D. Phosphorus Bioavailability and Loads

importance, recent history, and variability

Outline

1. Phosphorus importance and forms
2. Runoff events, phosphorus loading, and variability
3. Bioavailability: Background and results
4. Applying the bioavailability concept to phosphorus loads
5. Point source reductions to the shelf
6. Bioavailable loads to Cayuga Lake: LSC context
7. Summary

* see attached slides for added information on estimates of variability and uncertainty

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Importance of phosphorus (P) loads to lakes

- cultural eutrophication and associated water quality problems continue to be an important issue
- P is the limiting nutrient for algae growth in most inland waters, least available constituent necessary to support growth
  - Cayuga Lake is P-limited
- control of the supply of P (P_L; loads e.g., kg) is a primary management approach for lakes with excessive algal growth, described as culturally eutrophic
- earlier this was based on the concentration of total P (TP), and the development of TP loading rates ($TP_L = Q \cdot TP$; where Q is the flow rate of the input)
- focus here:
  - the evolution to the development of *bioavailable P loads (BAP_L)*

Forms of phosphorus (P)

- Total phosphorus (TP)
  - TP = PP + TDP (m)
  - Particulate P (PP) (m)
    - organic PP (PP_o)
    - minerogenic PP (PP_m)
    - $PP_m = PP_{m/u} + PP_{m/a}$

  advanced here

  - Total dissolved P (TDP) (m)
  - TDP = SRP + SUP (m)
    - Soluble reactive P (SRP) (m)
    - Soluble unreactive P (SUP) (m)

(m) – directly, or indirectly from measurement

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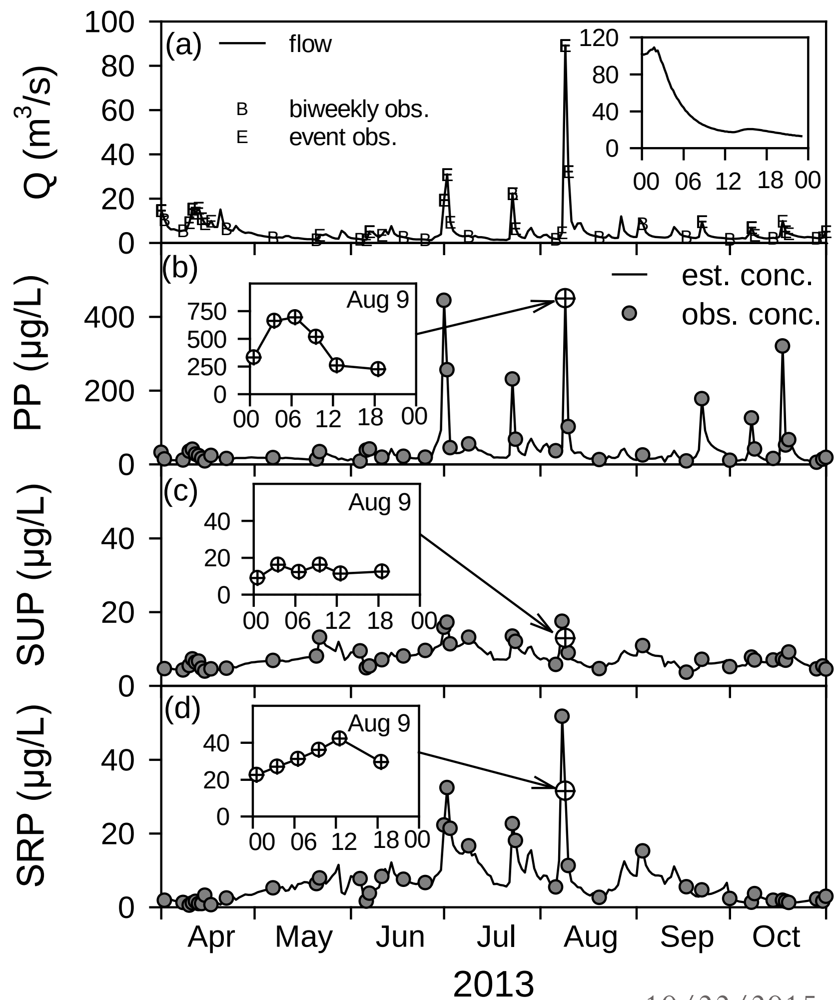
Inclusion of runoff-event based sampling was critical to support development of representative loading estimates and the overall P-eutrophication modeling initiative

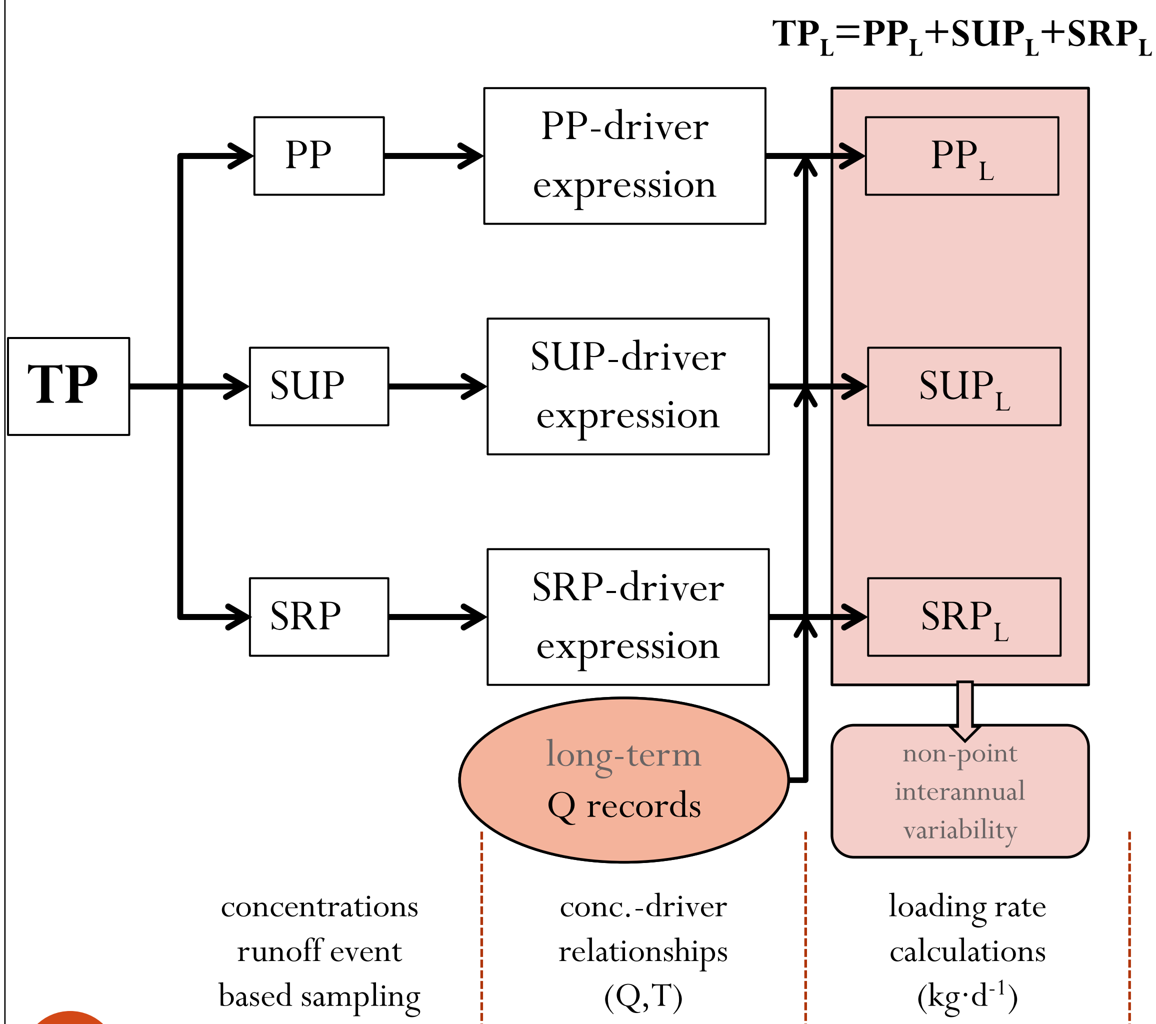
- strong dynamics in concentrations of forms of P are observed in most tributaries during runoff events
- these need to be resolved and parameterized to support credible loading estimates and related modeling
  - as promoted by NYSDEC (automated sampling equipment, and program support)
  - P_L as a major model driver has important management implications
    - apportionment according to sources is critical

\- Figure 3 (Fall Cr.) from Prestigiacomo et al., 2015



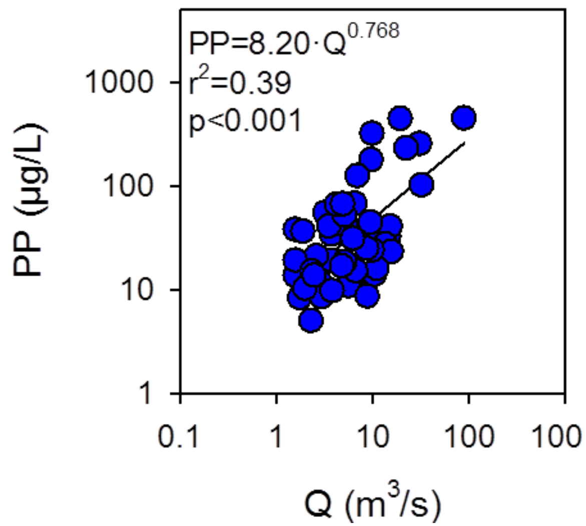

Sixmile Creek during high flow

Approach used for phosphorus load estimation: Independently for each stream



Loading estimates for the Cayuga Lake system: Context, importance of runoff event tributary monitoring

- tributary P loading methods and quantification – reported in Prestigiacomo et al. (2015), previous presentations
- P_L strongly dependent on P/Q relationships (stream, P-form dependent)
  - developed from 2013 program
- P/Q relationships were the sole basis for estimates for previous years
  - interannual differences in P loading – driven by interannual variations in Q
  - support from CSI program (Community Science Institute)
    - based on monitoring since early 2000s, no systematic changes in TP/Q relationships indicated, supporting the approach for historic P_L estimation
    - other historic P_L validations ongoing



positive dependency, but substantial variance

Sources of uncertainty in the estimation of P loads (P_L)

1. methods of load estimation
   - numerous protocols available
   - daily estimates required
2. dependencies of tributary P concentrations (various forms) stream flow rate (Q)
   - other environmental conditions, i.e., season
3. monitoring coverage adjoining tributary mouths
   - number, frequency of sample collection
4. application of bioavailability results

- uncertainty and variability common to loading analyses

detailed treatment of variability (uncertainty) for Fall Cr. available at end of presentation and for all tribs in Prestigiacomo et al. 2015

