E. Minerogenic Particulate Phosphorus Model

- the unavailable component ($PP_{m/u}$)
- development, testing, and application

Outline

1. background, supporting elements, and an empirical $PP_{m/u}$ model
2. conceptual mechanistic $PP_{m/u}$ model, input considerations and development
3. model performance
4. model analyses
5. applicability, advancements, and summary

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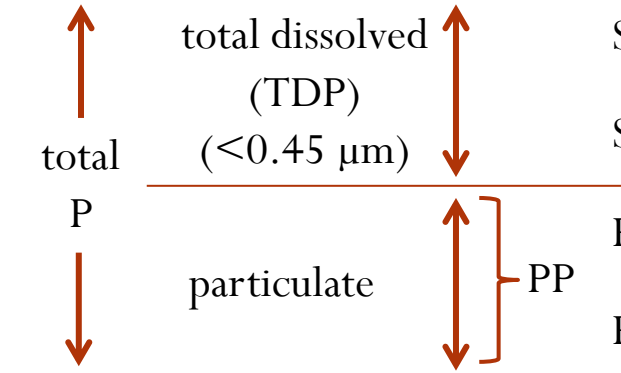
Unavailable minerogenic particulate phosphorus ($PP_{m/u}$), other P fractions, and bioavailability

- (Prestigiacomo et al., 2015)



P fraction	bioavailability (assays)	
SRP	complete	soluble reactive
SUP	mostly	soluble unreactive
PP_o	mostly	organic particulate
PP_m	limited	minerogenic particulate

partitioning $PP_m = PP_{m/u} + PP_{m/a}$

$PP_{m/u}$	none	minerogenic unavailable particulate
$PP_{m/a}$	complete	minerogenic available particulate, small fraction here

$PP_{m/a} \div PP_m \approx f_{BAP}$ for PP

Implications for Water Quality Model Structure

- PP needs to be partitioned according to PP_o and PP_m
- PAVm or a proxy is a potentially valuable state variable to represent minerogenic particles
- external loads of PAVm or a proxy would be necessary
- longitudinal segmentation needed to differentiate near-shore versus pelagic waters conditions

based on: Effler et al. 2014. *Inland Waters* **4**:179-192

consistency with implemented tool

Independent estimates of $PP_{m/u}$ and the ratio $PP_{m/u}$:PAV_m from an *empirical* model: A test for the *dynamic* mechanistic model

- development and testing for the lake documented (Effler et al. 2014)
- stoichiometry – based model for lake PP, PP_o, and $PP_{m/u}$

$$PP = PP_o + PP_{m/u}$$

$$PP = (PP_o{:}Chl)\cdot Chl + (PP_{m/u}{:}PAV_m)\cdot PAV_m$$

1.53

stoichiometric ratios

- from optimization analysis of lake observations, 1999-2006

7.1 mg/m^3

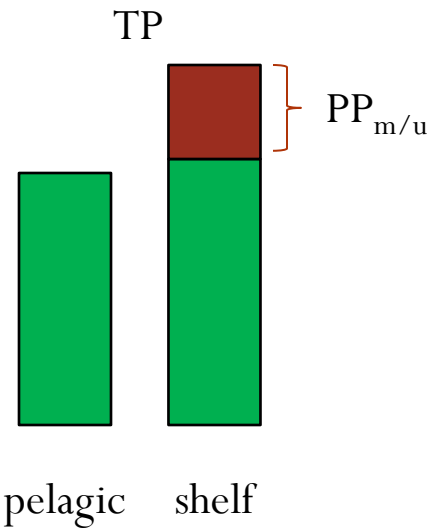
temporal uniformity in stoichiometric ratios invoked

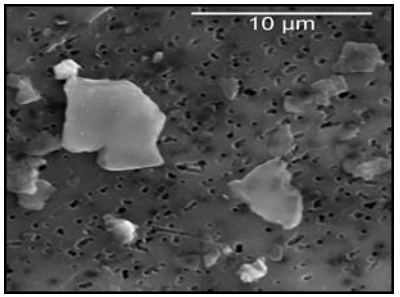
Chl – chlorophyll a

- supports the partitioning of PP
  - $PP = PP_o + PP_{m/u}$

Implications of $PP_{m/u}$ concentrations in lakes and related challenges for its modeling

- noteworthy contributions of $PP_{m/u}$ compromise TP concentration as a metric of trophic state because of the unavailability of $PP_{m/u}$ to support plant (e.g., algae) growth
- differences in time and space within individual lakes, and between lakes, are to be expected, associated with coupled differences in responsible minerogenic particles (PAV_m) – runoff event effects important
- runoff events expected to promote higher PAV_m and thereby $PP_{m/u}$
- challenges to model $PP_{m/u}$ in lakes, quantification of:
  1. delivery, transport, and fate of minerogenic particles (PAV_m), and
  2. P associated with these particles (PP_m) and its bioavailability ($PP_{m/u}$ vs $PP_{m/a}$)





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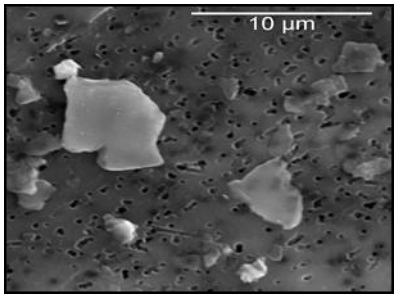
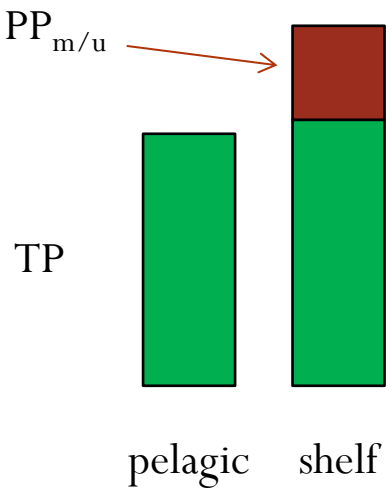
Extensive technical program support for mechanistic $PP_{m/u}$ model for Cayuga Lake

