# Forces united: How physical and chemical processes combine to impact soil phosphorus desorption on the way to the drain

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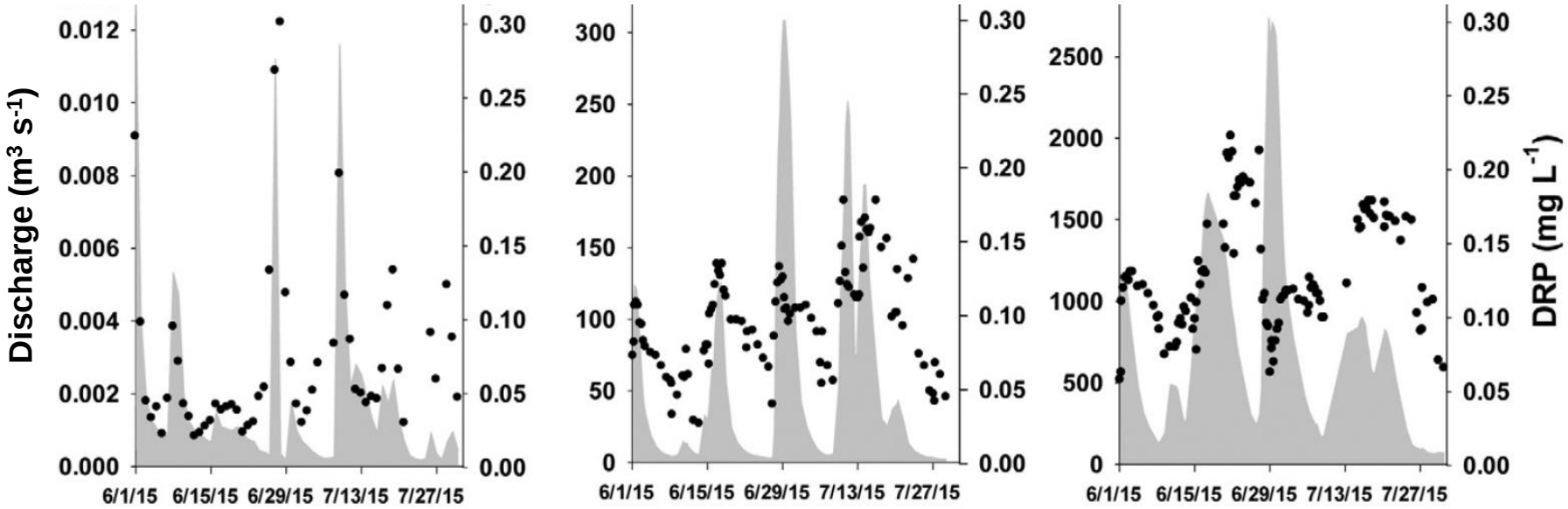
# Dissolved P is Dynamic

Field tile drain
(0.18 km$^2$)

Portage River
(1100 km$^2$)

Maumee River
(16000 km$^2$)




*King et al., 2017*

- DP loss is flashy with most loss in large events
  - True concentrations follows discharge flow rate
    - Solid:solution dynamic impacted by hydrology
- Current models cannot capture this variability. Why not?

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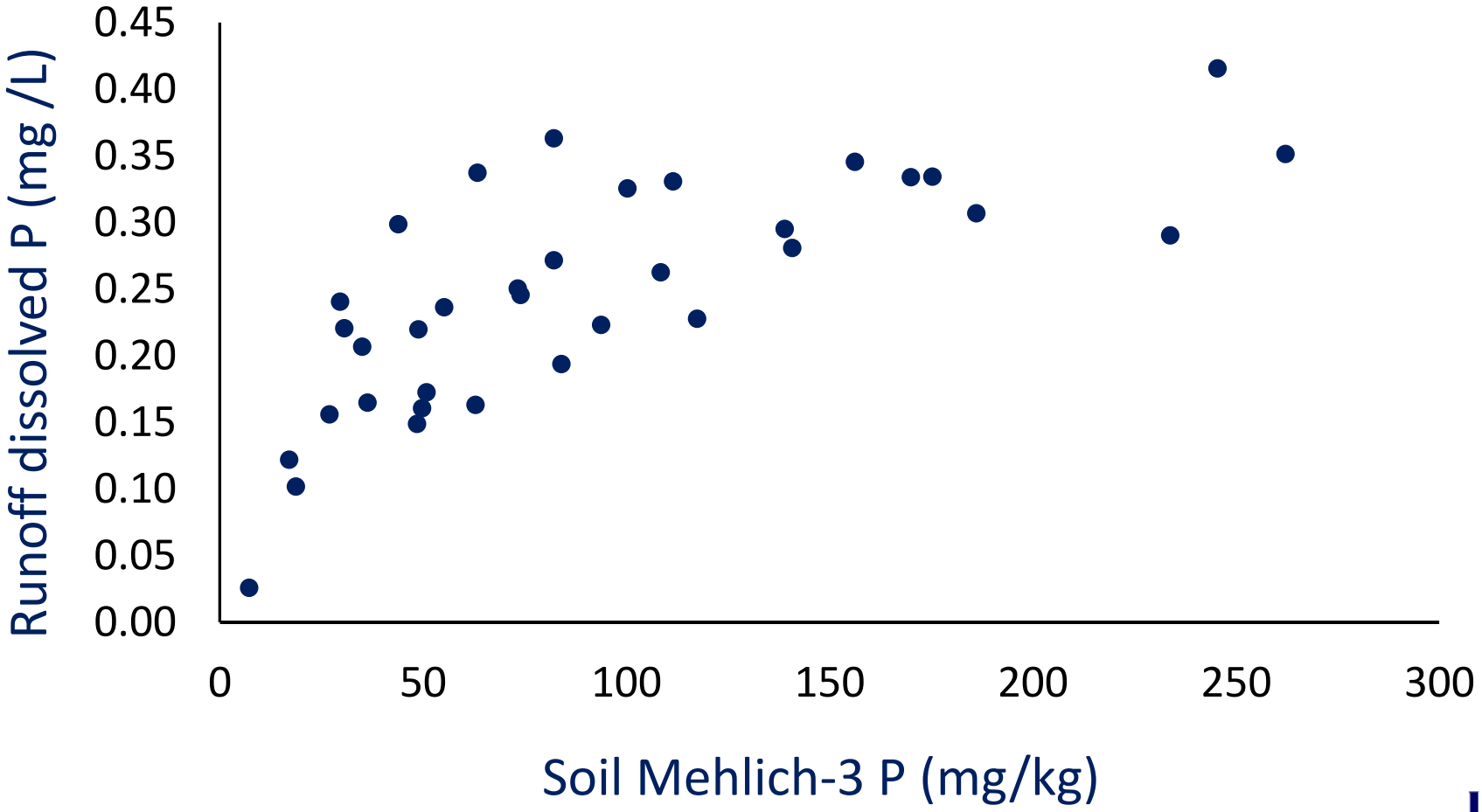
# Currently: Static estimate of DP concentrations in flow

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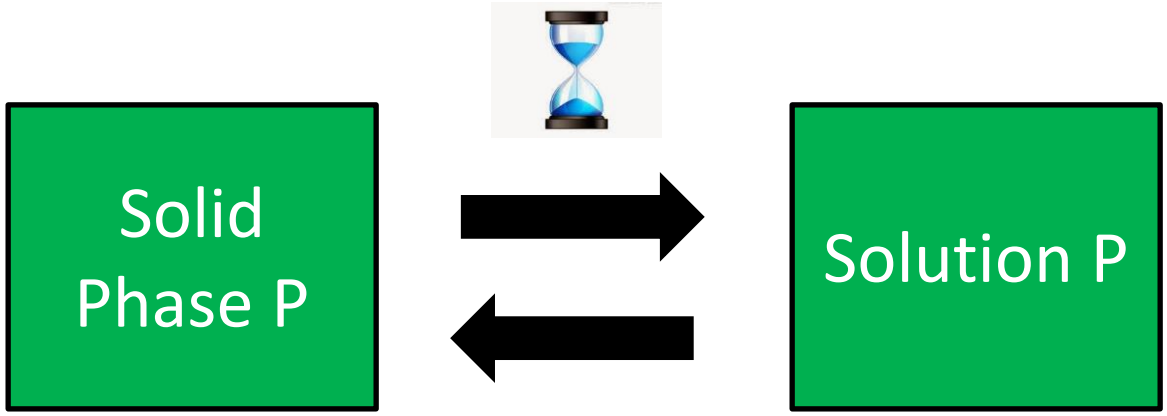
# Movement between pools requires time, not just thermodynamics




