Assessment of Sediment P Contributions to the Water Column in Small Watersheds

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Problem Statement

- P loading to lakes may continue despite application of best management practices and reductions in P discharges to surface waters.
- Sediment P may act as a source for long time periods under certain environmental conditions.
- Management requires an understanding of sediment P phases.

Background

- Potential mobile forms of P (Rydin, 2000)
  - Ca and Al bound P are stable and the Ca fraction tends to increase with time (depth).
  - P release from all phases is low under aerobic conditions
  - Reducible P from Fe and Mn oxyhydroxides becomes available under reducing conditions
  - Organic P fractions are more difficult to characterize

Background

- Fe-P as a source of internal loading (Petticrew and Arocena, 2001)
  - Hypolimnetic anoxia associated with SRP
  - A significant relationship was observed between reducible (Fe bound) P in sediment and SRP in the hypolimnion.
  - No significant relationship was seen between SRP and sediment organic P

P Speciation

- Distribution of P among various sediment physicochemical phases.
  - P associated with sediment solids and pore water
  - Determined by selective removal of each phase in a sequential extraction procedure

Sequential Extractions

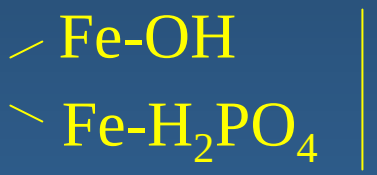
- Removal of elements associated with discrete phases
  - Optimized for a specific element of group of elements
  - Optimization based on chemical reactivity and associations in the sediment
  - Extractions become “operationally defined” fractions

P Chemistry in Sediments

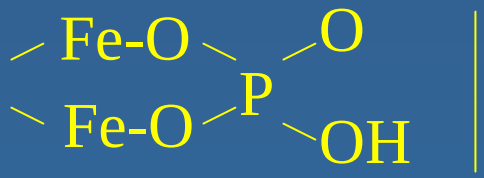
- Exists primarily as phosphate in inorganic fractions
  - $H_2PO_4^-$ or HPO_4^{-2}
- Forms strong bonds through ligand exchange with oxyhdroxides
  - Fe, Al and Mn
- Sparing soluble Ca-phosphate phases
- Organic fractions are complex and variable

P Interactions with Oxyhydroxides

Easily exchangeable outer sphere complex (hours)



Specifically adsorbed inner sphere complex (days)

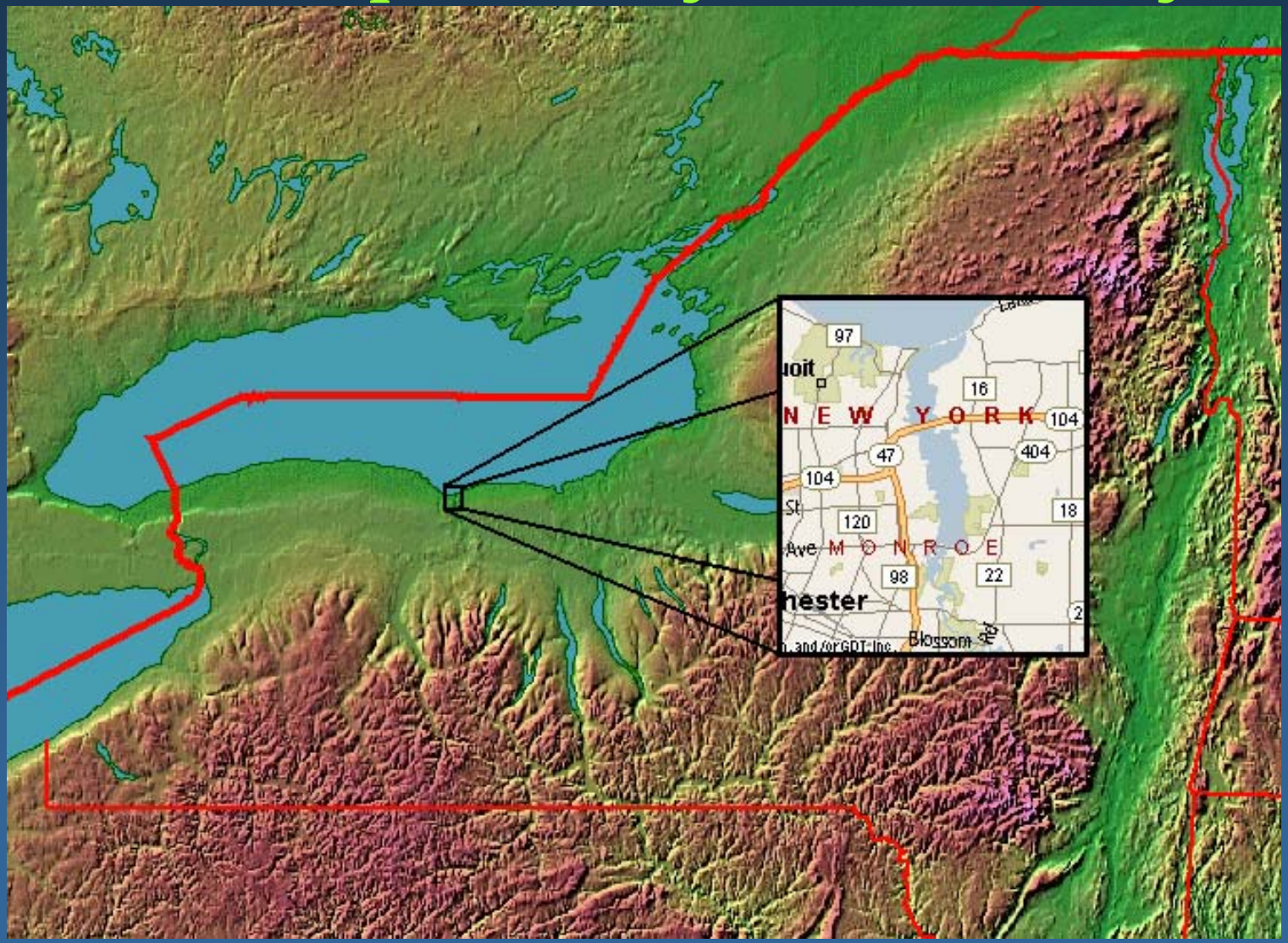


Anion penetration by ligand exchange (weeks)

Method

- Commonly used routines separate P into 5 primary phases. Psenner et al. (1988)
  - Pore water P
  - Organic P
  - Al bound P
  - Reducible P
  - Ca bound P