- lake monitoring – LSC program 1999-2006, plus 2013
  - P fractions, Chl-*a*, PAV_m (size classes and type)
- primary tributaries
  - P fractions, sediment (ISPM, SPM), PAV_m (size classes)
- bioavailability assays (NYSDEC recommended)
- submodels
  - (1) 2-D transport, (2) PAV_m (4 size classes)
- loading estimates – PAV_m and $PP_{m/u}$
  - runoff event sampling focus (NYSDEC recommended), Inlet (extra, UFI and Cornell)
- sediment trap (extra, UFI and Cornell)

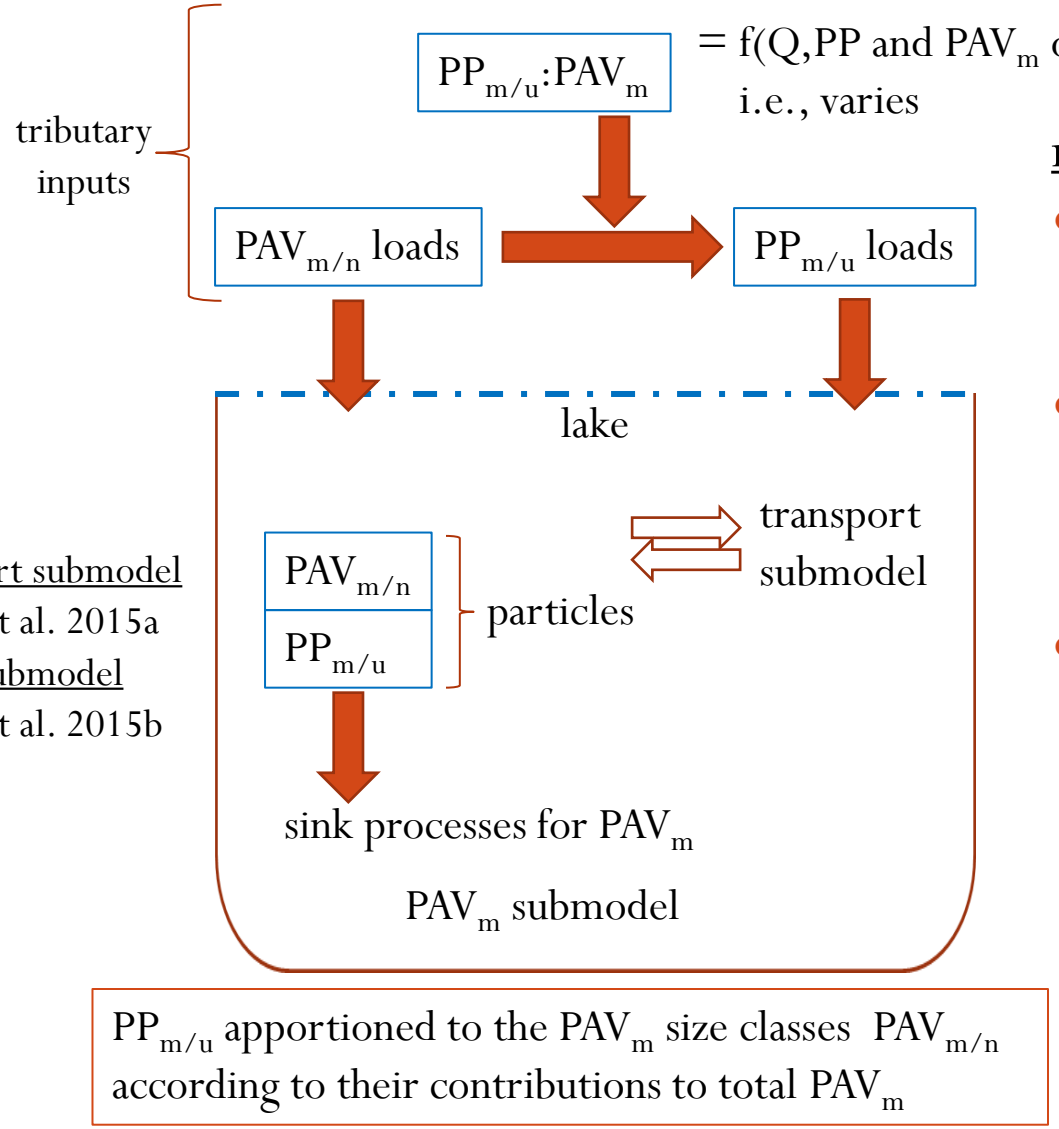


A mechanistic model for unavailable minerogenic particulate P ($PP_{m/u}$) for Cayuga Lake: Background

- P associated with minerogenic particles ($PP_{m/u}$) delivered by the watershed interferes with the use of TP concentration as a trophic state metric in lacustrine systems because of its limited bioavailability
- a mechanistic mass balance model for $PP_{m/u}$ has been developed and tested, as described here
- supporting components
  - long-term and intensive 2013 monitoring
  - LSC monitoring (1999-2006)
  - bioavailability assessments
  - loading estimates, PAV_m and $PP_{m/u}$
  - transport and PAV_m submodels



Conceptual model for dynamic mechanistic $PP_{m/u}$ model

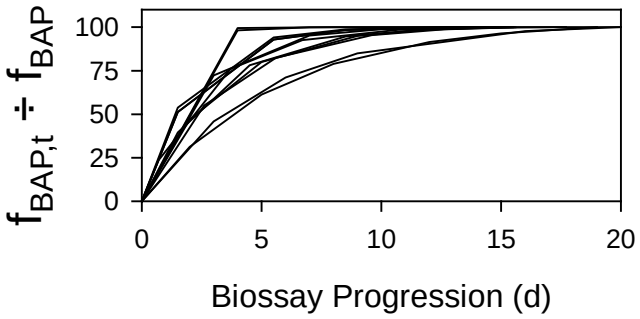


model features

- $PP_{m/u}$:PAV_m of delivered particles subject to variation
- in-lake behavior of $PP_{m/u}$ is assumed to be that of PAV_m with which it was associated upon entry
- in-lake dynamics of $PP_{m/u}$ reflect external load of $PAV_{m/n}$, the dynamics of the $PP_{m/u}$:PAV_m ratio in the tributaries and the progression of in-lake PAV_m loss processes