$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y$$

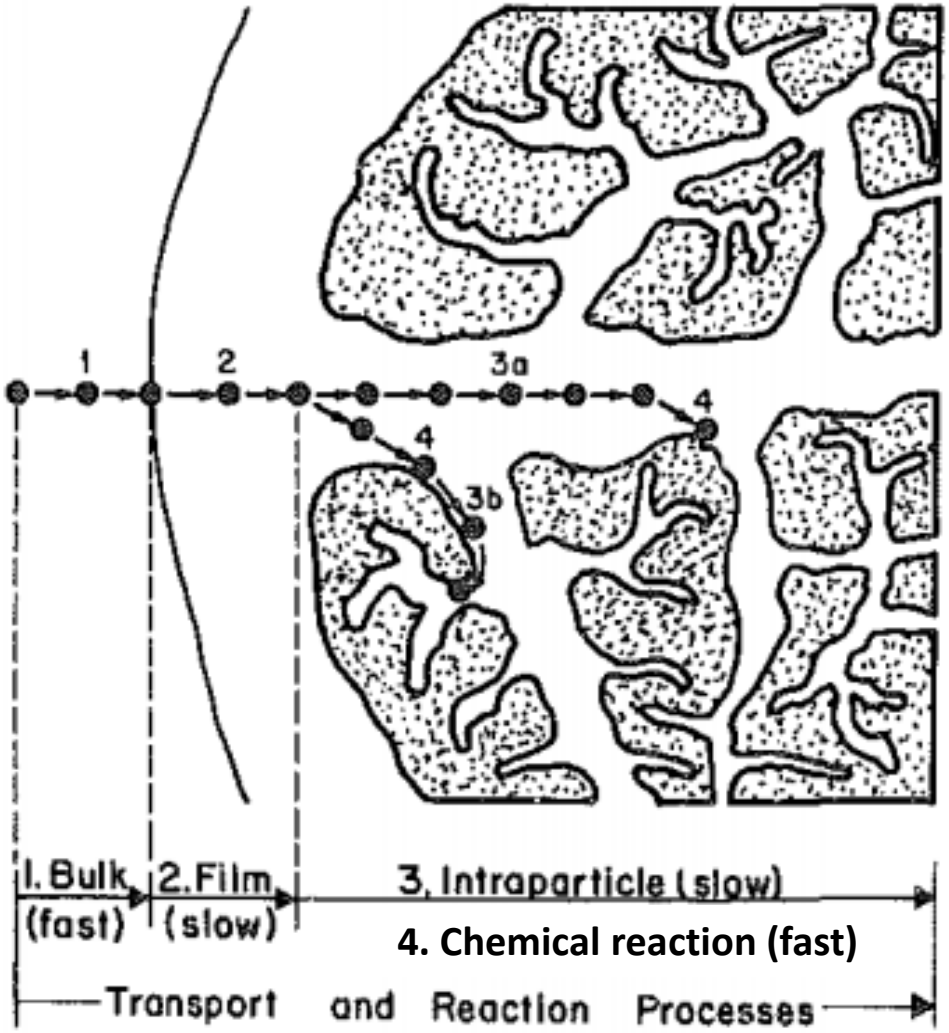
$$\frac{d[A]}{dt} = -k_1\,[A][B] + k_{-1}[Y]$$

- Kinetics
- Depends on same properties that impact equilibrium

# It takes time and water to desorb P

- ….Which is just another way of saying “kinetics and thermodynamic equilibrium”

# Not just speed of chemical reaction:




*Weber, 1984*

# P desorption is not a purely chemical process

- Chemical process of desorption is only realized through physical processes
  - Chemical alone: extremely difficult and rare
- How does physical interaction of water impact net measured desorption?
  - Quantity
  - Rate
- Thoroughly studied a single high P soil to understand this process before working on other soils

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# Physio-chemical interaction

- Two most important physio-chemical aspects to process of P desorption:
  - Reaction order
    - i.e. how does concentration affect desorption rate
  - Diffusion
- Both will impact P desorption quantity, rate, and buffering

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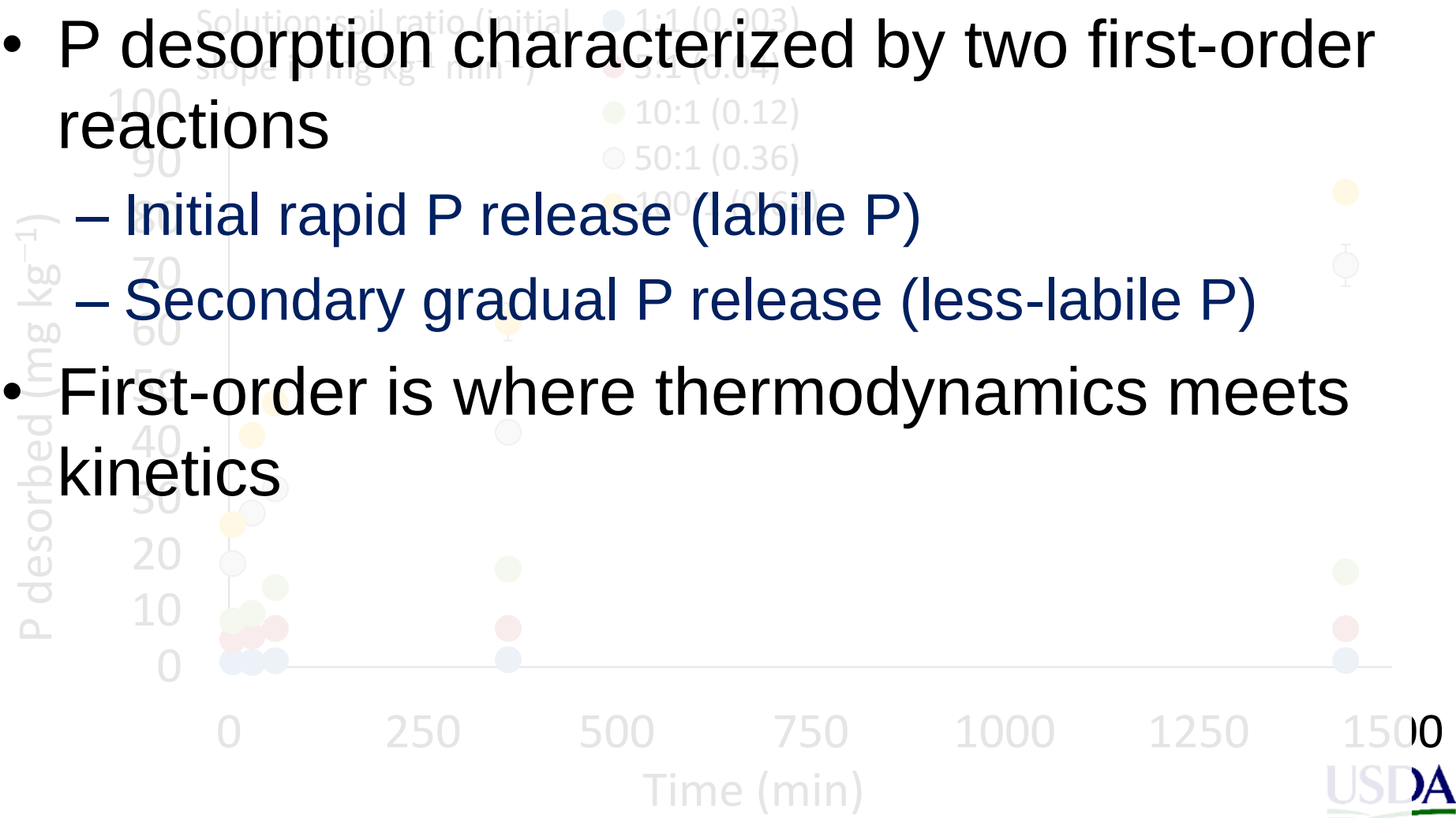
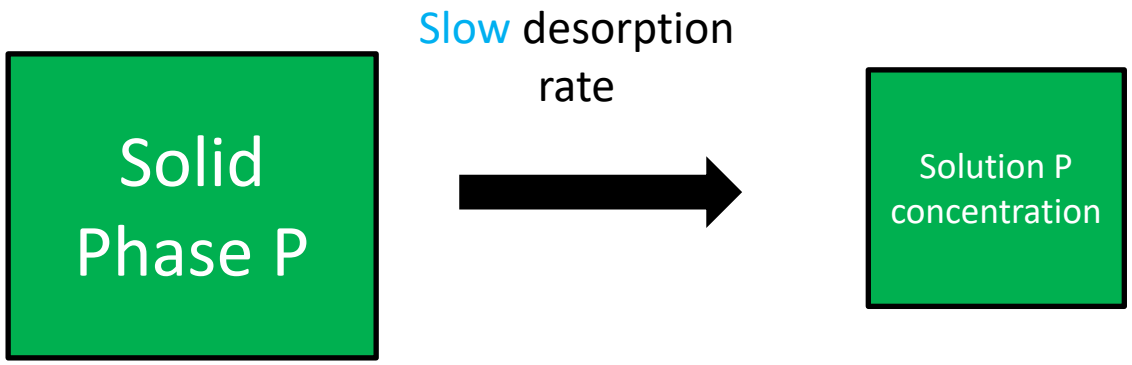
# P desorption is first-order