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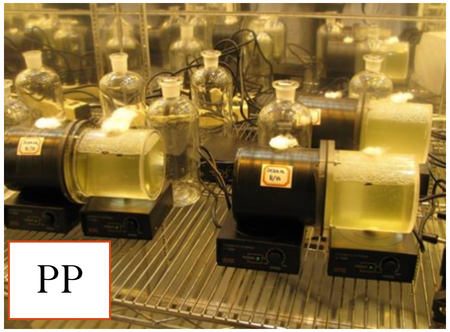
Phosphorus bioavailability: An established protocol

1. established bioassay protocol
   a. review by Auer 2015, others
2. applications in New York
   a. NYC – reservoir tributaries
   b. Onondaga Lake – NYSDEC
      - Metro/Actiflo
      - tributaries
3. Cayuga Lake (NYSDEC)
   - 4 main tributaries
   - IAWWTP/Actiflo
   - CHWWTP
   - LSC



PP

Importance of the bioavailability of phosphorus loads delivered to lakes

- a major problem has emerged for the simple approach of focusing strictly on TP
  - P exists in multiple chemical forms that differ substantially in their availability to support algal growth
- differences in availability according to P forms
  - TP = PP + TDP (PP – particulate P ; TDP – total dissolved P)
  - TDP = SRP + SUP (SRP – soluble reactive P; SUP – soluble unreactive P)
  - PP = PP_o and PP_m (PP_o – organic PP; PP_m – minerogenic PP)

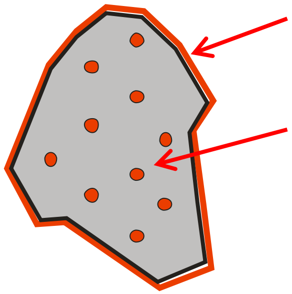
P form	bioavailability
SRP	~ completely
SUP	mostly
PP	low
PP_o	intermediate, variable
PP_m	low (<< PP_o)

Consideration of bioavailability causes the effective external P loads (BAP_L) to be diminished relative to the TP load (TP_L)

- the failure to consider bioavailability in most contemporary mechanistic P-eutrophication models is problematic
  - TP loads overestimate the amount of P that grow algae and that leads to compensating by misrepresentation of source and/or sink processes for P as part of model calibration
- key examples of the importance of appropriate representation of BAP_L are emerging for prominent cases
  - re-eutrophication of western Lake Erie
  - Onondaga Lake –Metro discharge and rehabilitation
  - Cayuga Lake – emerging in these analyses, based on related NYSDEC recommendations

Phosphorus (P) associated with clay particles: Simple concepts

1.



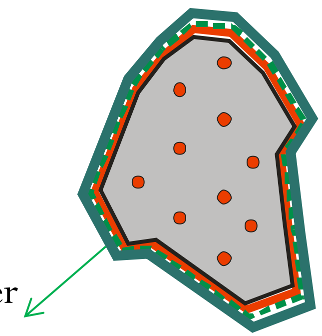
red border – strongly bound

red dots – strongly bound

such P would not be mobilized following delivery to the lake and thus is uncoupled from trophic state

- not bioavailable

2.

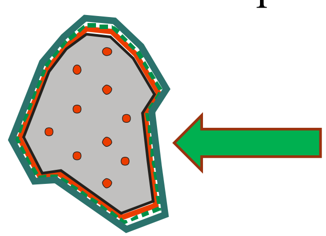


green layer subject to release

adsorption/desorption processes

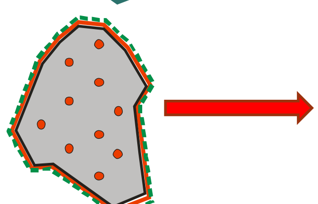
- driven by ambient SRP
- potential bioavailability

a.



adsorption – in tributaries where SRP is higher

b.



desorption, low SRP – in lakes, bioavailable P released, where SRP is lower

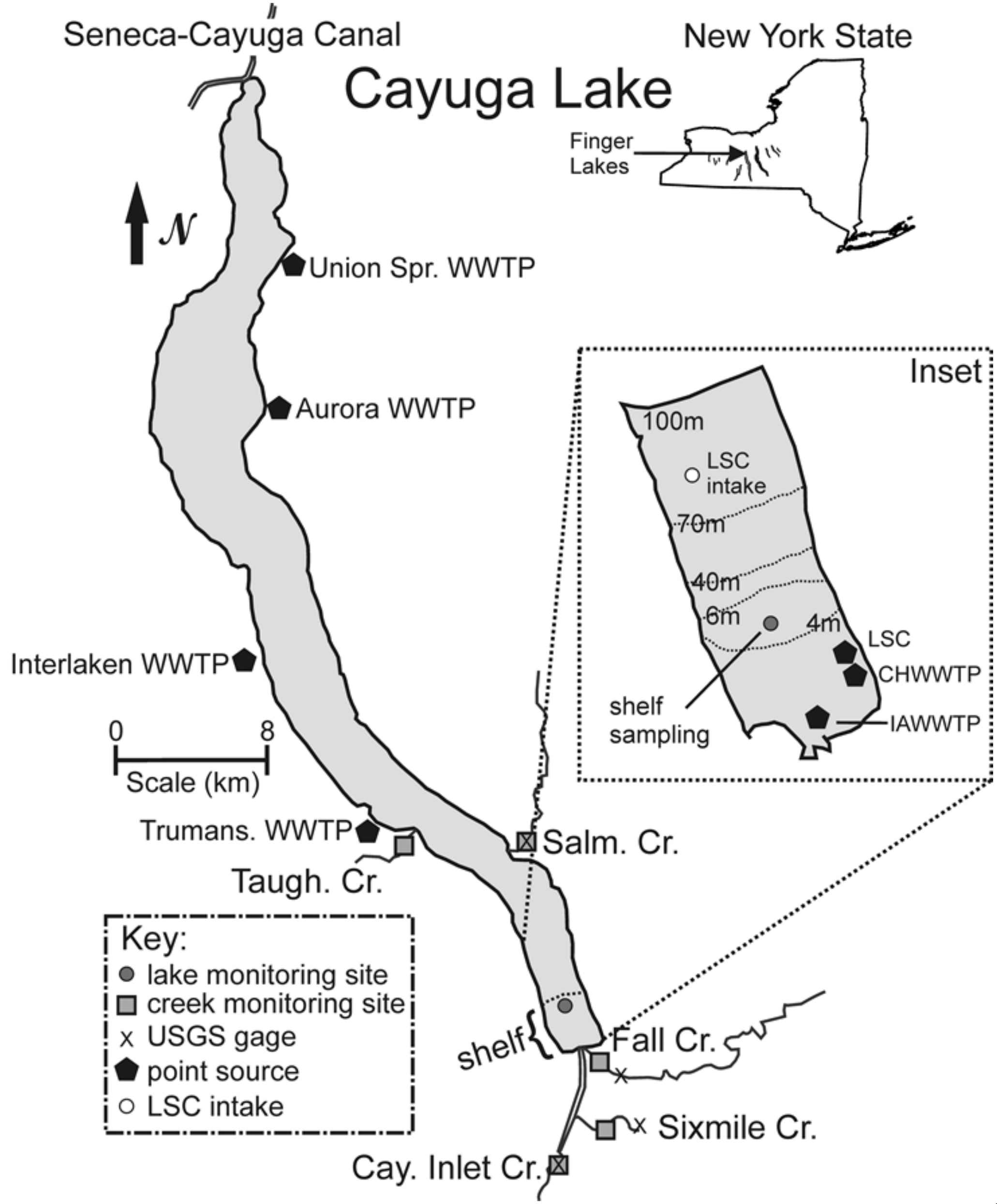
- giving up the green layer

The BAP_L initiative for Cayuga Lake

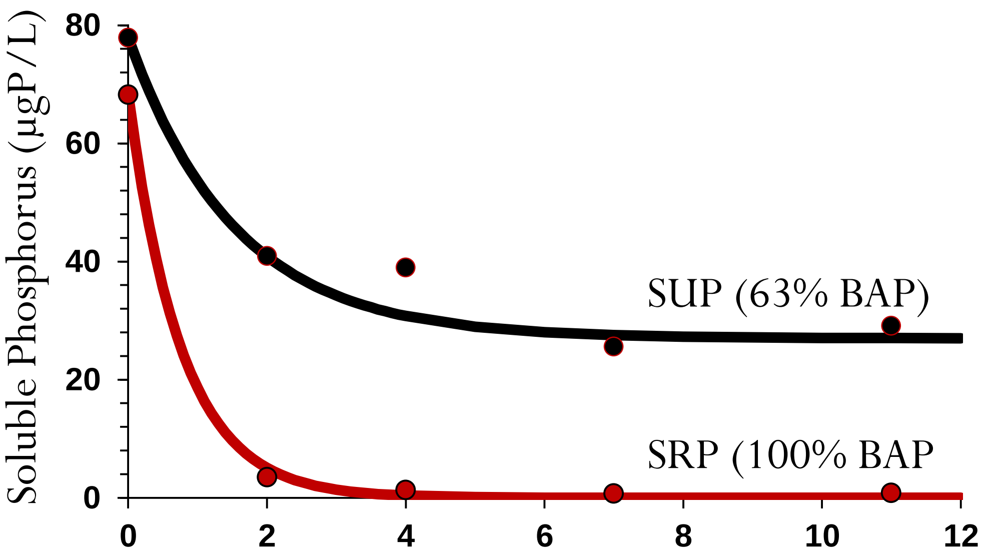
- supporting components
  - monitoring forms of P in critical inputs
  - development of empirical concentration-Q relationships, supported by runoff event sampling
  - bioassay-based bioavailability (fraction f_{BAP}) assessments of PP, SUP, and SRP – multiple sources
  - estimates and apportionment of BAP_L
  - estimates of interannual variation in loads associated with variations in stream flow
- importance
  - apportionment of BAP_L according to sources
  - model credibility
  - management deliberations/transferability

External loading to shelf of bioavailable P, 2013: Sites

- April through October, 2013
- tributaries
  - Fall Cr.
  - Cayuga Inlet mouth
    - Cayuga Inl. Cr.
    - Sixmile Cr.
    - Cascadilla Cr. (estimates)
- point sources
  - IAWWTP
  - CHWWTP
  - LSC
  - minors (estimates)



Methods for assessing P-bioavailability: Soluble phase assays



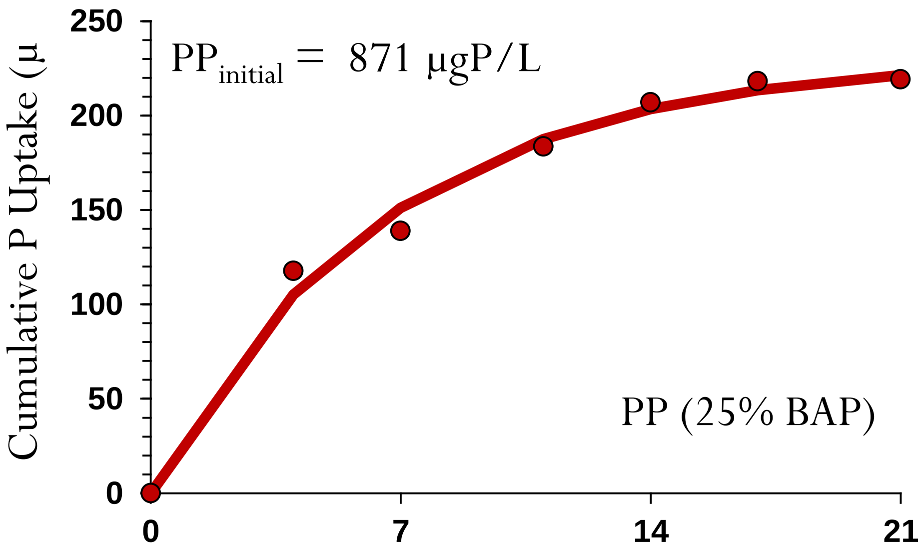
Soluble Phase Assay Setup

Precision: <11%, n=3

Adopts the procedure of **W.E.Miller and J.C. Greene. 1978**.

