

Emerging Threats to Groundwater and Surface Water

Water Arabia 2009

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Background

- Big Blue River STP, Kansas City 1976
- Germany, early 1990's
 - Stan & Linkerhäger, 1992
 - Clofibric acid in groundwater
- USGS – Toxic Substances Hydrology Program
 - 139 streams, 95 chemicals, 75% > 1 chemical present
 - Steroids, insect repellent, and caffeine
- Trent University
 - Aspirin, ibuprofen, indomethacin, bezafibrate, and carbamazepine in ten sewage samples

Concerns with PPCPs

- Widely used
- Improper disposal and inadequate treatment
- Promotion of pathogenic resistance
 - Bactericides, pesticides
- Reproductive/development effects
 - Estradiol (female sex hormone) shown to alter sex characteristics at concentrations of 20 ppt (Raloff, 1998)

Concerns with PPCPs

- Increased use of graywater
 - Aquifer storage and recovery (ASR) projects
 - Soil aquifer treatment systems (SAT)
 - Biosolids
 - Septic systems
- Little to no regulatory guidelines
 - California
 - Florida
 - Europe (max. 100 ng/L)

Questions with PPCPs

- Can aquifer/vadoze zone “filter” out the PPCPs?
- Mobility of PPCPs?
- Transformation rates?
 - Different geochemical environments
- Can transformation reactions be enhanced?
- Accumulation of PPCPs?
- Are concentrations significant?

Characteristics

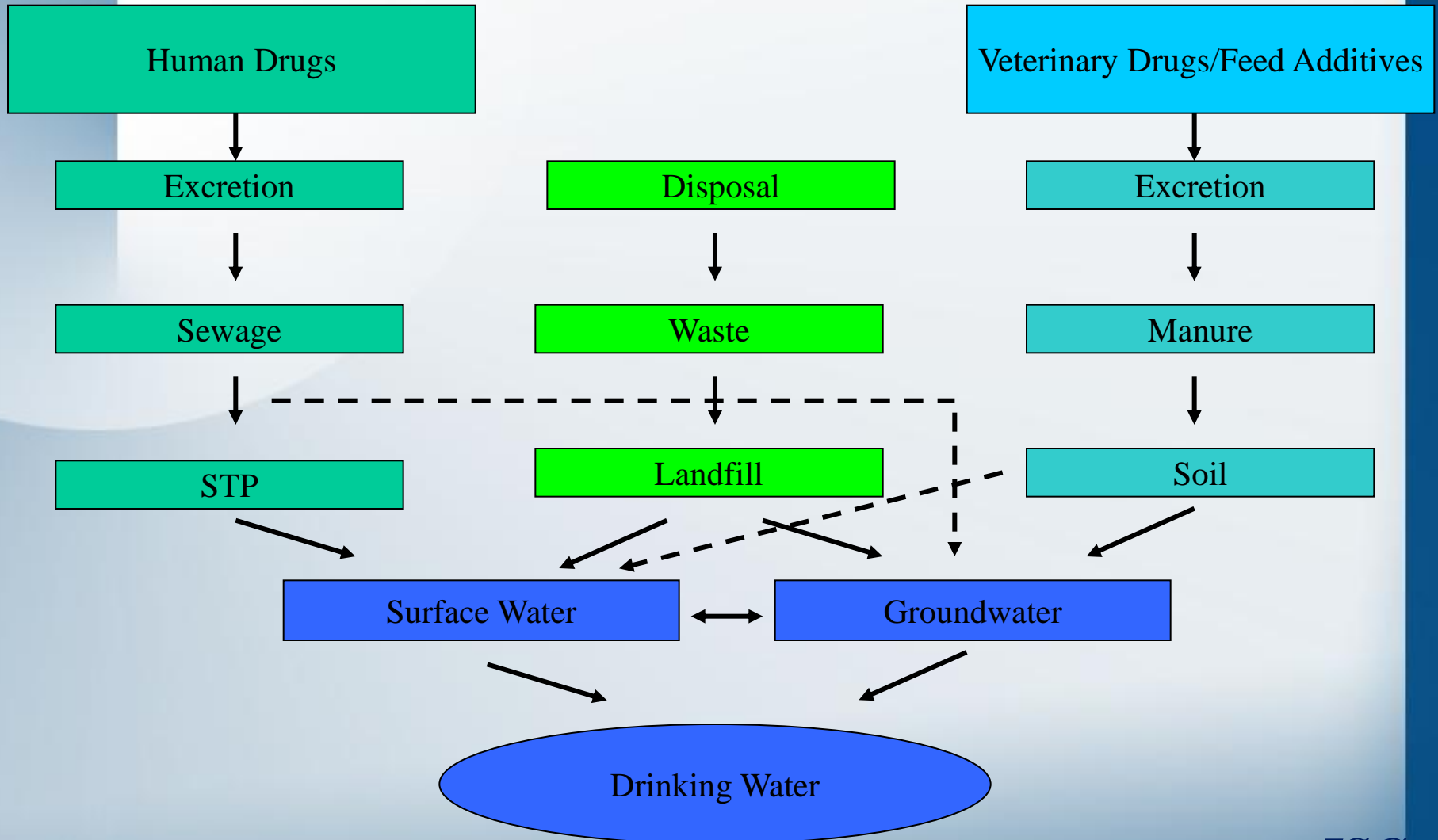
- Hydrophilic vs Lipophilic
 - 30% lipophilic (dissolves in fat), concentrate in larger predators
- Persistent
 - 50% to 90% excreted in original form
 - Remainder as metabolites
- K_{ow}
 - Low <3.0
 - Medium 3.0 to 4.0
 - High >4.0