Specifications for modeling $PP_{m/u}$

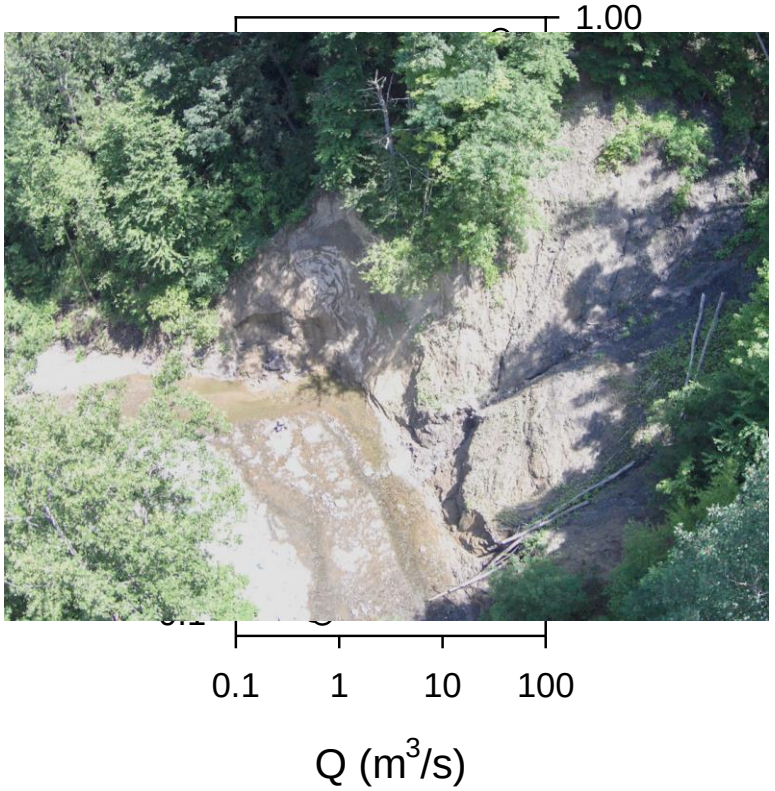
- well-mixed upper waters targeted (epilimnion)
- linear dependency of PP_m on PAV_m
  - described by Effler et al. (2014), conceptual consistency
  - partitioning of PP_m according to size class contributions
- PP_m from tributary inputs of PP according to:
  - $PP_m = PP \cdot (ISPM:SPM)$; ISPM:SPM generally > 0.9
- PP_m subject to temporal variability in tributary inputs according to variations in the PP_m:PAV_m ratio
  - tributary loads of PP_m from PAV_m load estimates
  - PP_m load = PAV_m load·(PP_m:PAV_m)
- $PP_{m/u}$ loads incorporate tributary-specific bioavailability results
  - $PP_{m/u}$ load = $(1-f_{BAP}) \cdot PP_m$ load
  - supported by rapidity of the transformation
- in-lake behavior of $PP_{m/u}$ equivalent to that of the PAV_m with which it is associated



- f_{BAP} = fraction bioavailable for completed bioassay
- $f_{BAP,t}$ = fraction bioavailable through progression of bioassay

Considerations for modeling $PP_{m/u}$: Tributary conditions and loads of minerogenic particles

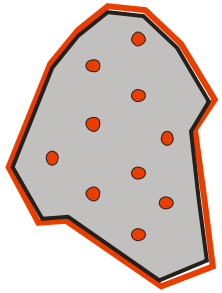
- positive dependencies of particle concentration (ISPM), and the minerogenic component on stream flow (Q)
- implications of runoff events
- dominance of minerogenic particles – glacial lacustrine stream deposits (Nagle et al. 2007)
- origins of variance in dependencies
- e.g., character of stream banks



Fall Creek examples

Consideration for modeling $PP_{m/u}$: Tributary conditions, dependence of PP on PAV_m

- strong positive dependence of PP in streams on PAV_m
  - most of PP is as $PP_{m/u}$
- the P content of clay mineral particles delivered



associated with PAV_m

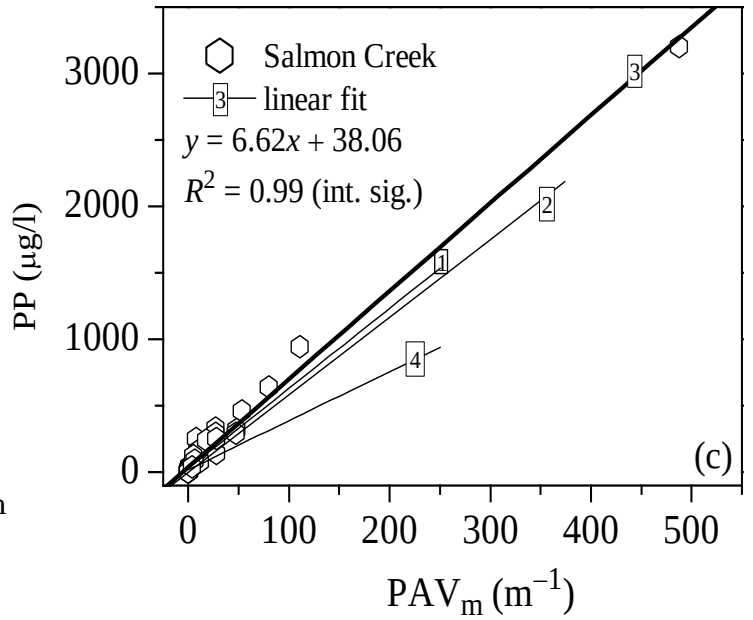
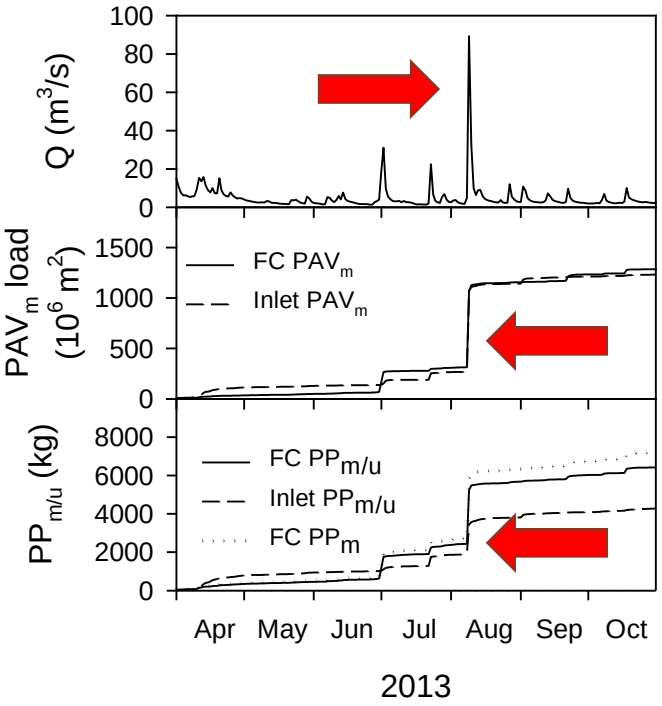


