Importance of sample timing, handling and other methods to low-level analysis of phosphorus in lake water

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Thank you

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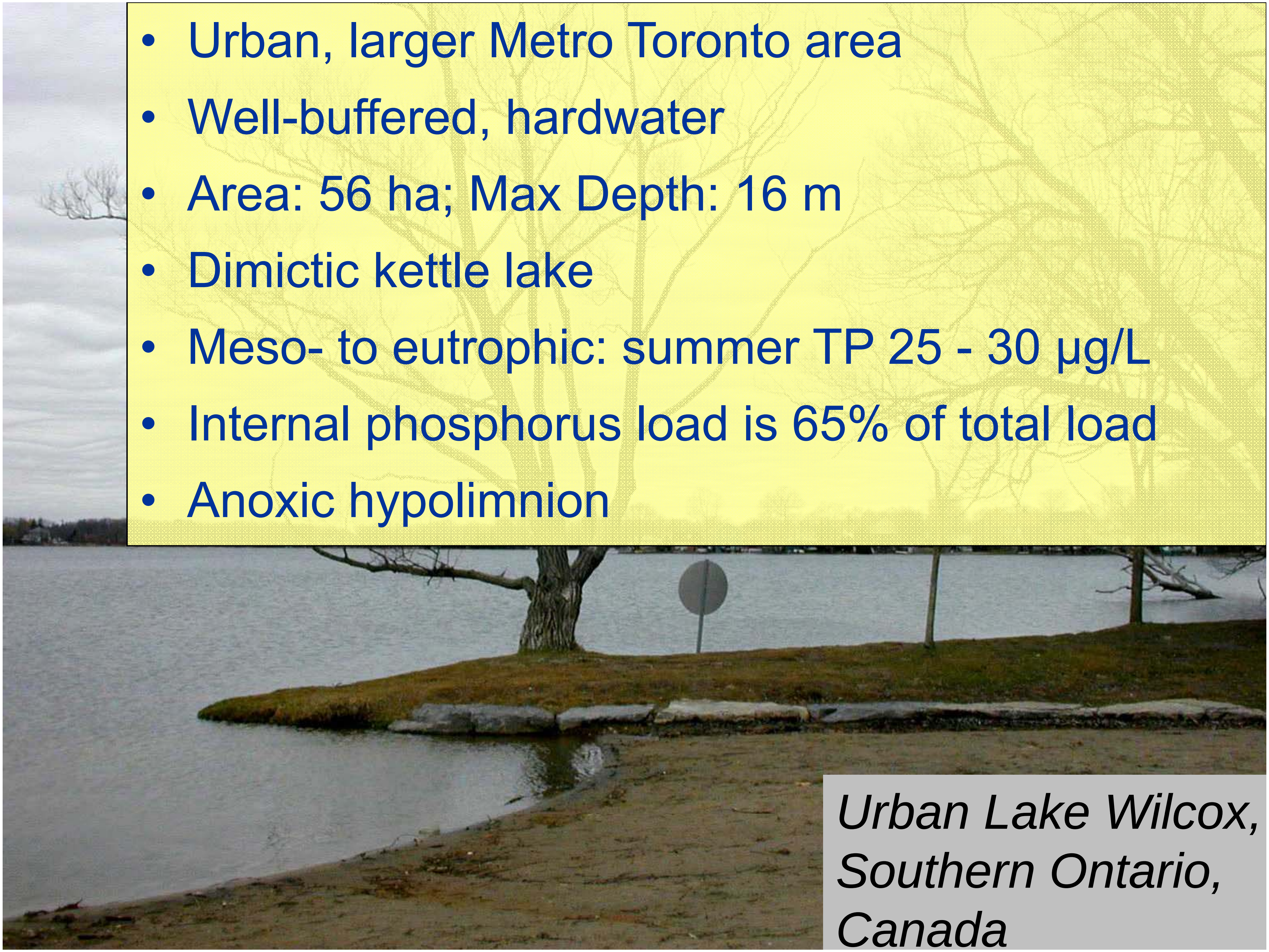
- Travel grant by NEMC
  Conference Coordinator, *Jerry Parr* of the NELAC Institute

Charlie Patton

1. Reasons NOT to use low-level analysis
2. What may be more important instead

Problems with low level analysis

- Contamination
- Need a lot of replicates (high analytical effort)
- Few comparative data from other studies/ systems available
- High cost, effort, specialization, etc. “Trade off”
- Transient “Snapshot”: not reproducible (high sampling effort) – example “Blooms”

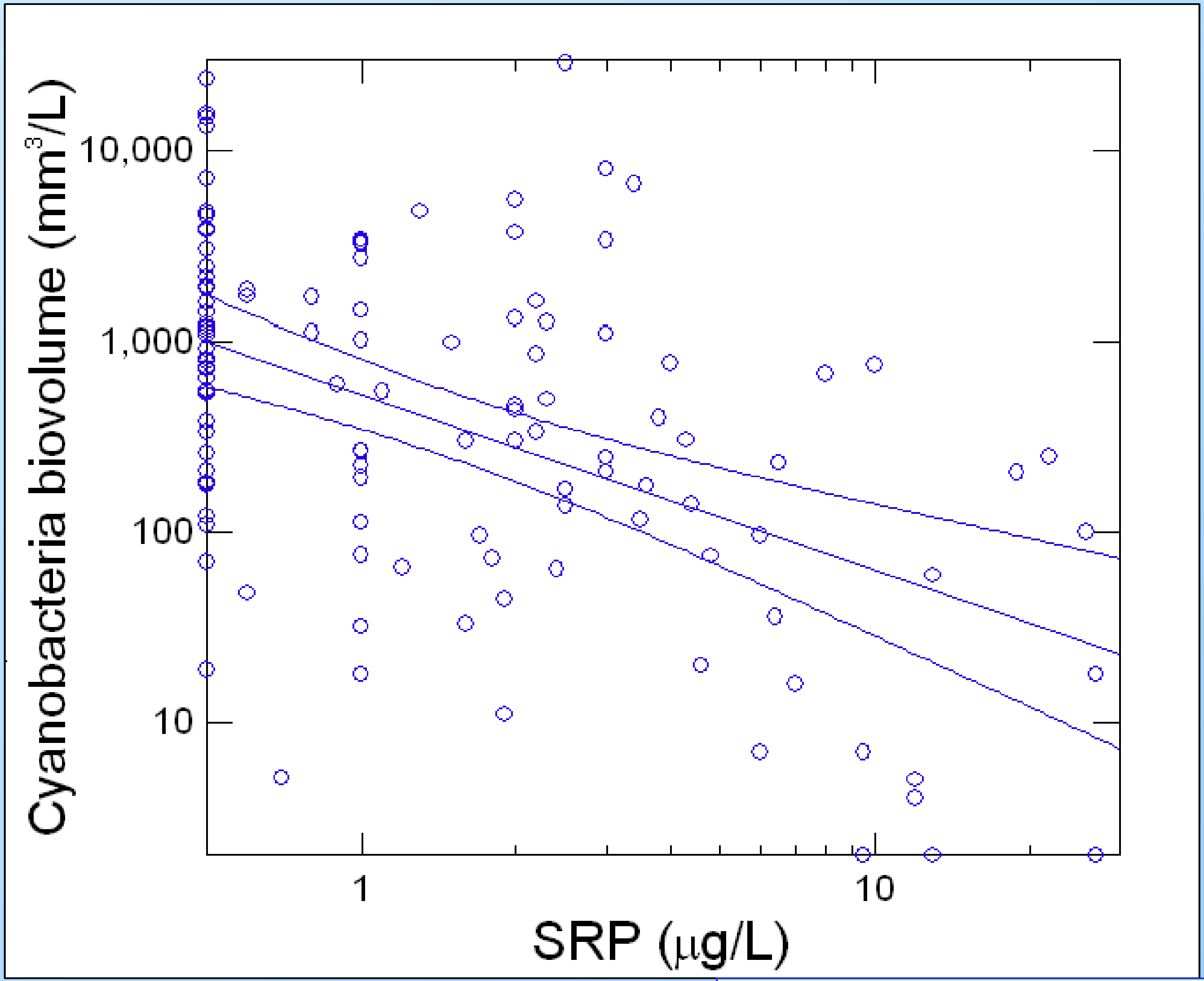


- Urban, larger Metro Toronto area
- Well-buffered, hardwater
- Area: 56 ha; Max Depth: 16 m
- Dimictic kettle lake
- Meso- to eutrophic: summer TP 25 - 30 µg/L
- Internal phosphorus load is 65% of total load
- Anoxic hypolimnion