Irondequoit Bay Case Study



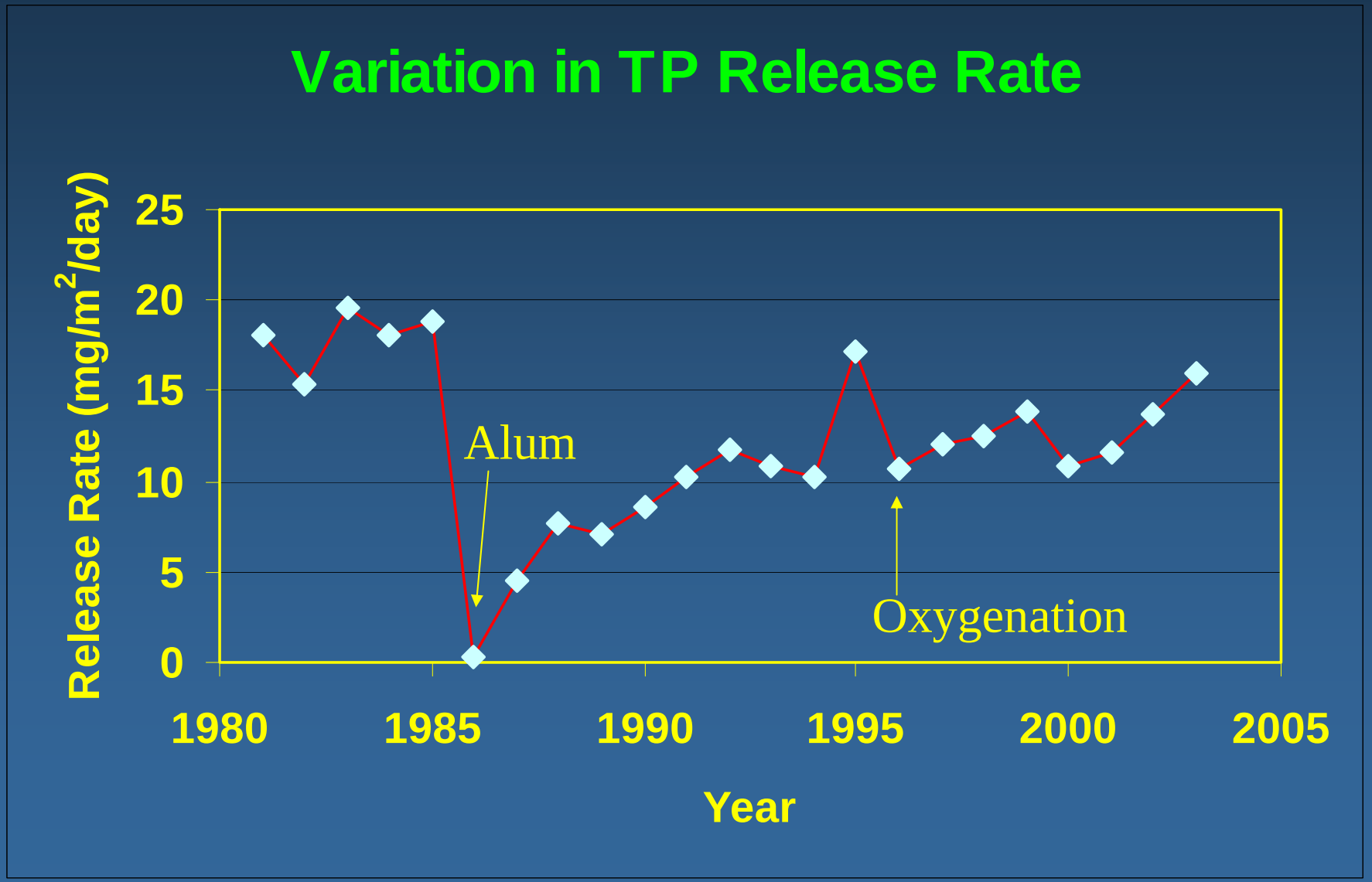
Irondequoit Bay Background

- Dimictic lake, stratifies early May to June
- Maximum Depth – 23 meters
- Surface Area – 6.68 km^2
- Length – 6.44 km
- Max. Width – 0.97 km

Irondequoit Bay Background

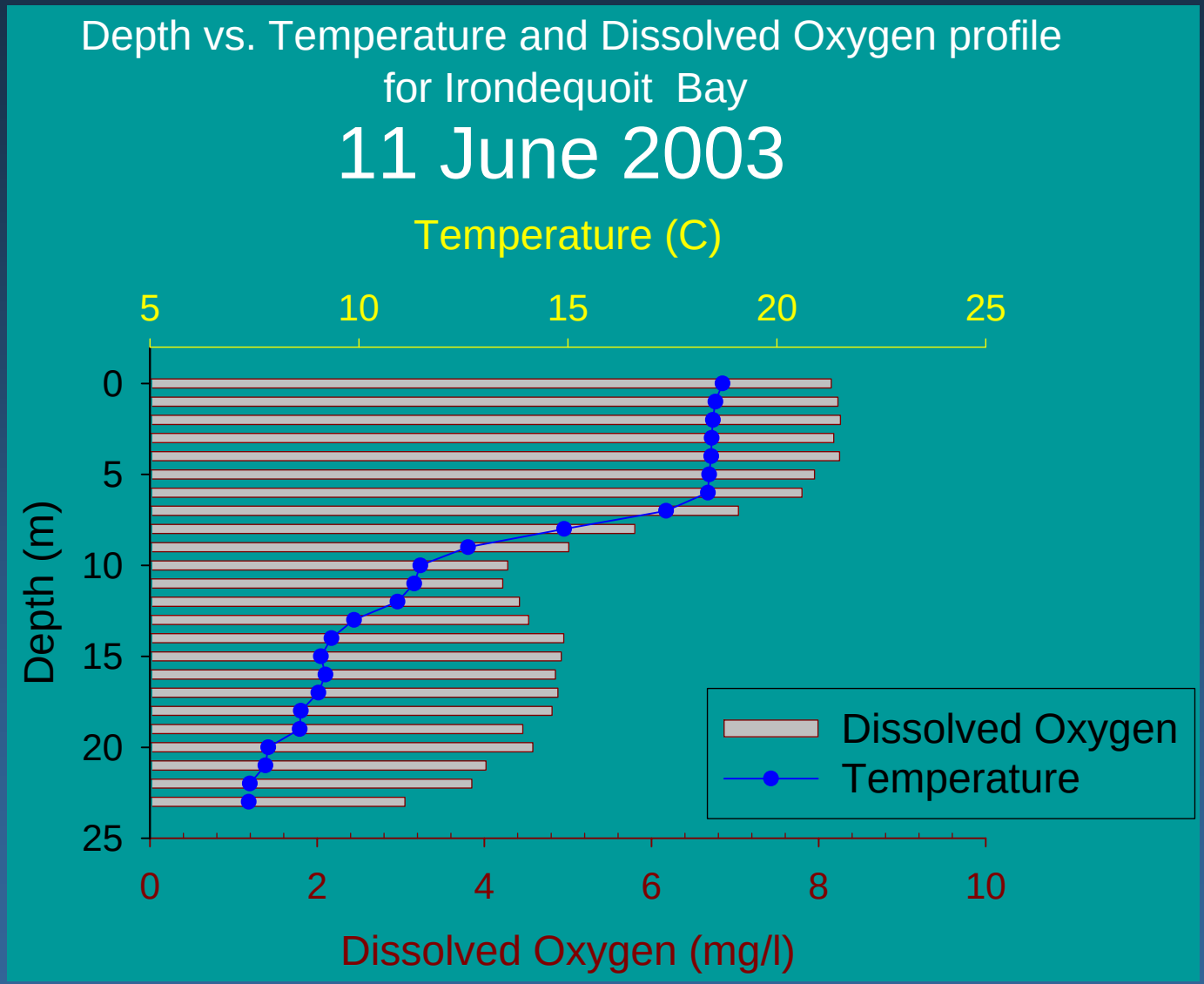
- Severe eutrophication noted since early 1900's
- Irondequoit Bay Framework Plan, early 1980's
  - Reduce external loading of nutrients
    - 298 kg/day to 60 kg/day
  - Alum treatment in 1986
- Oxygen supplementation starting in 1993