Fig. 4c from
Peng and Effler 2015

- during a runoff event large quantities of PAV_m and associated P (PP_m) are delivered

Specifications for modeling $PP_{m/u}$: Tributary conditions and loads

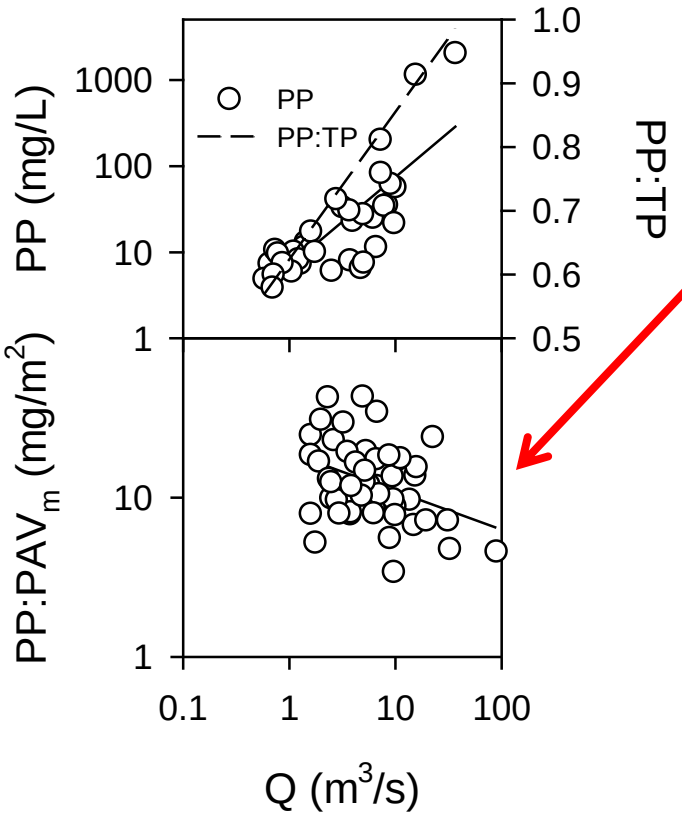
- temporal patterns
- runoff events dominate



- Fall Cr. Q time series 2013, prominent runoff events
- cumulative format for PAV_m and $PP_{m/u}$ loads
- early July and August runoff events dominate

Specifications for modeling $PP_{m/u}$: Tributary conditions and loads

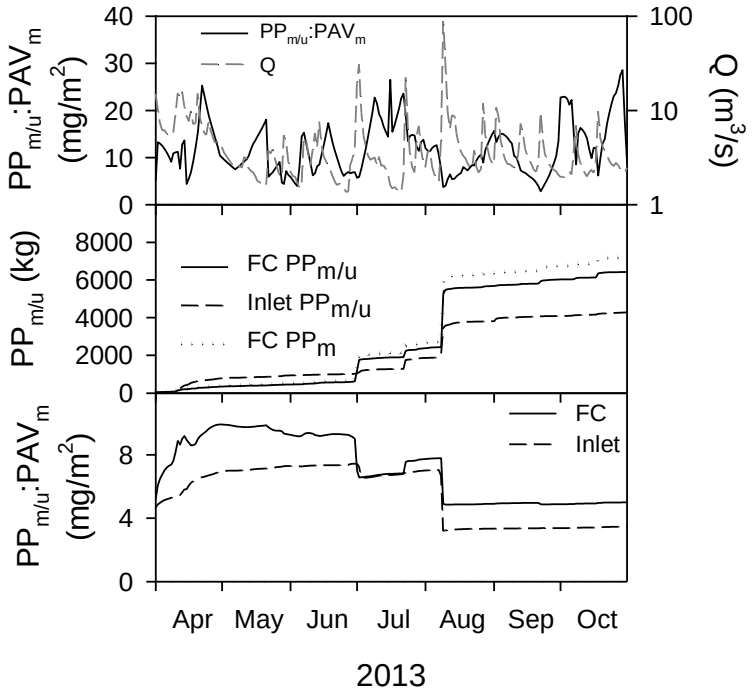
- positive dependencies on stream flow (Q)-PP, PP:TP



- Fall Cr. examples
- PP_m:PAV_m ratio supports estiamtes of PP_m (and $PP_{m/u}$) loads from PAV_m loads
  - negative, but variable dependency on Q

Specifications for modeling $PP_{m/u}$: Tributary conditions and loads

- temporal patterns
  - example for Fall Cr, $PP_{m/u}$:PAV_m and Q
  - cumulative formats for $PP_{m/u}$ load and the ratio



- $PP_{m/u}$:PAV_m highly variable, negative dependency on Q
- dominance of runoff events for $PP_{m/u}$ loads
- PP_m loads just slightly higher, consistent with low f_{BAP}
- cumulative change for ratio will drive changes in-lake relationship

