#### The Unsaturated Zone is NOT a Black Box

2007 WRD Research Lecture Series



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#### Soil scientist

#### unsaturated zone guy?

#### Hydrologist

#### Why is the unsaturated zone understudied?

- Not a contaminant receptor
- Limited Relevance to Plant Fertility
- Data difficult to collect Multiple phases
- Its not time yet?



... Often conceptualized as a black box despite that we may know about ...

- geology
- residence time (even in the east!)
- Variable mineral content
- Microbes
- a gaseous phase
- water table interface







Spatially variable rechargeand Mineralogic Controls on NO<sub>3</sub><sup>-</sup> sorption and transport

#### **Natural Attenuation at Gasoline Spills**

# The atmosphere as a source of MTBE in ground water-

**Current Activity and Outreach** 

#### Black box - uniform recharge for watershed



#### Basic data collection only provides an average ...



# ... but to study chemical loading better resolution is needed







# Calculation made in lowermost unit



Mehaffey Nursury C01

#### **Distribution of Recharge Estimates**



Median 11.5 inches/yr.



dillution effect?...

#### ... or some other UZ process

unsaturated zone

#### Black Box Treatment for storage

#### all nitrate stored in the unsaturated zone is available for transport with recharge

- 8 Km<sup>2</sup>
  watershed
  Upper
  Deerfield
- Nearly 100% agricultural
- Mostly Bridgeton formation
- 11 sites







### **NJ Geoprobe**



#### Nitrate







# sorption indicated

# **Sorption coefficient**

 $S = K_d C$ 

- S = sorbed concentration (mg/kg)
- $K_d$  = sorption coefficient (L/kg)
- C = aqueous concentration (mg/L)

# **Measurements**

- T = total conc. in UZ (mg/kg)
- W<sub>ave</sub> = avg. moisture content (L/kg)
- C = shallow GW conc. (mg/L)







#### Flux variability--

Not only depends on land use and application rates (black box) but also on Kd and recharge

# Mineralogy of Upper Deerfield UZ

(quantitative XRD by Neil Fishman – USGS GD-Denver)

| A Contraction         | Mineral   | Median<br>(wt %) | Min<br>(wt %) | Max<br>(wt %) |
|-----------------------|---|------------------|---------------|---------------|
|                       | Goethite -<br>FeO(OH)   | 2.0              | 0.6           | 6.5           |
|                       | Ilmenite -<br>FeTiO <sub>3</sub>  | 0.5              | 0.0           | 5.8           |
| 1 State Barris States | Kaolinite -<br>Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> | 6.9              | 1.0           | 20.7          |

minerals capable of anion sorption at lower pH

#### Tropical Soils with high anion exchange capacity similar to UZ sediments of NJ Coastal plain



#### Latosol

Rich in iron, alumina, or silica. Formed in tropical woodlands under very humid climate with relatively high temperature.



#### Oxisol Soils with no more than 10 percent weatherable minerals. High concentration of iron (III) and aluminum oxides and hydroxides.

# **Implications**



- UZ storage can be greater than expected for NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>--</sup>, and Cl<sup>-</sup> due to sorption
  - UZ can be a significant reservoir for N and other elements and needs to be considered in hydrologic cycles ....

#### ... Increased residence times imply aquifer cleansing will take longer ...



# ... Expect same through Atlantic Coastal Plain ...



## ... Land use ≠ Loading ...

![](_page_28_Picture_1.jpeg)

#### ... The UZ is not a Black Box

![](_page_29_Picture_1.jpeg)

# **Current Project Activity**

- . Pesticides/Fungicides
- . Field Data
- . Sorption process research

![](_page_30_Picture_4.jpeg)

# Natural Attenuation at Gasoline Spill Sites-

![](_page_31_Picture_1.jpeg)

![](_page_32_Figure_0.jpeg)

# The black box treatment... All of mass is solubilized and enters gw system eventually...

![](_page_33_Figure_1.jpeg)

# But...

![](_page_34_Figure_1.jpeg)

The Addition of the Gaseous Phase Results in Additional Interfaces to Consider

### Gaseous Aqueous Product Solid 6 possible phase interfaces

![](_page_35_Picture_2.jpeg)

Product - Aqueous (solubilization) black box

- Product Gaseous (volatilization) TBD
- Aqueous Gaseous (volatilization) TBD

G-S A-S P-S

![](_page_36_Figure_0.jpeg)

![](_page_36_Figure_1.jpeg)

![](_page_36_Figure_2.jpeg)

![](_page_36_Figure_3.jpeg)

# **Scaling Model**

![](_page_37_Picture_1.jpeg)

![](_page_37_Picture_2.jpeg)

# **Scaling Model Results**

![](_page_38_Figure_1.jpeg)

#### **Scaling Model - Biodegradation**

![](_page_39_Figure_1.jpeg)

![](_page_40_Figure_0.jpeg)

#### **Degradation / volatilization**

![](_page_40_Picture_2.jpeg)

**Natural Attenuation** 

![](_page_41_Picture_0.jpeg)

![](_page_41_Picture_1.jpeg)

![](_page_42_Figure_0.jpeg)

science for a changing world

![](_page_43_Figure_0.jpeg)

![](_page_44_Figure_0.jpeg)

Science for a changing world

![](_page_45_Figure_0.jpeg)

![](_page_46_Figure_0.jpeg)

Approximate extent of north oil pool, August 1998 modified from Lakehead Pipe Line Co., written commun., 1998

a) 1985, Gas concentrations modified from Hult and Grabbe (1988).

![](_page_47_Figure_1.jpeg)

# **USGS Toxics Hydrology Research**

![](_page_48_Picture_1.jpeg)

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# VOC's Through the Hydrologic Cycle Point or Non-point Sources ?

![](_page_49_Picture_1.jpeg)

![](_page_49_Picture_2.jpeg)

![](_page_50_Picture_0.jpeg)

#### **Source Concentrations of MTBE**

<u>Gasoline Spills</u> MTBE ≈ 7500 mg/L BTEX ≈ 100 mg/L

<u>Used motor oil</u> MTBE ≈ 28 mg/L BTEX ≈ 3 mg/L

Auto exhaust

![](_page_51_Picture_4.jpeg)

![](_page_51_Picture_5.jpeg)

## **Ambient Environment**

- shallow ground water
- atmosphere
- lakes and streams

![](_page_52_Figure_4.jpeg)

Location of Glassboro, New Jersey study area

![](_page_53_Figure_0.jpeg)

#### Distribution of MTBE Concentrations In Ambient Shallow Ground Water

![](_page_54_Figure_1.jpeg)

![](_page_55_Picture_0.jpeg)

![](_page_56_Figure_0.jpeg)

#### Distribution of MTBE Concentrations In Ambient Shallow Ground Water

![](_page_57_Figure_1.jpeg)

#### Distribution of MTBE Concentrations In Ambient Shallow Ground Water

![](_page_58_Picture_1.jpeg)

# OR

![](_page_58_Figure_3.jpeg)

Plume Migration point source(s)

![](_page_59_Figure_0.jpeg)

#### Schematic of Sampling to Achieve Low Concentrations of VOCs in Unsaturated Zone Gas

![](_page_60_Figure_1.jpeg)

#### Black box -

# Shallow GW in equilibrium with atmosphere

![](_page_61_Picture_2.jpeg)

![](_page_62_Figure_0.jpeg)

![](_page_63_Figure_0.jpeg)

![](_page_63_Figure_1.jpeg)

#### ... but actually....

![](_page_64_Figure_1.jpeg)

# **USGS Toxics Hydrology Research**

![](_page_65_Picture_1.jpeg)

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