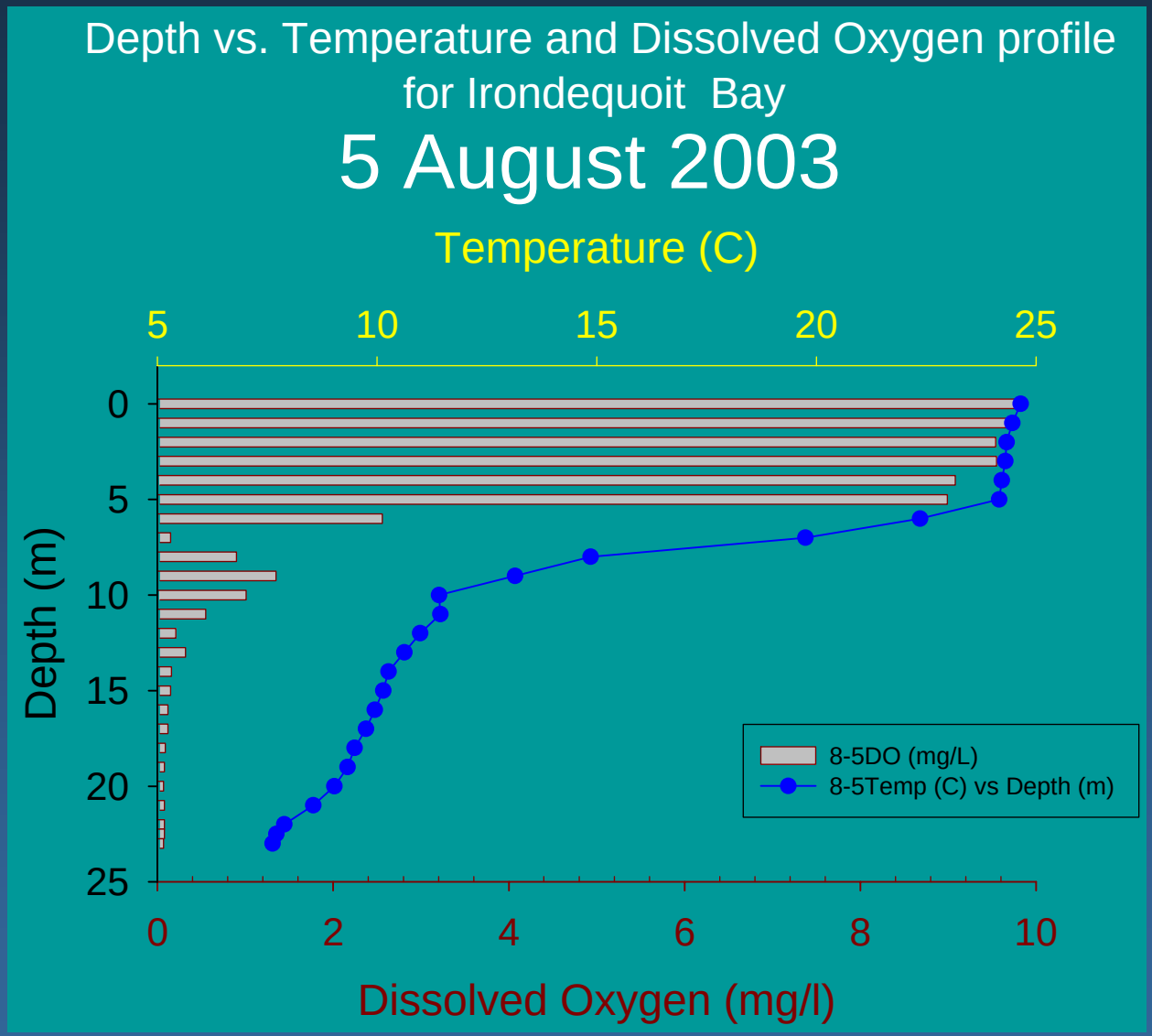
P Release in Irondequoit Bay

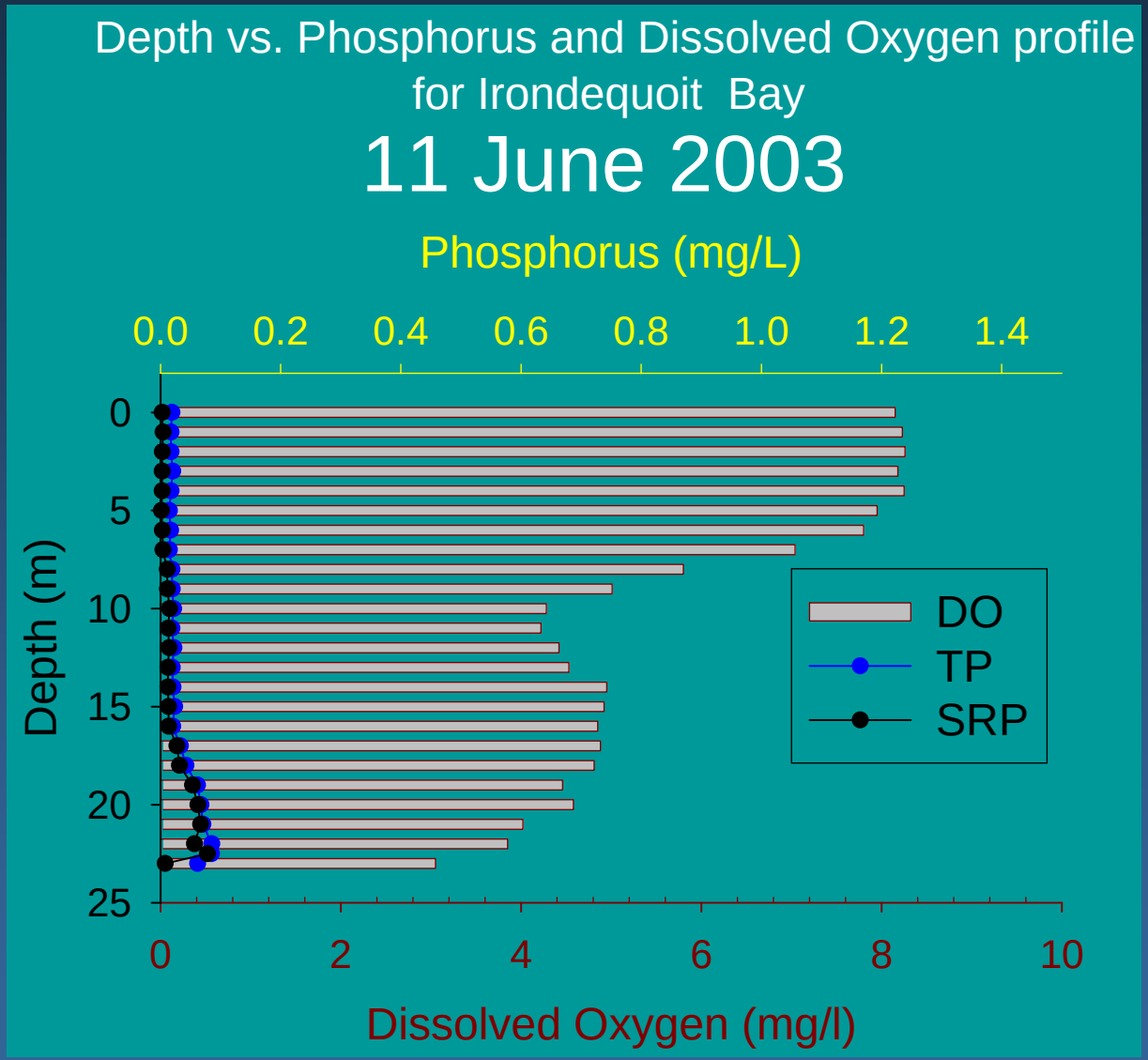


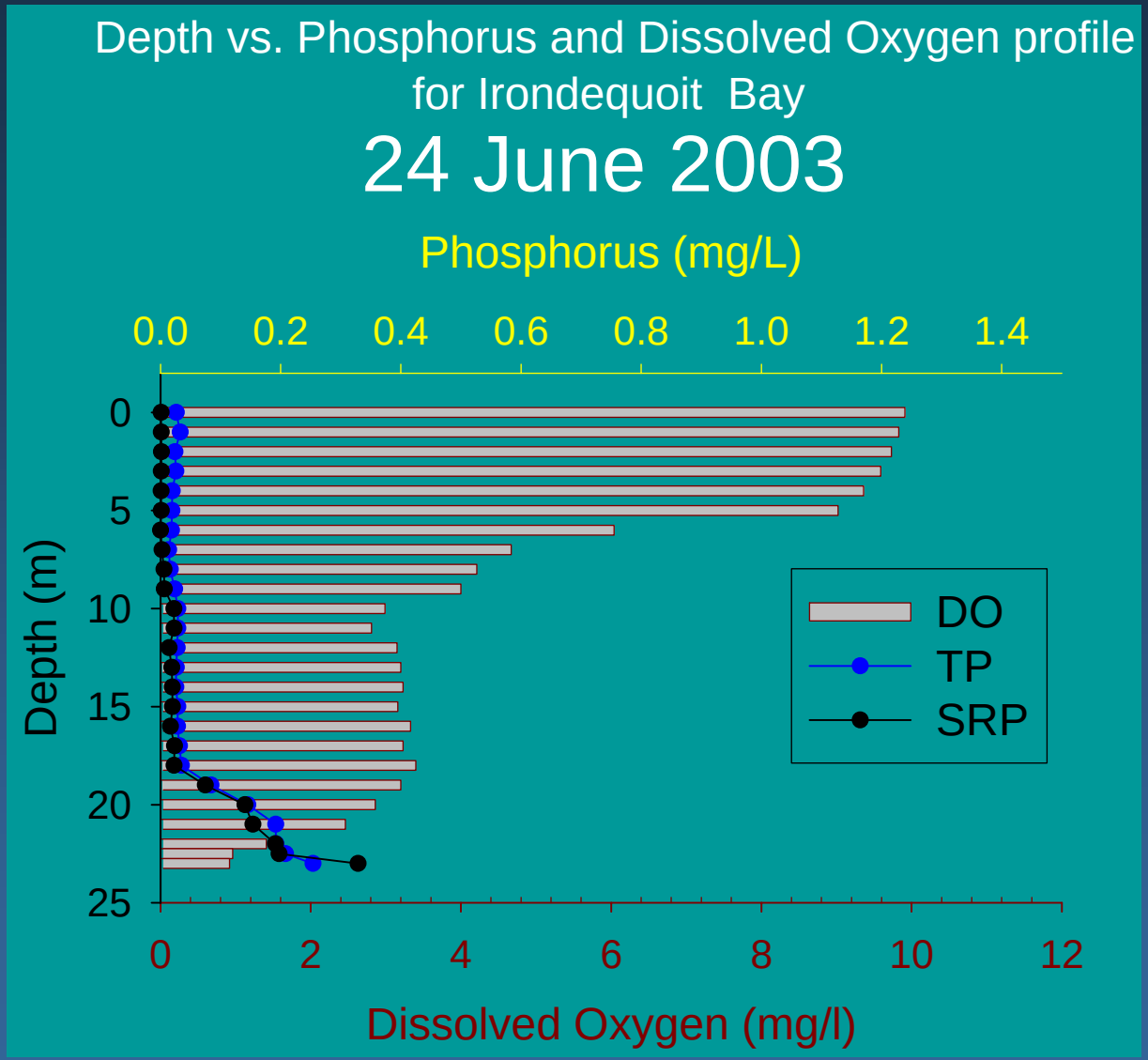
Water Column Observations

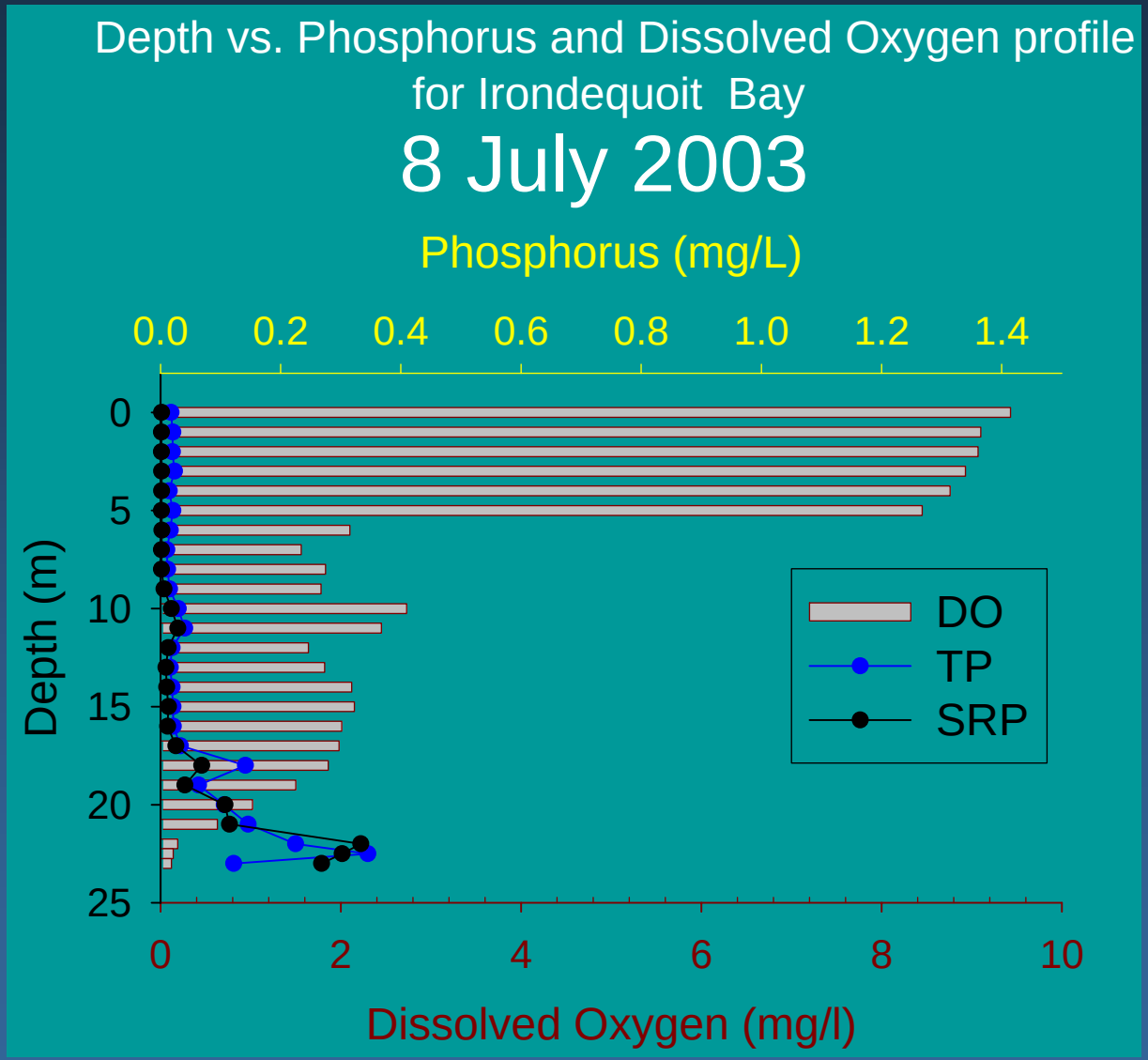
- Water Samples taken weekly from 11 June 2003 to 5 August 2003
- Water samples taken at 1 m interval throughout the water column
  - Total Phosphorus (TP)
  - Soluble Reactive Phosphorus (SRP)
  - Dissolved Oxygen (DO)
  - Total Metals