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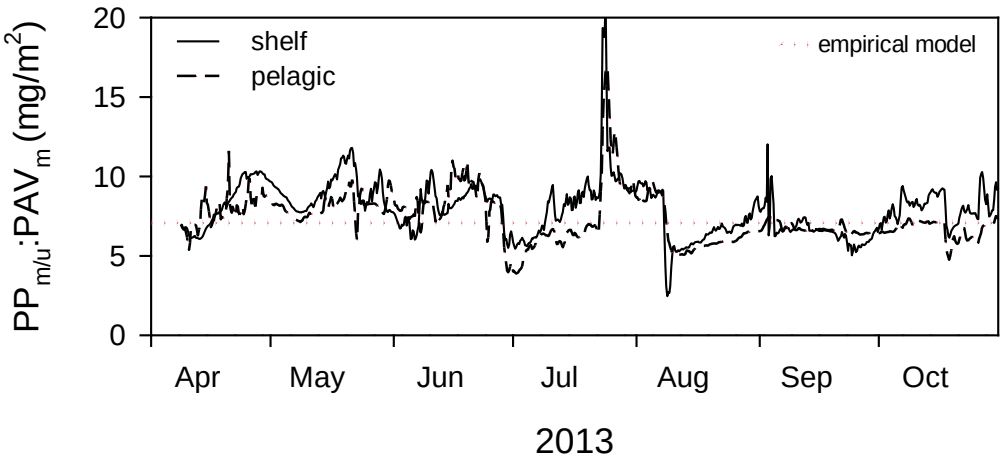
Mechanistic dynamic $PP_{m/u}$ model performance: Targeted attributes for testing

tests of consistency

- extent of closure with prediction of independently tested empirical PP model
  - in-lake $PP_{m/u}$:PAV_m ratio
  - in-lake $PP_{m/u}$
- $PP_{m/u}$ with historic TP and PP shelf observations, following runoff events
- predicted $PP_{m/u}$ deposition on shelf from runoff event inputs with sediment trap observations

Mechanistic dynamic $PP_{m/u}$ model performance: Lake $PP_{m/u}$:PAV_m ratio vs. empirical model value

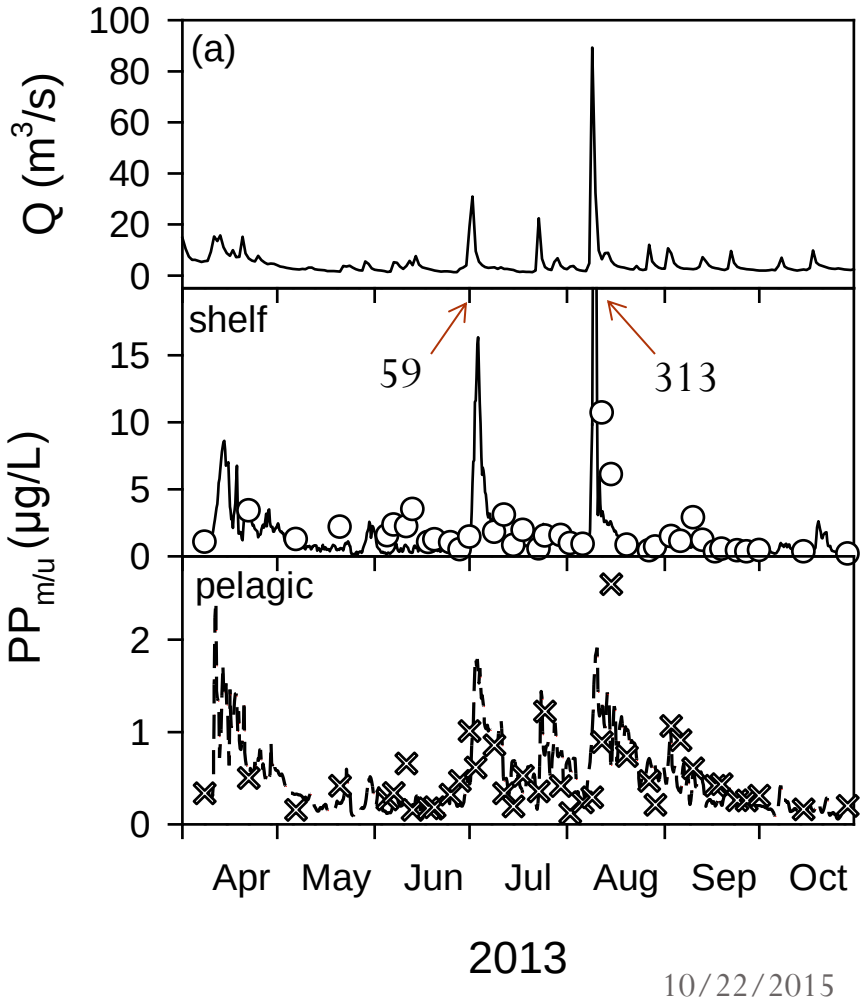
- predictions of in-lake $PP_{m/u}$:PAV_m ratio
  - only minor shelf vs. pelagic differences
  - averages (shelf – 8.0 mg/m^2; pelagic – 7.4 mg/m^2) closed well with single empirical model value (7.1 mg/m^2; Effler et al. 2014)



- in-lake variations (cv=0.22) driven by tributary variations (cv=0.46)
  - tributary dynamics linked to variations in Q

Mechanistic dynamic $PP_{m/u}$ model performance: Comparison of $PP_{m/u}$ predictions, mechanistic vs empirical models

- comparisons for both the shelf and pelagic waters
- predictions for 2013, with Fall Cr. Q for runoff event context
- empirical model predictions limited to sampling occurrences
  - reasonably strong relationships
  - shelf vs pelagic different scaling
  - magnitudes consistent overall



Mechanistic $PP_{m/u}$ model performance: Consistency with historic TP and PP observations following runoff events

- identifying runoff events from LSC monitoring
  - record
- same runoff events considered for PAV_m (sub)model
  - Table 2 (Gelda et al. 2015b)
- signatures of increased PP_m expected on shelf following runoff events

Features of selected Fall Creek runoff events and subsequent PAV_m and PP monitoring observations for the shelf of Cayuga Lake, NY for the 2000-2013 period.

