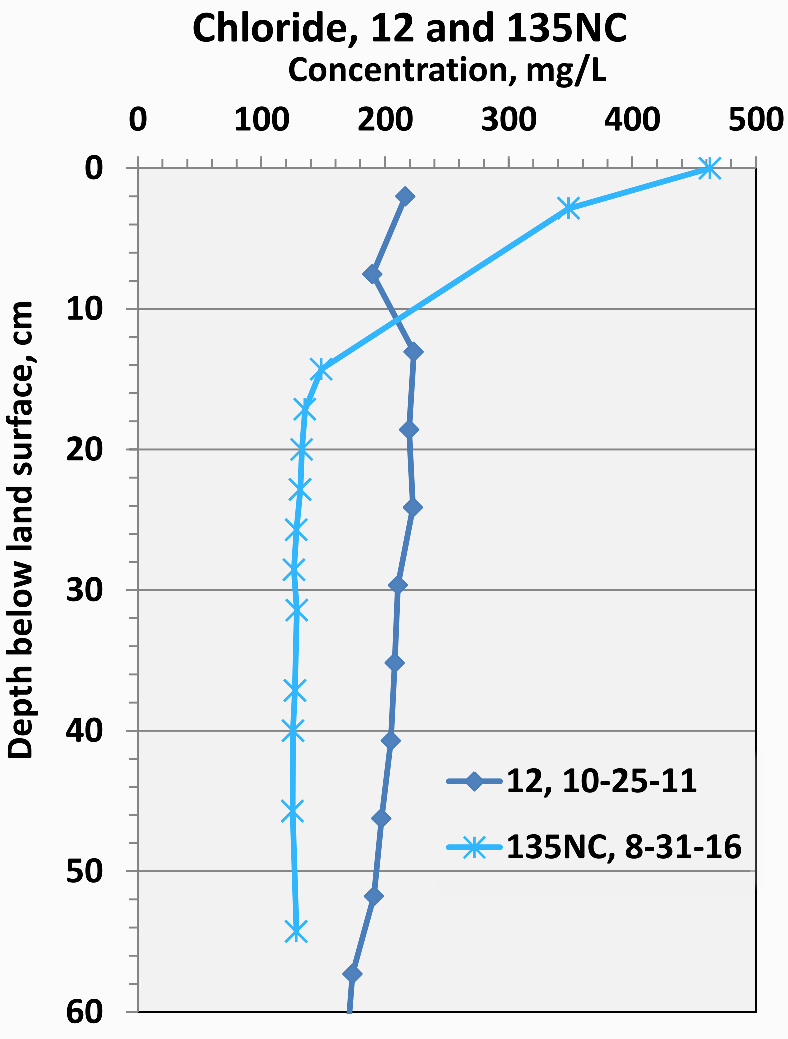




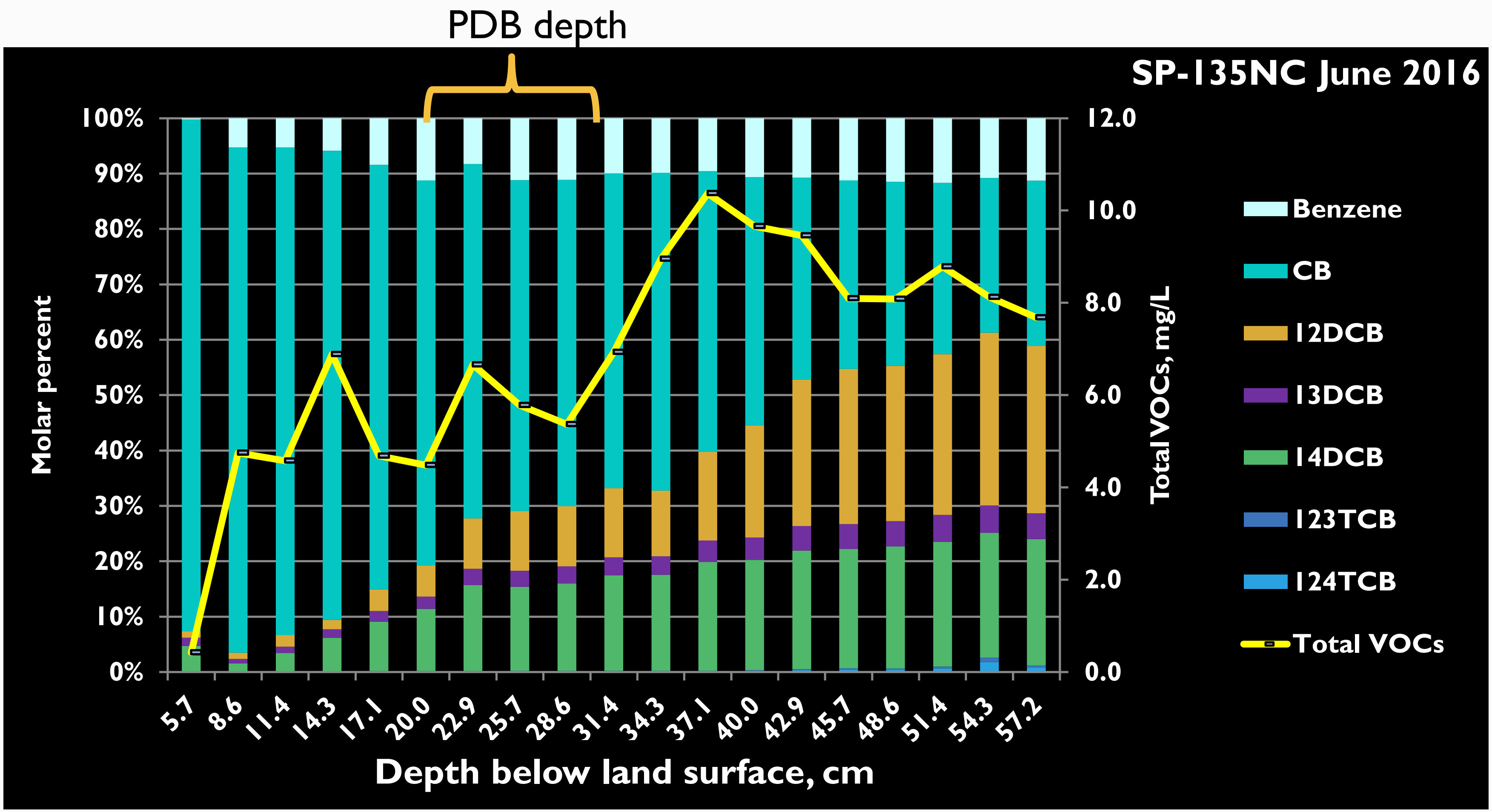
In 2015,VOC composition showed higher percent MCB (median > 80 percent), but equal or lower percent benzene compared to 2011.