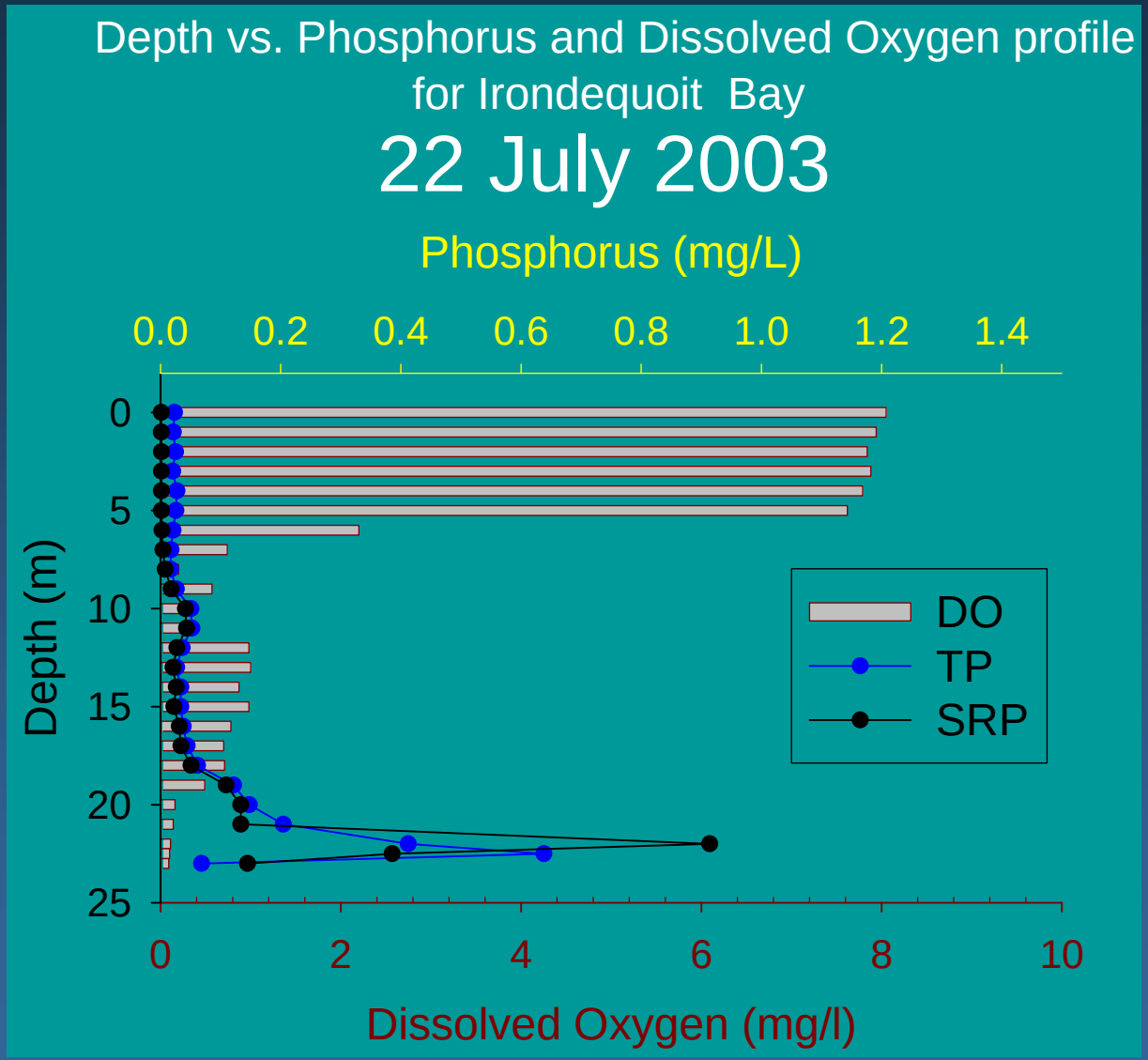

Depth vs. Temperature and Dissolved Oxygen profile
for Irondequoit Bay
11 June 2003
Temperature (C)
5
10
15
20
25
Depth (m)
0
5
10
15
20
25
0
2
4
6
8
10
Dissolved Oxygen (mg/l)
Dissolved Oxygen
Temperature

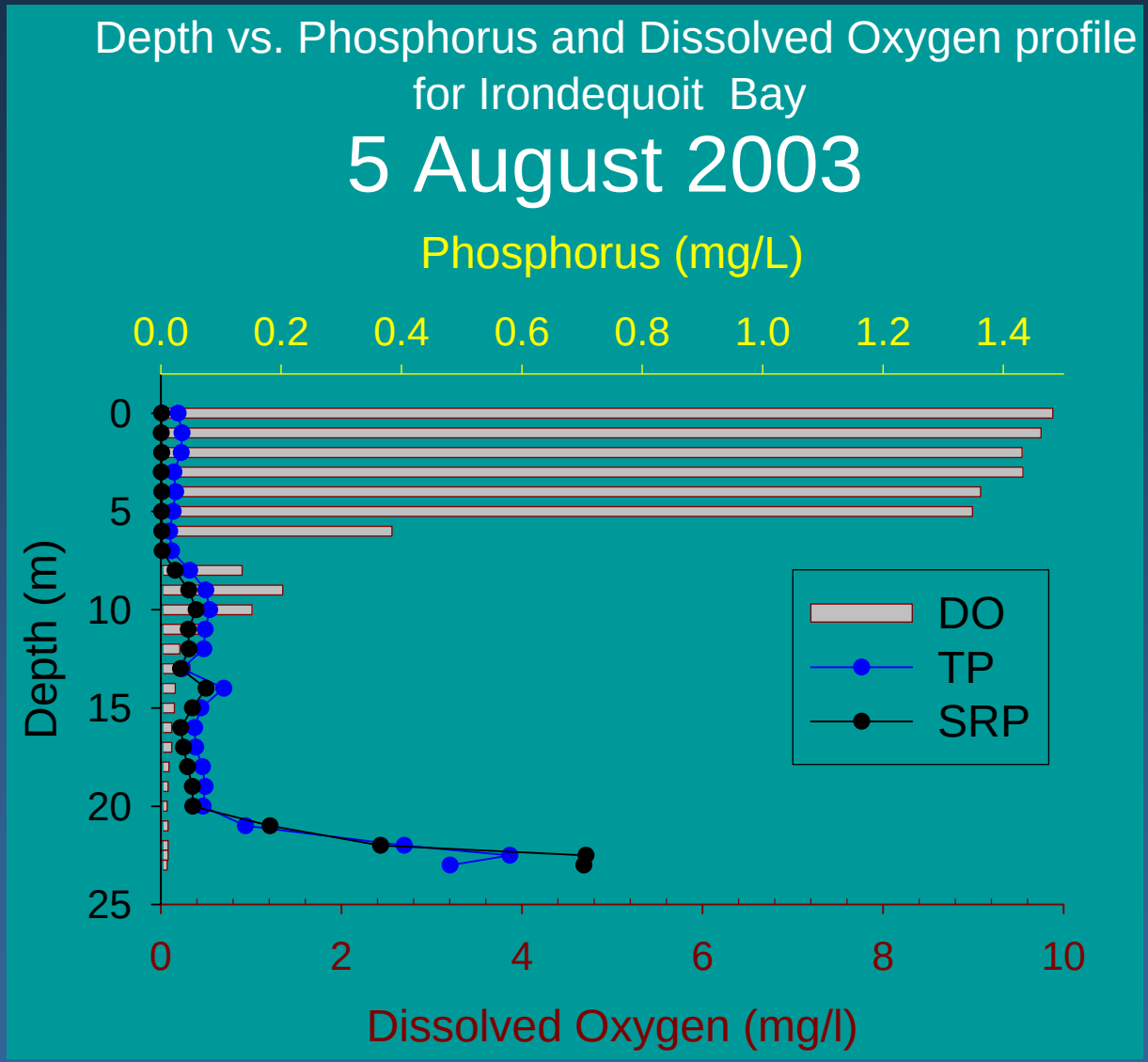

Depth vs. Temperature and Dissolved Oxygen profile for Irondequoit Bay
5 August 2003
Temperature (C)
5
10
15
20
25
Depth (m)
0
5
10
15
20
25
0
2
4
6
8
10
Dissolved Oxygen (mg/l)
8-5DO (mg/L)
8-5Temp (C) vs Depth (m)

