Honing in on Sources of Dissolved P: Targeting Legacy Soils with Phosphorus Removal Structures

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Why we care about the dissolved pool:

- It’s what plants truly uptake
- Stronger eutrophication agent
- More difficult to control or manipulate compared to solid-bound/particulate P
  - With regard to plant availability
  - With regard to non-point drainage losses
- Dissolved P is dynamic
  - Solubility varies with chemical conditions
  - Behavior is a function of more than simple solubility
    - Physical location, hydrology, kinetics
Precipitated minerals:
- Ca-P & Mg-P
- Al-P & Fe-P

Intensity (solution phase)
- sorption
- precipitation
- de-sorption

Quantity (Solid phase)
- precipitation
- anion exchange

Soil Components
- ligand exchange
- Plant uptake
- Runoff & leaching

Plant uptake

Runoff & leaching
• DP loss is flashy with most loss in large events
  – True concentrations follows discharge flow rate
    • Hydrology is partly controlling desorption from soil, not just loads!
• Current models cannot capture this variability. Why not?
Movement between pools requires time, not just thermodynamics

- Kinetics
- Depends on same properties that impact equilibrium

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

- Kinetics
- Depends on same properties that impact equilibrium
It takes time and water to desorb P

\[ \text{P in water} \]

\[ + \]

\[ = \]

….Which is just another way of saying “kinetics and thermodynamic equilibrium”
Not just speed of chemical reaction:

Chemical process of desorption is only realized through physical processes

Weber, 1984
P desorption is not a purely chemical process

Objective:
How does physical interaction of water impact net measured desorption?
  • Quantity
  • Rate

We thoroughly studied a single high P soil to understand this process before working on other soils (Penn et al., 2022; Soil Processes)
Physio-chemical interaction

- Two most important physio-chemical aspects to process of P desorption:
  - Reaction order
    - i.e. how does concentration affect desorption rate
    - First-order is where thermodynamics meets kinetics
      - Dilution!
  - Diffusion

- Both will impact P desorption quantity, rate, and buffering
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
Flow-Through Method

Inflow from Mariotte bottle

Soil

0.45 μm filter

Constant water level

Peristaltic pump

Outlet: solution to be analyzed

Tested a “fast” and “slow” flow rate (7 vs 0.13 mL/min)
Flow rate makes a big difference

Fast flow rate produces lower concentrations:
Flow rate makes a big difference

BUT, higher flow rate desorbs P much faster than the slow flow rate

Cumulative desorbed P (mg kg⁻¹)

Slope = P desorption rate

Desorption rate decreases as soil P is exhausted
Flow rate makes a big difference

However, slow flow rate desorbs a greater P quantity at any given volume than fast flow rate.
2-stage first-order kinetics:

- Initial rapid desorption depletes labile pool
- Secondary gradual desorption limited by less-labile pool
Diffusion and buffering

• Interruption tests indicate P desorption is diffusion-limited
  – Less diffusion limitation with slow flow rate

• Diffusion IS buffering
Mineral Film sorption-desorption
• More effective diffusion to replenish labile pool
• Labile pool depleted slowly
  – Less-labile pool replenishment “keeps up” for a time
• Less effective diffusion

• Labile pool depleted rapidly
  – Labile pool depleted MUCH faster than it can be replenished
What we know

• P desorption quantity and rate are a function of:
  – Time and Water!
    • Both captured by flow rate
    • Physio-chemical process

• 2-stage first-order kinetics
  – Initial rapid rate, secondary gradual release
  – Dilution: via thermodynamics increases rate

• Desorption and buffering limited by diffusion

• Slow flow desorbs more P than fast flow, but does it at a slower rate
How do soil properties affect how flow rate influence P desorption degree and kinetics?
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
Changes in flow rate have a more dramatic effect on clay soils than sandy.

Clay soils are more buffered and therefore a much larger less-labile pool

- Have much more total P for a given level of M3-P compared to sandy soils
- Less-labile pool able to keep feeding the labile pool faster for clays because of first order kinetics (bigger pool = faster)

  • BUT this potential is more fully realized at slower flow rates
    - Clay soils have much more physical restrictions than sand, and therefore are diffusion limited
      » You overcome diffusion limitations at slower flow rates
      » i.e. fast flow rates do not allow for less-labile P and diffusion as much
Who Cares?