- P desorption characterized by two first-order reactions
  - Initial rapid P release (labile P)
  - Secondary gradual P release (less-labile P)
- First-order is where thermodynamics meets kinetics

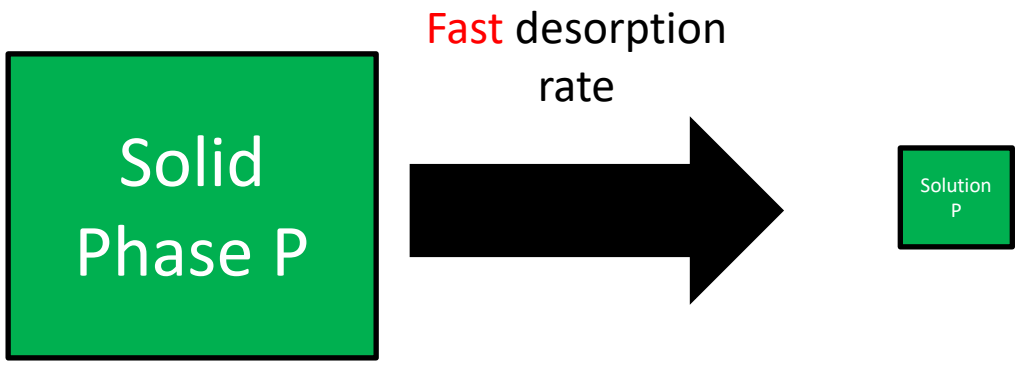


# First-order means desorption rate is concentration dependent

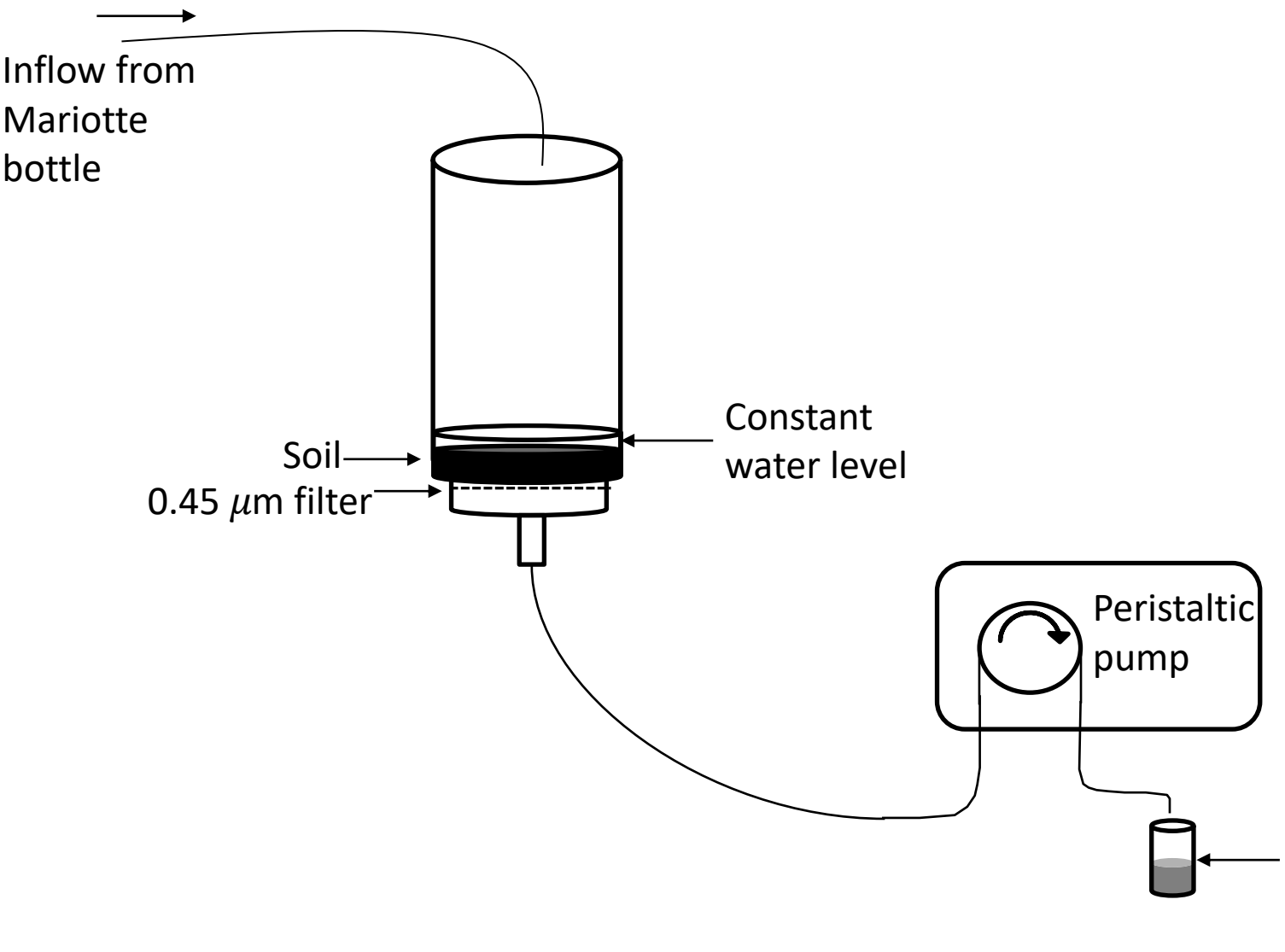



- P desorption rate increases with disparity between solid and solution phase concentration
  - i.e. P desorption rate decreases with less dilution or accumulation of solution P
    - Lesser solution:soil ratio

# First-order means desorption rate is concentration dependent

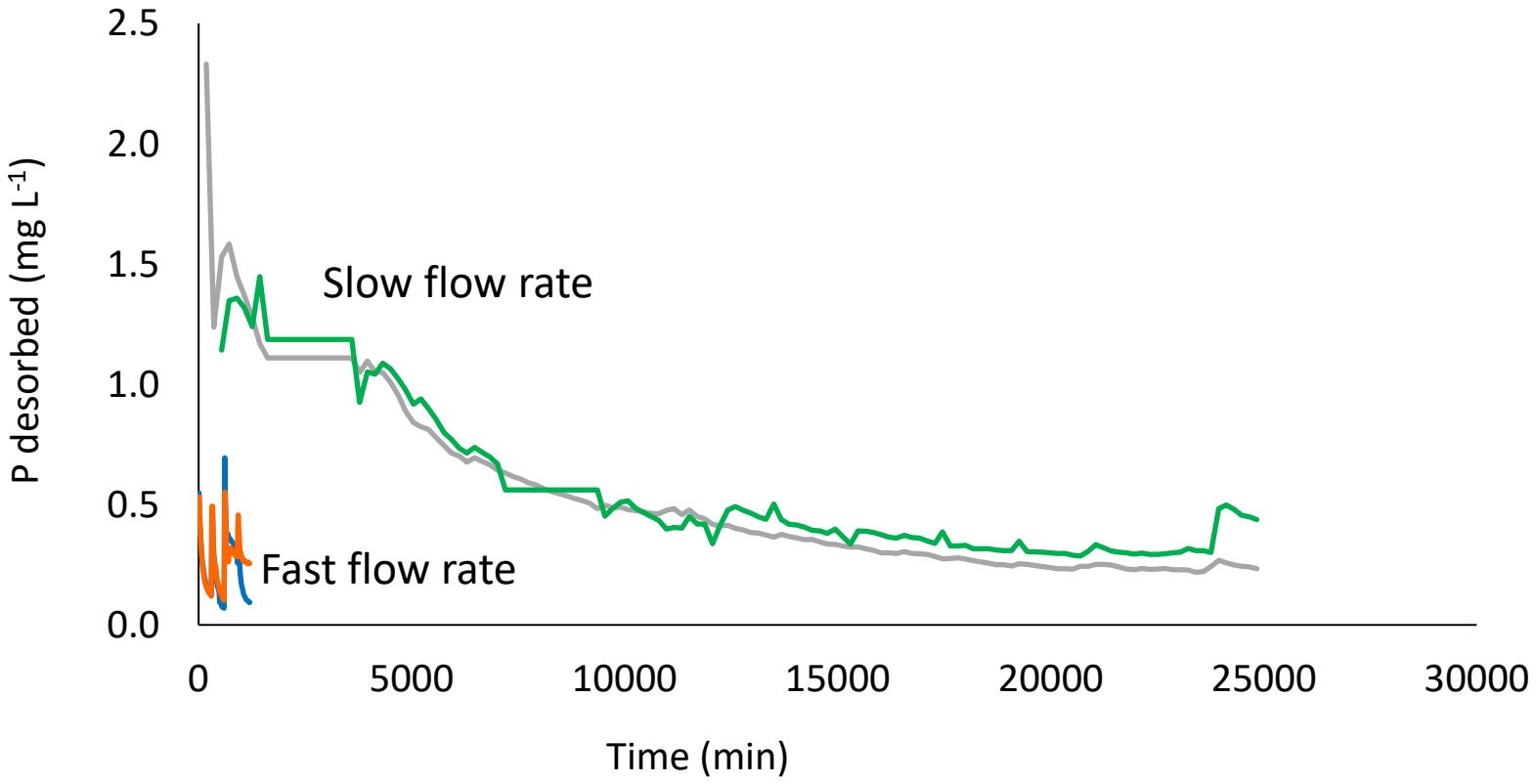



- P desorption rate increases with disparity between solid and solution phase concentration
  - i.e. P desorption rate increases with dilution and removal of solution P
    - Greater solution:soil ratio