Urban Lake Wilcox, Southern Ontario, Canada

Cyanobacteria vs SRP

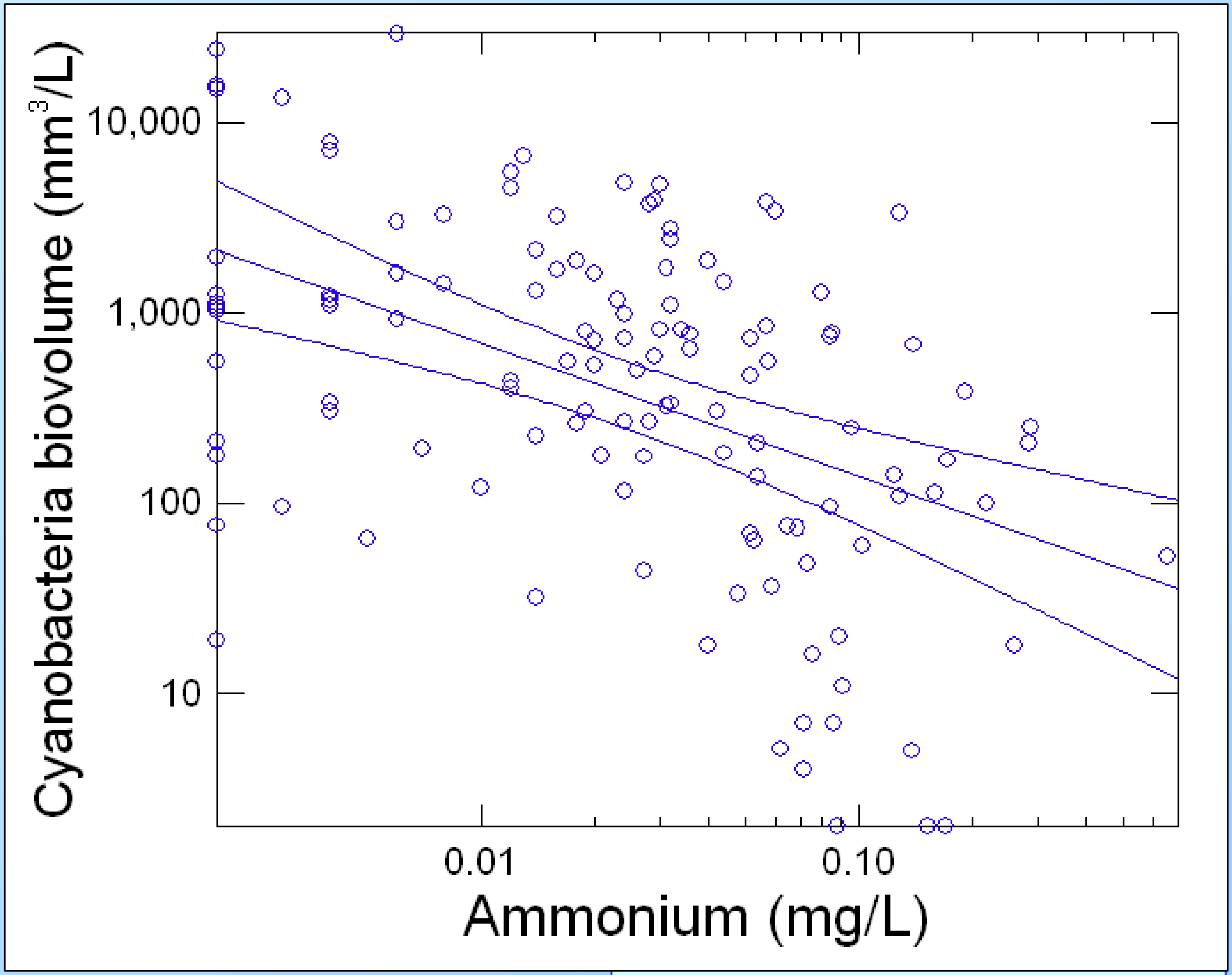
(dissolved reactive P, detection limit 0.5 µg/L)