Yearly Prescribed Amounts - Germany

Bezafibrate	45 tons
Carbamazepine	80 tons
Metoprolol	52 tons
Sulfamethoxazol	60 tons
Diclofenac	75 tons
Ibuprofen	180 tons
Acetylsalicylic acid	>500 tons
Iopromide	130 tons

Source: Ternes,2003

Fate of PPCPS



Treatment Efficiency - STP

■ Ibuprofen	90%
■ Clofibric acid	51%
■ Acetylsalicylic acid	81%
■ Phenazone	33%
■ Bezafibrate	75%

Flocculation removal poor

GAC moderate

Ozone best

- Source: Ternes, 2001

Caffeine

- Stimulant
- Omnipresent
 - Natural
 - Found in over 60 species
 - Synthetic
 - Theobromine is methylated
 - Found in
 - Wastewater effluent
 - Landfill leachate
 - Fly ash
 - Average global consumption ~ 70 mg/person/day (WHO, 1997)



Caffeine

■ Surface Water Studies

➤ USGS

- Mississippi River (Pereira et al., 1995)

- Detected at all sites during 3 sampling events, ~70 ng/L

➤ Poiger et al. 2003

- Switzerland

- Detected in all lake and river samples except most remote mountain lakes
- Correlated with rainfall
- Slow degradation from biological activity

Caffeine

- Groundwater Studies
 - McQuillan et al. (New Mexico)
 - No residues found in groundwater
 - Heberer et al. (Germany)
 - Artificial recharge
 - Residues found in groundwater
 - USGS (United States)
 - Detected in groundwater supply wells
 - McGregor et al. (Canada)
 - Detected in groundwater from septic

Clofibric Acid

- Cholesterol lowering medication
- ~200 tons produced annually in Germany
- Berlin tap water 10 to 165 ppt
- Conservative ???
- K_{ow} 3.1
- Similar to 2,4 D (weed killer)
- Algae and invertebrates shown to be sensitive

Ibuprofen

- Anti-inflammatory
- Acidic
- Low adsorption
- Susceptible to biotransformation
- ~125 tons prescribed annually in Germany



