

Environmental Water Quality BAE 452/552

Session 10
Specific Pollutants & Interactions in Soils I

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Specific Pollutants in Soils

- Soil Phosphorus
- Nitrogen in soils
- Organic chemicals
- Metals
- Soil microorganisms
- Pathogenic microorganisms

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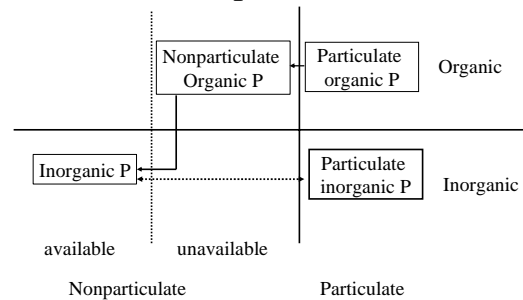
Soil Phosphorus (P)

Phosphorus (P) forms in soils:

1. Soluble Reactive P (SRP) or orthophosphate or soluble inorganic P
2. Particulate organic P
3. Non-Particulate organic P
4. Particulate inorganic P (sorbed P onto clay, apatite P, P complexed with solid matter such as FeOH_3)

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Phosphorus (P)



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Soil Phosphorus (P)

- At higher pH (calcareous soils): P precipitates in combination of Ca
- At lower pH (acidic soils with high clay and organic matter): P reacts with Fe and Al ions in soils
- Maximum phosphate concentration in soils around 10^{-5} mole L^{-1} or 0.3 mg L^{-1}
- As pH decreases, max phosphate concentrations in pore water reduce to 0.1 mg L^{-1}

Note: limit for eutrophication in open water is 0.02 mg L^{-1}

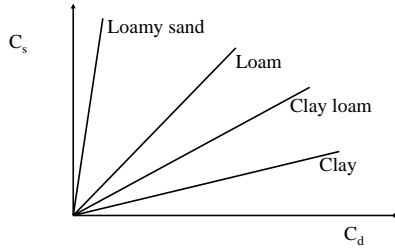
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Soil Phosphorus (P)

- Sandy soils do not react much with soil P
- Fertilizer P resides mostly in 5 cm of surface soil
- Organic matter contributes to P adsorption
- Langmuir isotherm tends to fit P adsorption better than Freundlich because Langmuir models a maximum

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Soil Phosphorus (P)



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Soil Phosphorus (P)

Novotny reports Langmuir coefficients for acid soils:

- $C_{s,max} = -3.5 + 10.7(\% \text{ clay}) + 49.5(\% \text{ org. C})$
- Unit: ($\mu\text{g g}^{-1}$)
- $K_1 = 0.061 + 170,000 \times 10^{-\text{pH}} + 0.027(\% \text{ clay}) + 0.76(\% \text{ org. C})$
- Unit: (L mg^{-1})

Note: Organic matter (%) $\approx 1.67 \times$ organic carbon (%)

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Soil P: Example

Fertilizer was applied to a field at a rate of 100 Kg/ha uniformly to depth of 0.3 m. Soil was a silt loam with 20% clay, porosity 40%, pH 6.0, org. C 1%, and ρ_{dry} 1500 Kg m^{-3}

Estimate dissolved and adsorbed P concentration during a long rain event at 1 cm/hr. Assume full infiltration and equilibrium between adsorbed and dissolved P, antecedent adsorbed P was negligible.

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Soil P: Example Solution

- $C_{s,max} = -3.5 + 10.7(20) + 49.5(1) = 260 \mu\text{g g}^{-1}$
- $K_1 = 0.061 + 170,000 \times 10^{-6} + 0.027(20) + 0.76(1) = 1.531 (\text{L mg}^{-1})$

$$C_T = \frac{100(\text{kg/ha}) \times 10^9 (\mu\text{g/kg})}{0.3(\text{m}) \times 10^4 (\text{m}^2/\text{ha}) \times 1000 (\text{L/m}^3)} = 33,300 \mu\text{g/L}$$

- $C_T = \theta_v C_d + \rho_{dry} C_s$ with $C_s = \frac{C_{s,max} K_1 C_d}{1 + K_1 C_d}$

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Soil P: Example Solution

- $C_{s,max} = 260 \mu\text{g g}^{-1}$
- $K_1 = 1.531 (\text{L mg}^{-1}) = 0.00153 \text{ L } \mu\text{g}^{-1}$
- $C_T = 33,300 \mu\text{g L}^{-1}$
- $\theta_v = n = 0.4$
- $\rho_{dry} = 1500 \text{ kg m}^{-3} = 1500 \text{ g L}^{-1}$

$$C_T = \frac{260 \times 0.00153 \times C_d}{1 + 0.00153 \times C_d} \times 1500 + 0.4 \times C_d$$

Solve for $C_d = 57 \mu\text{g L}^{-1}$

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Soil P: Example Solution

- $C_{s,max} = 260 \mu\text{g g}^{-1}$
- $K_1 = 0.00153 \text{ L } \mu\text{g}^{-1}$ $C_s = \frac{C_{s,max} K_1 C_d}{1 + K_1 C_d}$
- $C_d = 57 \mu\text{g L}^{-1}$

$$C_s = \frac{260 \times 0.00153 \times 57}{1 + 0.00153 \times 57} = 20.85 \mu\text{g/g}$$