Event No.	Sampling Date	Peak Q[a] ($m^3 \cdot s^{-1}$)		Δt[b] (hr)	PAV_m (m^{-1})	PP[d] (NTU)	
1	15-Jun-2000	41.6	(0.4)	74	1.01	11.1	(0.4)
2	28-Jun-2001	51.0	(0.6)	107	0.98	14.0	(0.2)
3	18-Apr-2002	35.1	(0.2)	84	0.90	15.6	(0.2)
4	16-May-2002	72.8	(1)	63	2.60	26.6	(0.2)
5	5-Jun-2003	34.3	(0.2)	94	0.60	12.1	(0.3)
6	6-May-2004	21.7	(0.1)	71	0.55	4.46	(0.5)
7	14-Apr-2005	175	(12)	272	0.95	15.3	(0.3)
8	29-Jun-2006	65.7	(1)	32	7.63	48.5	(0.2)
9	1-May-2007	15.5	(<0.1)	120	0.28[c]	10.6[f]	(0.2)
10	16-Apr-2008	10.6	(<0.1)	92	0.20[c]	8.6[f]	(0.1)
11	20-Apr-2011	51.5	(0.1)	75	2.03[c]	20.5[f]	(0.1)
12	27-Apr-2011	38.2	(0.1)	89	4.47[c]	27.9[f]	(0.2)
13	3-Jul-2013	20.3	(<0.1)	37	1.98[e]	58	(-)
14	9-Aug-2013	113	(3.5)	12	86.02	2.2	(-)
15	12-Aug-2013	113	(3.5)	86	2.67	25	(-)

[a] event peak return, in years, parenthetically
[b] time from event peak in Fall Creek to shelf sample collection
[c] estimated from T_n samples
[d] Site 2 PP with coefficients of variation of multiple shelf observations, parenthetically
[e] average of July 3-4 estimates of PAV_m
[f] estimates from TP

The complications of turbidity plumes on the shelf following major runoff events

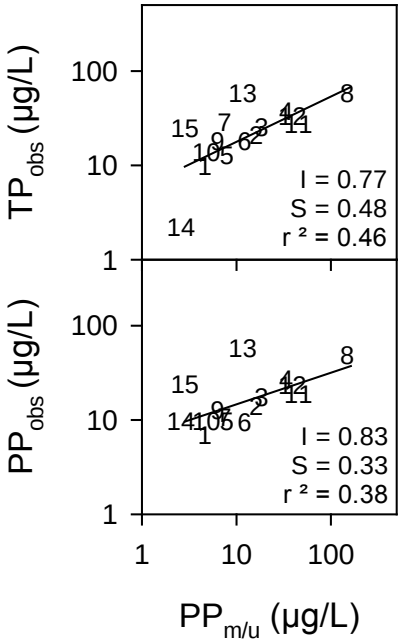
issue for $PP_{m/u}$ model evaluation as with the PAV_m model

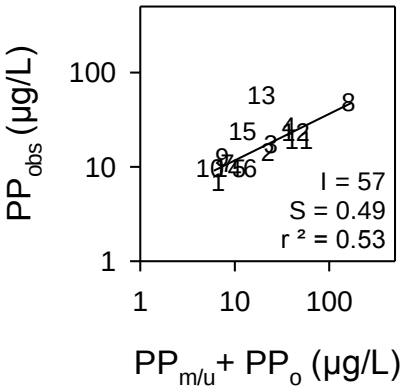
The complications of turbidity plumes on the shelf following major runoff events

issue for $PP_{m/u}$ model evaluation as with the PAV_m model

Mechanistic $PP_{m/u}$ model performance: Consistency with historic TP and PP observations following runoff events

- variations is predicted $PP_{m/u}$ for long-term (1999-2006) simulations performed reasonably well in explaining observed differences for historic events
- recall this is an imperfect match of P fractions
- performance improves somewhat with representation of the effects of PP_o (phytoplankton biomass) variation also





- numbers correspond to the various historic runoff events listed in previous table (Table 2, Gelda et al. 2015b)

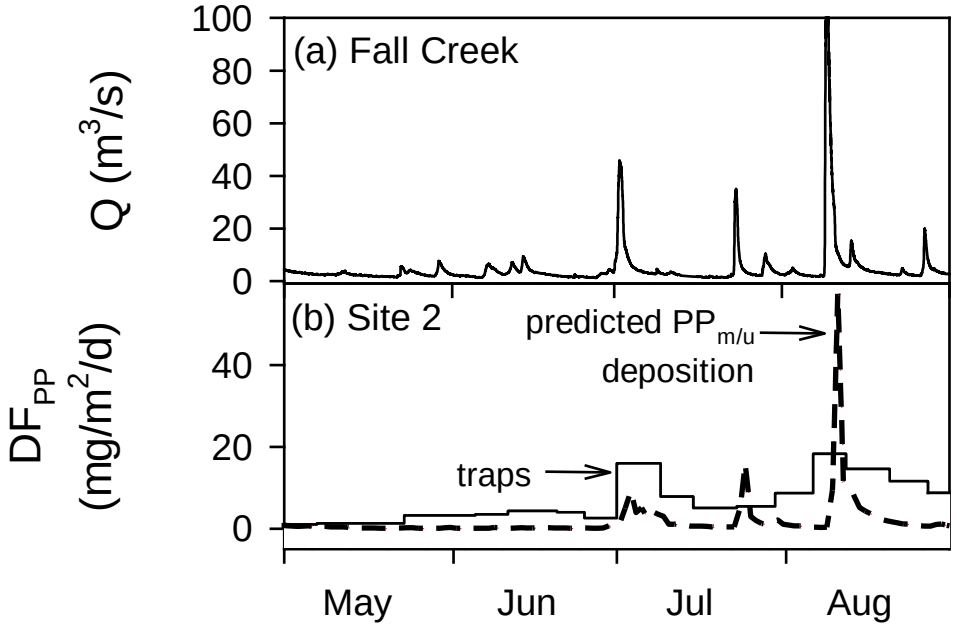
$$PP = (PP_o : Chl) \cdot Chl$$

1.53

Effler et al. (2014)

Consistent mechanistic $PP_{m/u}$ model performance for local deposition from runoff events