Inflow from
Mariotte
bottle
Soil
0.45 $\mu$m filter
Constant
water level
Peristaltic
pump
Outlet:
solution to
be analyzed

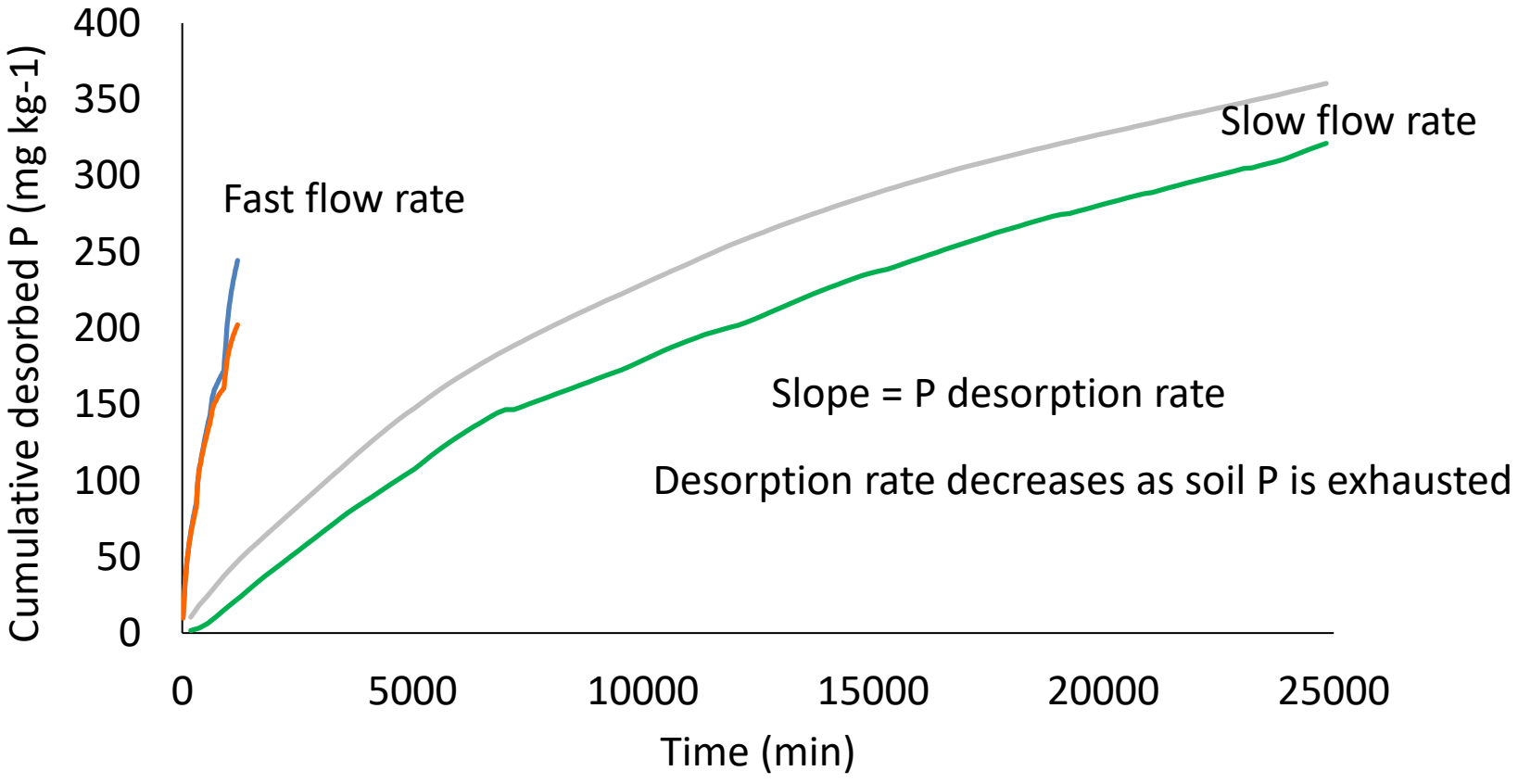
# Flow rate makes a big difference

Fast flow rate produces lower concentrations:



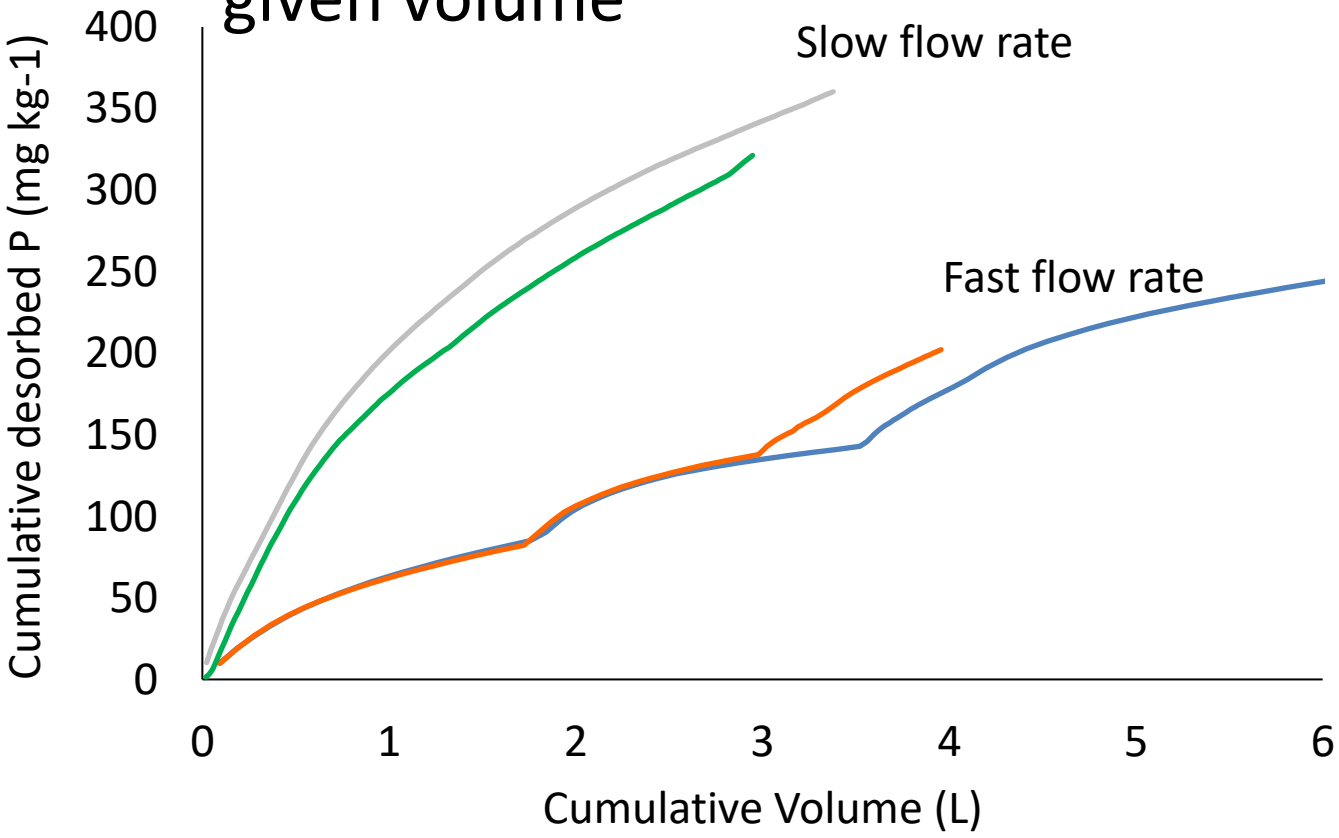
# Flow rate makes a big difference

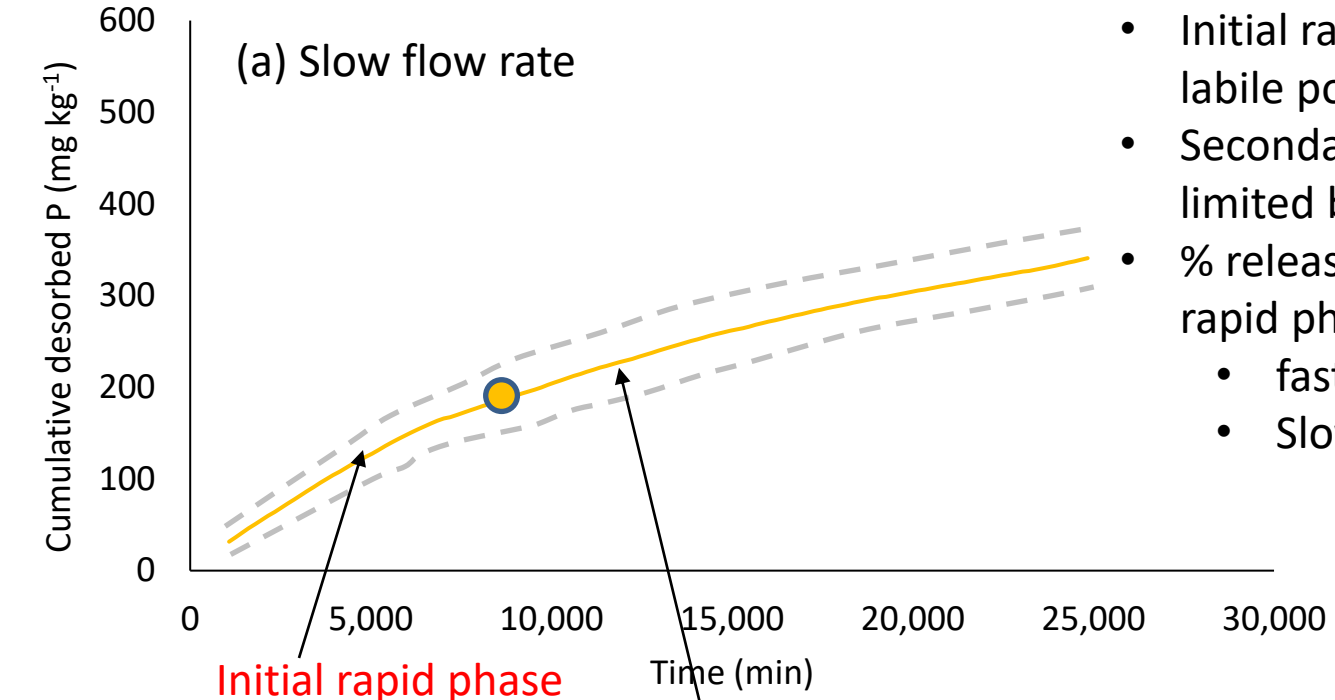
BUT, desorbs P much faster than the slow flow rate (first order kinetics)



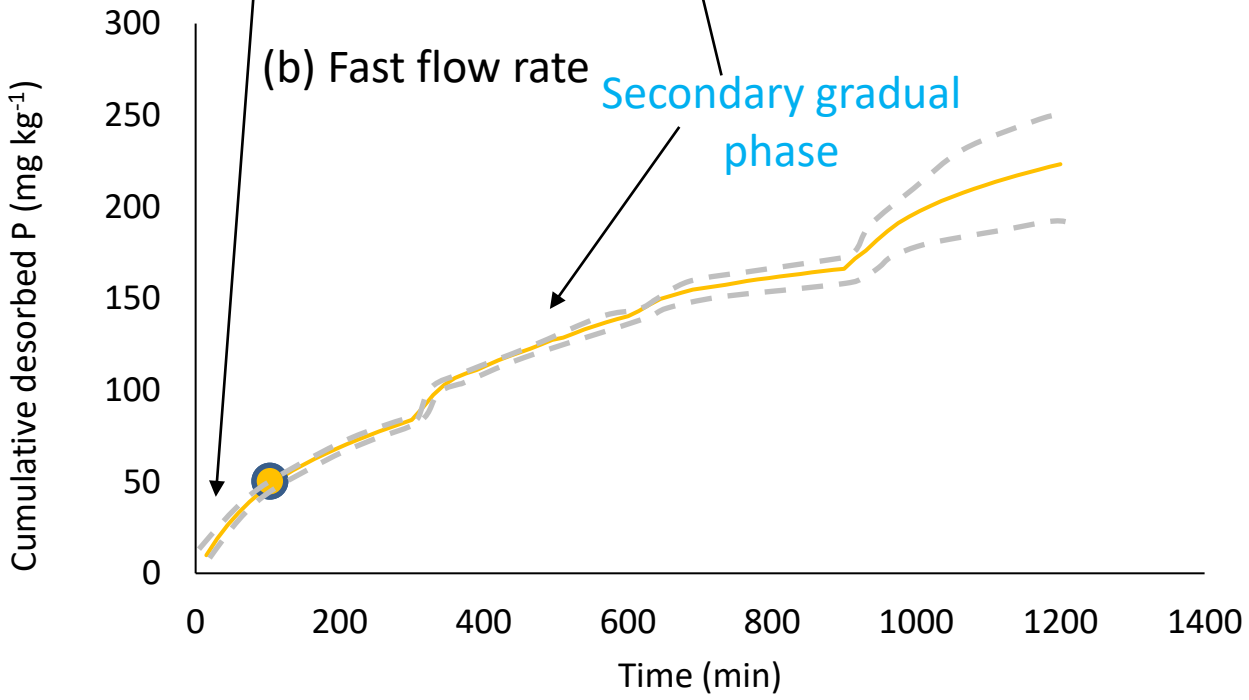
# Flow rate makes a big difference

Yet slow flow rate desorbs a greater P quantity at any given volume

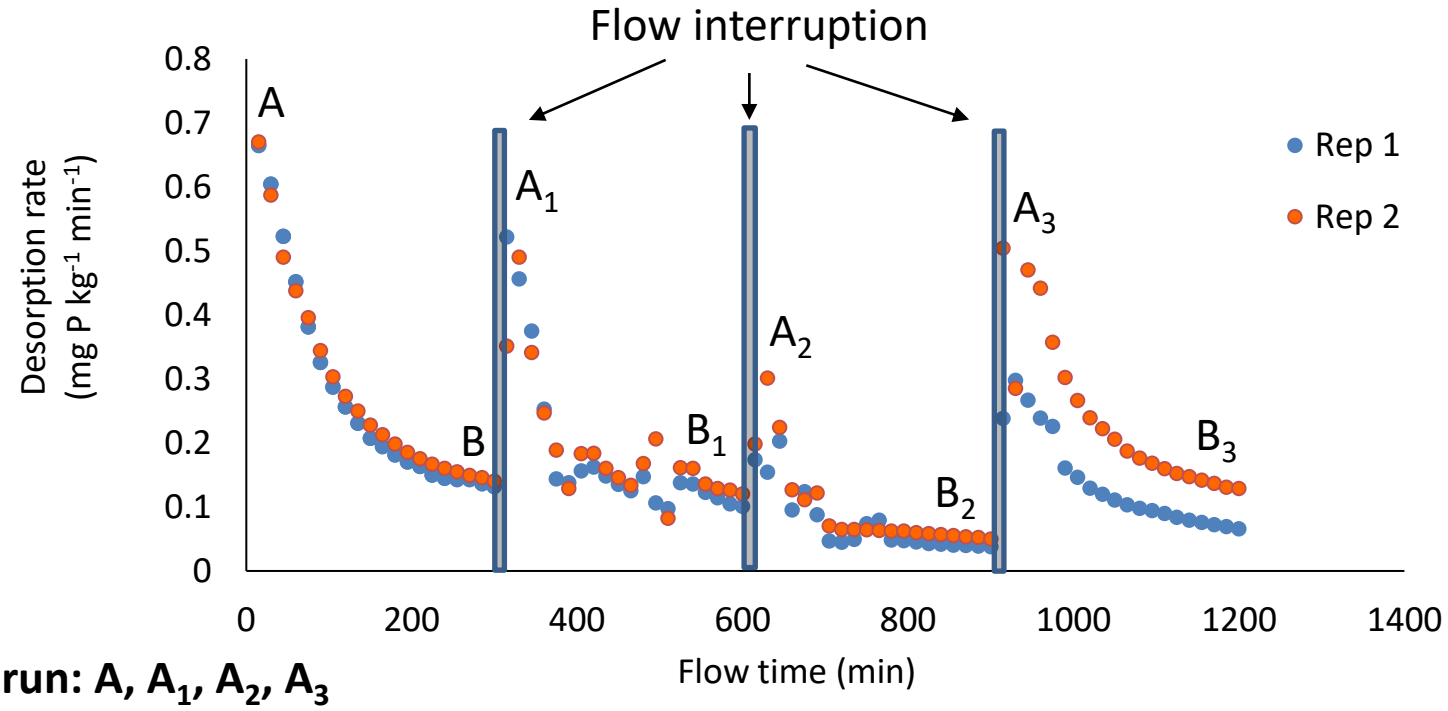





- Initial rapid desorption depletes labile pool
- Secondary gradual desorption limited by non-labile pool
- % released P desorbed in initial rapid phase:
  - fast flow rate- 22%
  - Slow flow rate- 55%