Chloride with Depth (Peepers)- effect of surface-water infiltration or ET?



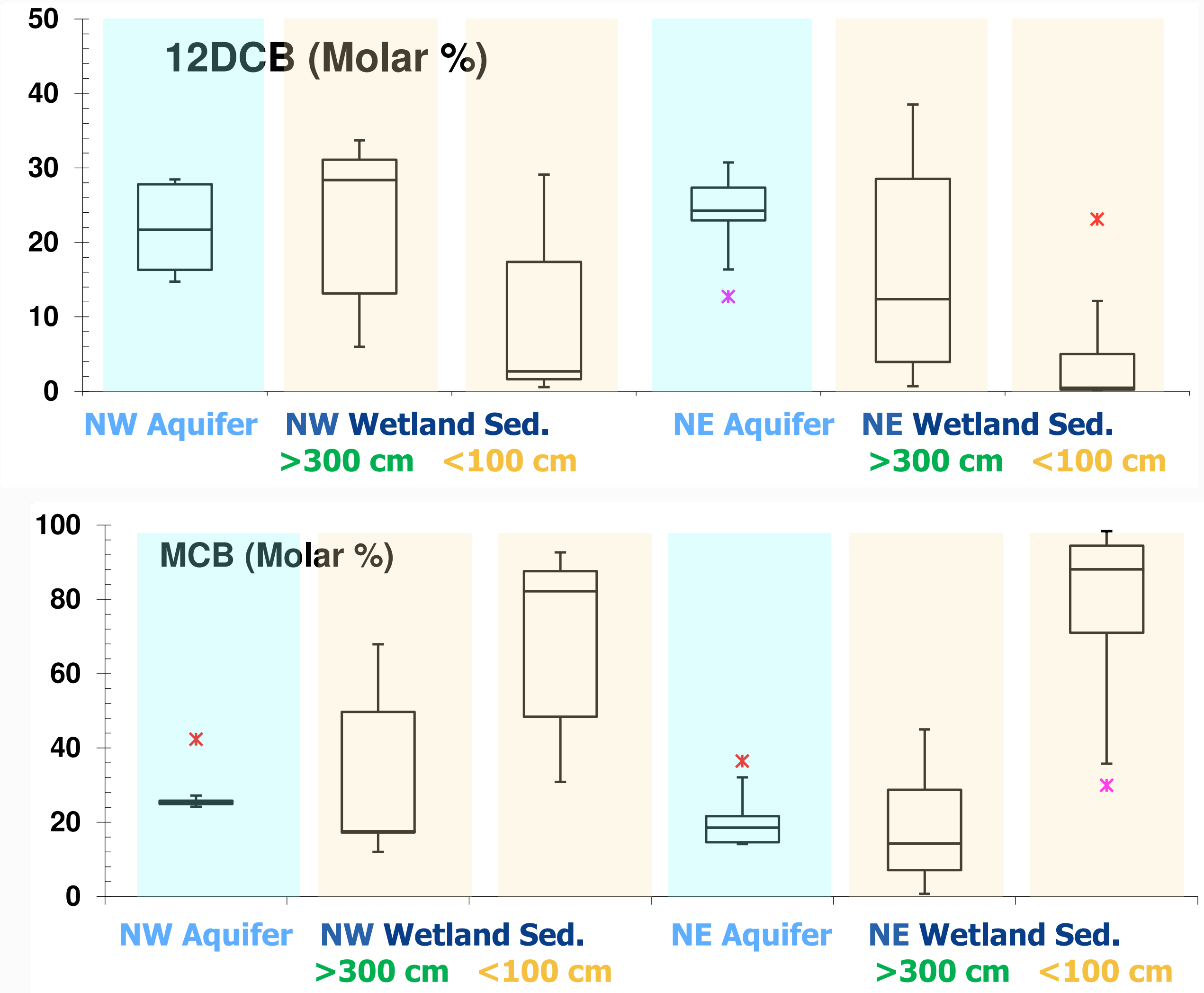


VOC Composition with Depth (Peepers)- effect of surface-water infiltration or ET?