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Soil Phosphorus (P)

$C_{s,max}$ and K_1 higher/lower for eroded sediments than for parent soils, respectively

In Wisconsin watershed:

$C_{s,max}$:

500 - 2000 $\mu\text{g g}^{-1}$ vs 189 - 287 $\mu\text{g g}^{-1}$

K_1 :

0.00011 - 0.000451 $\text{L } \mu\text{g}^{-1}$ vs 0.0009 - 0.0045 $\text{L } \mu\text{g}^{-1}$

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Soil Phosphorus (P)

Enrichment ratio (ER): concentration of the contaminant on sediment in runoff divided by concentration in parent soil

ER > 1:

- Selective removal of fine materials with higher pollutant concentrations
- Deposition of coarse materials

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Soil Phosphorus (P)

Enrichment ratio (ER): concentration of the contaminant on sediment in runoff divided by concentration in parent soil

ER > 1:

- Selective removal of fine materials with higher pollutant concentrations
- Deposition of coarse materials

ER = 2 for annual loads

ER = 7.39/Sed^{0.2} for event loads, where Sed is in kg ha^{-1}

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Soil Phosphorus (P)

P_2O_5 contains 44% P. The map of P (as P_2O_5) in the surface foot of soil shows P_2O_5 in percent, equivalent to 10,000 mg kg^{-1}

$$C_s = 0.44(\% \text{P}_2\text{O}_5) 10^4$$

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Nitrogen

Nitrogen (N) facts:

- 7 to 30% of Total N in top 15 cm (=1500 - 6000 kg ha^{-1})

Sources:

- Fertilizer application (46% in US)
- N fixation (20%)
- Manure application (7%)
- Plant residue (17%)
- Precipitation (10%)

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Nitrogen (N)

N is mobile in soils and may leach to ground water and reappear with groundwater discharge as base flow in streams

Downward movement of mobile forms (NO_3^- and NH_4^+) occurs when soils are above field capacity, with maximum flow during saturation (potentially with preferential flow mechanisms)

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Nitrogen (N)

The map of N in the surface foot of soil shows N in percent, equivalent to $10,000 \text{ mg kg}^{-1}$

$$C_s = (\%N)10^4$$

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Nitrogen

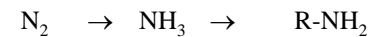
Nitrogen (N) forms in relation to natural waters :

- Free nitrogen (N_2)
- Ammonium (NH_4^+)
- Ammonia (NH_3)
- Nitrite (NO_2^-)
- Nitrate (NO_3^-)
- Organic N

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Nitrogen Cycle: Fixation

1. Fixation: N_2 to plant protein



- (nitrogen gas) (ammonia) (organic nitrogen)

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N Fixation

Legumes (soybeans, peas, beans) and some algae can fix nitrogen. The rate is assumed to be related to root growth:

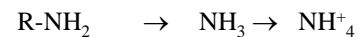
$$N_f = K_f r_g$$

where N_f is fixation rate ($\text{mg N cm}^{-1} \text{ day}^{-1}$), K_f is a constant ($0.011 \text{ mg N cm}^{-2}$), and r_g is the rate of root growth (cm day^{-1})

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Nitrogen Cycle: Mineralization

2. Mineralization: organic N decomposes into mineral form facilitated by microorganisms



- (organic nitrogen) (ammonia) (ammonium)

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Mineralization

Breakdown of organic N to NH_4^+ is a rate-limiting process described by 1st order decay with the remaining soil N as substrate:

$$\frac{dN}{dt} = -k_N N$$

where k_N can be estimated as 0.29 ± 0.007 (wk^{-1}) at 25 °C.

$$\log k_N = 6.16 - \frac{2299}{T} \quad \text{where } T \text{ is in } ^\circ\text{K}.$$

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Nitrogen Cycle: Nitrification

3. Nitrification: microorganisms in soil convert ammonium to nitrite and nitrate



- (ammonium) (nitrite) (nitrate)
- Rapid in moist, warm, well-aerated soil
- Bacteria: *Nitrosomonas* and *Nitrobacter*

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Nitrification

Growth of nitrifying bacteria is slow. The Monod equation may be used to simulate the NH_4^+ oxidation using $\mu_S = 0.41 \text{ mg L}^{-1} \text{ day}^{-1}$ and $k_s = 1.1 \text{ mg L}^{-1}$

$$\frac{dC_d}{dt} = \frac{-0.41 C_d}{1.1 + C_d}$$

Optimum temperature is 22°C, pH is 8.5, and nitrification rate decreases with moisture content

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Nitrogen Cycle: Denitrification

4. Denitrification: anaerobic bacteria in soil convert nitrate to gaseous forms of N



- (nitrate) (nitrite) (nitrous oxide)
- ↓ ↓
- NO N₂
- (nitric oxide) (nitrogen)

- Accelerated in poorly aerated and/or waterlogged soils

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Denitrification

A 1st order decay can describe the denitrification process where nitrate concentration in interstitial water is:

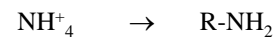
$$\frac{d\text{NO}_3^-}{dt} = -k_b \text{NO}_3^-$$

where k_b ranges with temperature and oxygen composition. For example, at 19.5 °C and 34 °C (20% O₂ composition), $k_b = 0.002 \text{ hr}^{-1}$, and 0.035 hr^{-1} , respectively.