The *Selenastrum capricornutum* Printz Algal Assay Bottle Test: Experimental Design, Application, and Data Interpretation Protocol. U.S. Environmental Protection Agency, Office of Research and Development, Corvallis Environmental Research Laboratory.

Methods for assessing P-bioavailability: Particulate phase assays



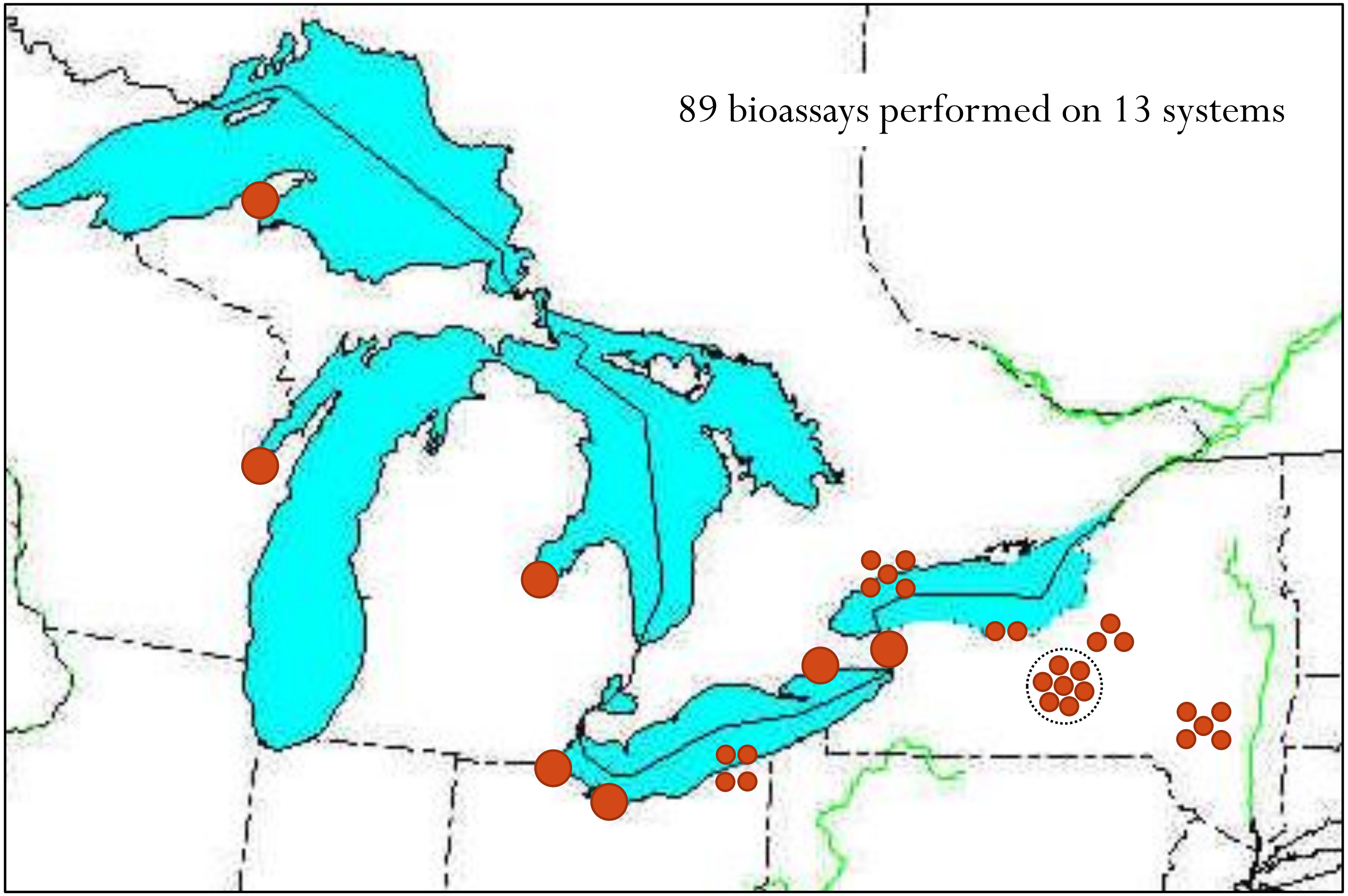
Dual Culture Diffusion Apparatus

Precision: <4%, n=3

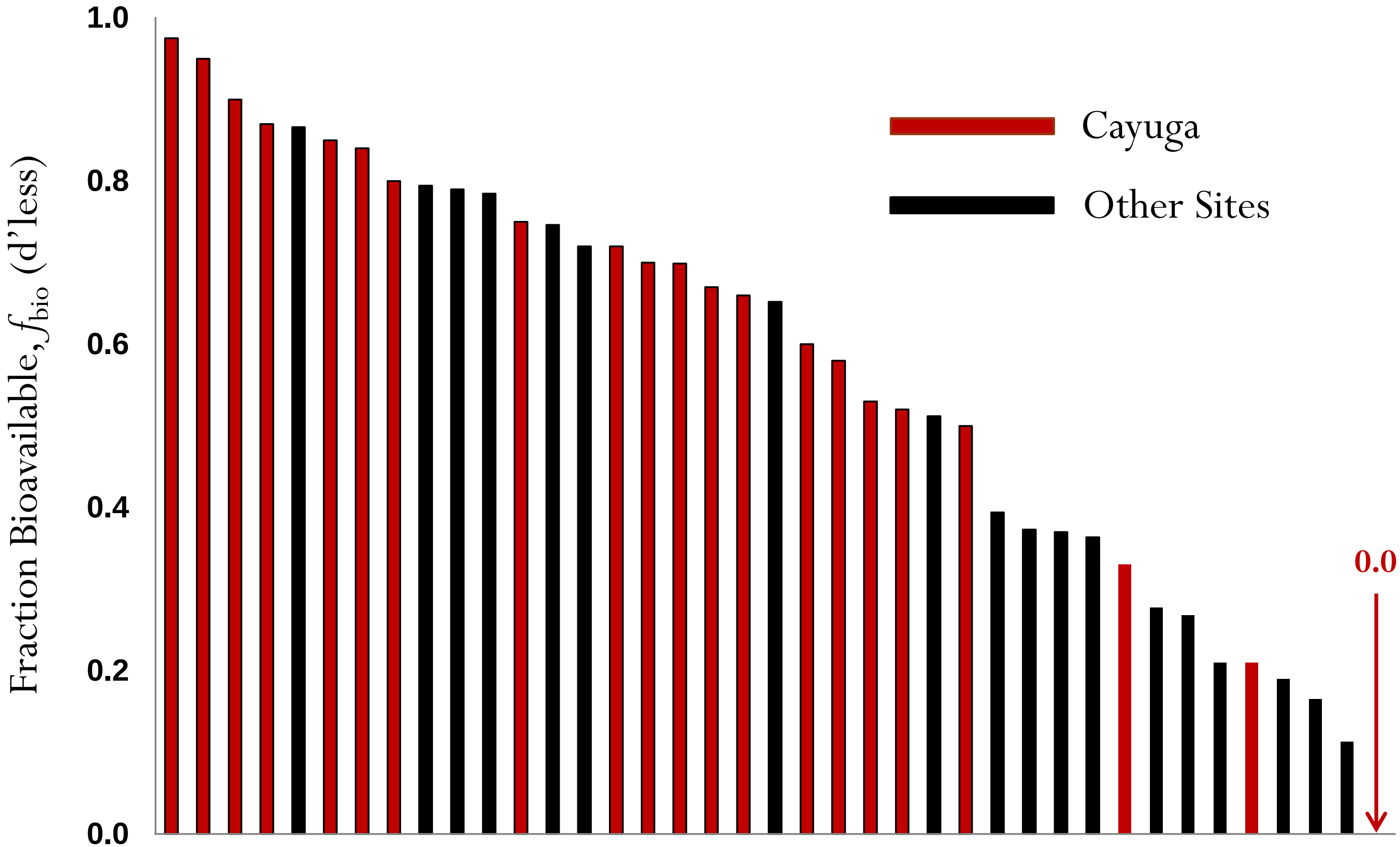
Adopts the procedure of **J.V. DePinto. 1982**.

An experimental apparatus for evaluating kinetics of available phosphorous release from aquatic particulates. *Water Research*, 16: 1065-1070.