Case Studies

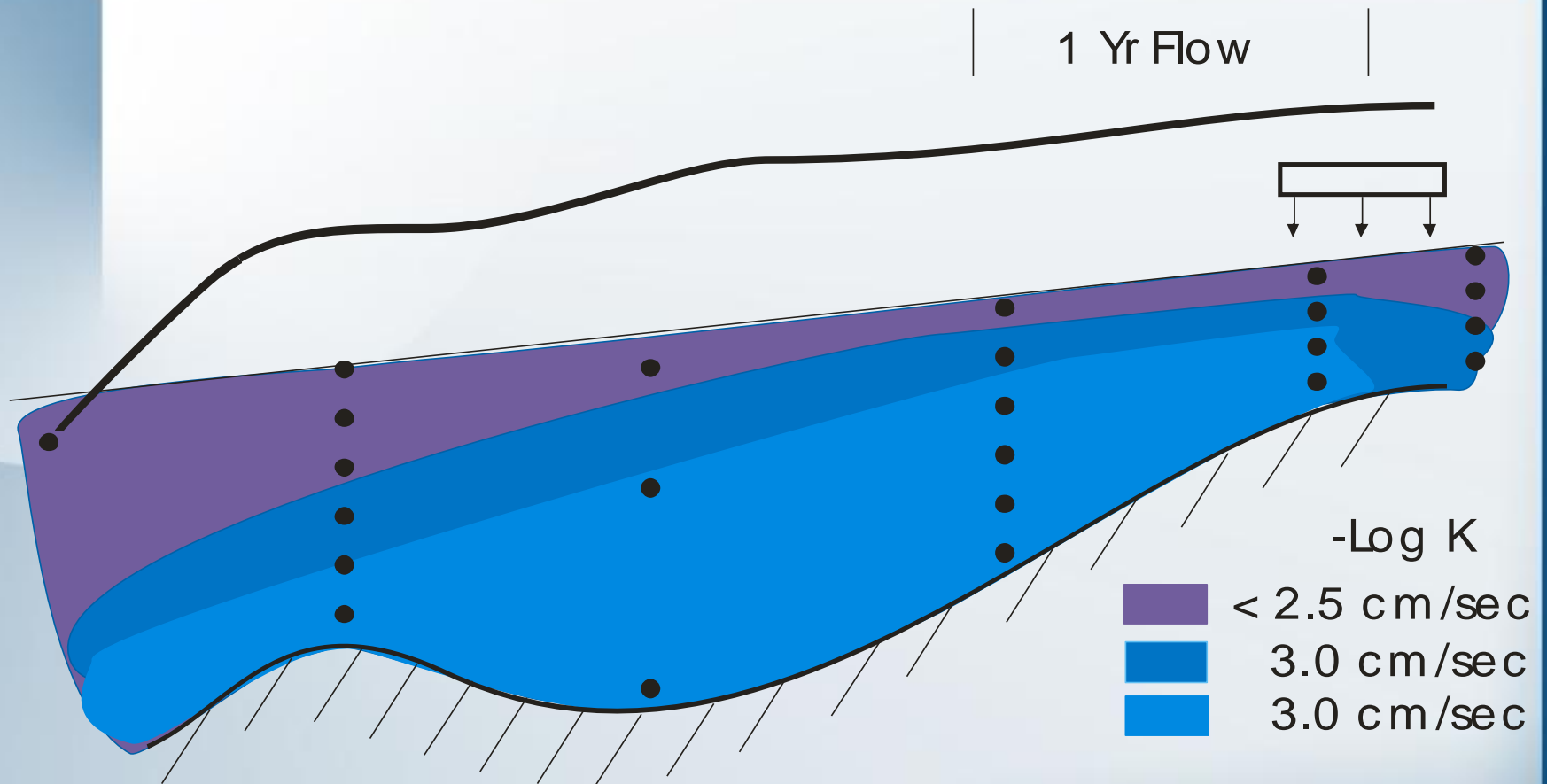


Site 1

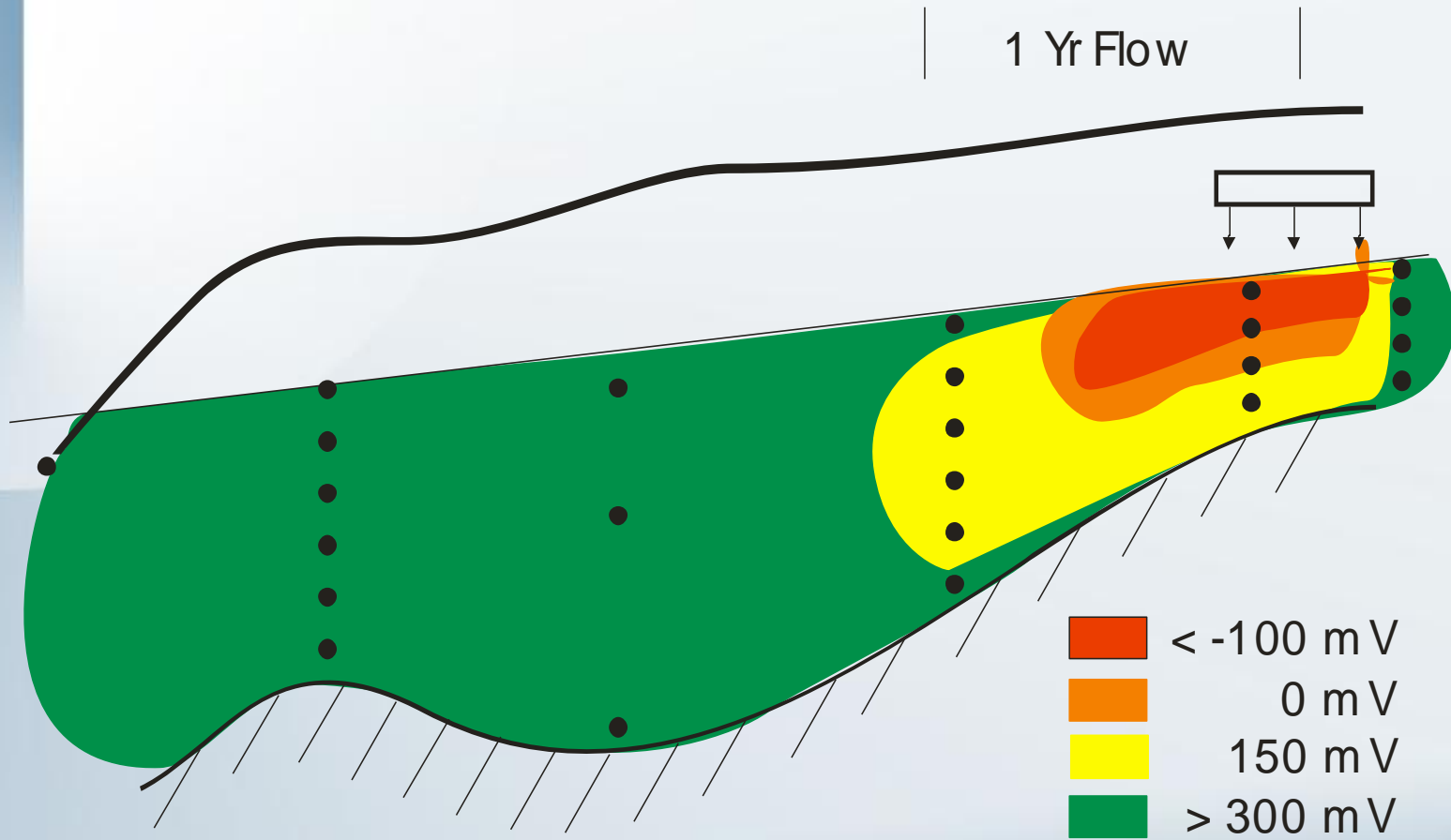
- Northern Canada
- Septic System
 - Family residence
 - ~1 metre vadoze zone
- Geology
 - Sandy overburden
 - Granite bedrock
- Hydrogeology
 - ~20 m/yr