R^2= 0.25, p<0.0001, n=123

Cyanobacteria vs Ammonium

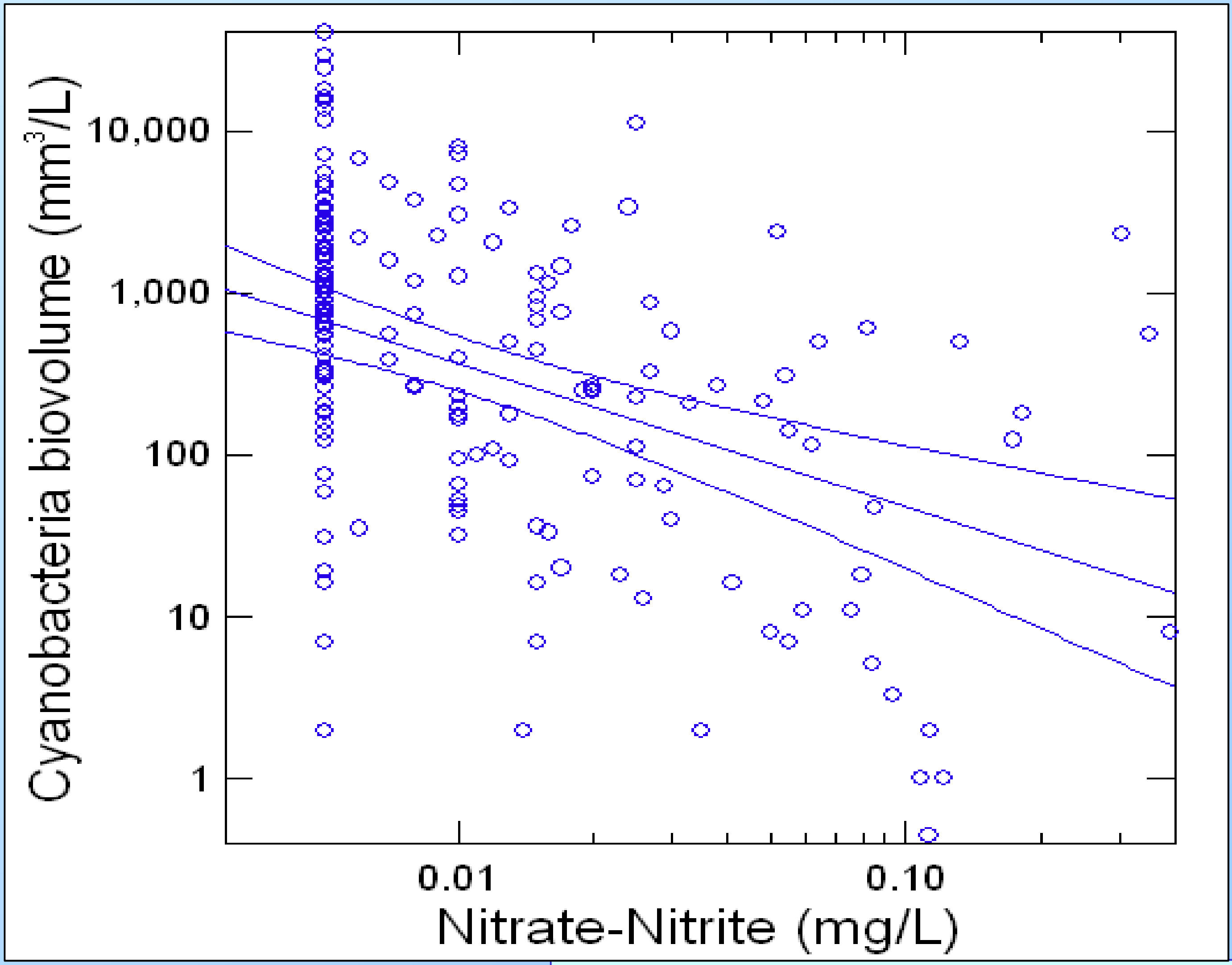
Detection limit: 0.002 – 0.005 mg/L



R^2= 0.22, p<0.0001, n=124

Cyanobacteria vs Nitrate&Nitrite

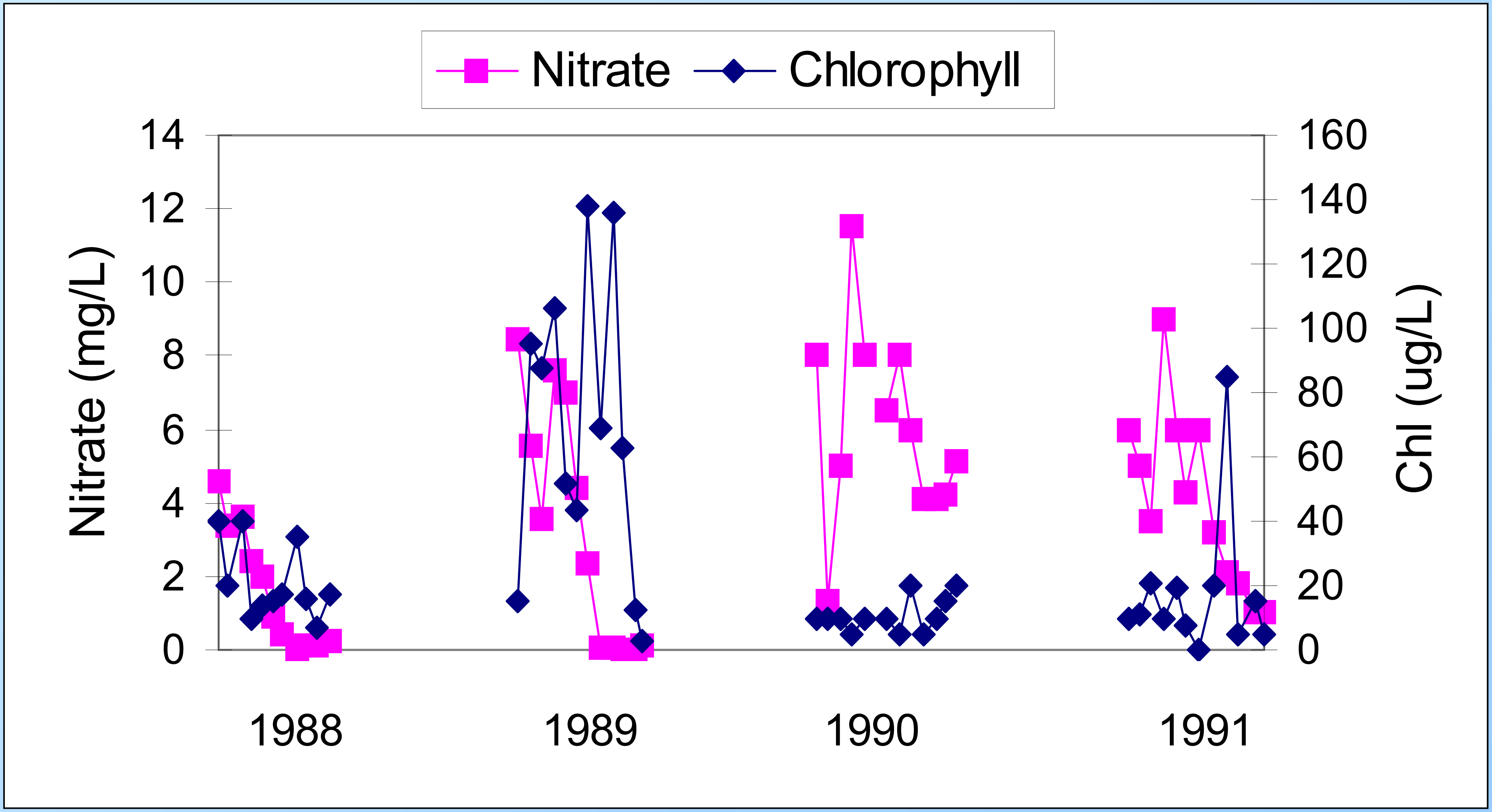
Detection limit 0.005 mg/L



$R^2 = 0.17$, $p<0.0001$, $n=181$

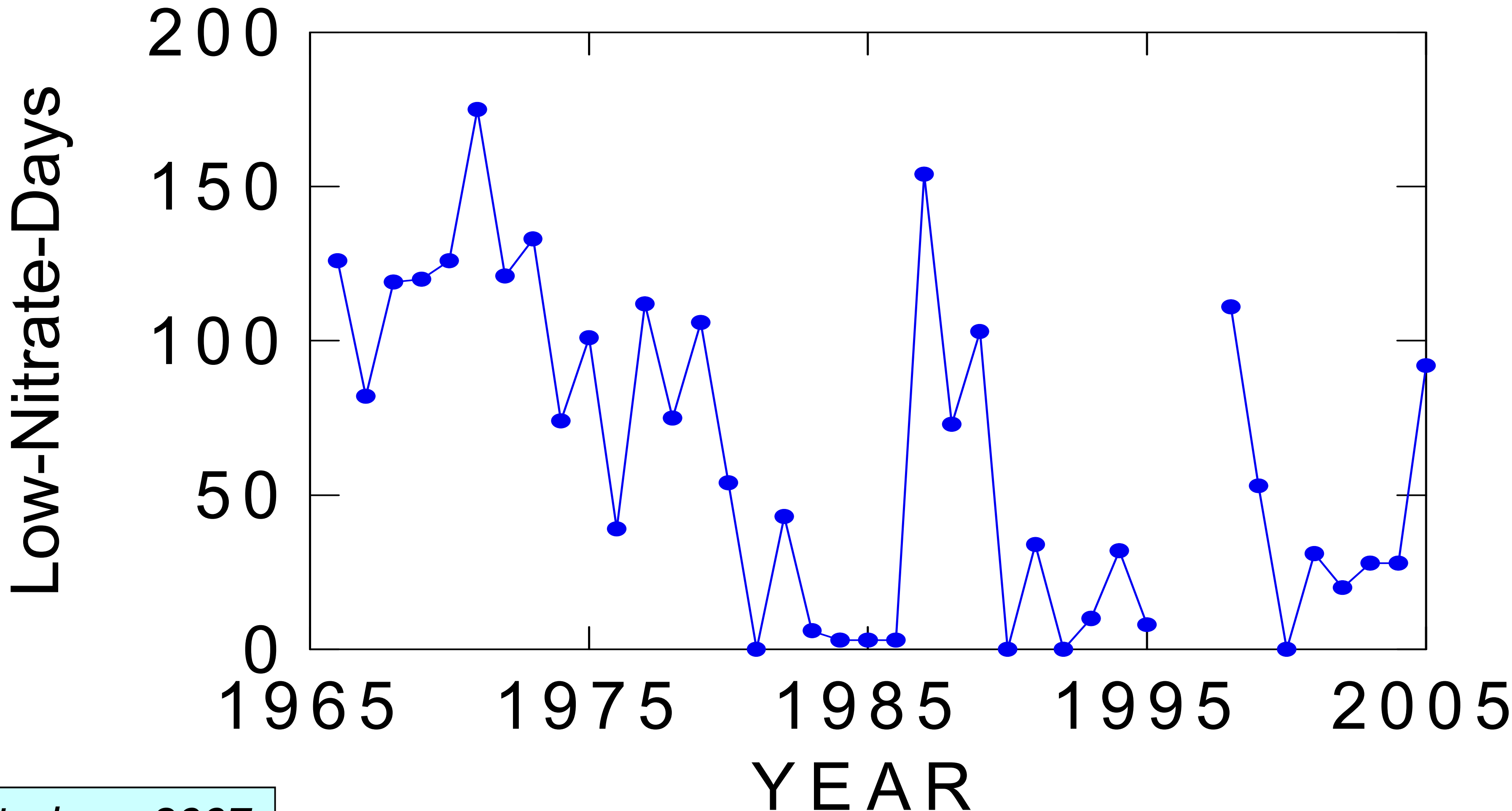
Bluegreen algal bloom in Fanshawe Lake on August 26, 2005

Fanshawe Lake
Nitrate and Chlorophyll



Bloom Indicator: Low-Nitrate-Days

The period of time during summer and early fall, when nitrate concentration is below 1-2 mg/L



Nürnberg 2007

The quest for adequate phosphorus measurements in lakes

What is the analysis for?

- Assessment for nutrients by routine monitoring, trophic state definition (Country, State, County)
- Remediation of eutrophication problems (Specific lake or watershed)
- Modelling (Scenarios, TMDLs)
- Specific scientific questions

What may be more important than LLA
- Outline -

- Background knowledge
  - Limnological characteristics
  - Historic data (“blooms”, fish kill)
  - Knowledge from other studies/systems
- Adequate sampling & handling, w/o contamination
- Determine related variables (instead or in addition)
- Adequate monitoring plan
  - Spatial and temporal sampling
  - Specific fractions to be determined
- Use a model instead

(MOST) Important background knowledge

- Surface water
  - Eutrophication
  - Cyanobacterial blooms

  What is limiting algal growth?

- Hypolimnia in lakes and reservoirs
  Anoxic or not?

Background knowledge
Water is anoxic

SRP, dissolved reactive P

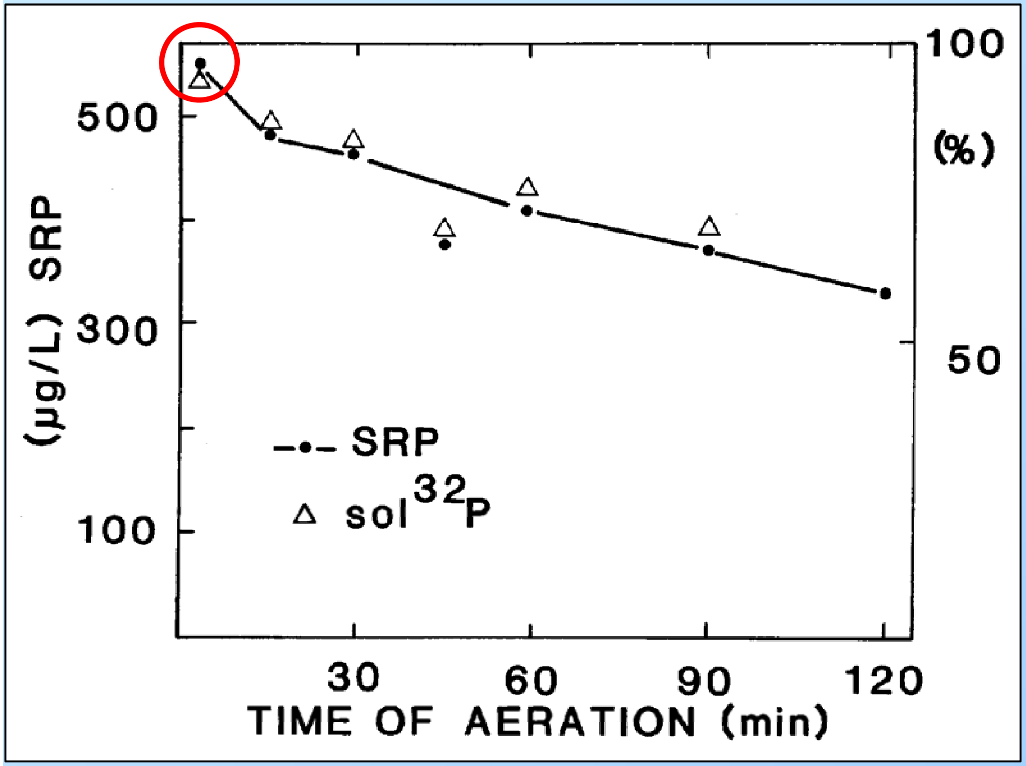
filtered through 0.45 µ, colorimetric assay, molybdenum blue - ascorbic acid

Sampling & handling: aeration or gas-tight

- Interference: H_2S, Fe, organic (humic) acids
- Differs with method
  - Auto analyser
  - Dilution
  - Holding & bench time

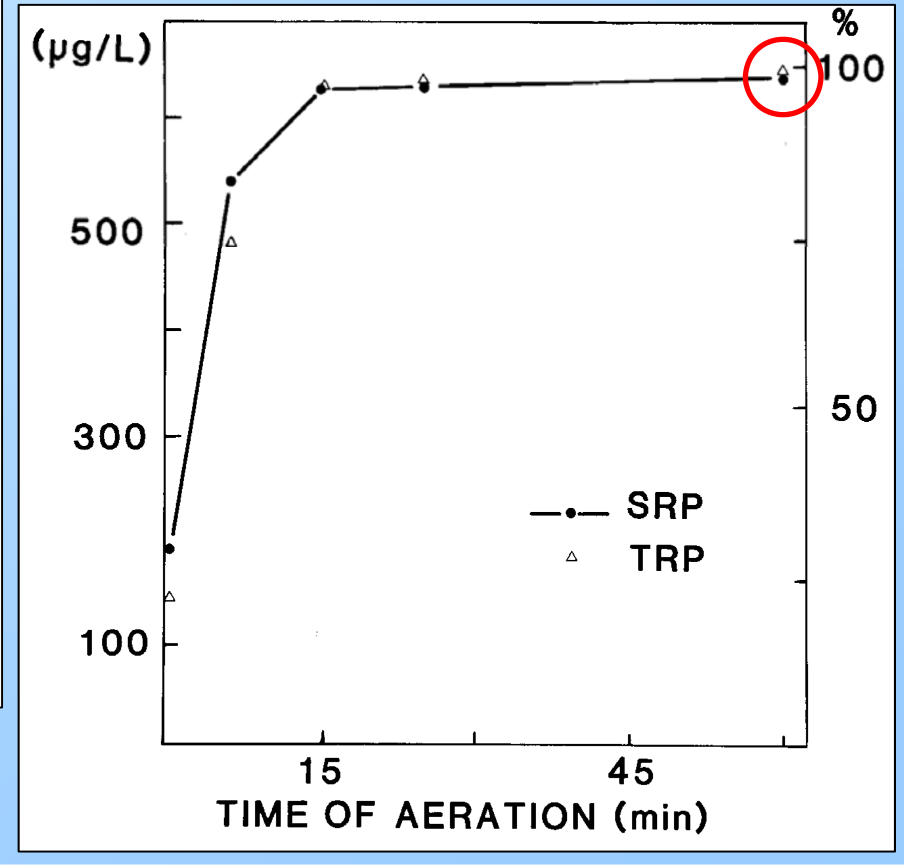
Interference Fe & H_2S in SRP analysis
Effect of Aeration