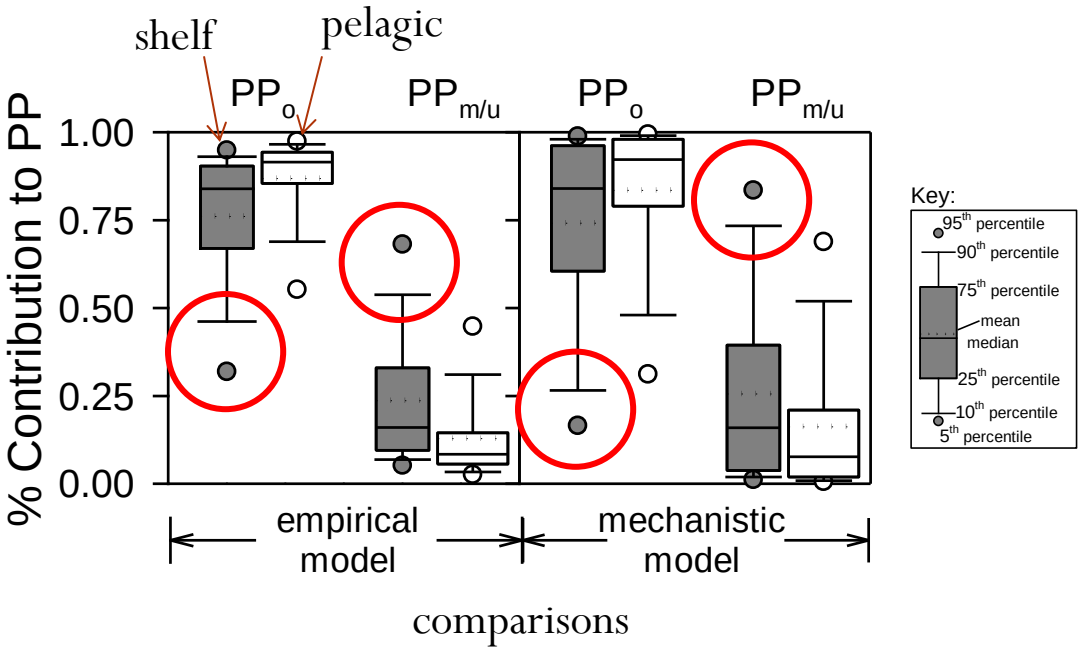
- comparison of simulations of deposition of $PP_{m/u}$ (i.e., associated with PAV_m) with sediment traps observations of PP downward flux
- simulations and observations both elevated for major runoff events
- semi-quantitative support, given the variable operation and trajectories of turbid plumes



DF_{PP} – downward flux of PP

Consistency of the mechanistic and empirical models in representing contributions of $PP_{m/u}$ and PP_o to PP for shelf vs pelagic waters

- recall, Chl-*a* (e.g., phytoplankton biomass) not significantly different on shelf vs pelagic waters
- recall $PP = PP_o + PP_m$
- both models
  - higher $PP_{m/u}$ values on shelf vs pelagic
  - greater variability on shelf
- median values – shelf vs pelagic waters, contributions of $PP_{m/u}$
  - 20 vs 11%, mechanistic
  - 16 vs 8%, empirical
    - reasonably good closure



- $PP_{m/u}$ much greater, and PP_o much smaller contributions on the shelf for the extremes of runoff events

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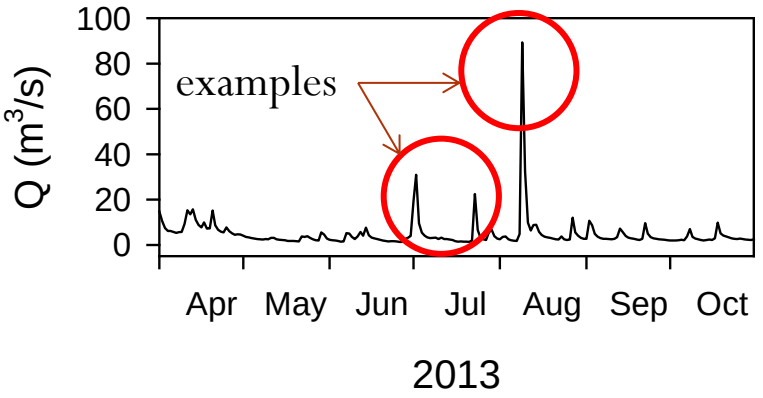
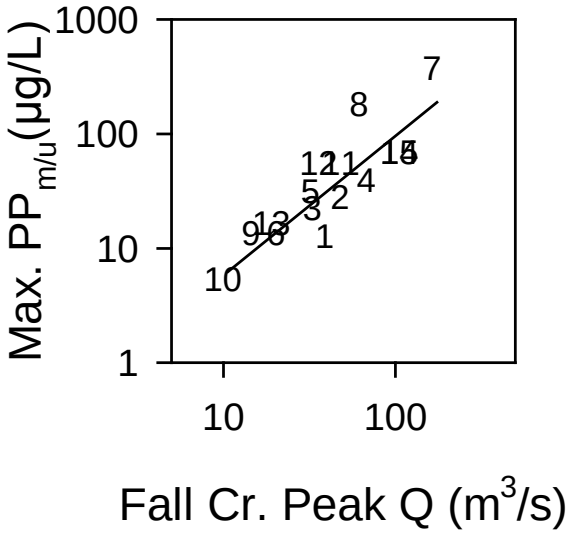
Analyses with the tested $PP_{m/u}$ model: Dependence of shelf response on runoff event magnitude, $PP_{m/u}$ vs. Q peaks