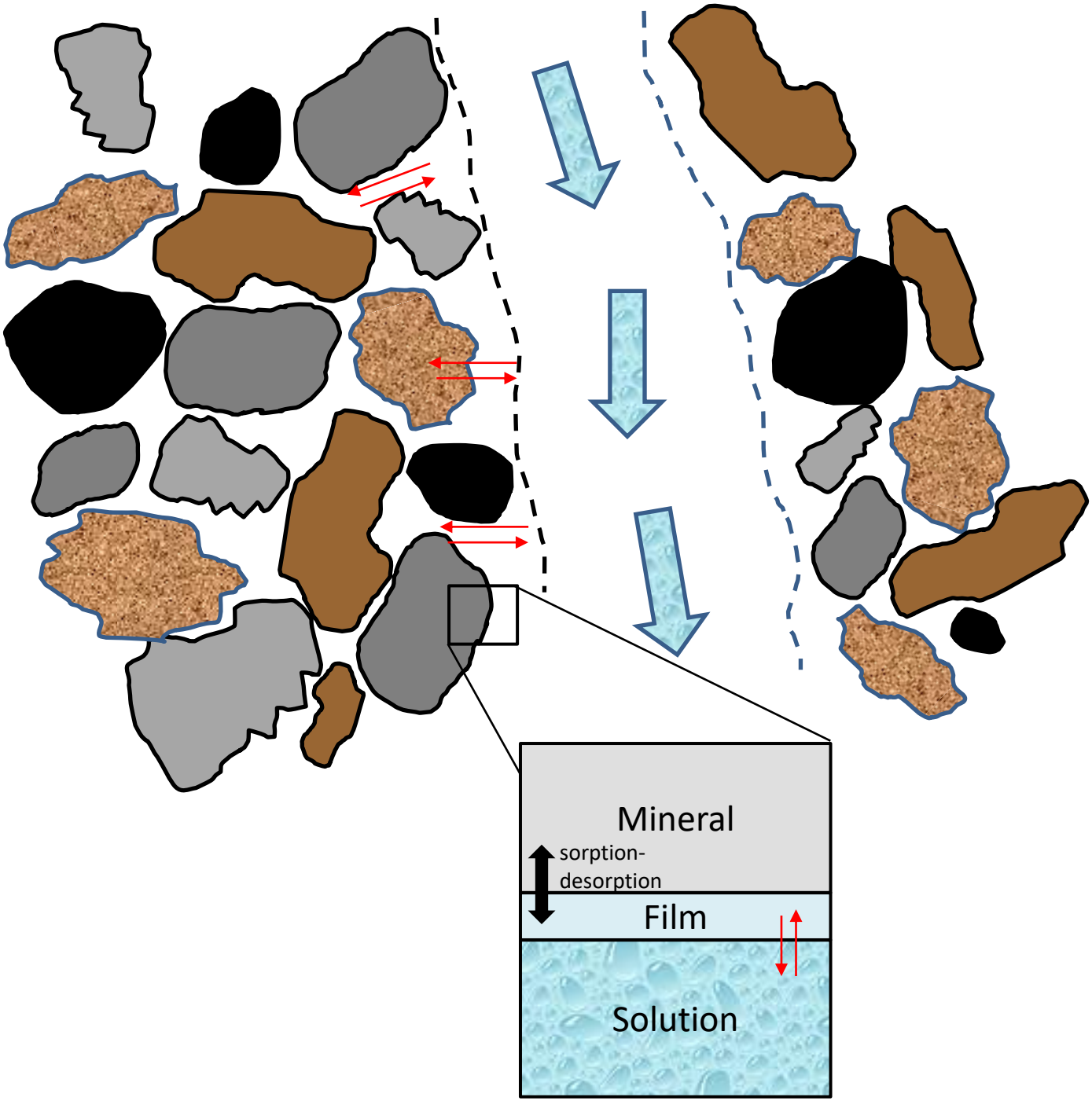


# Diffusion and buffering

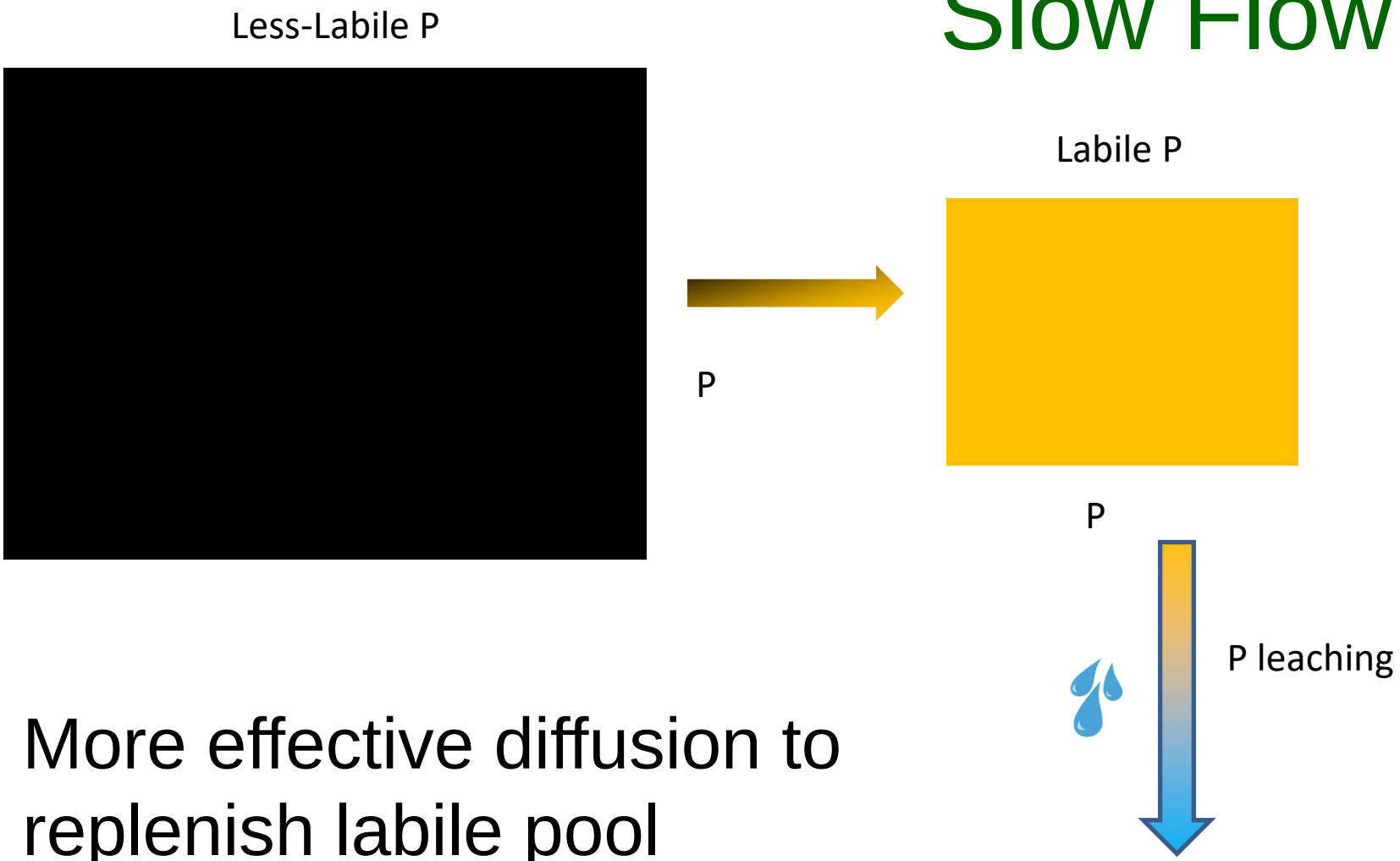



**Start of run: A, $A_1$, $A_2$, $A_3$**

- Interruption tests indicate P desorption is diffusion-limited
  - Less diffusion limitation with slow flow rate
- Diffusion IS buffering