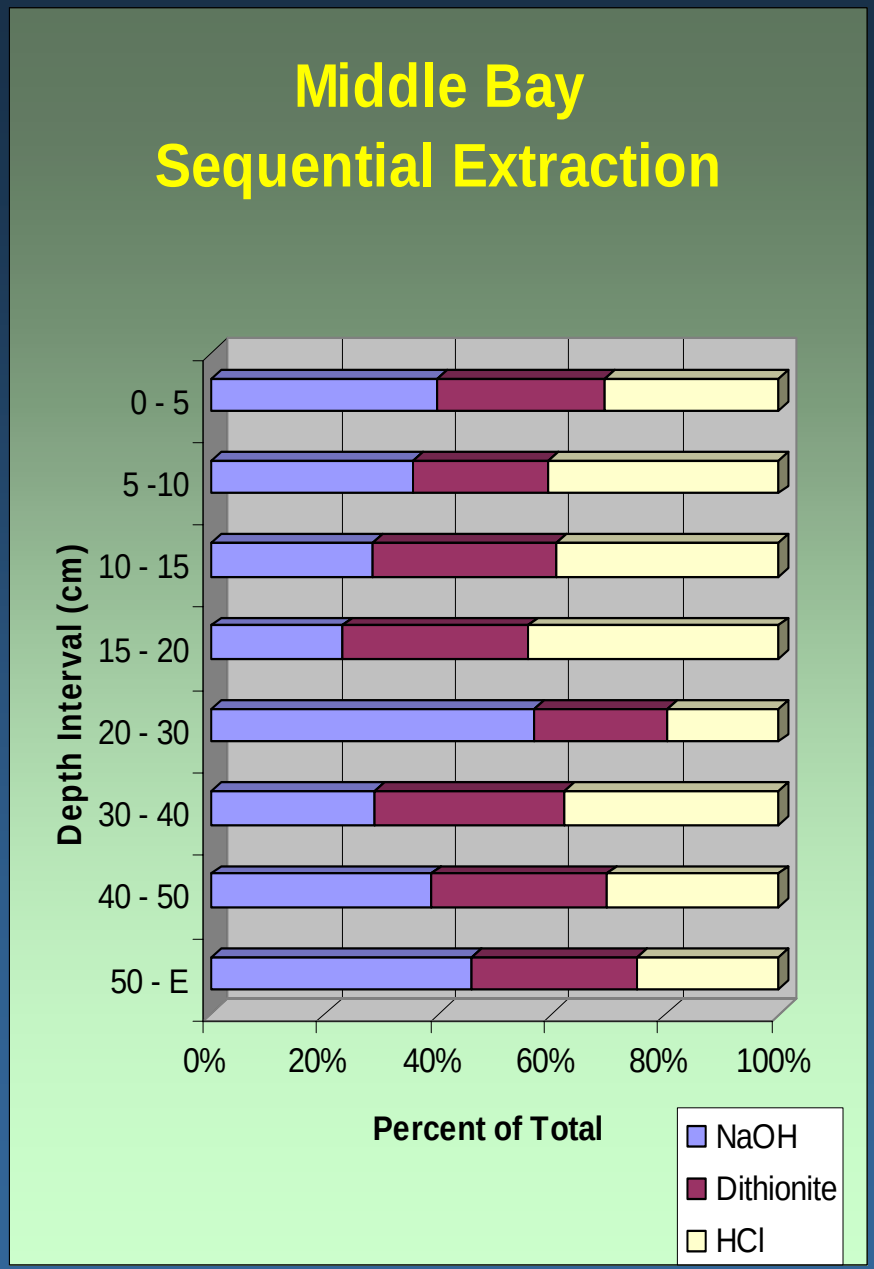

Depth vs. Phosphorus and Dissolved Oxygen profile for Irondequoit Bay
11 June 2003
Phosphorus (mg/L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Depth (m)
0
5
10
15
20
25
DO
TP
SRP
0
2
4
6
8
10
Dissolved Oxygen (mg/l)


Depth vs. Phosphorus and Dissolved Oxygen profile for Irondequoit Bay
24 June 2003
Phosphorus (mg/L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Depth (m)
0
5
10
15
20
25
DO
TP
SRP
0
2
4
6
8
10
12
Dissolved Oxygen (mg/l)


Depth vs. Phosphorus and Dissolved Oxygen profile for Irondequoit Bay
8 July 2003
Phosphorus (mg/L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Depth (m)
0
5
10
15
20
25
DO
TP
SRP
0
2
4
6
8
10
Dissolved Oxygen (mg/l)


Depth vs. Phosphorus and Dissolved Oxygen profile for Irondequoit Bay
22 July 2003
Phosphorus (mg/L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Depth (m)
0
5
10
15
20
25
DO
TP
SRP
0
2
4
6
8
10
Dissolved Oxygen (mg/l)