Soluble Fe: 3.15 mg/L
16m Lake Magog, 11 Aug 1981



Nürnberg 1984
Water Research 18: 369-377

H_2S: 15 mg/L, SRP= 719 µg/L
12m Lake St. George,
24 June1982



Analytical complexities in anoxic waters

Iron and hydrogen sulfide interferences with SRP

- **Iron:** oxygenation of Fe^{2+} to Fe^{3+} and formation of oxy-hydroxides that adsorb PO_4
  $\rightarrow$ SRP is underestimated

  Prevention by anoxic filtration

  Further interference by **humic acids**

- **H_2S:** Interference with molybdenum blue PO_4 assay (reductant)
  $\rightarrow$ SRP is underestimated

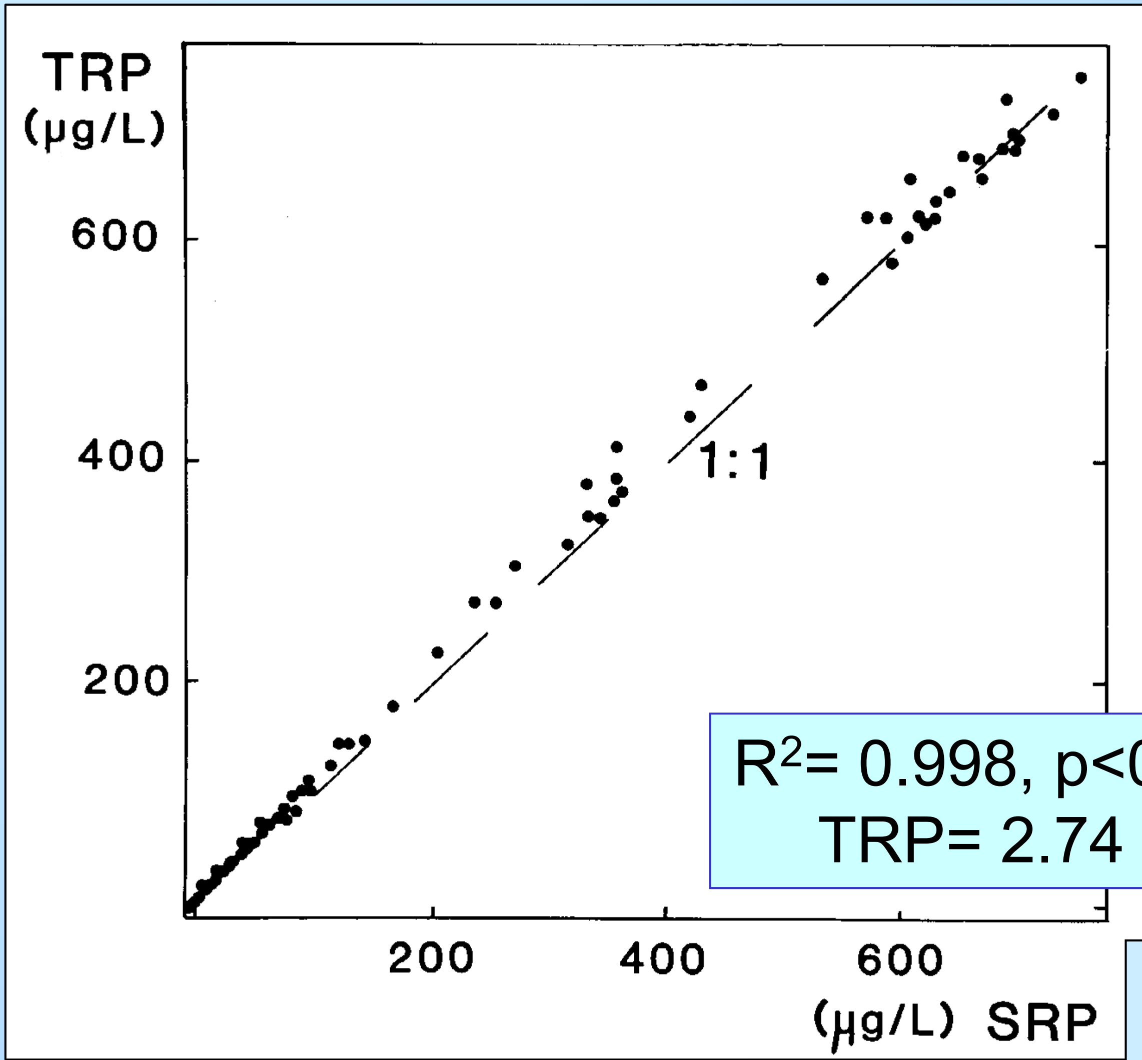
  Prevention by aeration before filtration

Solution: total reactive P (TRP), aerated

SRP vs TRP in anoxic hypolimnetic samples

from 5 softwater lakes with high Fe

3 hardwater with H_2S



R^2= 0.998, p<0.0001, n=174
TRP= 2.74 + 1.02 SRP

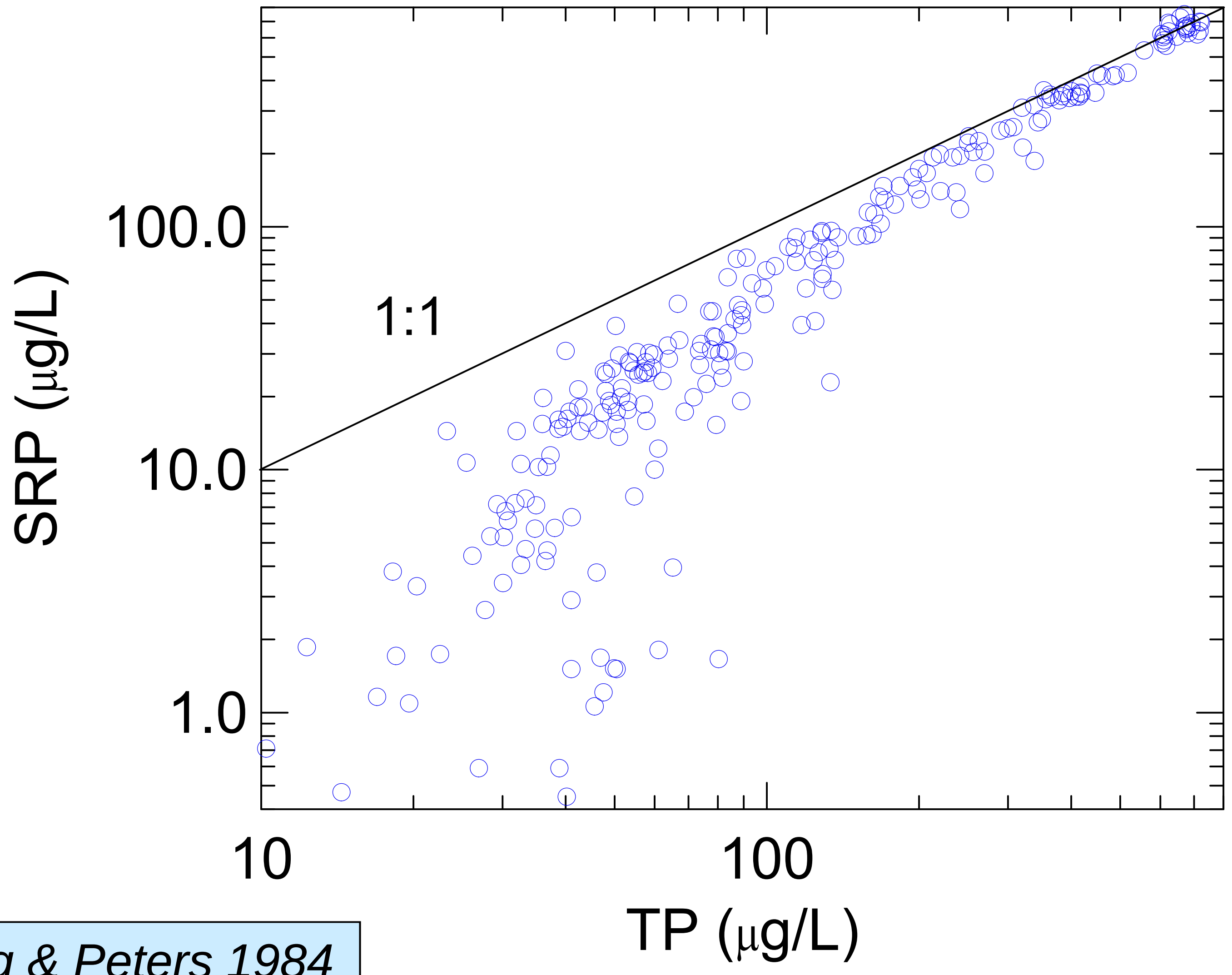
Nürnberg 1984
Water Research 18: 369-377