• Understanding the nature of P behavior will help us
  – Improve transport models
  – Create new P fertility recommendations
  – Better target best management practices

• …..Because water-soil interactions matter!
Water sources from near the soil surface = greater DRP concentration
Discharge and water sources vary with antecedent conditions impacting DRP

WT<1m
Lower, less variable DRP

WT>1m
Greater, more variable DRP
**WET conditions**
- Water table at/above tile depth
- Large flows $\propto$ precipitation
- Groundwater dominated
- Lower, less variable DRP

**DRY conditions**
- Water table at/below tile depth
- Small or negligible flows
- Soil water/precip. dominated
- Greater, more variable DRP
Soil-water Interaction matters:

STP is not the only factor controlling P loss!

More frequently above target for Mar-July DRP load
What to do when you have a legacy P soil?
“Legacy Phosphorus”

Cease P application and begin P drawdown with crops in 1998

Soil test P (mg/kg)

Fiorellino et al., 2017

Safe soil P level
P Removal Structure Theory

Retained P in PSM

Dissolved P from flow

Low-P water

PO₄³⁻
Fe
PO₄³⁻
Fe
PO₄³⁻
Al
PO₄³⁻
Al
PO₄³⁻
Al
PO₄³⁻
Al
3 Necessary Components

- Effective PSM in sufficient quantity
- Sufficient flow rate and contact time
- Ability to retain and replace PSM
Many Types of Structures
Phosphorus Sorption Materials

- Metal filings
- Steel slag
- Mine drainage residuals
- Manufactured PSMs
- Fly ash
- Waste recycled gypsum
Physical Components

• Distribution system for un-treated inflow water
  – Usually perforated pipe

• PSM bed

• Drainage/collection pipes for removing treated water from structure
  – Treated water must be removed so un-treated water can enter
    • Usually perforated pipe
DEFINITION
A system designed to remove dissolved phosphorus (P) from surface runoff, subsurface flow, or groundwater usually consisting of a portion media with a high affinity for dissolved P, a containment structure that allows flow through the media and retains the media so that it does not move downstream, and a means to remove and replace the media.

PURPOSE
This practice is applied for the following purpose:
To improve water quality by reducing dissolved phosphorus loading to surface water through the sorption of phosphate (dissolved) P from drainage and runoff water.

CONDITIONS WHERE PRACTICE APPLIES
This practice applies where phosphorus (P) presents a resource concern to surface water bodies and is mobilized and transported as a dissolved constituent and where a phosphorus sorption product is available locally. Sources of phosphorus sorption material (PSM) include steel slag, dredging materials, acid mine drainage residuals, fly ash, and gypsum waste. PSMs are typically high in Calcium (Ca), Aluminum (Al), and Iron (Fe). Sources of dissolved P in agricultural areas include cloches, livestock heavy use areas, manure storage and handling areas, fields saturated with P relative to the soil sorption capacity, and other areas with high impervious surface area and converging flow. Sites typically have runoff containing dissolved phosphorus > 0.5 mg L⁻¹.

This standard is not for treatment of particulate phosphorus, which is typically bound to soil particulate. If untreated P is a concern, use the criteria found in NRCS Conservation Practice Standard (CPS) 180, Sediment Basin or CPS 638, Water and Sediment Control Basin.

CRITERIA
General Criteria Applicable to All Purposes
Divert phosphorus-rich flow into a bed of sorption media where the water is in contact with the media for a certain amount of time (retention time, RT), before being able to freely flow out of the material by gravity.

*Refer to Stone et al., 2012, and PHROCS software. **These are critical assumptions that need testing.
## P-TRAP Design Software

### Input
- **Site hydrology**
  1. Peak flow rate
  2. Annual flow volume
  3. Dissolved P level
  4. Max footprint
- **P removal & lifetime**
  1. Target P removal (%)
  2. Target lifetime
- **PSM characterization**
  1. P sorption
  2. Safety
  3. Physical properties

### Output
- **Design parameters**
  1. Area
  2. Mass of PSM
  3. Depth of PSM
  4. Pipe reqmt

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**Model**
P-TRAP Software

Google: “P-Trap phosphorus”

https://www.ars.usda.gov/nserl/ptrap
If a site is worth treating, it will require a large mass of PSM.