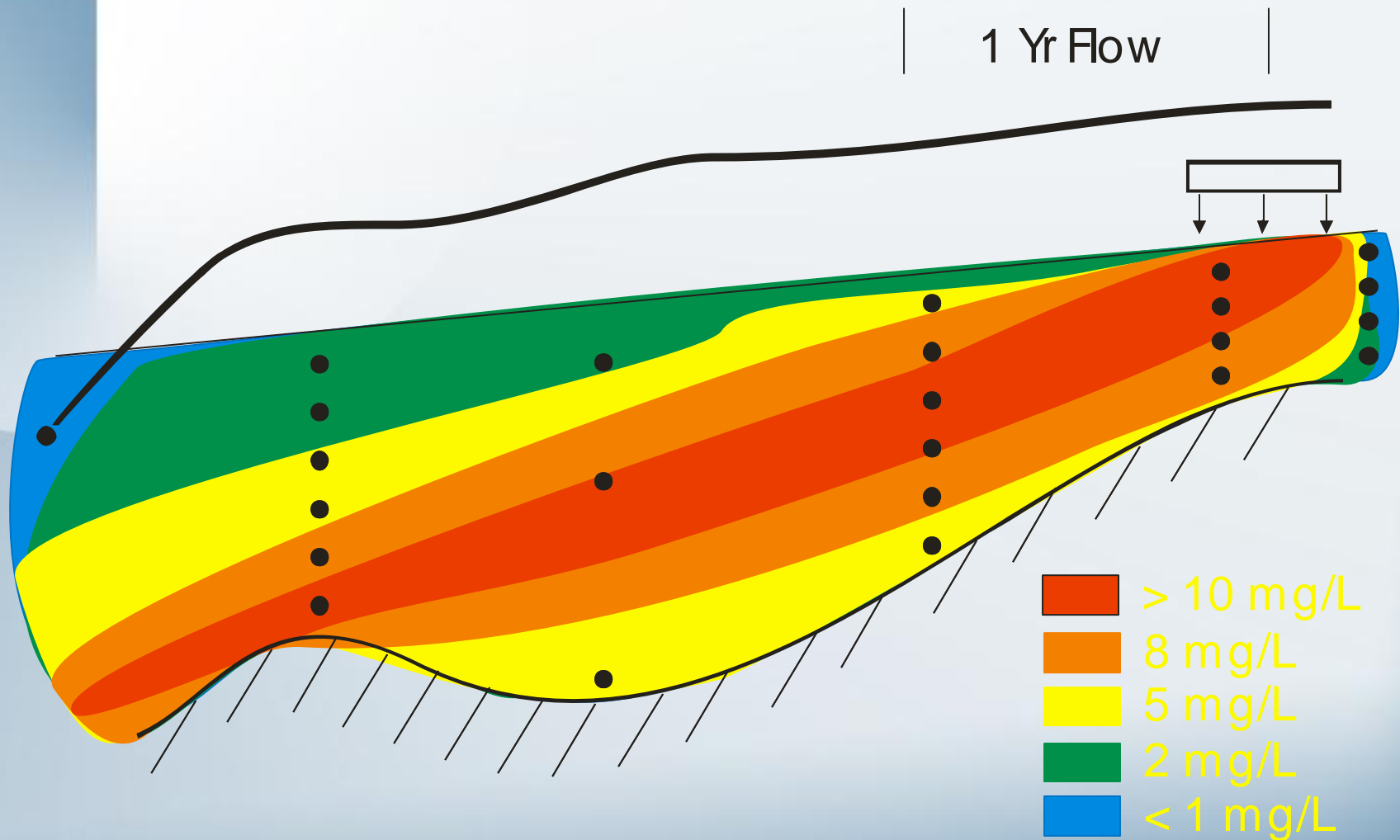
Site 1 – Hydraulic