Determine related variables

- Simpler to measure:
  - In anoxic water:
    - TRP instead of SRP
    - TP instead of SRP
    - SRP instead of BAP
    - Dissolved iron (SFe) for SRP
  - Secchi transparency for chlorophyll *a* pigment
  - Hydrogen sulfide smell or low redox potential instead of low dissolved oxygen

TP instead of SRP in anoxic hypolimnia

Hypolimnetic SRP versus TP



Nürnberg & Peters 1984

In anoxic hypolimnia

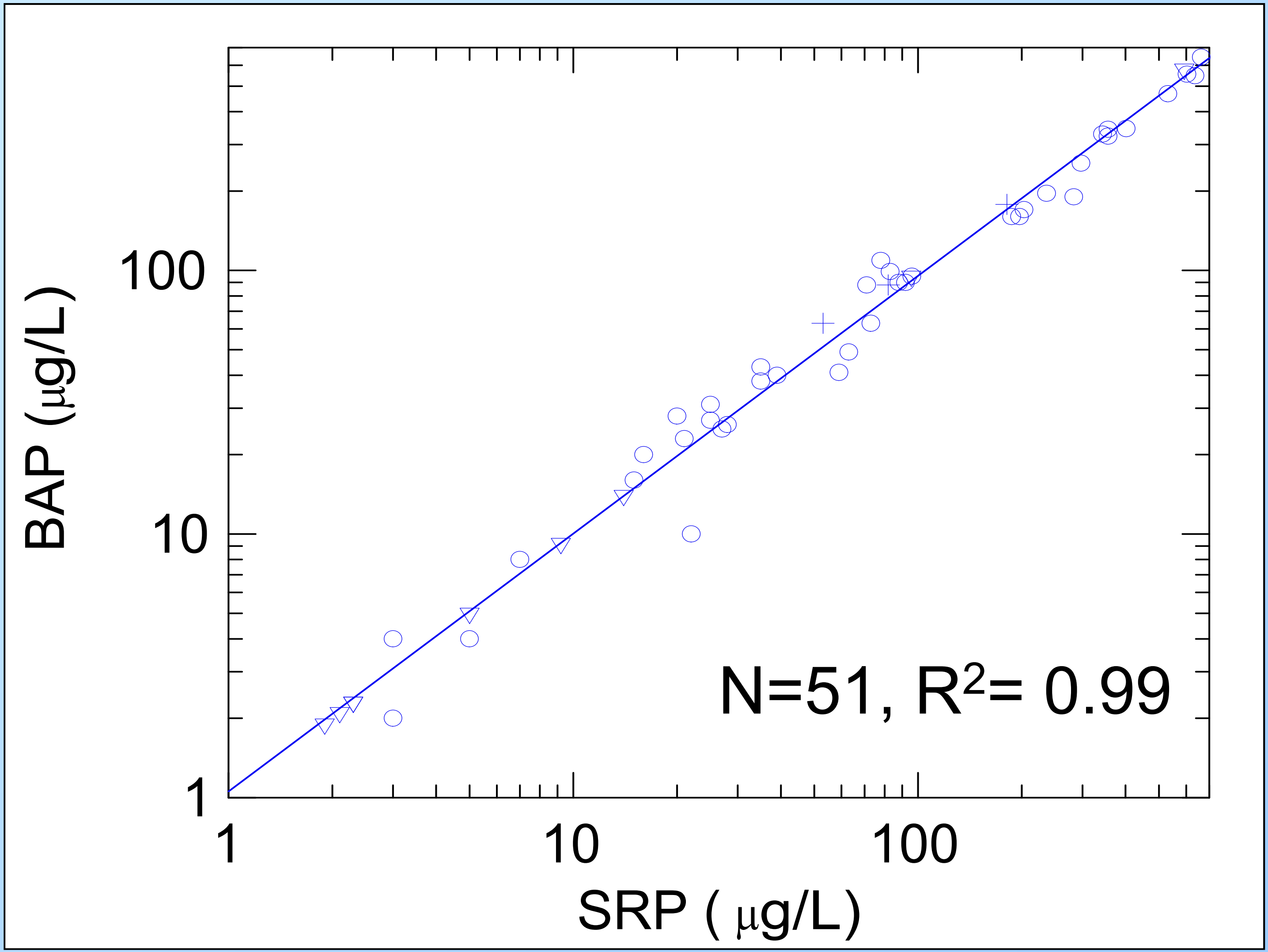
- With increasing TP, an increasing proportion is SRP, at 100 µg/L about 80%
- Almost all SRP is biologically available BAP*

  At least 90%, when small amounts of hypolimnetic water are added to large amounts of surface water

*Using radioactive bioassays that analyze for PO_4

Nürnberg & Peters 1984

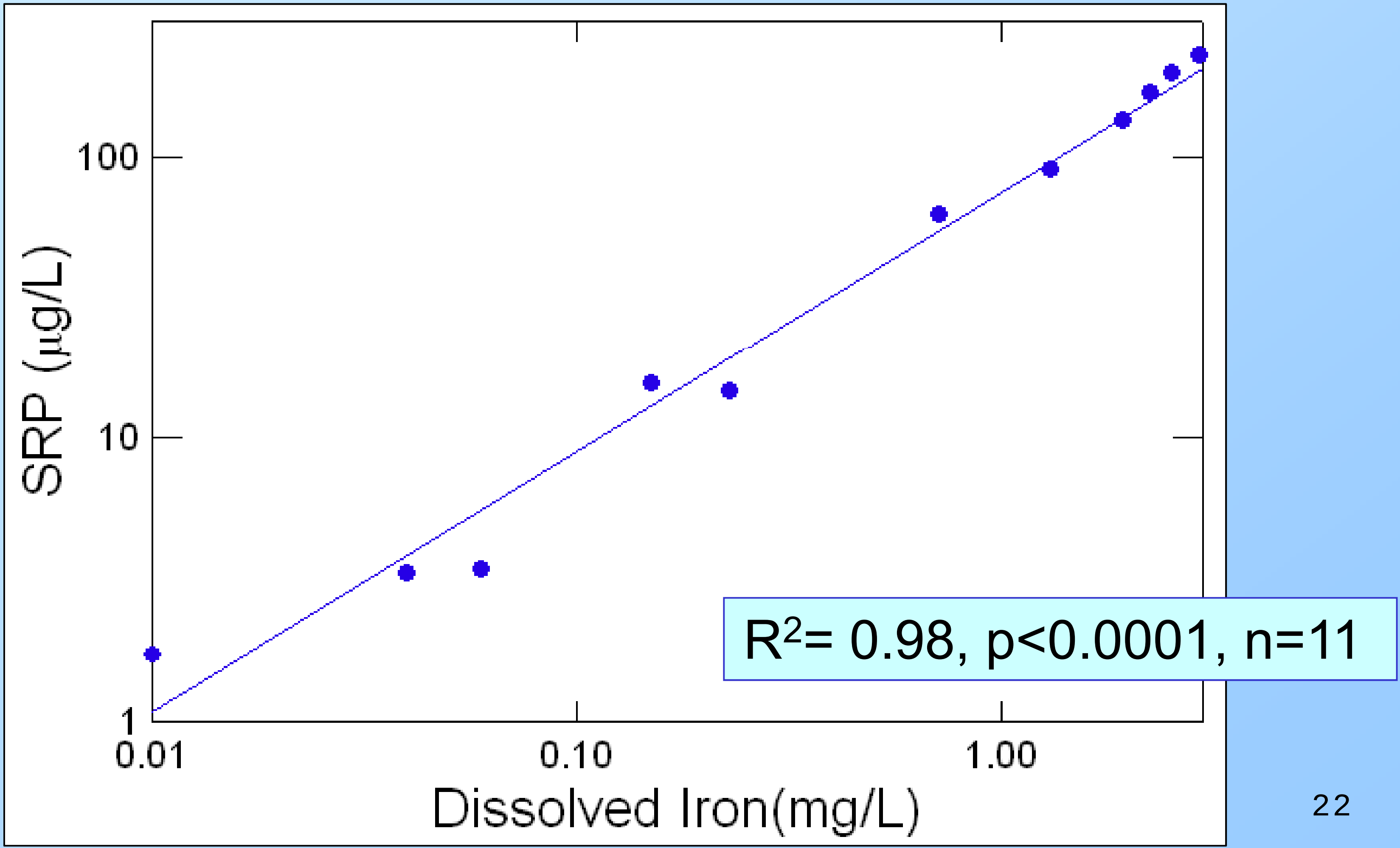
SRP instead of BAP in anoxic hypolimnia



Data from Nürnberg & Peters 1984

Dissolved iron (SFe) for SRP

Anoxic samples of Fitch Bay,
Lake Memphremagog, QU, VT



What may be more important than LLA
- Outline -

- Background knowledge
- Adequate sampling & handling
- Determine related variables
- Adequate monitoring plan
  - Spatial and temporal sampling
  - Variables to be determined
- Use a model instead