- High flow rate
- Sufficient contact time
- Useful lifetime

Useful lifetime
Cartridge Filters and small modular boxes?

- Portable, easy to install
- Only works in limited situations
  - Is it worth using them?
  - Limited amount of PSM
- Poor flow rate
Filter Sock?
Limited mass, contact, and contact time

Flow over the PSM: 6% P removal
Flow through the PSM: 32% P removal
Current State

• The technology is effective but can always be improved

  – Many structures constructed and monitored throughout the world

  • Penn et al., 2017; Water (review paper)

• Current research is dedicated to decreasing cost and improving efficiency
Confined Bed Structure

- 40 tons treated slag
- Handled ~ 1000 gpm flow
- $5 K

Penn et al., 2014; JSWC
Ditch Filter

• Allows large amount of material to be used
• Easy to build
• Use flow control to build head
• Low cost (< $4K)
• Probably best option for ditches
Blind Inlets

- Replacement of tile riser with gravel bed within field depressions
- Reduce particulate P via sediment filtration
  - Variable performance: ~ 40% over 12 yr
- Little to nothing for dissolved P

Gonzalez, Penn, Livingston; Water, 2020.
Blind Inlets

- Runoff flow into depression
- Downward flow through gravel-sand
- Treated water collection manifold
- Treated water outlet to tile or ditch

Diagram showing a blind inlet system with treated water collection manifold.
Modified blind inlet: Auburn, IN

- Alternative to limestone: 12 inches of sieved steel slag over railroad ballast
- Installed 2016; 15 tons slag. Treats surface water only.
- 2018: > 46% of the load
- 2018: removed 80% of glyphosate, 94% dicamba
- Gonzalez, Penn, Livingston: Water.
- 2021: Change to metal shavings/gravel for increased performance
- CHEAP: only about 3K
Modified bio-retention cell

- Urban blind inlet
- Same principle, but urban setting

Kandel et al. 2017; Water
Tile Drains

Drainage Ditch

Tile inlet: untreated water

Downward flow through PSM

Collection manifold for outlet

Treated water outlet

Distribution manifold for untreated water

Vertical pipe carrying untreated water downward

Collection manifold for untreated water

Impermeable liner/layer

Upward flow through PSM

Treated water outlet

Tile Drains

Drainage Ditch
Subsurface Tile Bed Filter, NE OH
In-tank tile drain structure

- 2 tons activated alumina
- Designed to remove 40% of 10 yr-load
- Currently monitored
- ~ $12K
Subsurface tanks: NW OH

- Site B: Metal shavings
  - effective removal of 49% of DRP load
- Site I: Alcan
  - effective removal of 45% of DRP load
  - 96% of DRP that enters P-filter is removed
  - Captured ≤5 kg of P over two years at each site
Metal shavings mix (sand or gravel)

- Pilot box: 300 lbs metal/sand or metal/gravel mix (8% metal)
- Received 130K gallons for overall 50% cumulative DP load reduction
- Cheap: $300/ton for metal
• Buried bed filter for tile drain: metal shavings/gravel
• Swine farm in Holland, MI
  – Top-down flow
  – Bottom drainage pipe layer shown
• Top-down flow
• Upper layer of inflow drainage manifold shown here
• Covered with a tarp before burial
• Completed
• Used flow-control as bypass
• Cost ~ $7,000
  – Levy Co./Plant Tuff
Combine with treatment wetlands or WaSCOBB

Contributing 20 Acre Watershed to Ag Runoff System

Jeremy Freund, Outagamie County Land Conservation Department
Combine with treatment wetlands or WaSCOB

• Advantage
  – Wetland drops out sediment
    • Removed particulate P
    • Prevents clogging of P removal structure
  – Provides a hydraulic buffer for surface water
    • Don’t need to treat 2000 gpm if you can store it and slowly release
      – Although it still needs to be treated at a reasonable flow rate
    • Water table control structure can do this for tile drainage
Do not use normal slag for treating subsurface drainage unless you plan to replace media annually

- Don’t use any Ca-based PSM for subsurface drainage
- Works fine for surface water
- Works good for silage runoff
Mobile P-removal demo unit
Training Modules In-Process: 2022

Designing a Phosphorus Removal Structure

Some trade names are used in this course to provide an understanding of equipment form and function. The USDA does not endorse any specific company.
Questions?
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