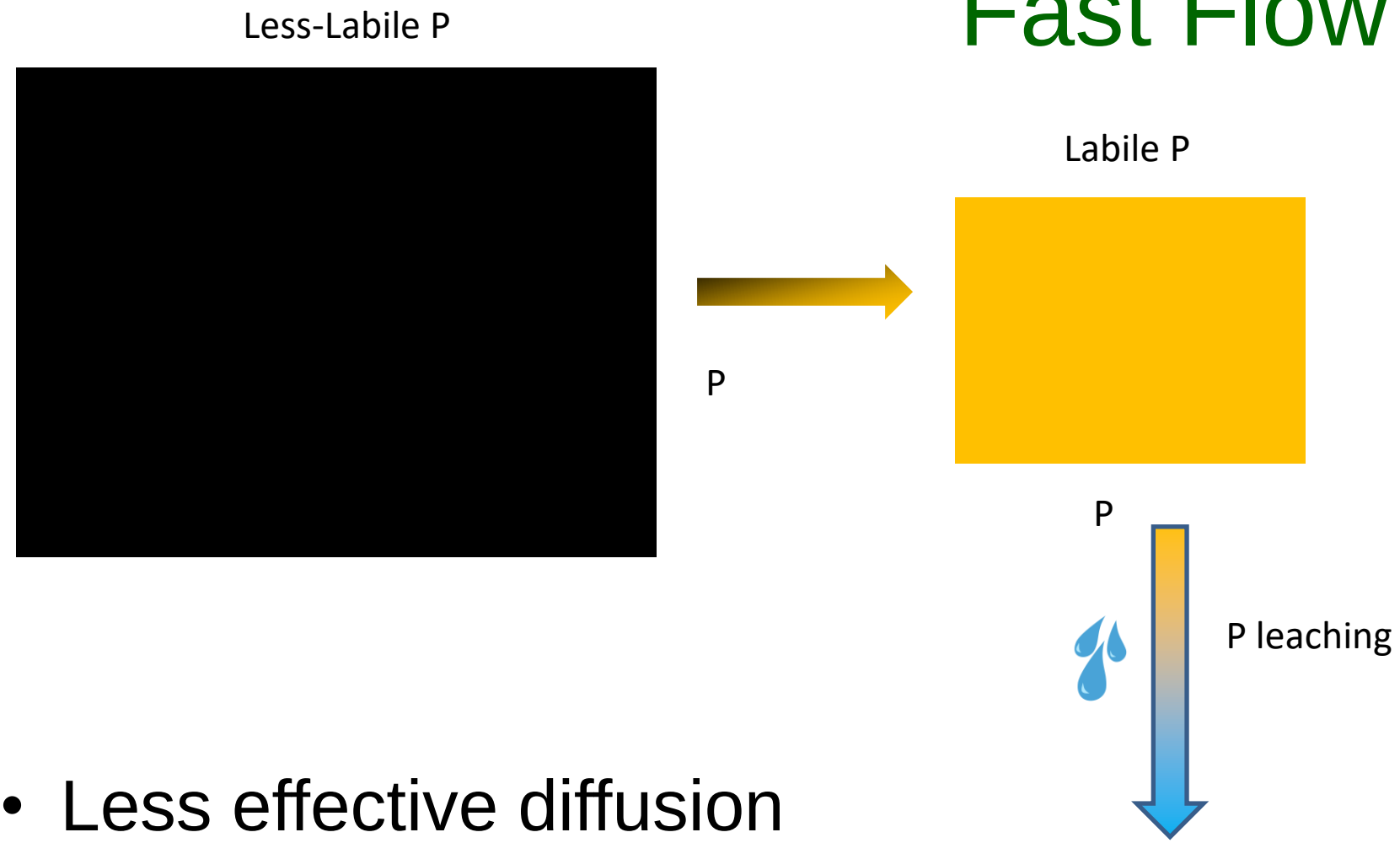

Mineral
sorption-
desorption
Film
Solution

# Slow Flow




- More effective diffusion to replenish labile pool
- Labile pool depleted slowly
  - Less-labile pool replenishment "keeps up" for a time

# Fast Flow




- Less effective diffusion
- Labile pool depleted rapidly
  - Labile pool depleted MUCH faster than it can be replenished

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# What we know

- P desorption quantity and rate are a function of:
  - cumulative solution volume, cumulative time, and discrete contact time
  - All capture by flow rate
- 2-stage first-order kinetics
  - Initial rapid rate, secondary gradual release
  - Dilution (thermodynamics) increases rate
- Desorption and buffering limited by diffusion
- Net desorption kinetics: physio-chemical

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# What we know

- Interaction between physical-chemical controls how P desorption is manifested
  - Physical process can enhance or depress desorption (quantity and rate)
    - Dilution disrupts equilibrium: promotes desorption and desorption rate
      - Faster flow rates reduces solution P concentrations, but desorbs at a higher rate than slow flow
    - Diffusion limits desorption for fast flow
      - Fast flow has lesser degree of desorption
  - i.e. what little P desorbed with fast flow rate occurred quickly, yet quantity was limited
    - Slow flow releases more P, but at slower rate and higher solution concentration

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# What we know

- Water alone can release a lot of soil P if the physical conditions are suitable
  - Depending on flow regime and time, 25 to >400 mg/kg P released with water
- Current models do not take any of this into account

# How will soil properties impact this?

- How do soil properties affect how flow rate impacts P desorption degree and kinetics?

# > 30 soils

| Soil property | range | mean | max | min | median |
|---|---|---|---|---|---|
| Clay content (%) | 16.7 | 6.5 | 17.5 | 0.8 | 6.0 |
| pH | 3.54 | 6.57 | 8.25 | 4.71 | 6.42 |
| Soluble C (mg/kg) | 501 | 284 | 616 | 115 | 207 |
| Total C (g/kg) | 34 | 20 | 39 | 5 | 18 |
| M3-P | 1378 | 260 | 1394 | 31.2 | 180 |
| Water soluble P (mg/kg) | 44.2 | 11.3 | 45.4 | 1.2 | 8.3 |
| $P_{ox}$ (mg/kg) | 7456 | 4003 | 7596 | 140 | 5379 |
| $P_{ox}$ Saturation (%) | 94 | 25.3 | 96.3 | 2.31 | 19.4 |
| M3-P Saturation (%) | 120 | 31.0 | 120 | 2.45 | 22.9 |
| Total P desorbed at 2 L: fast flow rate (mg/kg) | 218 | 50.3 | 228 | 9.7 | 37.3 |
| Total P desorbed at 2 L: slow flow rate (mg/kg) | 452 | 98.0 | 459 | 6.6 | 64.1 |