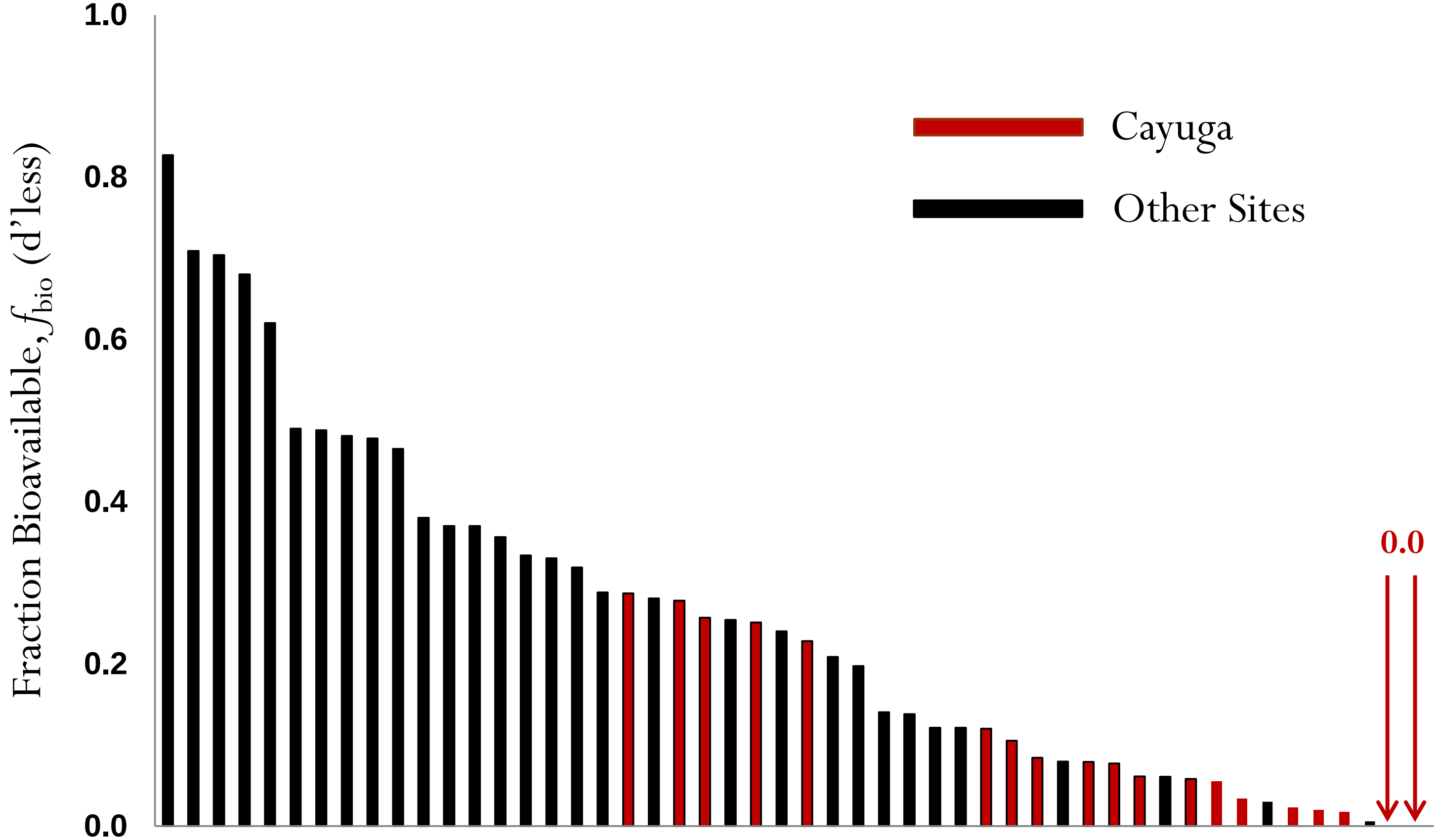
Application of P-bioavailability assays



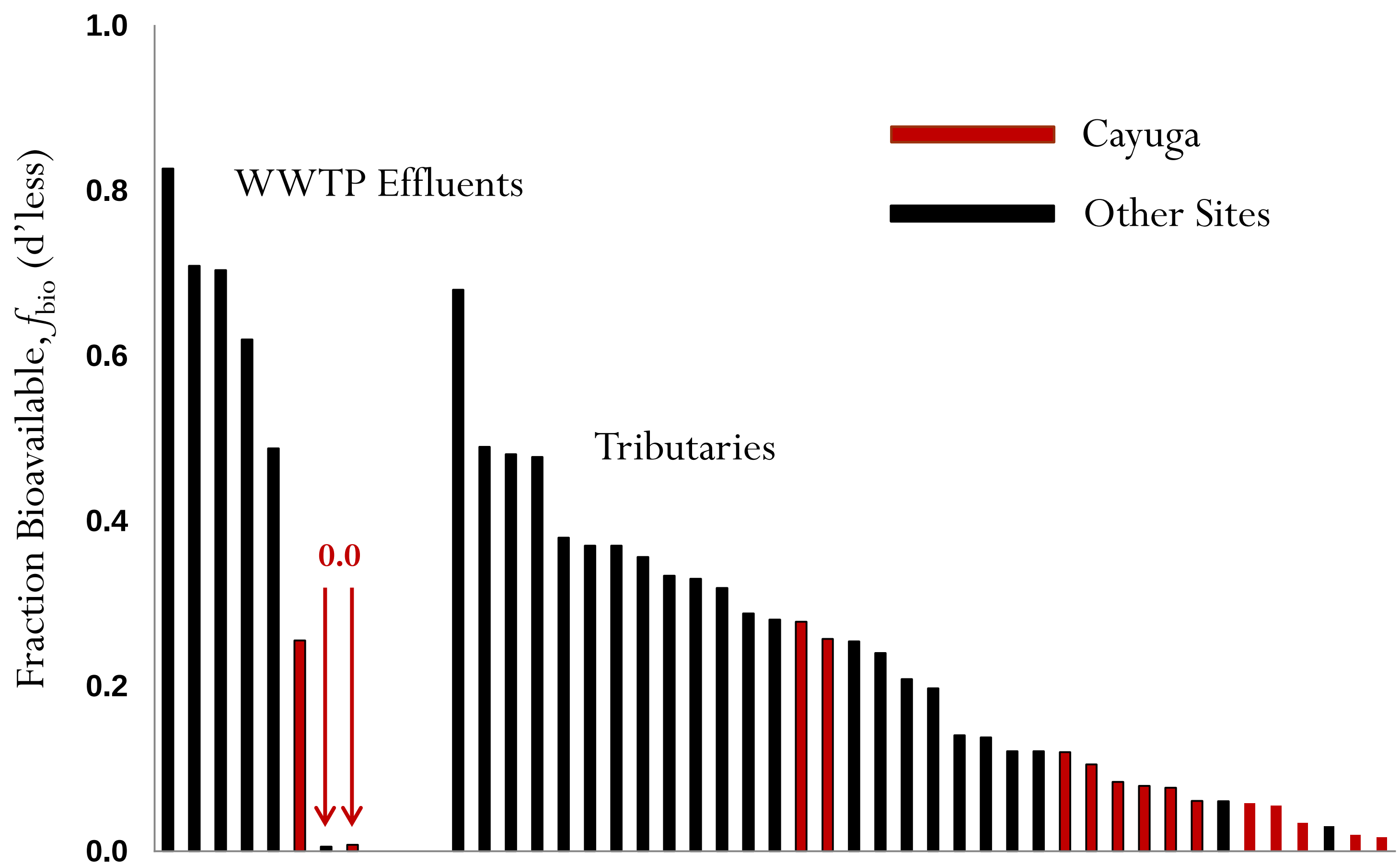
Range in P-bioavailability: Soluble unreactive phosphorus (SUP)



Range in P-bioavailability: Particulate phosphorus (PP)



P-bioavailability: Particulate phosphorus (PP), by discharge type



Cayuga Lake and tributaries: Sediment loading and bioavailability information

Tributary	Watershed (%)	PAV_m Load (%)[1]	ISPM Load (%)[1]	ISPM:SPM (%)[1]	PP Load (%)[1]	f_{BAP} PP (%)[2]
Fall Cr.	17.7	94	96	90	85	9
Inlet	22.0	89	87	90	78	-
Cayuga Inlet Cr.	12.9	96	99	93	98	6
Six Mile Cr.	7.20	97	90	97	89	6
Salmon Cr.	12.5	98	98	87	95	21
Unmonitored[3]	49.7	96	95	91	90	-

1 fraction received during high runoff intervals
2 fraction of PP bioavailable, average of three bioassays (Prestigiacomo et al., 2015)
3 estimated, based on monitored portion

minerogenic particles dominate in runoff event samples

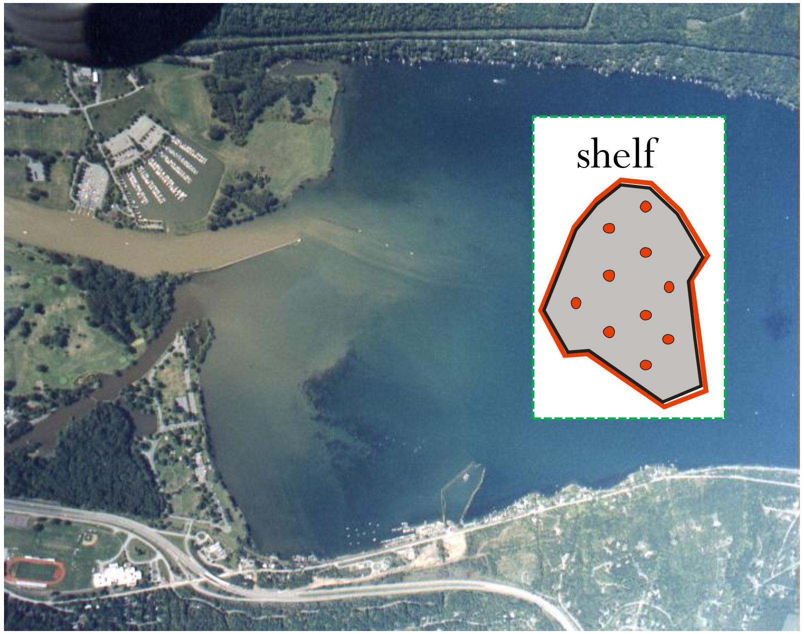
Bioavailability assay results (f_{BAP}) for P forms from multiple sources to Cayuga Lake

	f_{BAP}		
Source	PP	SUP	SRP
Fall Cr.	9	77	94
Cayuga Inl. Cr.	6	64	89
Salmon Cr.	21	84	98
Sixmile Cr.	6	62	94
IAWWTP	1	72	93
CHWWTP	26	63	98
LSC	not avail	10	97
shelf	2	95	97

- noteworthy features
  - tributary PP f_{BAP} - low, Salmon highest on average
    - some limited evidence that PP f_{BAP} correlated with land-use
  - LSC SUP - low
    - in-lake processing effect, enzymatic activity
  - IAWWTP PP f_{BAP} – low
    - Actiflo (similar to Syracuse Metro)
  - shelf, post event f_{BAP} – low
    - dominated by mineral particles

Bioavailability results for Cayuga Lake system: Context

1. Salmon Cr. vs shelf tributaries
   a. Salmon Cr. SRP ~ 25 μg/L
   b. shelf tribs SRP ~ 5-10 μg/L
   c. lake SRP ~ 1 μg/L



2. important implications of low shelf f_{BAP} (~ 1.7%), following the major runoff event of early July 2013

   PP = 368 μg/L; i.e., not related to trophic state

   TP = 387 μg/L

PP received by the shelf from major runoff events is nearly completely unavailable