Limited evidence of dilution or ET effect- primarily top sampling depth). ET would preferentially strip lighter VOCs.

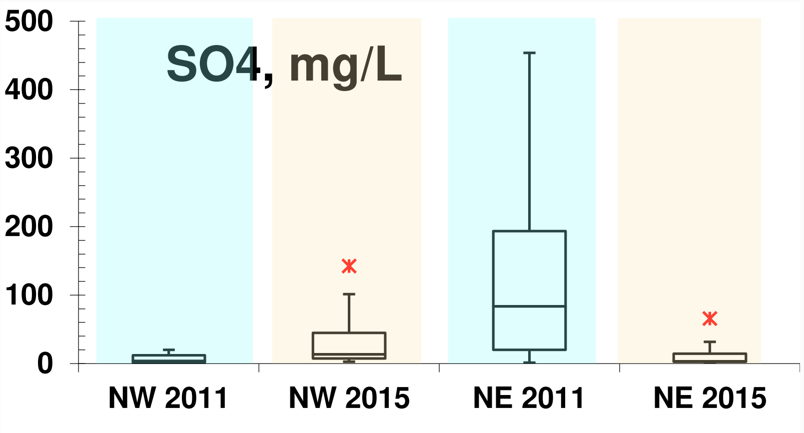
VOCs in Piezometers and PDBs, Aquifer to Shallow Wetland Groundwater

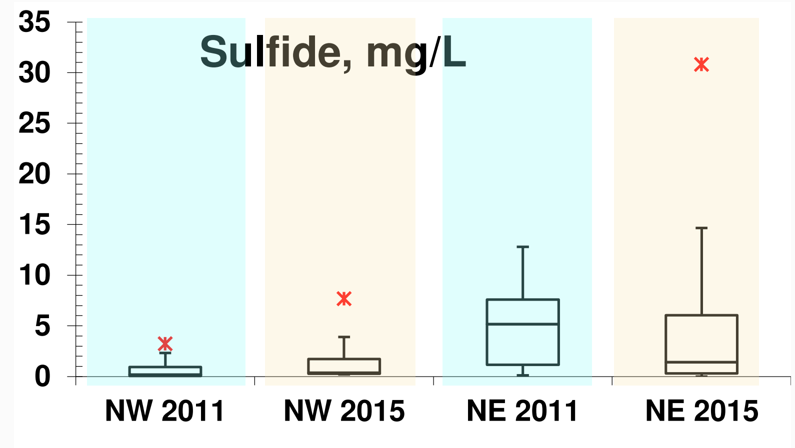


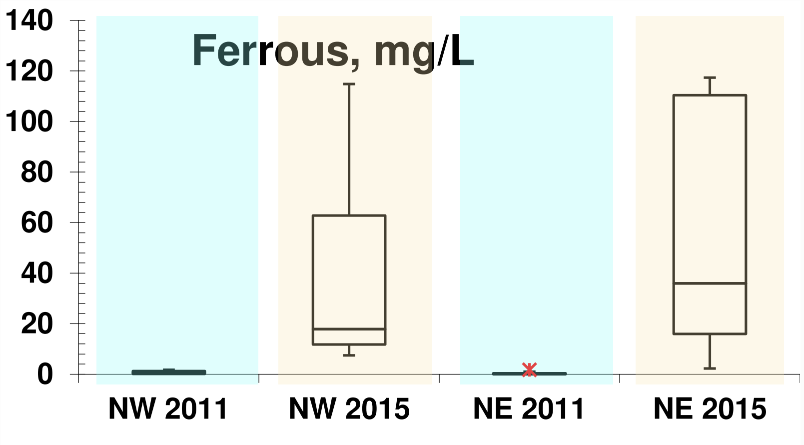
Greatest change occurs in the shallow wetland groundwater, not between aquifer and deep wetland groundwater.

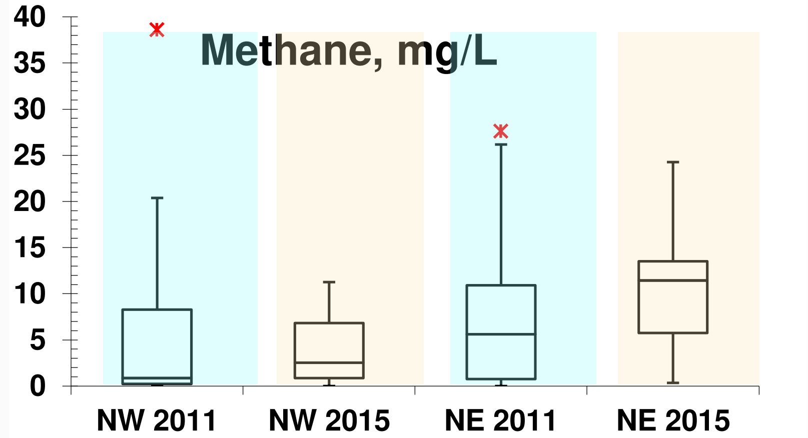
A change in the contaminant source feeding into aquifer is not the cause of the observed VOC changes.