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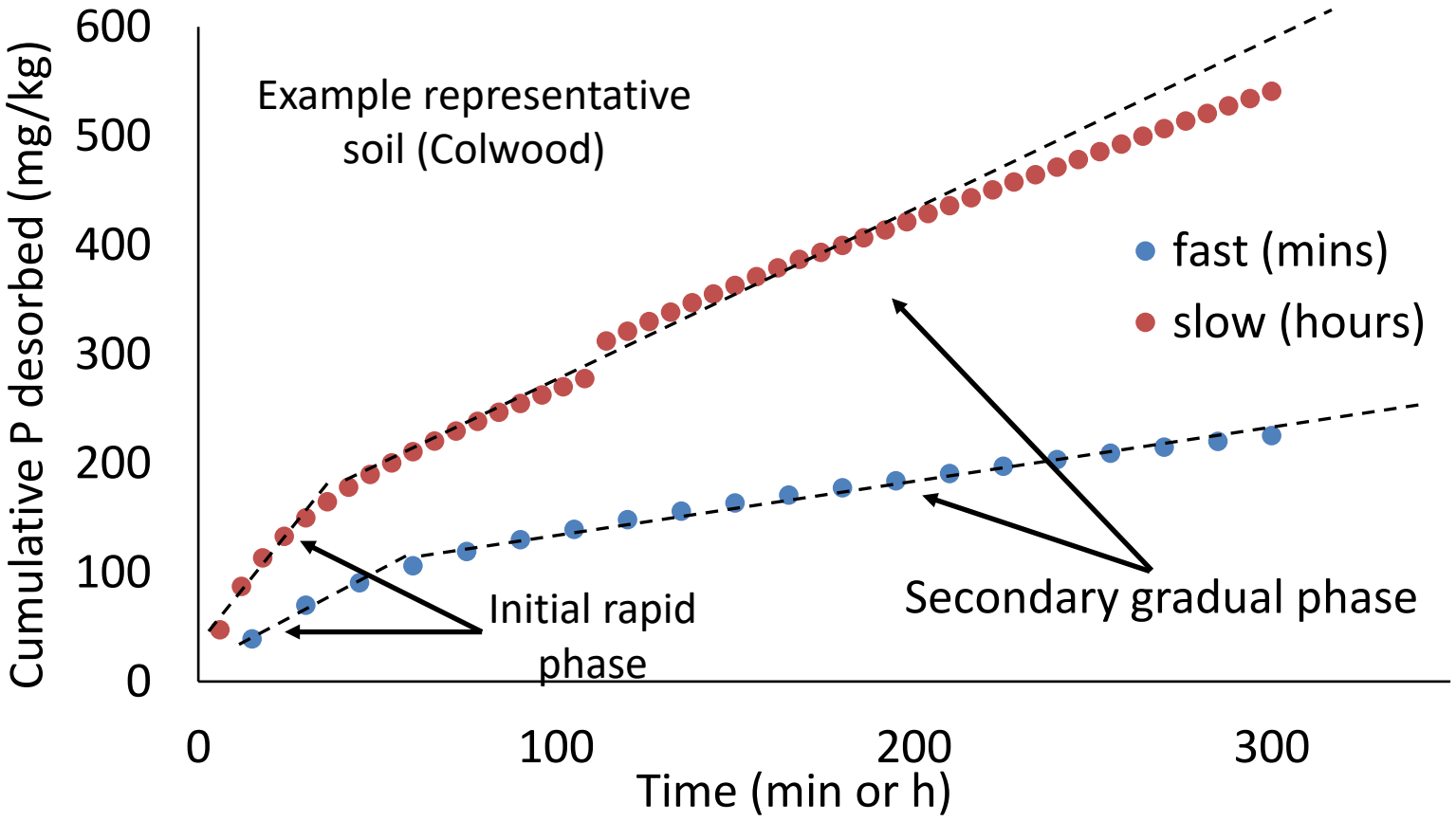
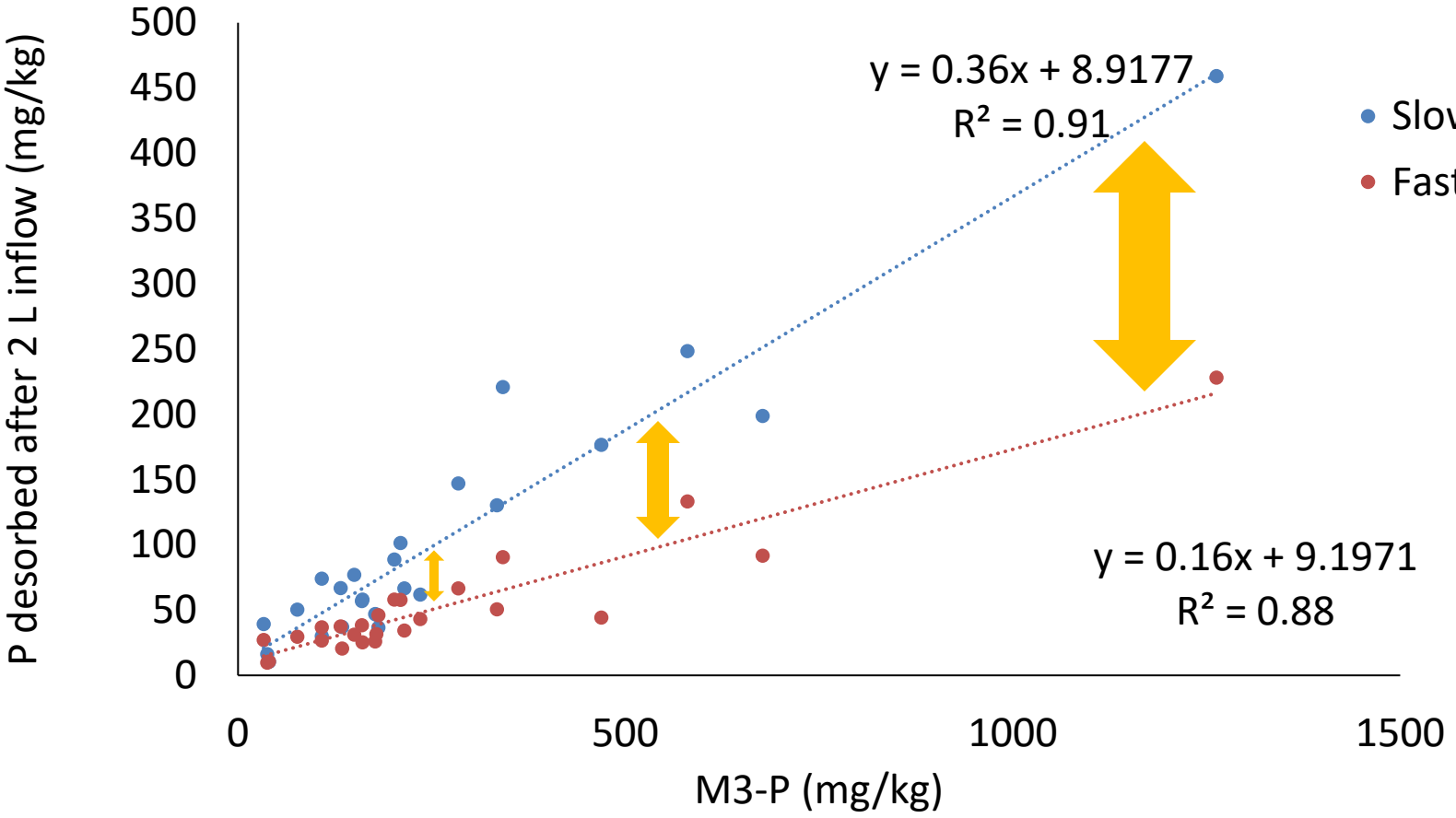
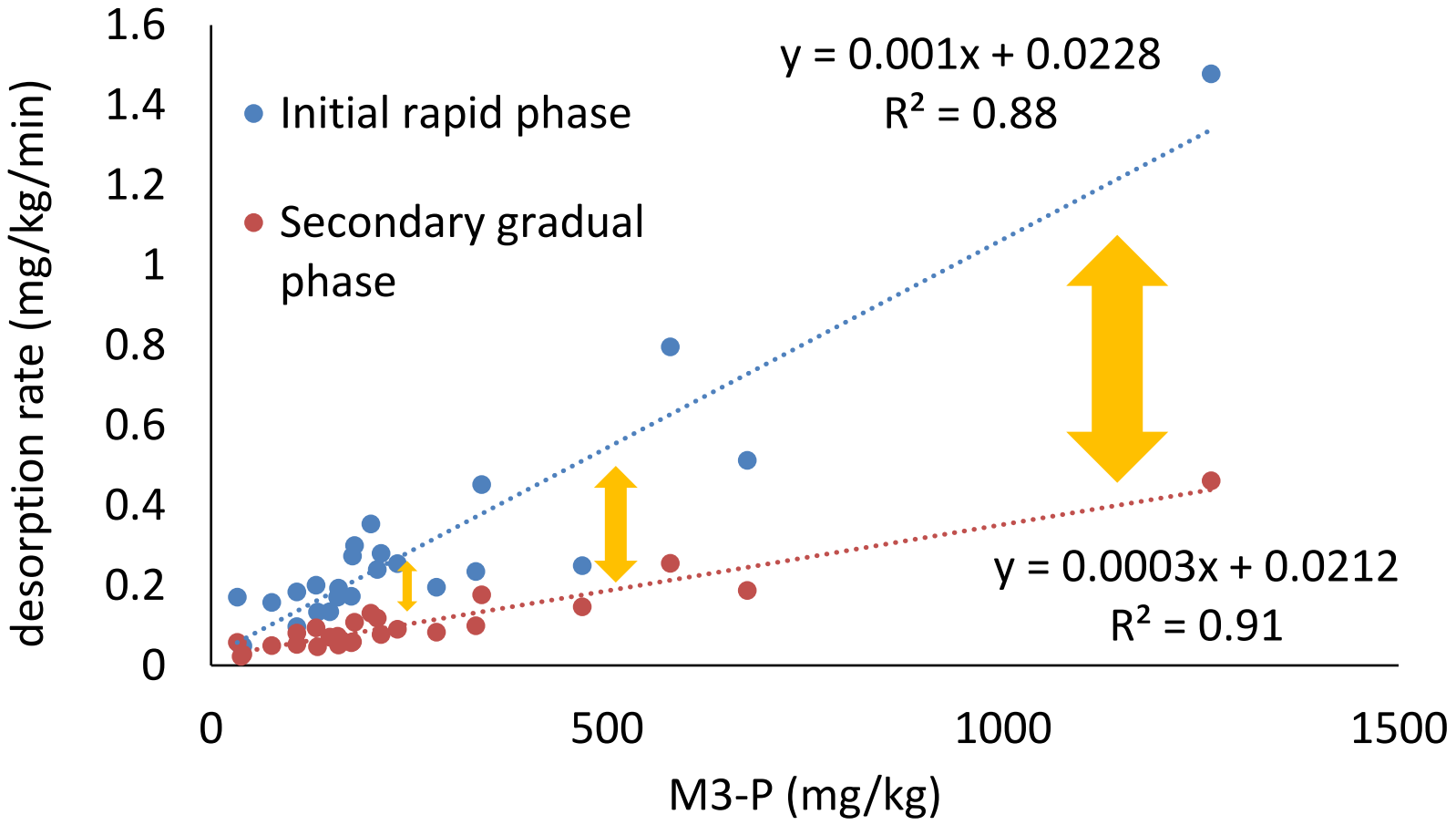
- Same trend for all
  - Dual phase P release (rapid followed by gradual)
  - Fast flow = less P released at a more rapid rate
  - Greater solution P concentrations with slow flow



- Desorption quantity:
  - Clearly more P released with slow flow and from soils with greater soil M3-P
  - Difference in P released between fast and slow flow increased with increasing soil M3-P content



- Desorption rate:
  - Increased soil P concentration means faster P release
    - i.e. First order kinetics
    - Difference in P desorption rate between initial rapid phase and secondary gradual phase increased with increasing soil M3-P content



# Who Cares?

- Understanding the nature of P behavior will help us
  - Improve transport models
  - Create new P fertility recommendations
  - Better target best management practices
- *Penn, C. J., Williams, M. R., Camberato, J., Wenos, N., & Wason, H. (2022). Desorption Kinetics of Legacy Soil Phosphorus: Implications for Non-Point Transport and Plant Uptake. Soil Systems, 6(1), 6.*

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Questions?
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