Salmon Creek during high flow

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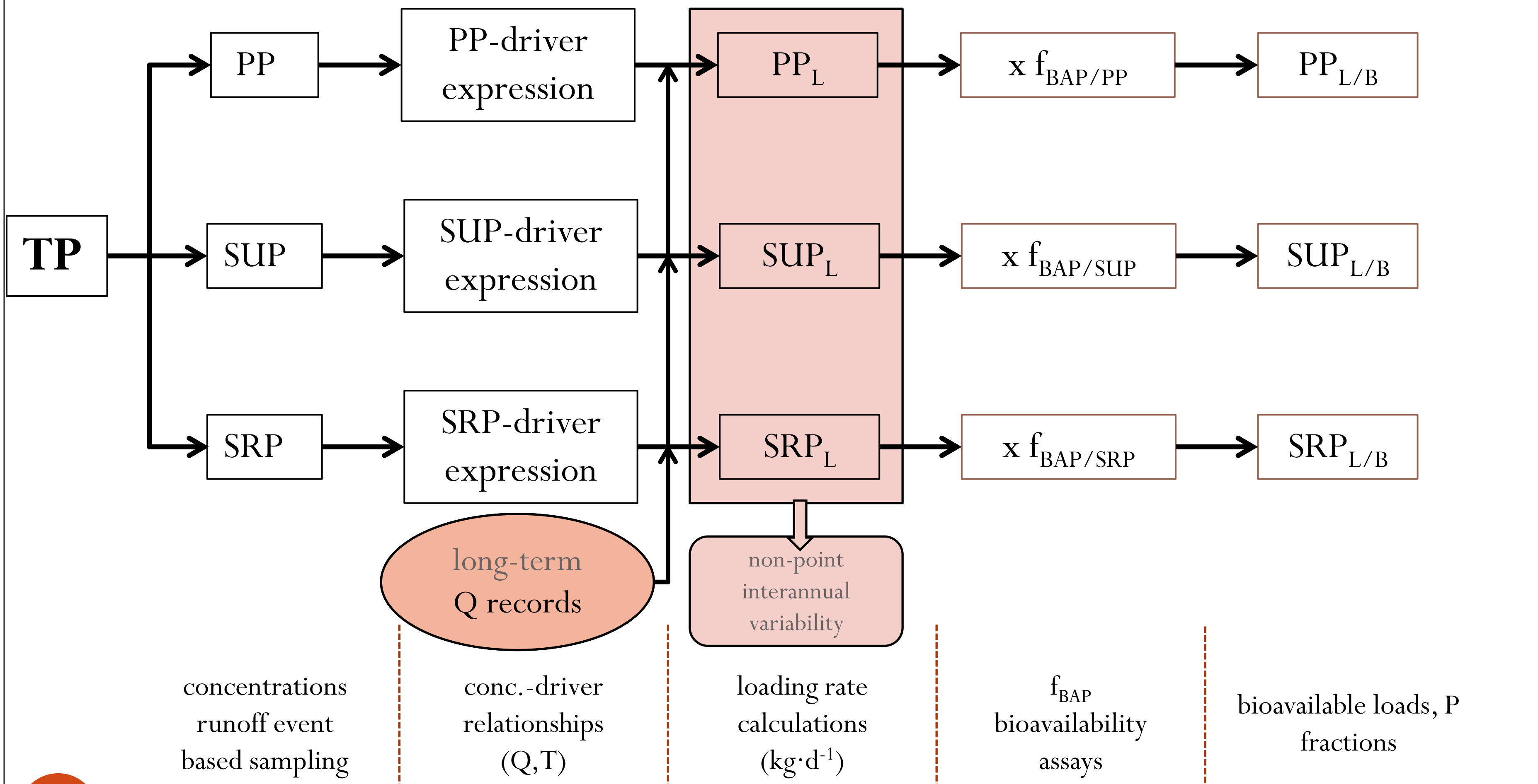
Application of the bioavailability concept

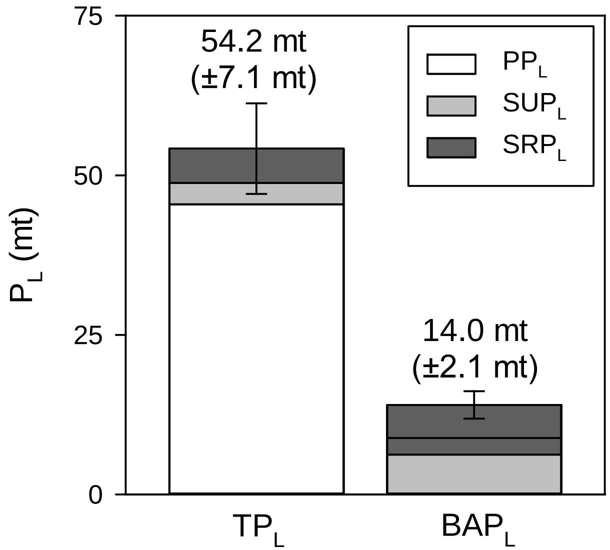
$TP_L = PP_L + SUP_L + SRP_L$

$BAP_L = PP_{L/B} + SUP_{L/B} + SRP_{L/B}$



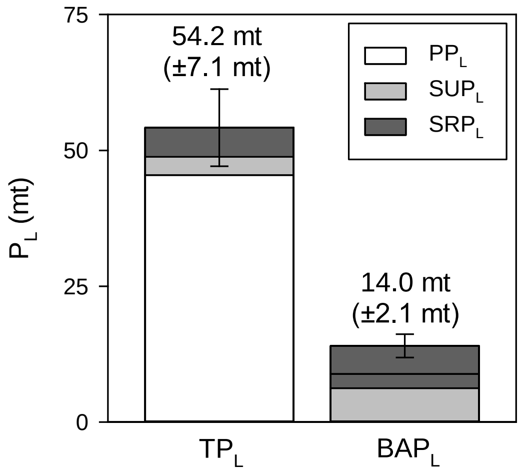
Phosphorus and bioavailability results for Cayuga Lake system: Context

- tributary P loading – totals, according to forms
  - TP = PP + SUP + SRP
    - PP dominant (~84%)
- 2013 study results (Apr.-Oct.)
  - documented in Prestigiacomo et al. (2015)
    - scope, NYSDEC input, event sampling
  - daily loads generated
    - summaries for different intervals (e.g., summer)
- **BAP_L ~ 26% of TP_L**
  - $PP_{L/B}$ ~ 40%
  - $SRP_{L/B}$ ~ 41%
  - $SUP_{L/B}$ ~ 19%



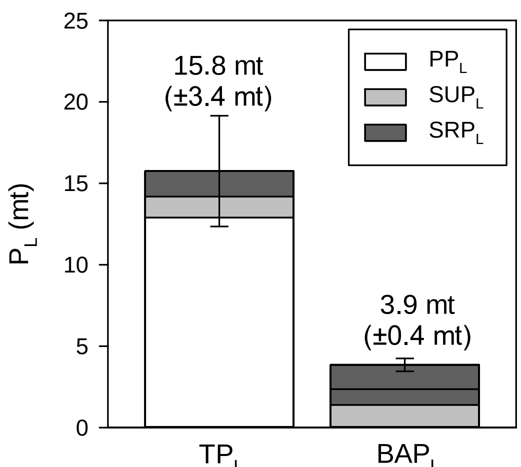
Comparison of total (TP_L) and bioavailable (BAP_L) load estimates to Cayuga Lake: Entire lake vs. shelf

* includes point and non-point sources



entire lake

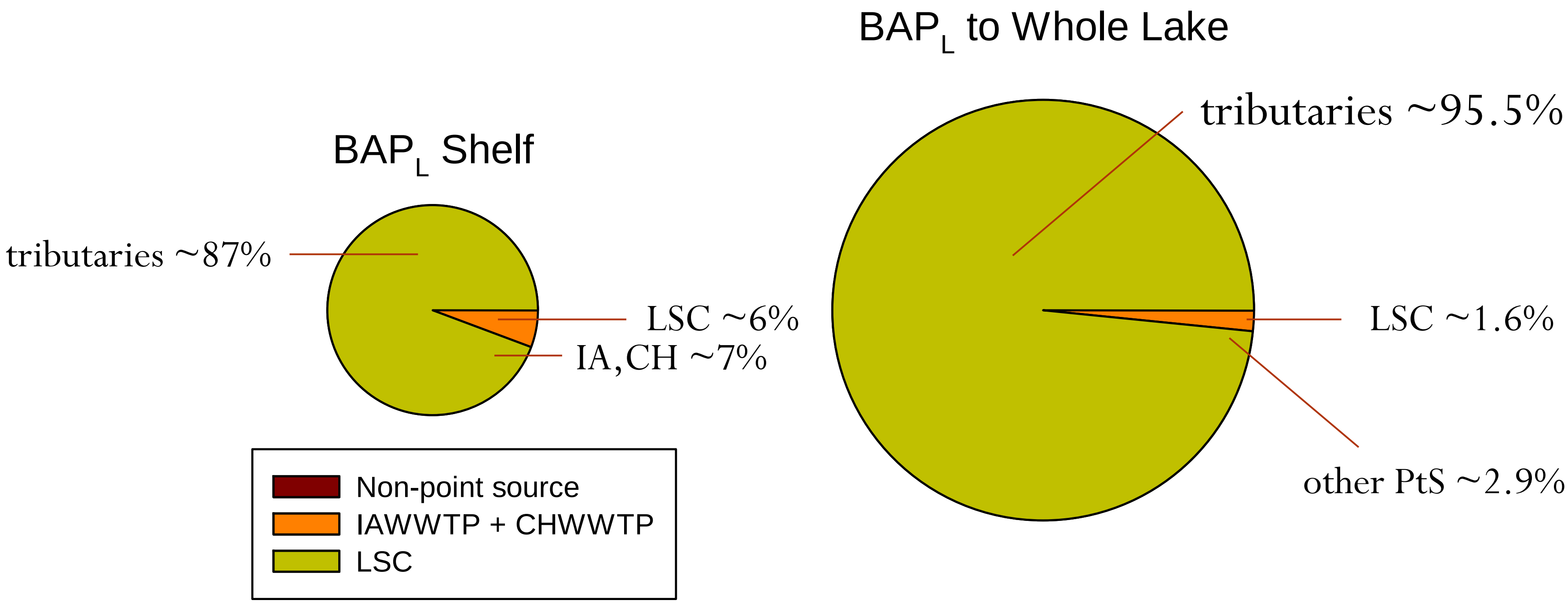
- dominant contribution of PP_L to TP_L, received mostly during runoff events
- BAP_L <<TP_L; ~25% due to low f_{BAP} of PP



shelf

- caution for related local interpretations, because of rapid flushing of shelf (subsequently)
- BAP_L remains much smaller (~ 22%) than TP_L locally

Comparison of BAP_L to the shelf and lake as a whole, 2013 conditions



Apportionment of BAP loads, 2013

		BAP_L (mt)	Percent Contribution to total BAP_L (%)
non-point sources	Fall Cr.	2.10	15
	Cayuga In.	0.79	5.6
	Salmon Cr.	**2.18**	**15.6**
	Six Mile Cr.	0.47	3.4
	Taugh. Cr.	1.10	7.9
	Unmon. Tribs.	6.75	48.1
	summed (%)	***13.4***	***95.5***
point sources	IAWWTP	0.21	1.5
	CHWWTP	0.08	0.5
	minor WWTP	0.14	1.0
	LSC	***0.22***	***1.6***
	summed (%)	***0.64***	***4.5***
	summed (%)	***14.0***	***100***