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Nitrogen Cycle: Immobilization

5. Immobilization: Plant uptake and soil microbes take up ammonium and nitrate

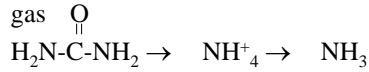


- (ammonium) (organic nitrogen)
- $\text{NO}_3^- \rightarrow \text{R-NH}_2$
- (nitrate) (organic nitrogen)

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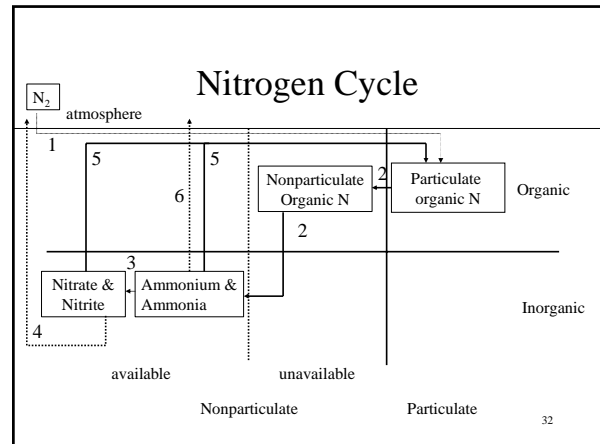
Nitrogen Cycle: Volatilization

6. Ammonia Volatilization: ammonia in urea containing fertilizer or manure converts to gas



- (urea) (ammonium) (ammonia)
- No loss of ammonia from acidic fertilizers such as ammonium nitrate or ammonium sulfate, unless pH is high

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Soil N: Example

A silt soil contains about 2.5% organic matter and 0.12% total N (organic N + $\text{NH}_4^+\text{-N}$) of which 75% is organic N. Effective θ_v is 20%, and $\rho_{\text{dry}} = 1500 \text{ Kg m}^{-3}$ ($=\text{g L}^{-1}$). The Freundlich isotherm parameters are $K_f = 7.0$, and $n = 1.25$.

Estimate mobile and immobile N concentration in this soil.

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Soil N Example: Solution

OM = 2.5%; TN = 0.12% organic N + $\text{NH}_4^+\text{-N}$
 75% = organic N; θ_v is 20%; $\rho_{\text{dry}} = 1500 \text{ g L}^{-1}$.

The dissolved fraction of TN is part of $\text{NH}_4^+\text{-N}$ content which is both dissolved and adsorbed.

Total $\text{NH}_4^+\text{-N}$:

$$(1 - 0.75) \times 0.12\% = 0.03\% \text{ or } 300 \mu\text{g g}^{-1}$$

Volumetric concentration:

$$300 \mu\text{g g}^{-1} \times 1500 \text{ g L}^{-1} \times 0.001 \text{ mg } \mu\text{g}^{-1} = 450 \text{ mg L}^{-1}$$

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Soil N: Example Solution

- $n = 1.25$; $K_f = 7.0$
- θ_v is 20%; $\rho_{\text{dry}} = 1500 \text{ g L}^{-1}$; $C_T = 450 \text{ mg L}^{-1}$
- $C_T = \theta_v C_d + \rho_{\text{dry}} C_s$ with $C_s = 7.0 C_d^{0.8}$

$$450 \text{ mg/L} = 0.2 C_d + 1500 (\text{g/L}) \times 7.0 C_d^{0.8} \times 0.001 (\text{mg}/\mu\text{g})$$

Solving for C_d gives: $C_d = 103.5 \text{ mg L}^{-1}$

$$\text{and } C_s = 7.0 \times 103.5^{0.8} = 286 \mu\text{g/g}$$

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Soil N: Example Solution

- Ratio of available $\text{NH}_4^+\text{-N}$ to TN:

$$100 \left(\frac{0.2 \times 103.5 (\text{mg/L})}{0.0012 \times 1500 (\text{g/L}) \times 1000 (\text{mg/g})} \right) = 1.15\%$$

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Nitrification Example

Following the previous example, how much nitrogen will be nitrified during a 2-week period if soil is at $T = 22\text{ }^{\circ}\text{C}$, $\text{pH} = 8.5$, and moisture is adequate.

Solution: Only dissolved ammonium can be nitrified: $C_d = 103.5\text{ mg L}^{-1}$.

$$\frac{dC_d}{dt} = \frac{-0.41C_d}{1.1 + C_d} = \frac{-0.41 \times 103.5}{1.1 + 103.5} = 0.41\text{ mg/Lday}$$

In 2 weeks: $14 \times 0.41\text{ mg L}^{-1}\text{day}^{-1} = 5.7\text{ mg L}^{-1}$