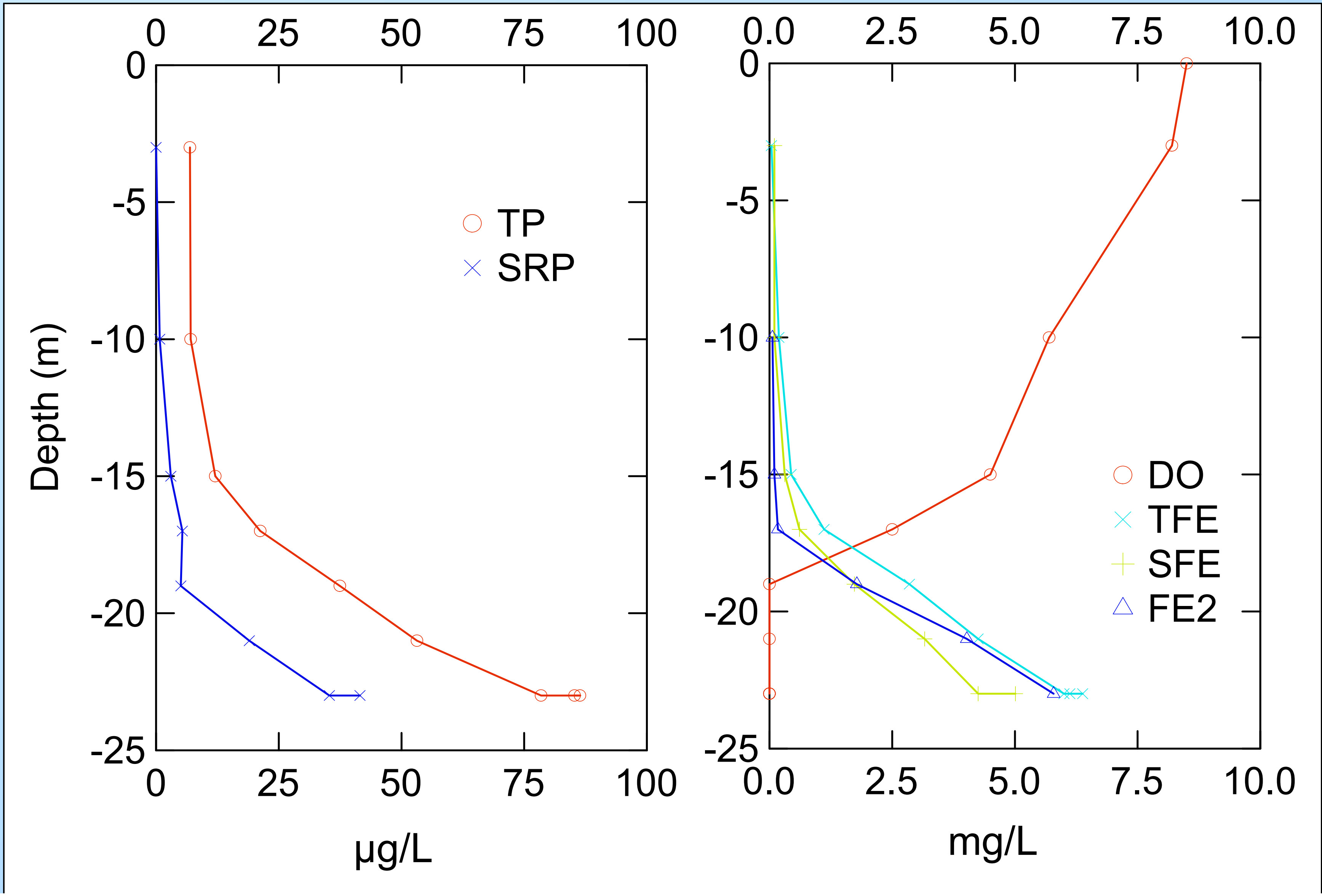
Adequate monitoring plan

1. Spatial and temporal sampling
   – Representative or worse conditions wanted?
   – Bays with polluted inlets or max depth location
   – Reservoir sections: riverine, transition, dam
   – Water intake location (reservoir)
   – Surface vs. hypolimnion
   – Growing season, fall turnover, under ice