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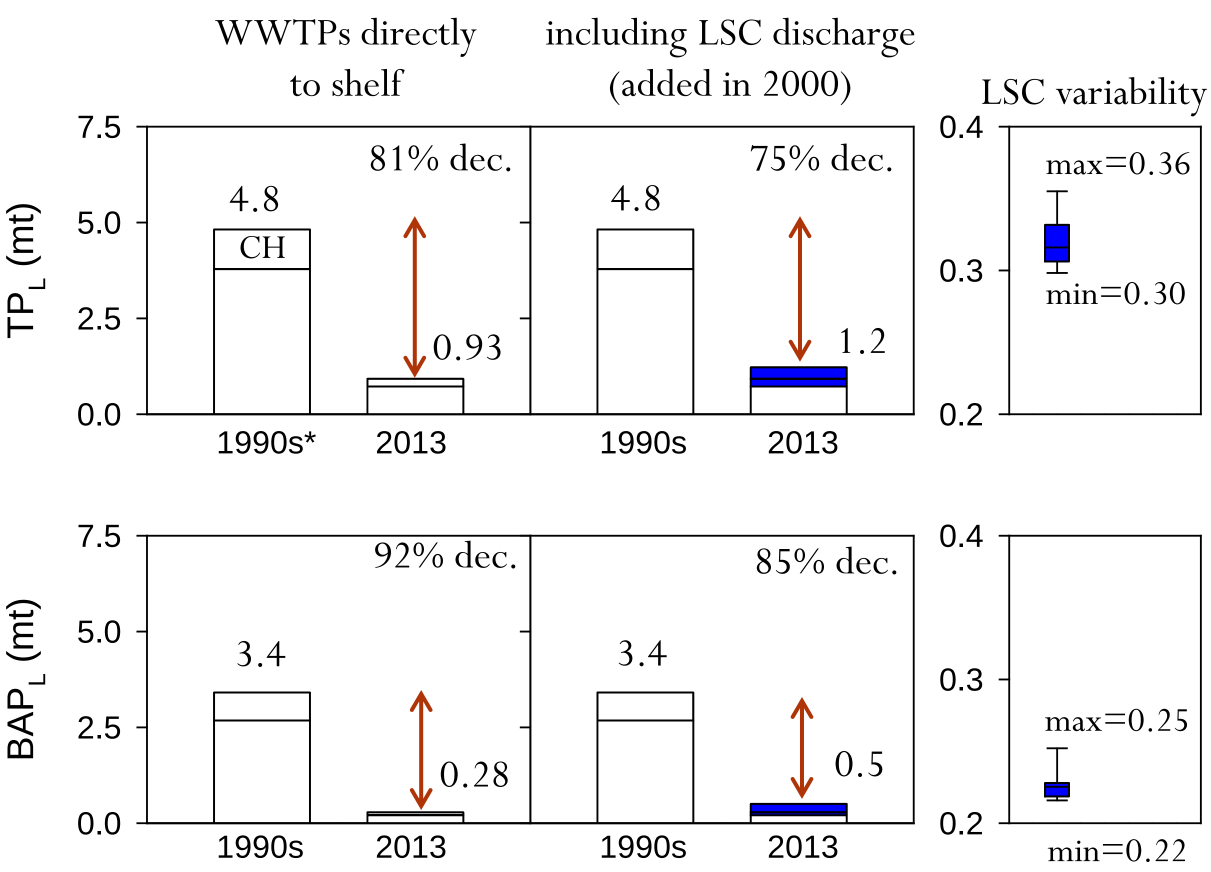
Reductions in P loading to the shelf from point sources



- April-October loads
- LSC (blue bar)
  - initiated in 2000
  - notable point source contributor in 2013
  - small relative to the overall decrease in point source inputs

* 1990s point source assumptions detailed in Prestigiacomo et al. 2015

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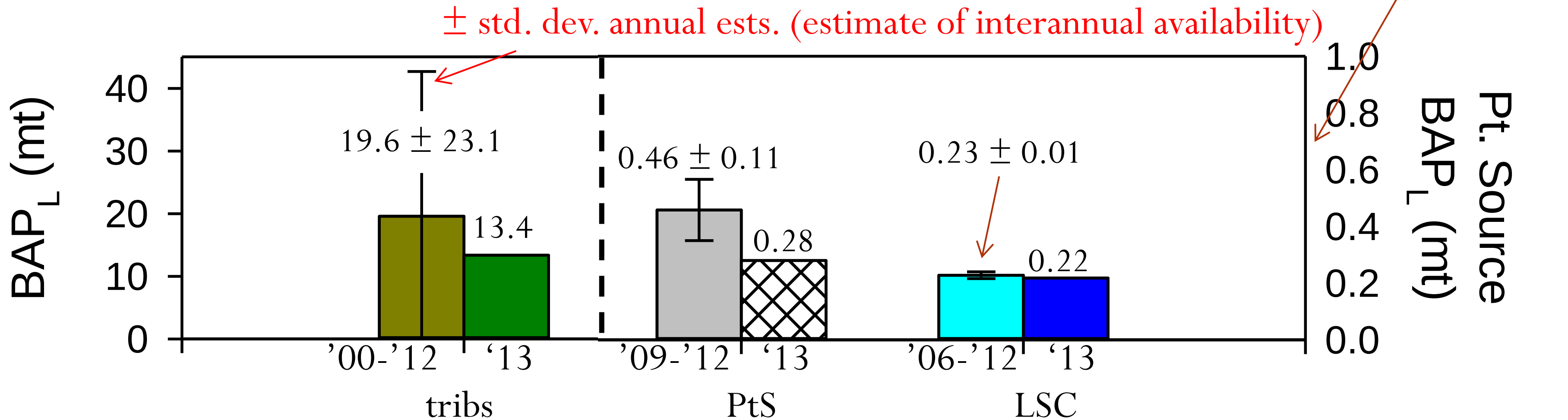
Representation of interannual variations in whole lake BAP_L, results

Prestigiacomo et al. 2015 (Figure 8)

- BAP_L variations according to source (± 1 std. dev.)



comparative features of LSC variability

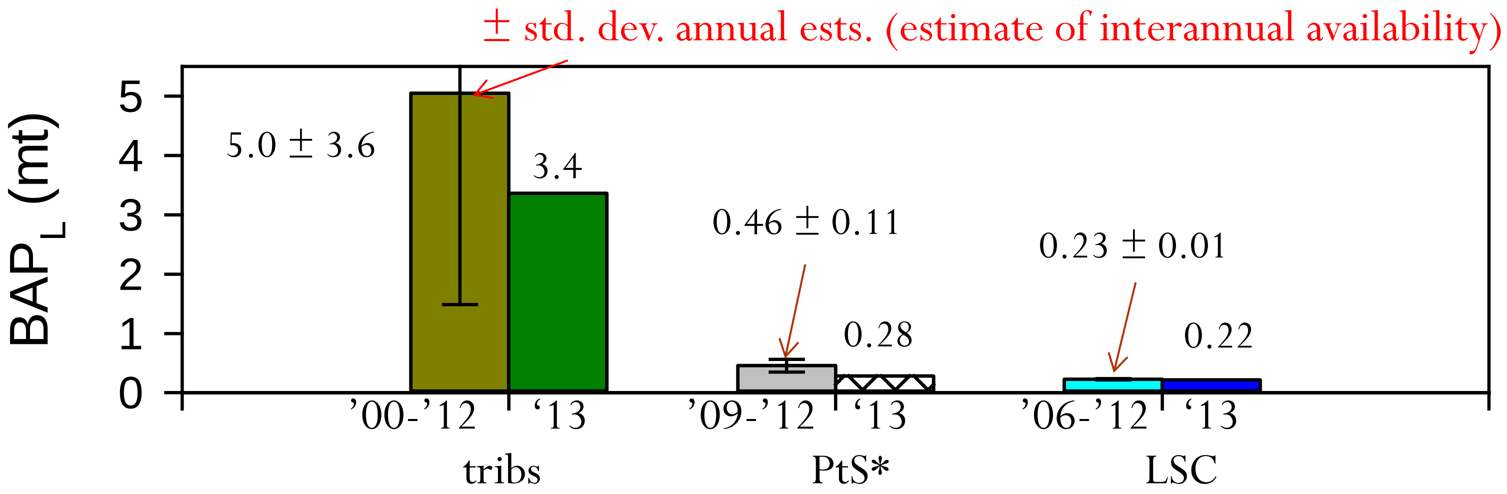
1. ± 1 std. dev. ~ 4.5 % of LSC load
2. ± 3.6 % of total PtS load
3. ± 0.07 % of total local 2013 load
4. ± 0.04 % of total estimated variability in BAP_L

variations in tributary loading dominate; potential climate change effects should be considered

Representation of interannual variations in <u>local</u> lake BAP_L, results

Prestigiacomo et al. 2015 (Figure 8)

- BAP_L variations according to source (± 1 std. dev.)



<u>comparative features of LSC variability</u>

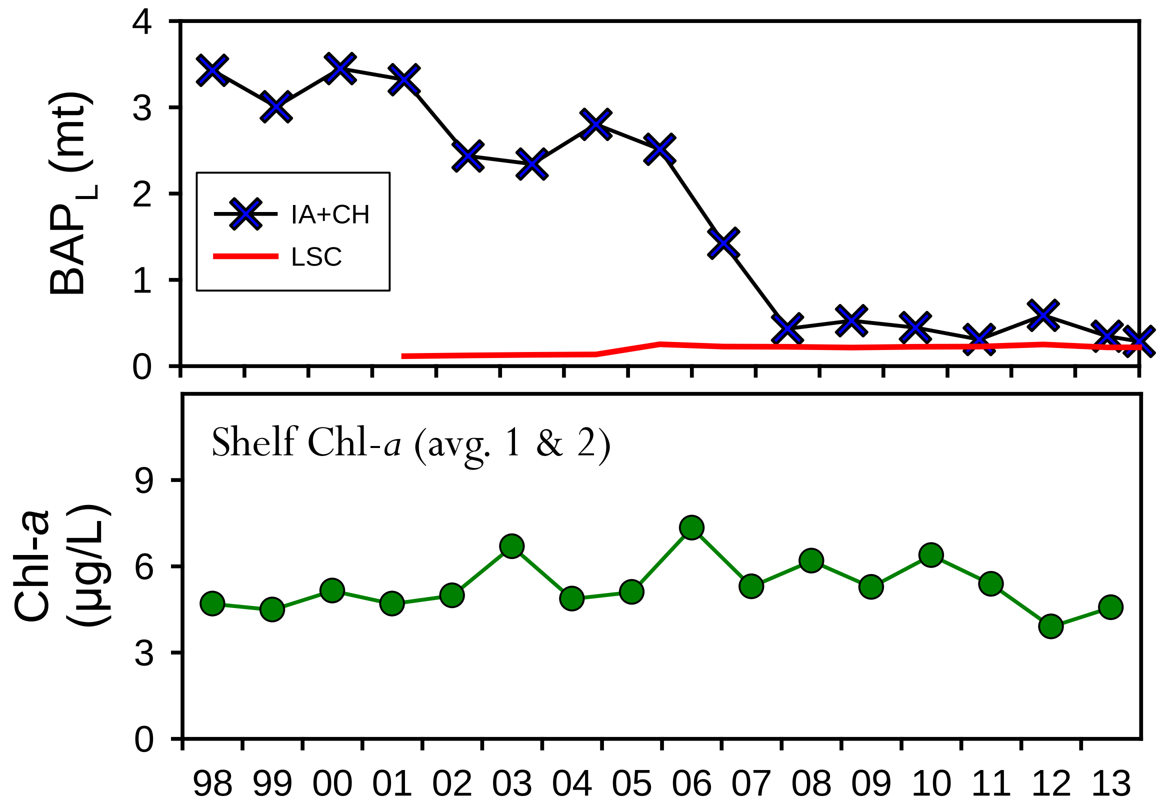
1. ± 1 std. dev. ~ 4.5 % of LSC load
2. ± 3.6 % of total PtS load
3. ± 0.3 % of total local 2013 load
4. ± 0.3 % of total estimated variability in BAP_L

variations in tributary loading dominate; potential climate change effects should be considered