PDBs, Shallow Wetland Groundwater (30-45 cm depth)



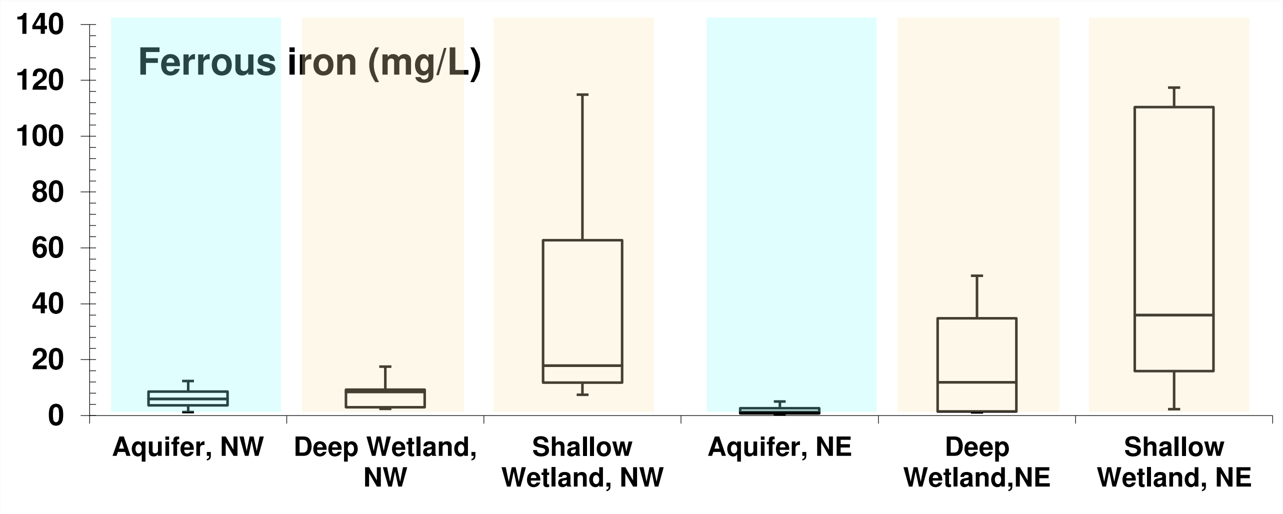


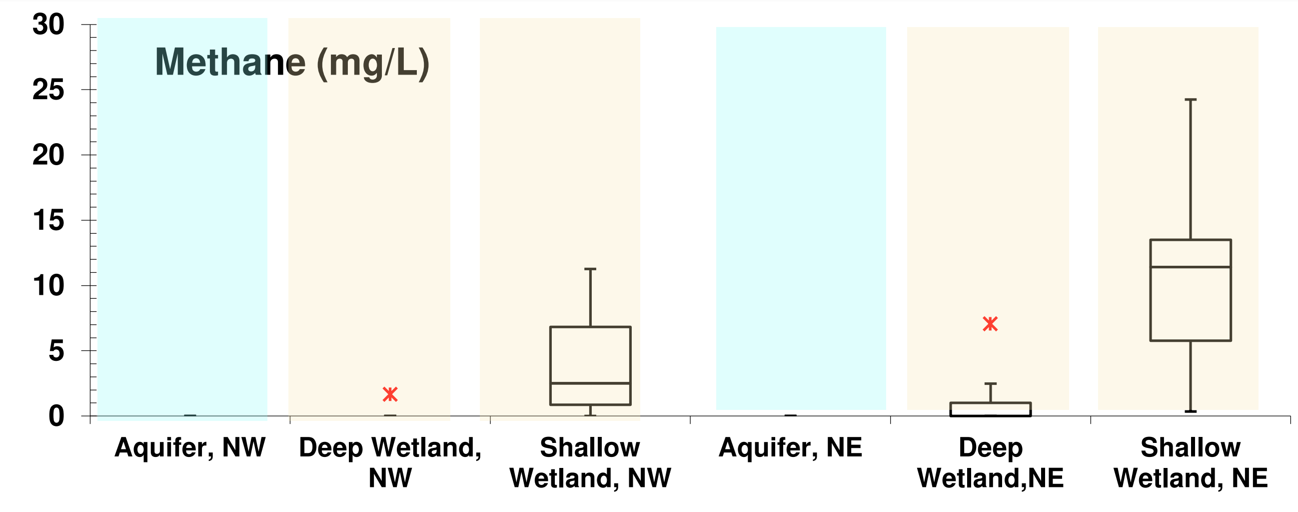




In 2015, general decrease in sulfate and increase in reduced species compared to 2011.