2. Careful selection of variables to be measured

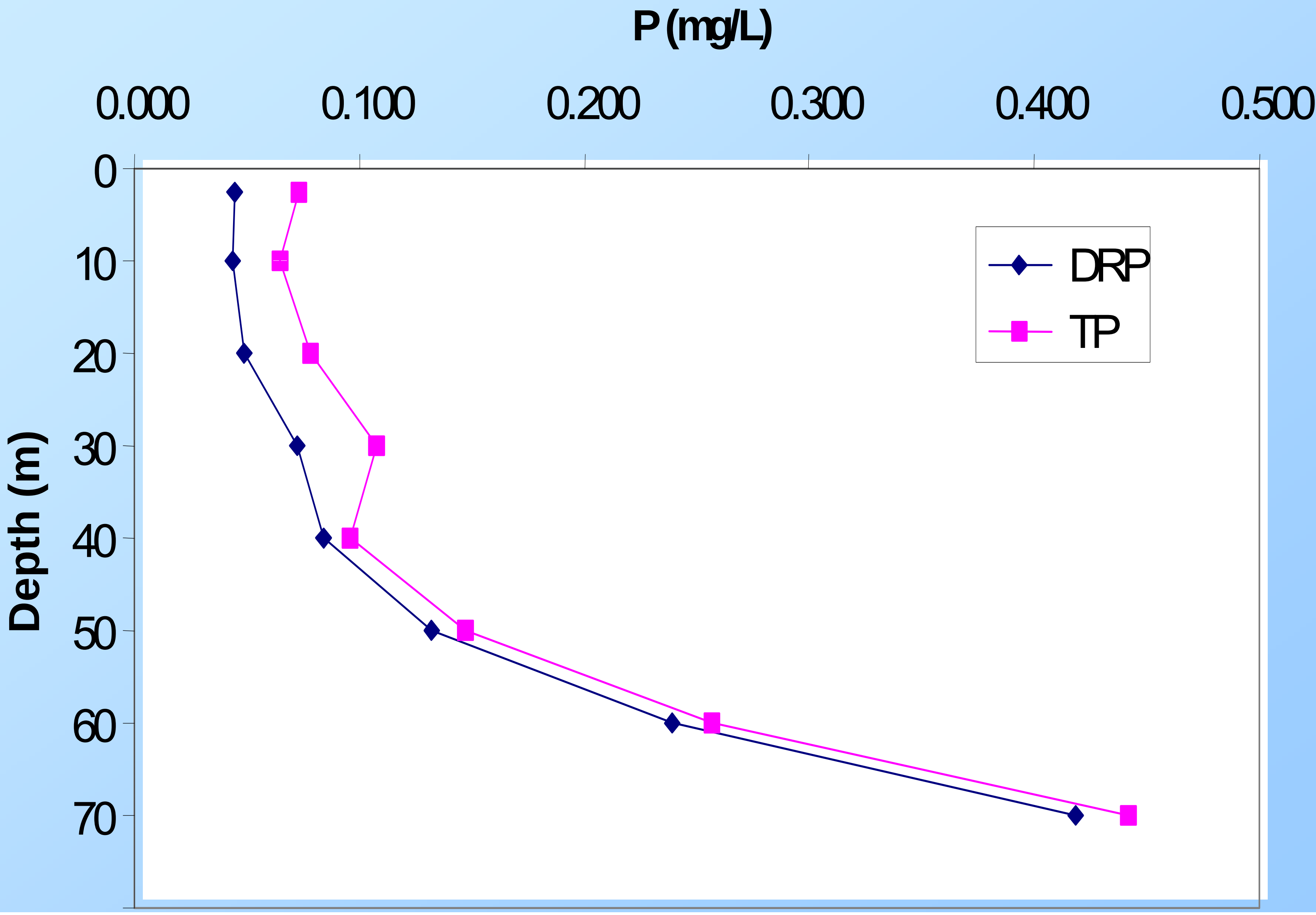
P and Iron Profiles

oligotrophic Chub Lake, ON, Sept. 13 1982



TP, SRP Profiles

at Dam of Brownlee Reservoir, 11 Aug 1999

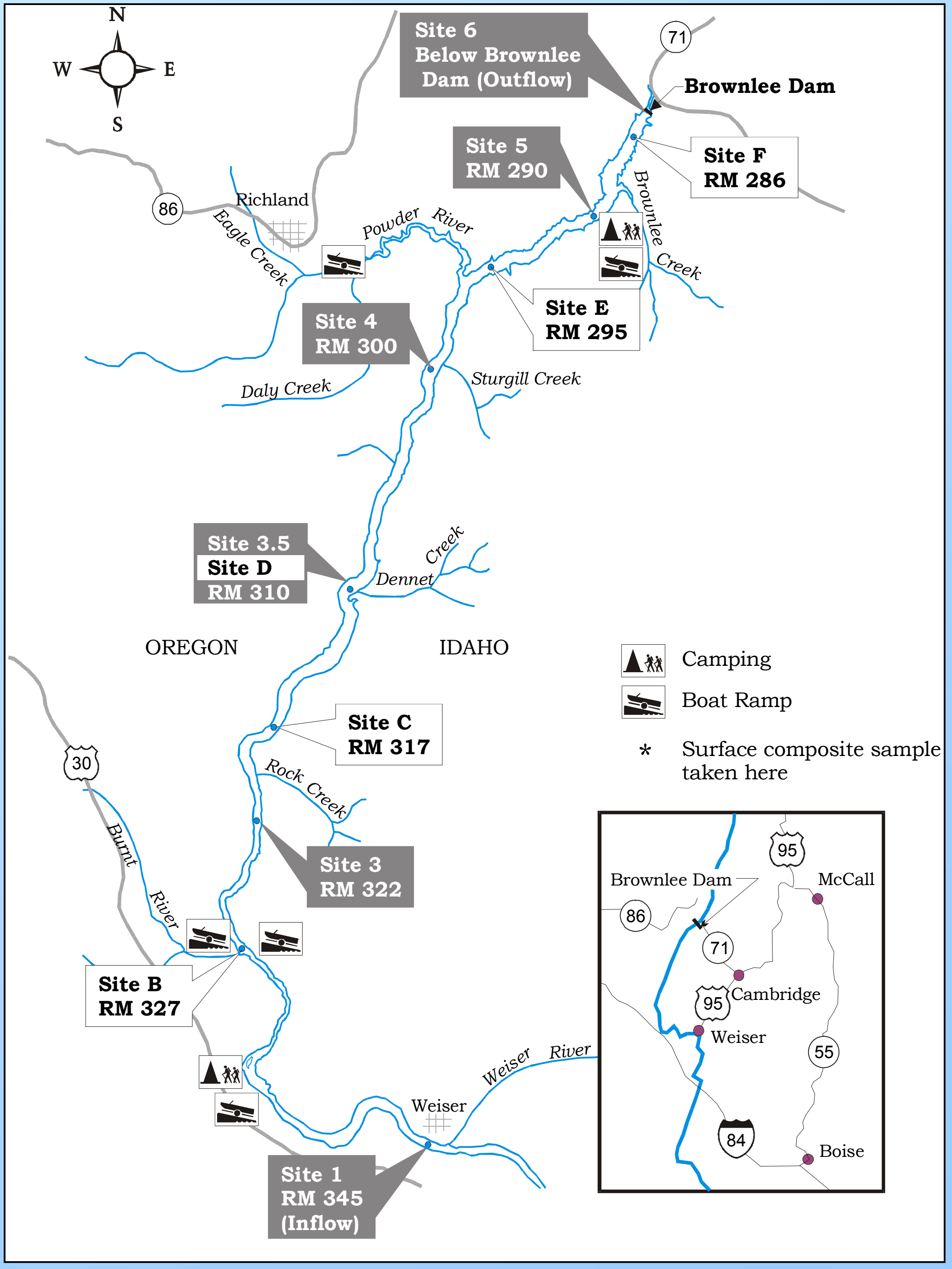


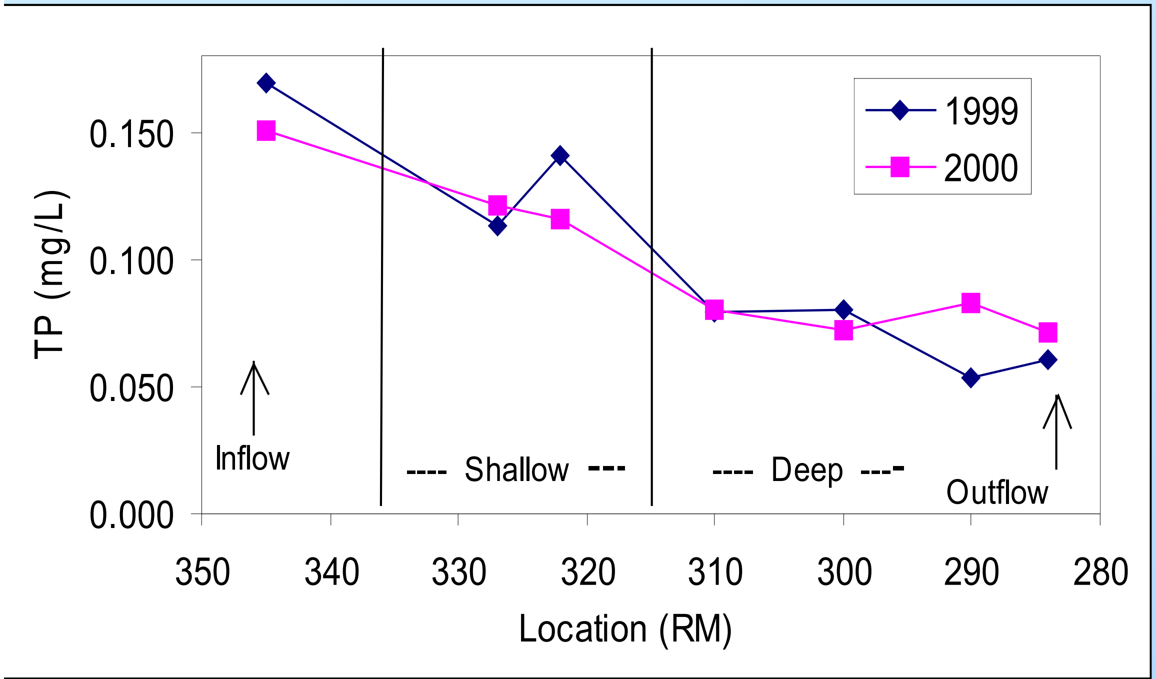

Brownlee Reservoir, Snake River
Hells Canyon Complex, ID/OR

Brownlee Reservoir, ID/OR

Total length: 100 km
Deep section: 48 km

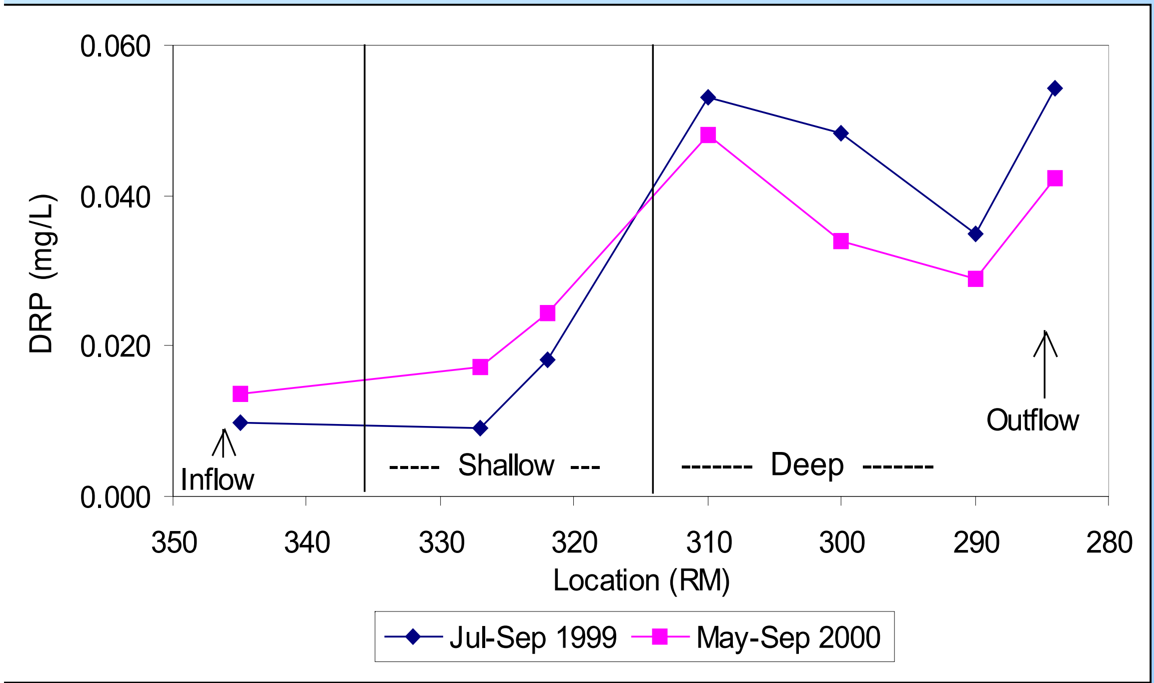
Depth: 60 m
Width: <1 km





Brownlee Reservoir, Gradient along axis

Total phosphorus concentration averages in the surface water in summer 1999 and 2000



SRP concentration averages in the surface water in summer 1999 and 2000

Adequate monitoring plan (2)

1. Spatial and temporal sampling locations
2. Careful selection of variables to be measured

   & determine limits necessary for meaningful study

   - That interfere with analytical procedures (Fe, H_2S)
   - That correlate with analyzed variable (SFe vs. SRP)
   - That can replace needed variable (NO_3 instead of blooms)
   - That are measured routinely and frequently in comparison studies (TP rather than SRP)
   - That are input to a specific model to be used (TDP instead of TP in river models)

Careful selection of variables to be measured (2)

P Fractions in Water

- **TP** - total P: digested then molybdenum-blue (MB) analysis for PO_4
- **SRP** (**DRP**) - soluble reactive P: filtered through 0.45 µ then MB (PO_4, biologically available)
- **TRP** - total reactive P: (unfiltered) MB
- **PRP** - particulate reactive P: TRP-SRP (Fe-P)
- **DP** - total dissolved P, filtered, then digested, then MB
- **PP** - particulate P: TP-DP (seston, plankton)
- **BAP** – biologically available P (bioassay)

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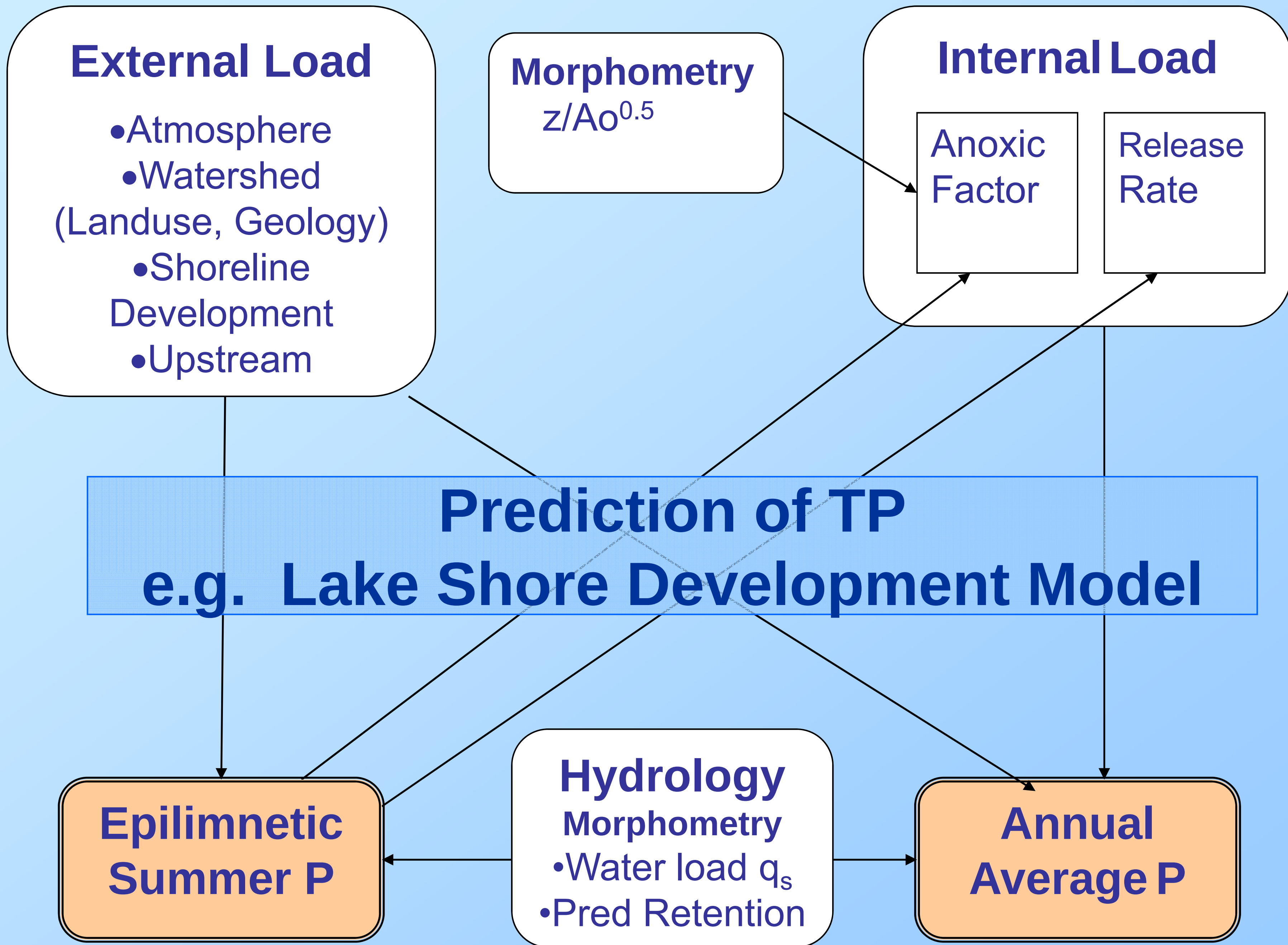
- Outline -