*summation of point sources

Representation of interannual variations in local lake BAP_l, results

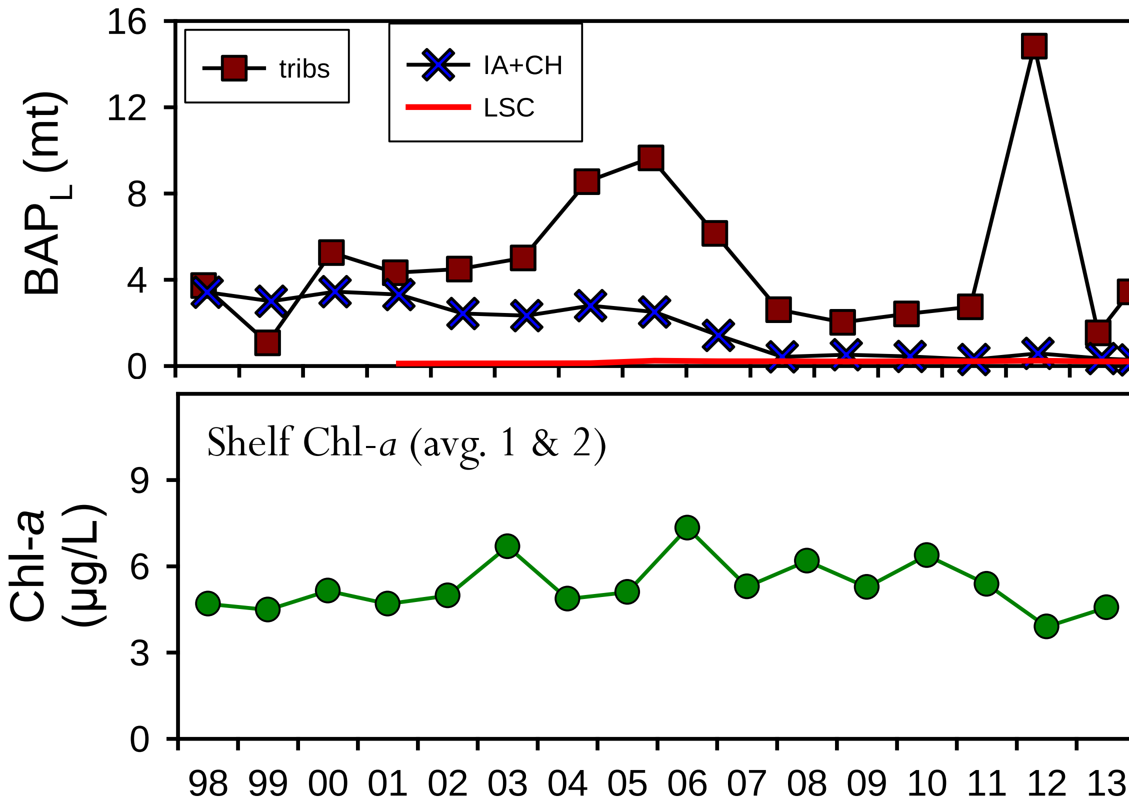
- local BAP_L for the April – October interval
  - 1998-2013 period
- systematic decrease in the WWTP BAP_L (IA nd CH) in ~ 2006
- increase in LSC BAP_L starting 2004-2005 evident



- no significant trends in Chl-*a* (or TP) despite those in point source BAP_L

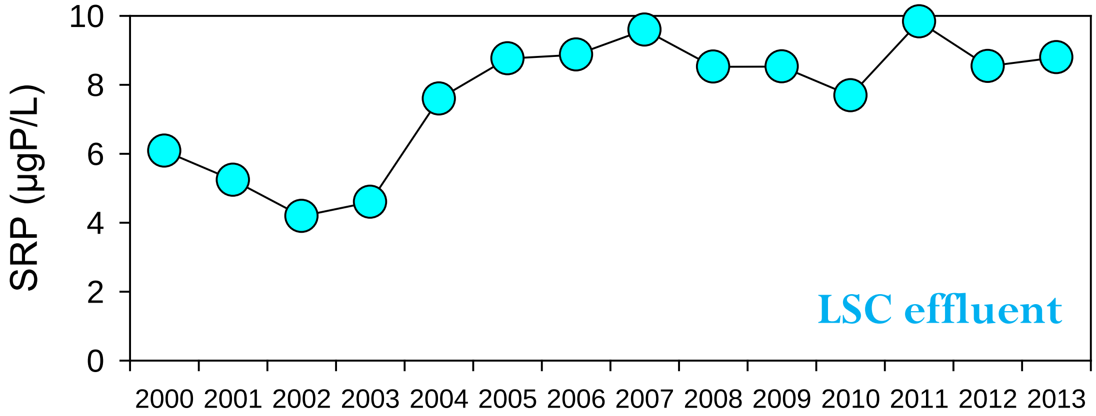
Representation of interannual variations in local lake BAP_l, results

- local BAP_L for the April – October interval
  - 1998-2013 period
- systematic decrease in the WWTP BAP_L (IA nd CH) in 2006
- increase in LSC BAP_L starting 2004-2005 evident
- the tributary *usually* dominates overall loading
  - exceptions, dry years, 2012
  - highly variable, dependent on hydrology
  - Prestigiacomo et al. 2015



- no significant trends in Chl-*a* (or TP) despite those in point source BAP_L

The increase in the LSC SRP levels: A limnological signature, but only a small increase in BAP_L



- indicative of shift in system metabolism
- zebra to quagga mussels?

- distinct increase in 2004
  - SRP concentration was 4-6 µg/L, now 8-10 µg/L
- current conditions represent, on average, an increase in the LSC BAP_L of ~0.1 mt
  - ~2.7% increase in BAP_L to shelf
- small component of overall load (all tribs, non-point sources)

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Summary: Phosphorus bioavailability and loads

- runoff event monitoring and P concentration-flow (P/Q) relationships critical to support loading estimates
- bioavailability concept (f_{BAP}) integrated into P loading analysis for Cayuga Lake
- components
  - multiple fractions of P monitored
  - algal bioassays of PP, SUP, and SRP – multiple sources and events
  - development of load estimates (TP_L and BAP_L)
    - including historic estimates (~late 1990s) and contemporary
- bioavailability findings for tributary inputs
  - PP (mostly minerogenic particles) – low (6-21%)
  - SUP – mostly (60-85%)
  - SRP – ~ completely (>90%)
  - other contrasting conditions – LSC/SUP, Actiflo/PP, Salmon Cr./PP, shelf post events/PP

Summary: Phosphorus bioavailability and loads

- tributary sources of BAP_L dominate the overall BAP_L to the entire lake and shelf
  - ~ 95% on a lake-wide basis
  - ~ 87% on the shelf
- April-October 2013 BAP_L was substantially lower than TP_L
  - ~ 26% of TP_L
  - received mostly during runoff events
  - large interannual variations anticipated from variations in hydrology - complications
- point source upgrades reduced BAP_L contributions lake-wide from ~20% (late 1990s) to ~5% (2013)
  - obvious benefits, quantification of benefits difficult due to tribs dominance

Questions

Detailed uncertainty and variability analyses

1. methods of load estimation
   - numerous protocols evaluated
   - results for Fall Creek
2. dependencies of tributary P concentrations (various forms) stream flow rate (Q)
   - loading calculations, FLUX32 Jackknifing
3. monitoring coverage adjoining tributary mouths
   - loading calculations, FLUX32 Jackknifing
4. application of bioavailability results
   - temporal, site specific variability in bioavailability
   - Monte Carlo analysis
5. estimates of interannual variations in tributary BAP_L

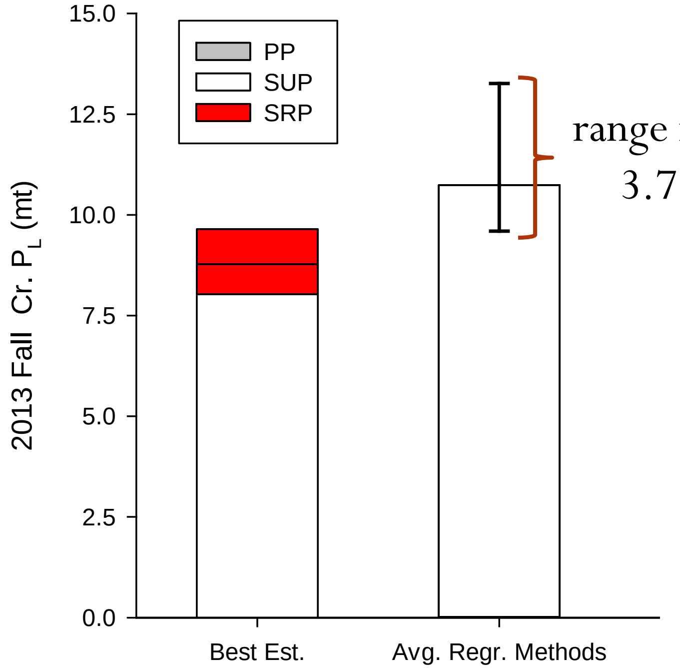
1. Variability in Fall Creek P_L estimation: Calculation protocol

Method	PP Load (kg)	SUP Load (kg)	SRP Load (kg)	TP Load (kg)
F32 method 6 C/Q interpolated, seasonal	**8,032**	**741**	**876**	**9,649**
F32 method 6 C/Q interpolated, flow	8,010	742	855	9,607
F32 method 6 C/Q	11,289	770	1,202	13,261
F32 method 5 C/Q adj.	8,156	755	893	9,804
F32 method 4 C/Q flow wtd. adj.	8,300	759	907	9,966
F32 Rising/Falling limb	8,008	739	850	9,597
Manual regr.	10,251	746	1,108	12,105
Manual regr. with events	10,223	645	1,153	12,021
Multiple Linear Regression	8,896	784	971	10,651
range (regression methods)	**8,008-11,289**	**645-784**	**850-1,202**	**9,597-13,261**