Reduced Species in Piezometers and PDBs, Aquifer to Shallow Wetland Groundwater

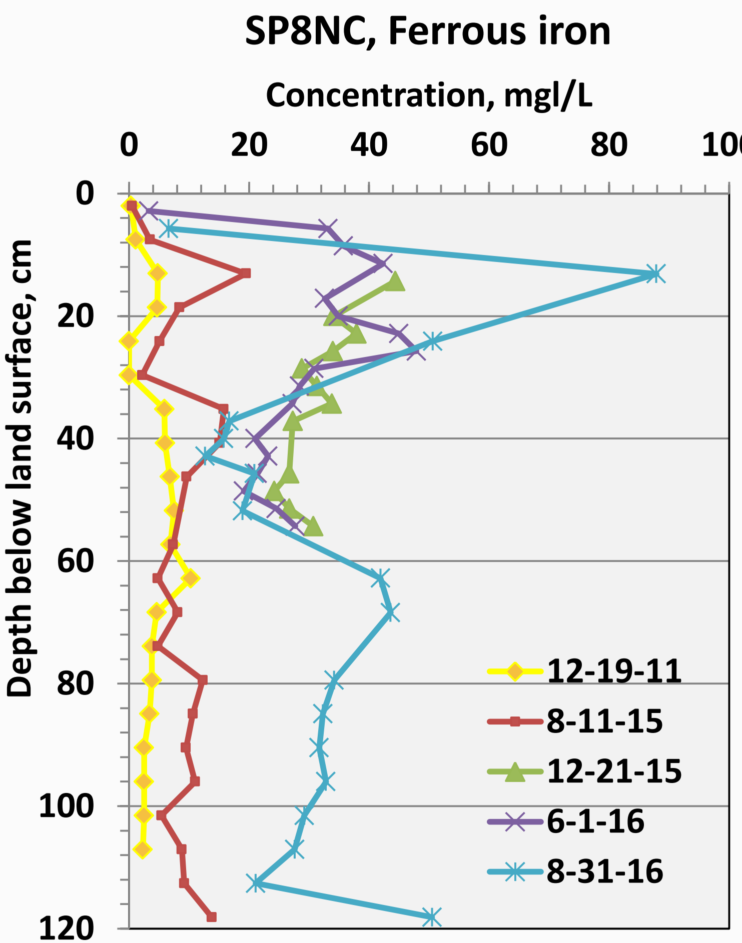


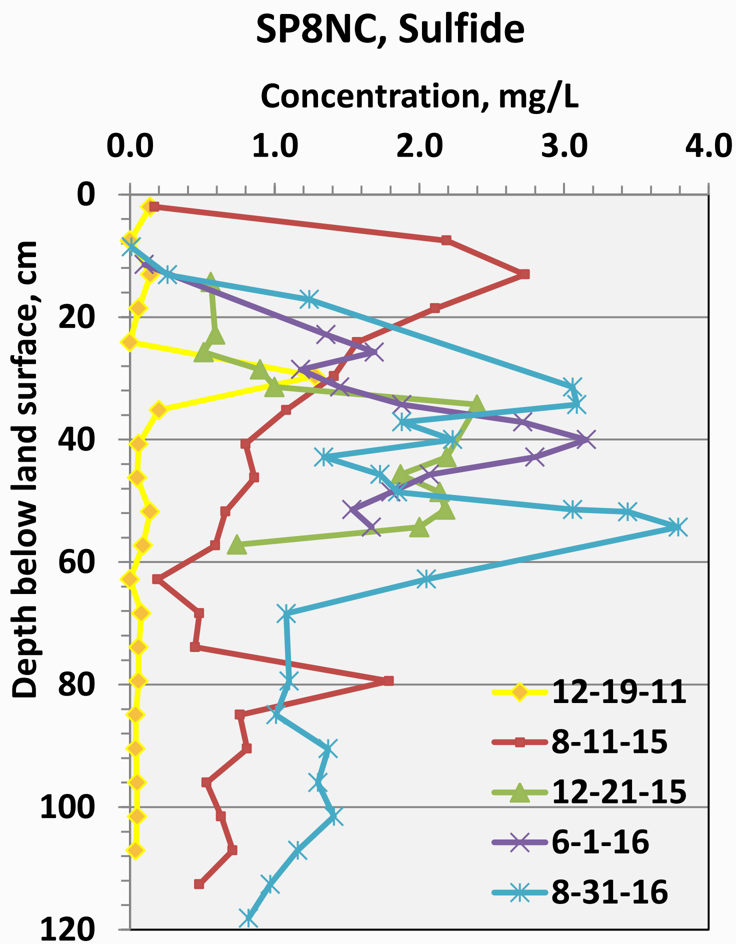


Iron, sulfide, and methane primarily about same in aquifer and deep wetland groundwater.