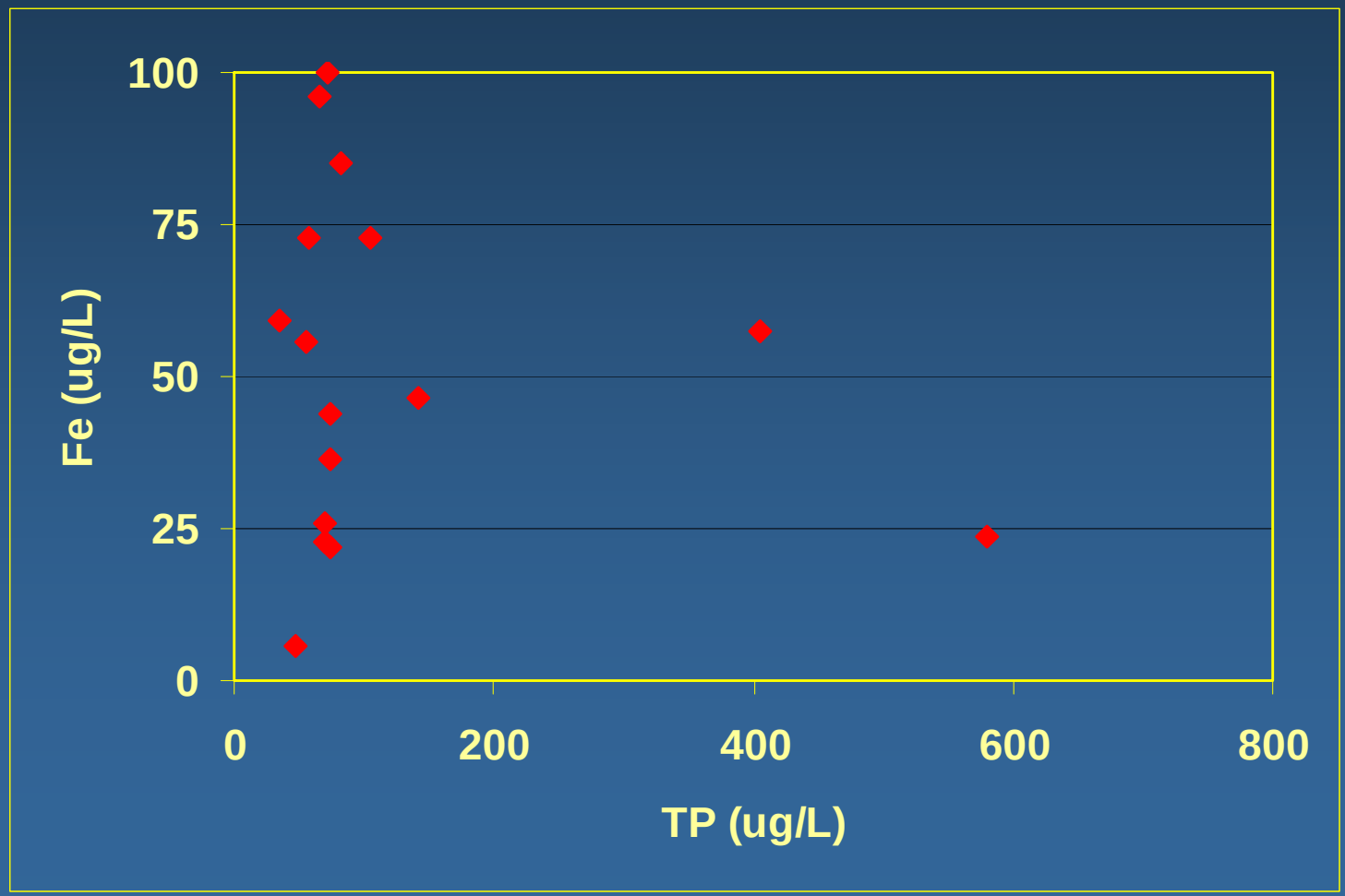

Depth vs. Phosphorus and Dissolved Oxygen profile for Irondequoit Bay
5 August 2003
Phosphorus (mg/L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Depth (m)
0
5
10
15
20
25
DO
TP
SRP
0
2
4
6
8
10
Dissolved Oxygen (mg/l)



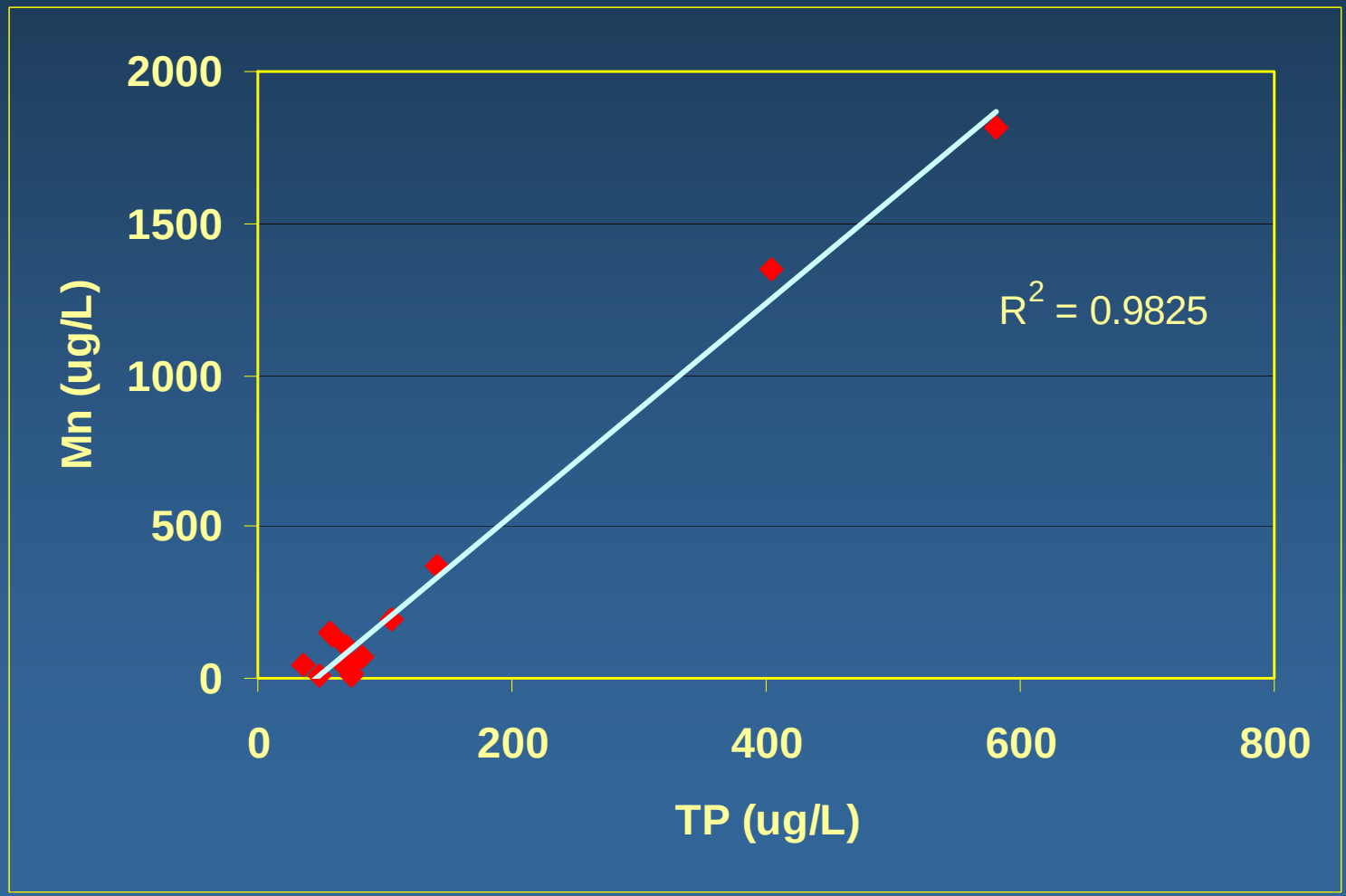
P Fractionation Summary Core sample collected May 2003

Depth Interval	P - Sum mg/kg (dry wt.)
0 - 5	1744
5 -10	1606
10 - 15	1346
15 - 20	1315
20 - 30	2127
30 - 40	1730
40 - 50	1641
50 - E	2253