- demonstration of some dependence of load estimates on the specifics of the loading calculation protocol adopted

1. Variability in Fall Creek P_L estimation: Calculation protocol

- April – October, 2013

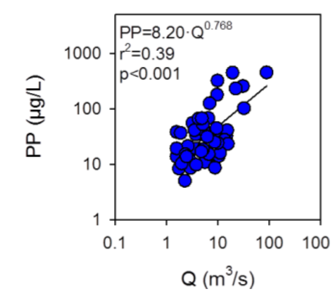


range in TP_L
3.7 mt

- best estimate Fall Cr. TP_L = 9.6 mt
  - PP_L = 8.0 mt;
  - SRP_L = 0.88 mt;
  - SUP_L = 0.74 mt
- range in estimates from regression protocols is typical
  - TP_L range = 3.7 mt (38% of best estimate TP_L)
    - PP_L = 3.3 mt;
    - SRP_L = 0.35 mt;
    - SUP_L = 0.14 mt

most uncertain

most certain

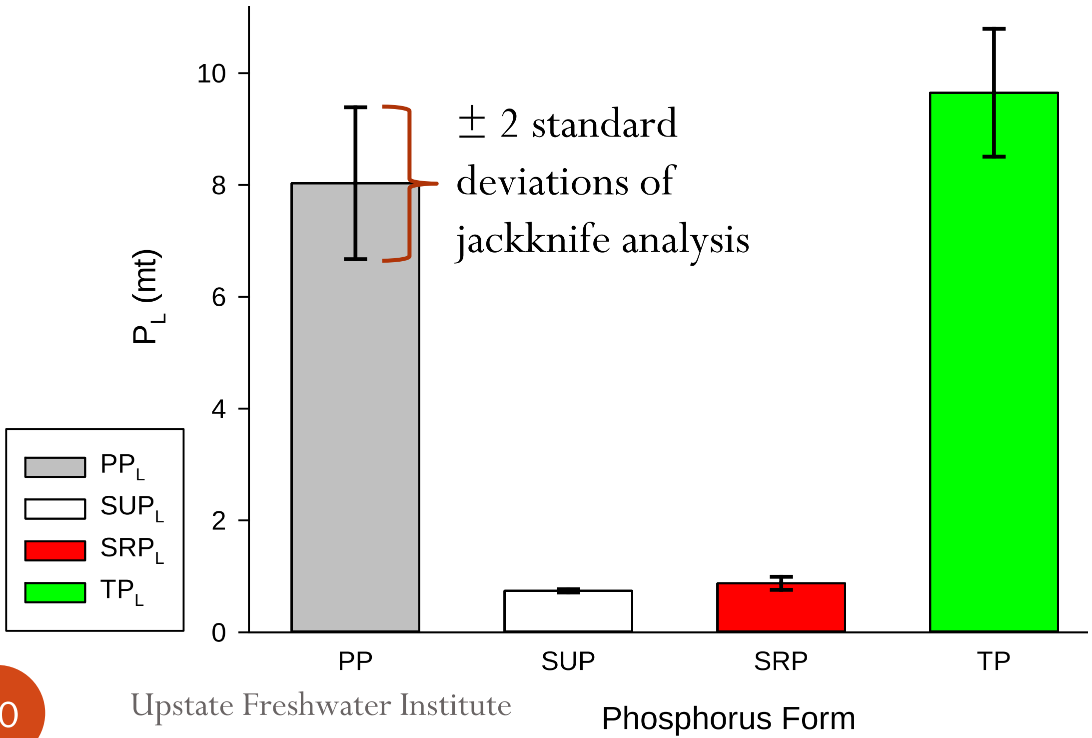


- protocol uncertainty due to:
  - uncertainty in C/Q
  - assumptions embedded in individual protocols
- methodological uncertainty similar for other tributaries

2-3. Uncertainty in Fall Creek load estimation associated with adopted method: Jackknife analysis

Jackknife procedure (FLUX32)

1. calculates the best estimate load using all observed concentration data
2. excludes one measured concentration one at a time, and recalculates the loads
3. repeated for n-1 number of iterations, where n is the total number of concentration observations
4. uncertainty statistics calculated on the n-1 number of load estimates

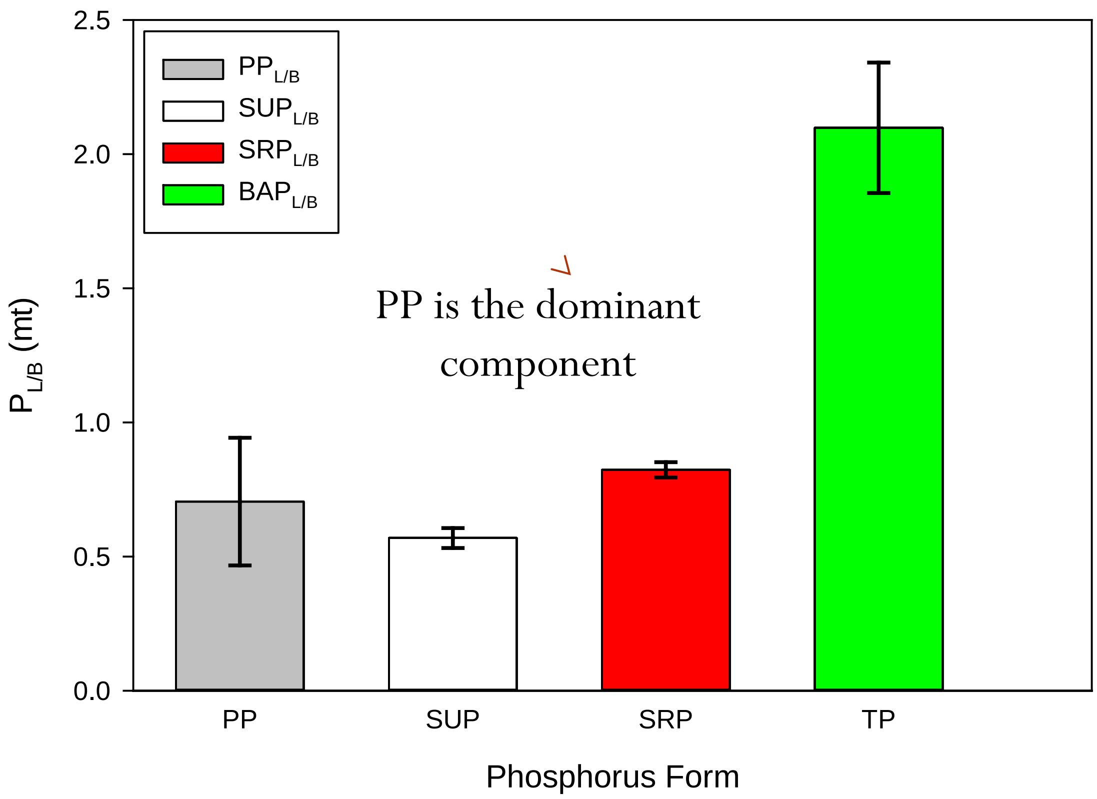


- unavoidable, associated with variability in the C/Q relationships and number of observations
- greatest uncertainty associated with PP, the dominant P component
- magnitudes of jackknife uncertainty
  - TP_L = 2.2 mt
  - PP_L 2.7 mt
  - SRP_L = 0.23 mt
  - SUP_L = 0.06

4. Uncertainty in BAP_L estimates: Monte Carlo analysis

- fully summarized in Prestigiacomo et al. 2015
- associated with temporal variations in f_{BAP} in the tributaries
  - beta distribution (StatSoft, 2003) was established for f_{BAP} for each tributary based on the three observations for each P form
  - values of f_{BAP} were selected randomly from these distributions for each day over the April-October interval of 2013 for each tributary (and P form) and associated loads were calculated (summed to BAP_L), as conducted for the original overall best estimate
  - process repeated for 2000 simulated April-October intervals
  - uncertainty in $P_{L/B}$ for each tributary and together is represented by 95% confidence limits of the calculated 2000 seasonal distributions

4. Uncertainty in BAP_L estimates: Monte Carlo analysis

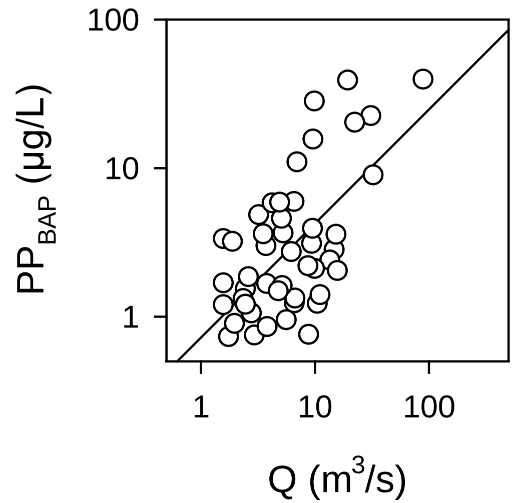


- Fall Cr. results
- greatest uncertainty associated with PP,
- magnitudes of Monte Carlo uncertainty
  - $BAP_{L/B}$ = 0.24 mt
  - $PP_{L/B}$ = 0.24 mt
  - $SRP_{L/B}$ = 0.04 mt
  - $SUP_{L/B}$ = 0.003 mt

5. Representation of interannual variations in local P_L and BAP_L, methods (2000-2012)

1. analyses of loads for tributaries
   a. evaluation of concentration-flow (C/Q) relationships
      - logarithmic relationships
      - positive, reasonably strong
      - "power law" format
      - important support for position that these dependencies have not systematically changed in recent years (historical CSI, UFI monitoring)
   b. FLUX32 calculations of P_L
      a. application of bioassay f_{BAP} results to daily P_L estimates
   c. enhanced credibility of load estimates from NYSDEC's call for event-based tributary monitoring
   d. uncertainty in estimates unavoidable, from real variations in P/Q relationships
2. point sources – discharge monitoring
3. uncertainty – estimates, real variations

- Prestigiacomo et al., 2015



e.g., high flow years will have higher concentrations and associated loads

Potential for interannual variations in local BAP_L to mask systematic benefits from reductions in point source loads

- the executed experiment:
  - Prestigiacomo et al. 2015

"Point source contributions to the total bioavailable P load (BAP_L) are minor (5%), reflecting the benefit of reductions from recent treatment upgrades. The BAP_L represented only about 26% of the total P load, because of the large contribution of the low bioavailable PP component. Most of BAP_L (> 70%) is received during high flow intervals. Large interannual variations in tributary flow and coupled BAP_L will tend to mask future responses to changes in individual inputs."