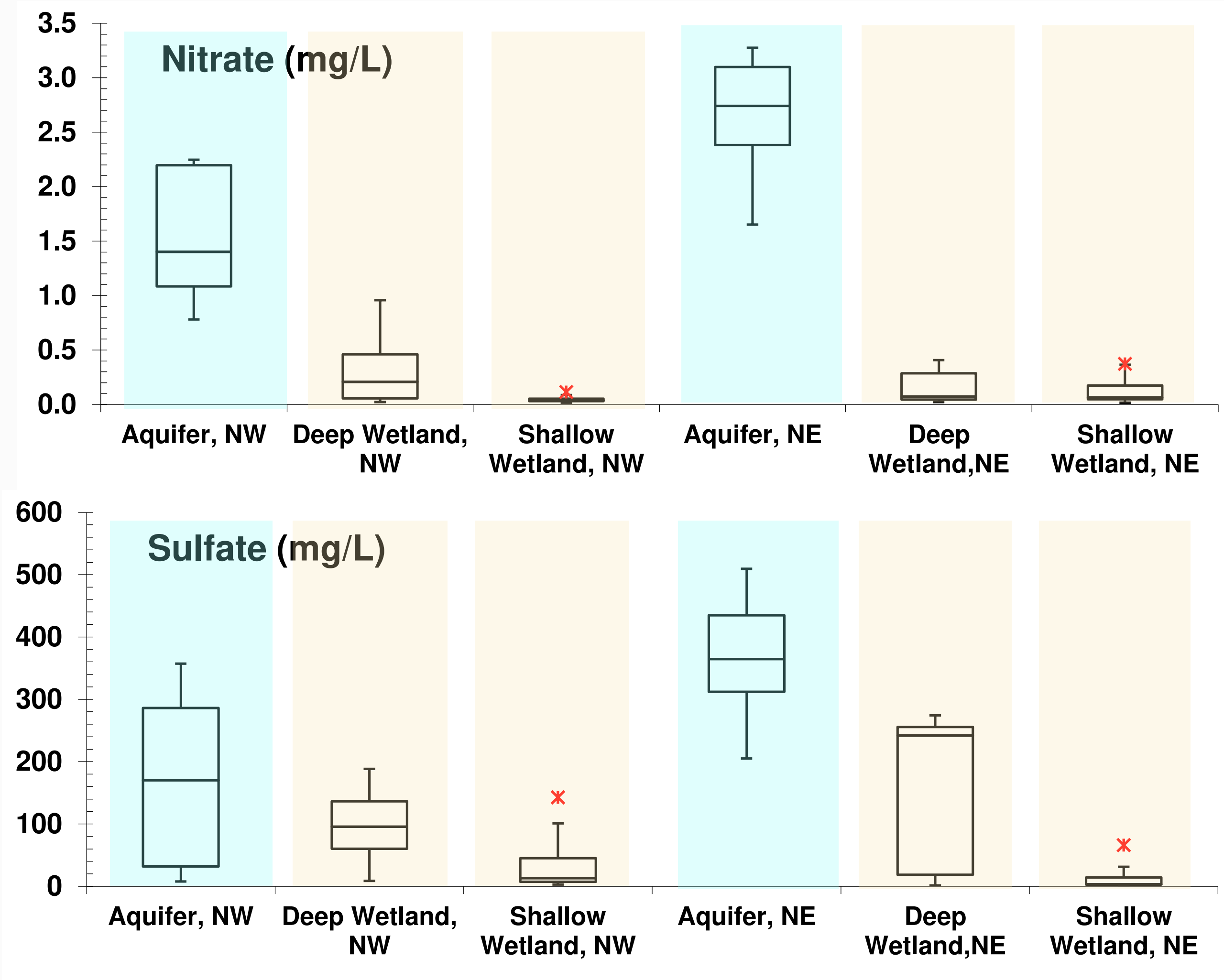
As for VOCs, change occurs primarily in the shallow wetland groundwater.

Reduced Species with Depth, 2011 and 2015-16





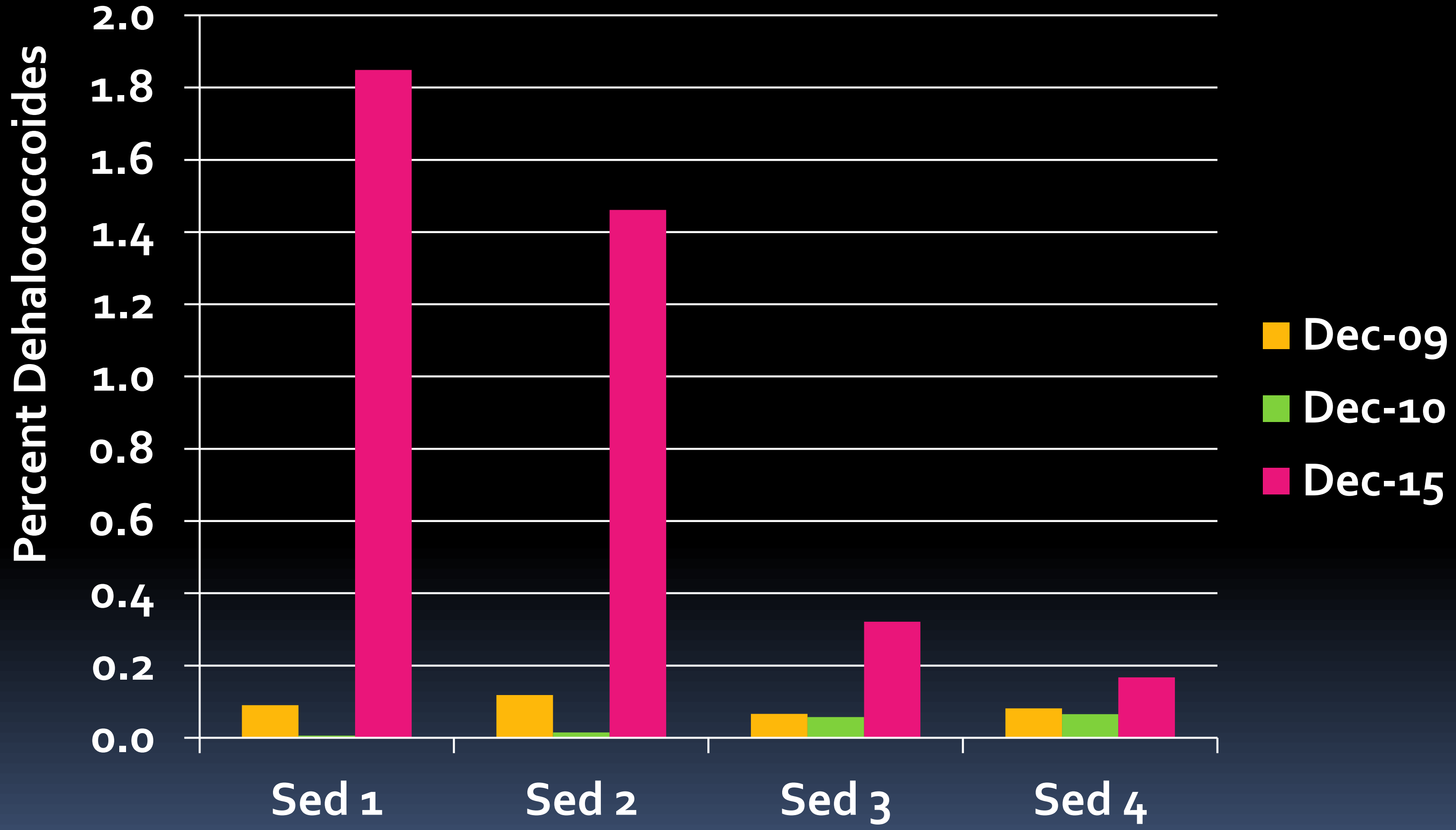
Nitrate and Sulfate in Piezometers and PDBs, Aquifer to Shallow Wetland Groundwater