TP vs Fe
Aug. 5, 2003



TP vs Mn
Aug. 5, 2003



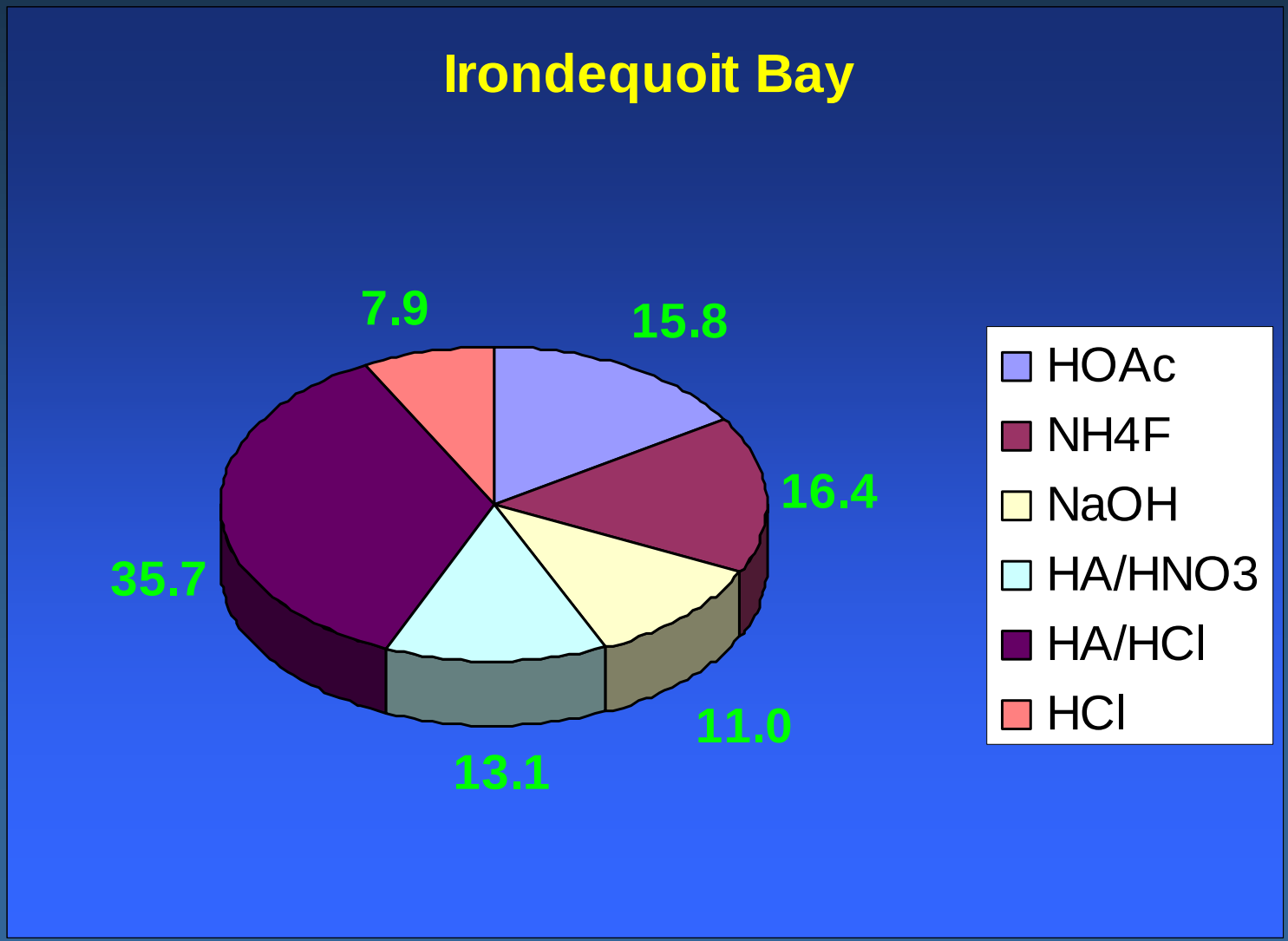
Old Method

- Commonly used routines separate P into 5 primary phases. Psenner et al. (1988)
  - Pore water P
  - Organic P
  - Al bound P
  - Reducible P
  - Ca bound P

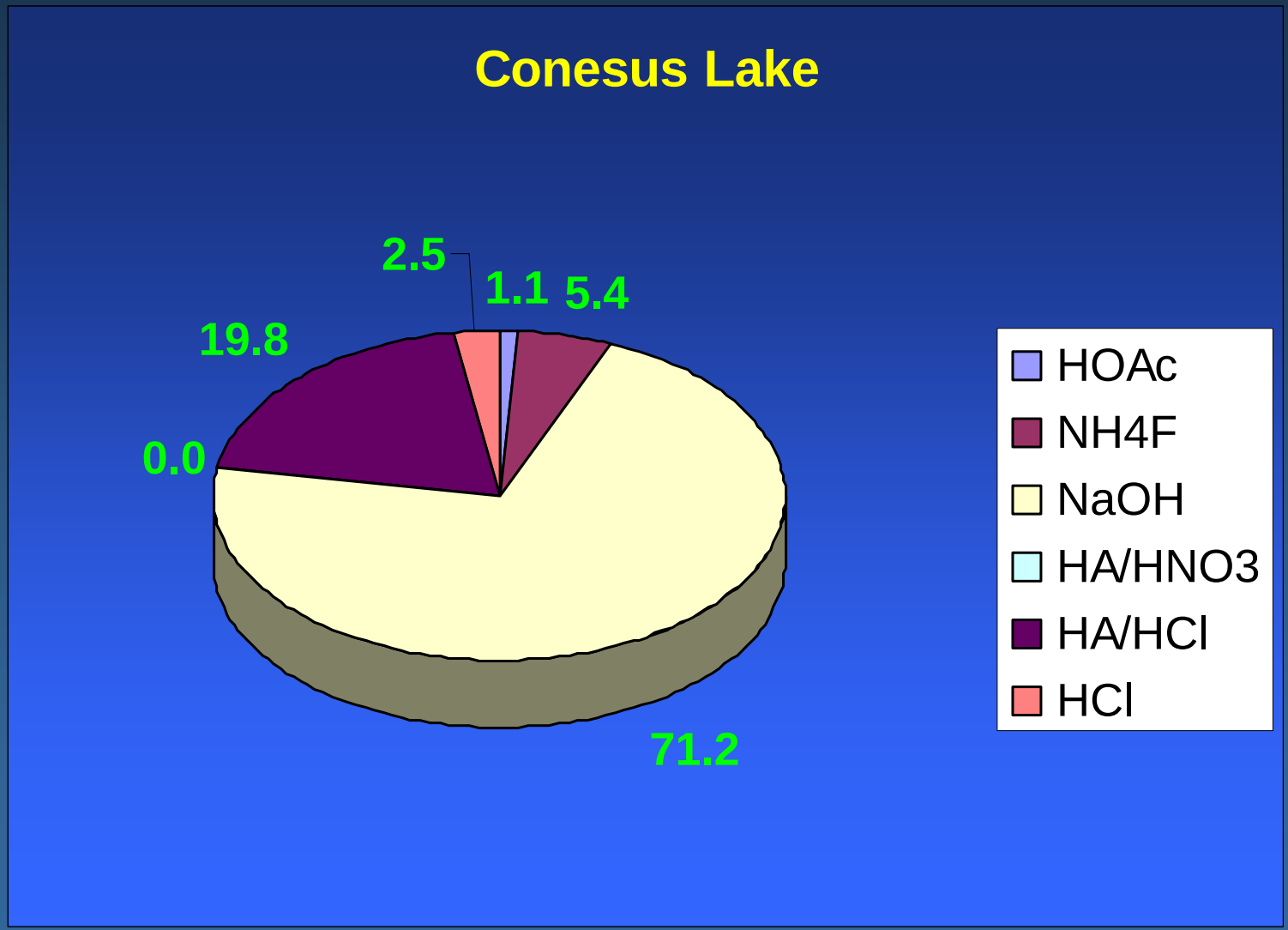
New Sequential Extraction Scheme

- Acetic Acid - removes free carbonates
- NH_4F - removes Al-P
- NaOH - removes organic P
- HA/HNO_3 - easily reducible OxHy
- HA/HCl - crystalline OxHy
- HCl - Ca-P

Sequential Extraction Results



Sequential Extraction Results



Conclusions/Future Work

- Sediment P may impact water quality despite reductions in external loading
- Alum treatments are limited
- Oxyhydroxides play an important role in annual cycling of P

Conclusions/Future Work

- Mn and/or amorphous oxyhydroxides are more active in cycling process
- Evaluate link between seasonal changes in sediment P distribution and water column chemistry