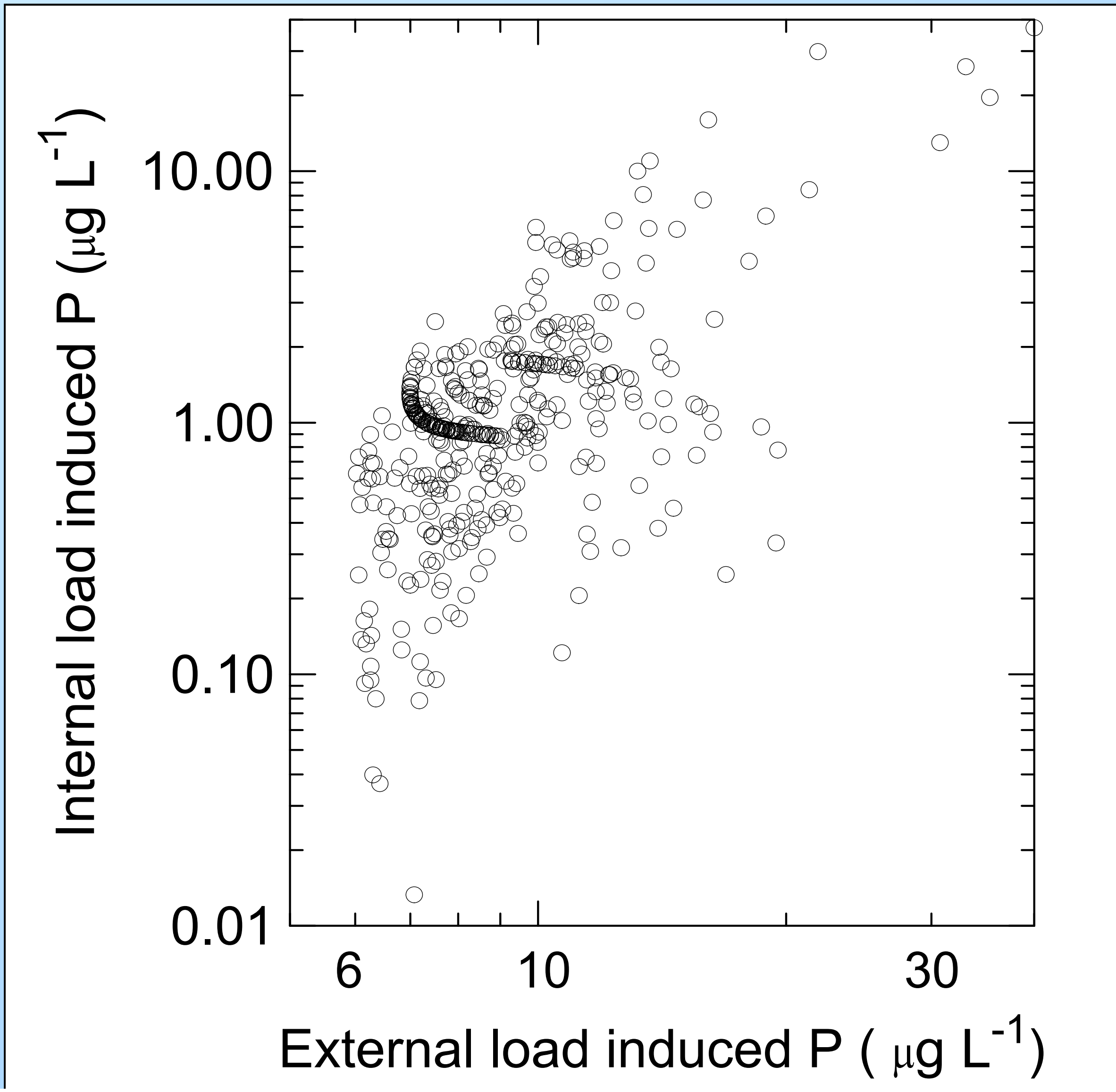
- Background knowledge
- Adequate sampling & handling
- Determine related variables
- Adequate monitoring plan
  - Spatial and temporal sampling
  - Variables to be determined
- Use a model instead
  - example Muskoka lakes

Muskoka lakes on the Canadian Shield (Central Ontario)

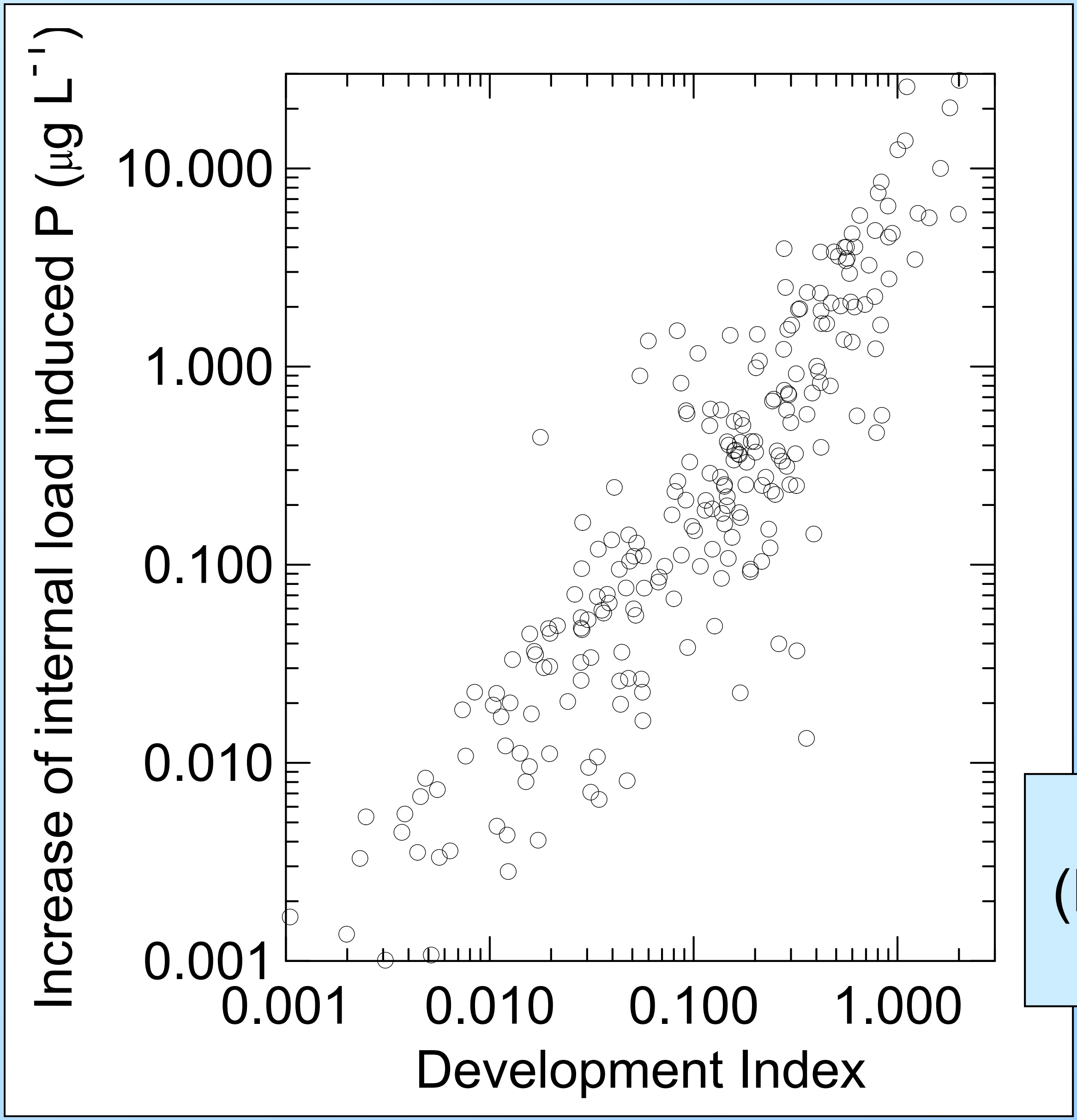


After Nürnberg & LaZerte 2004

TP concentration from Internal Load in 500 Muskoka Lakes



Internal Load Increases from Development in Muskoka Lakes



Development Index = ($P_{developed}$ – $P_{natural}$) / $P_{natural}$

Low Level Analysis

- Problems with LLA
- What may be more important
  - Know, what the analysis is for
  - Consider, what is known about the system: Background knowledge
  - Adequate sampling, handling, and monitoring plan