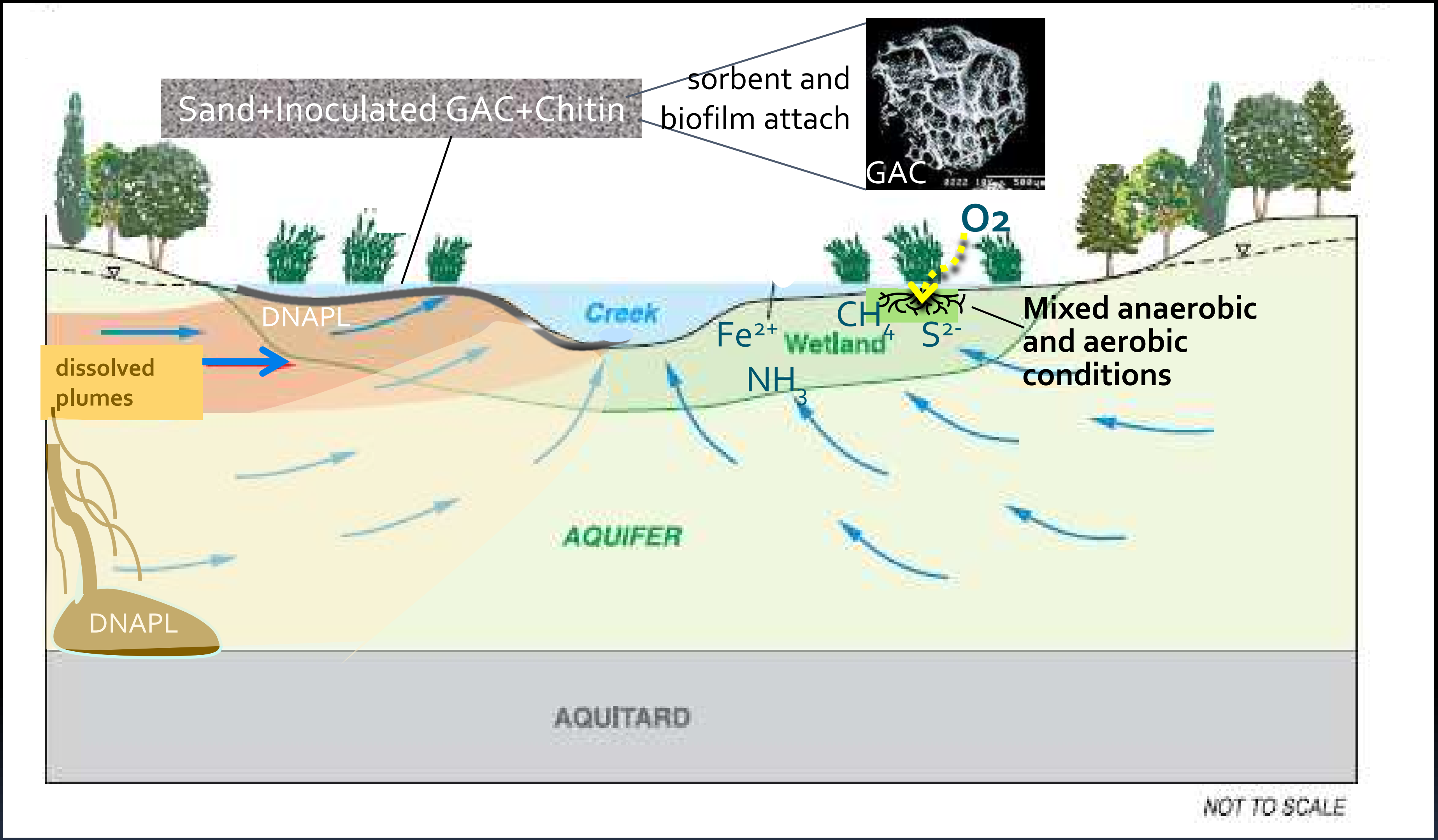


Terminal electron acceptors decreased between aquifer and between deep and shallow wetland groundwater.