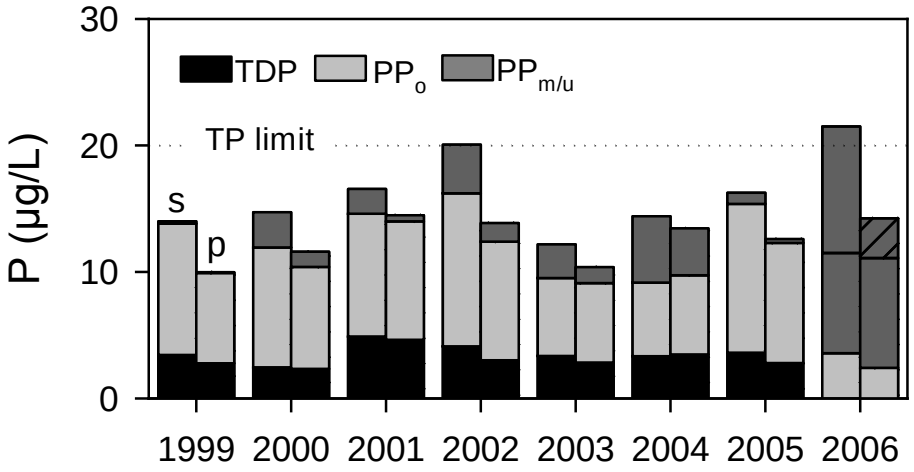
- Fall Cr. peak Q for the earlier (1999-2006) runoff events
- corresponding predicted peak $PP_{m/u}$ at Site 2 on shelf
- strong positive dependency of $PP_{m/u}$ on event magnitude
- sources of variance in the relationship-variations in ambient mixing, limitations in peak Q defining external $PP_{m/u}$ loads





Analyses with the tested $PP_{m/u}$ model: Interannual variations in predicted $PP_{m/u}$ explains much of the interannual and spatial variations in TP

- total P (TP) concentration is a trophic state metric, guidance value of 20 µg/L as summer average, in NY
- $PP_{m/u}$ variations important in regulating interannual and shelf vs pelagic differences in TP
- $PP_{m/u}$ lower at pelagic site each year
- interannual differences in $PP_{m/u}$ between sites explained much of the year-to-year differences in TP (45%)
- these interannual differences in $PP_{m/u}$ explain 47% of the year-to-year differences in TP at both sites

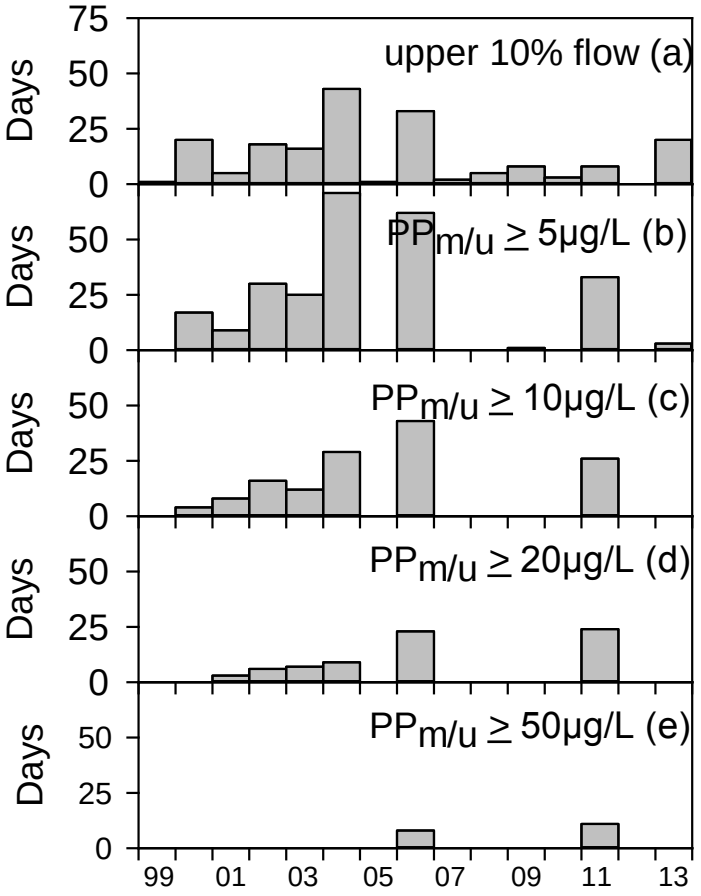


$PP_{m/u}$ – based on mechanistic model predictions

Analyses with the tested $PP_{m/u}$ model: Interannual variations in day counts of elevated concentrations on the shelf

- based on model simulations for the 1999-2013 period

- multiple $PP_{m/u}$ concentration thresholds chosen for Jun-Sept. interval, 1999-2013
- high flow events represented by number of days Fall Cr. Q was in the upper 10%
- high $PP_{m/u}$ concentrations coupled to runoff event occurrences
- major interannual variations predicted; consistency with observations
- timing of monitoring could be important to reported summer average and guidance value status
- extreme cases of high $PP_{m/u}$ predicted for 2006 and 2011



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Applicable findings from the $PP_{m/u}$ modeling initiative

- there has been a qualitative recognition of the interference of minerogenic particles for metrics of trophic state for decades
- the importance of these particles depicted here, relative to the application of TP, is likely broadly occurring
- advancements from, or value of, this $PP_{m/u}$ modeling
  - improved usage of TP as a trophic state metric
  - applicable to the numerous systems of similar setting and issues
  - advancement of water quality models to represent this issue and effects of minerogenic particles
- these advancements will be necessary to address the implications of predicted features of climate change (NOAA 2013) – more runoff events and severity of the events

Summary

- P associated with minerogenic particles (e.g., PP_m) delivered from the watershed interferes with the use of TP as a trophic state metric because of its limited bioavailability
- a mass balance-type model for unavailable PP_m ($PP_{m/u}$) has been successfully developed and tested
  - higher $PP_{m/u}$ on the shelf following runoff events is predicted , that causes irregular exceedances from TP guidance value, that is uncoupled from trophic state
- positive features of model performance included:
  - reasonable closure of predicted shelf and pelagic levels of $PP_{m/u}$ and $PP_{m/u}$:PAV_m with those from an independent empirical model (Effler et al. 2014)
  - consistency of predicted $PP_{m/u}$ shelf deposition with sediment trap observations
  - a consistent partitioning of the PP pool between $PP_{m/u}$ and PP_o (phytoplankton) for historic observations
  - consistency of post-runoff event TP and PP observations with $PP_{m/u}$ predictions
- this advancement in modeling is invaluable and appropriate for large initiatives addressing the trophic state issue through TP