However, marked change in anaerobic biodegradation of chlorinated benzenes observed only with increase in reduced species in the shallow groundwater.

Dehalococcoides Abundance in Shallow Wetland Sediment

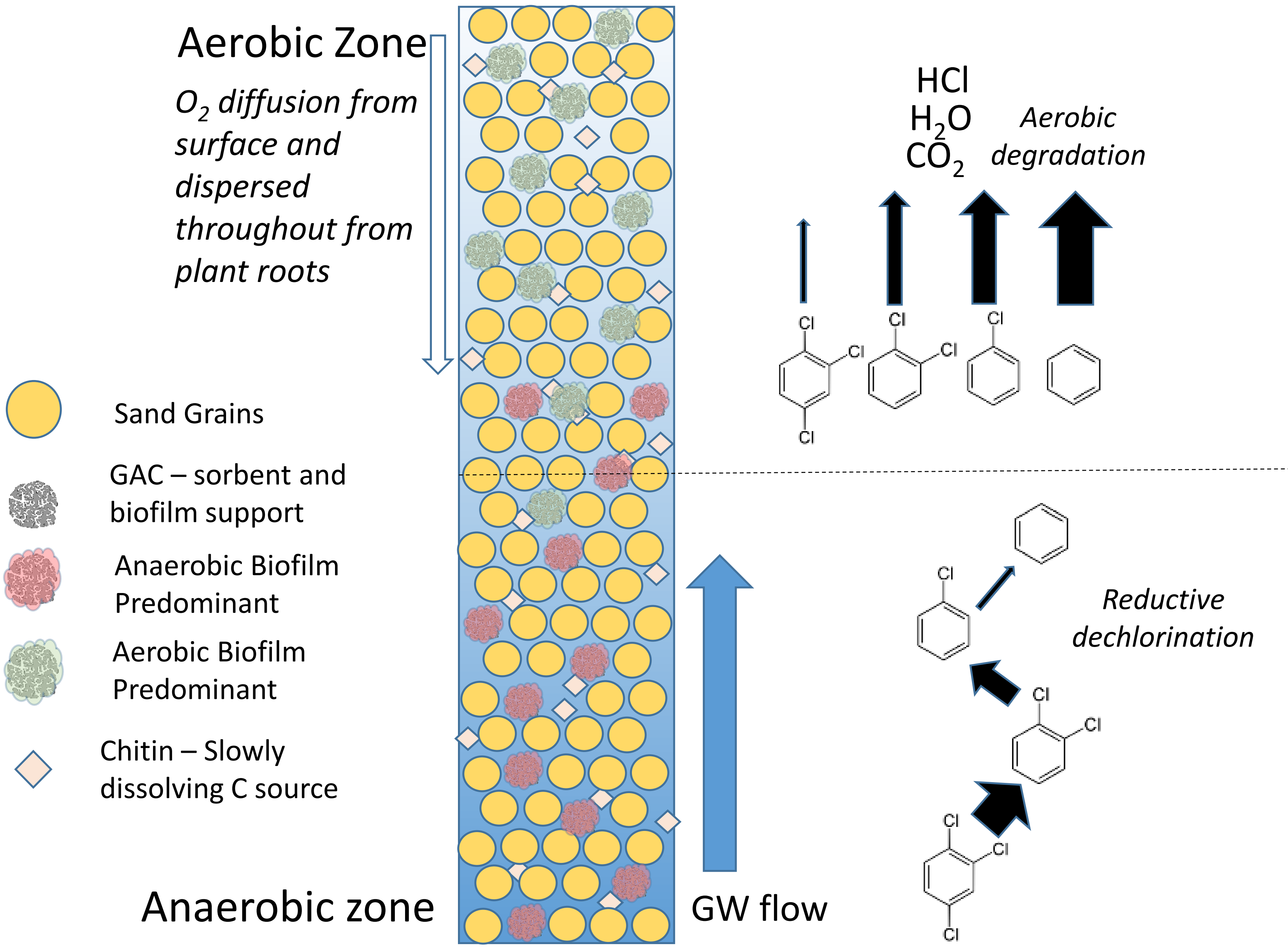




Conceptual model for contamination and dual-biofilm GAC barrier

Study funded by EPA, and NIEHS grant with co-PIs Dr. Bouwer (JHU) and Drs. Durant and Wadhawan (Geosyntec)

Reactive Barrier Concept



Conclusions

- **Biogeochemistry changes and increase in *Dhc* population in wetland sediment in 2015 -16 compared to 2010-11 indicate reductive dechlorination became prominent.**
- **Rise in surface water elevation after broken tide gates was only change between 2010-11 and 2015 to account for these biogeochemical changes.**
- **Percent MCB, still a toxic compound, increased to over 80 % of the VOC composition in 2015-16. Biodegradation needs to be complete to be a remedy.**
- **Increase in reducing conditions could make remedy that would combine anaerobic and aerobic chlorobenzene-degrading bacteria more difficult.**

Biodegradation reactions are a major factor in fate, toxicity, and remediation of organic contaminants in many wetland environments. These processes could change significantly with increased extent and duration of flooding with sea level rise.