Conductivity



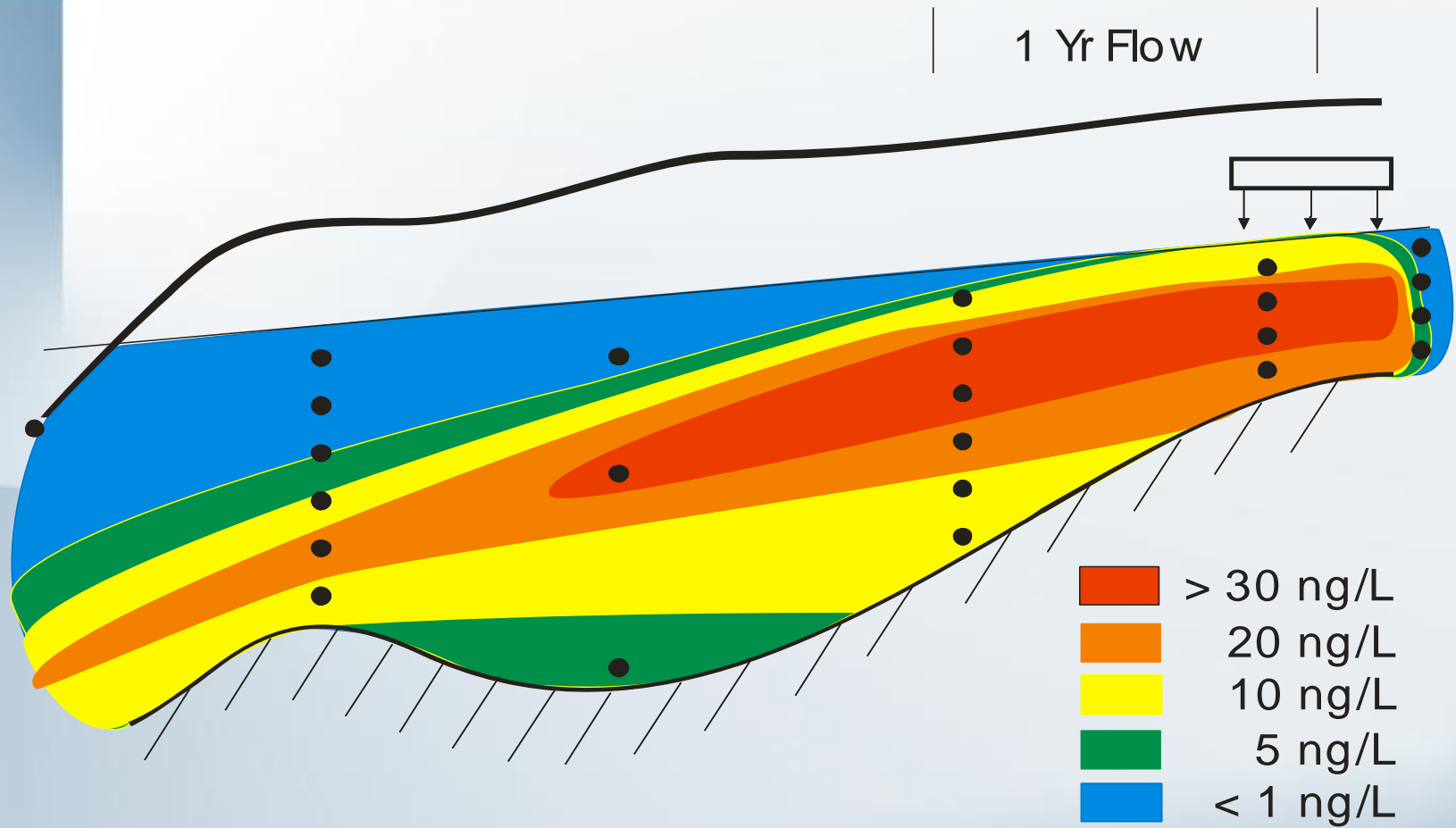
Site 1 – Eh



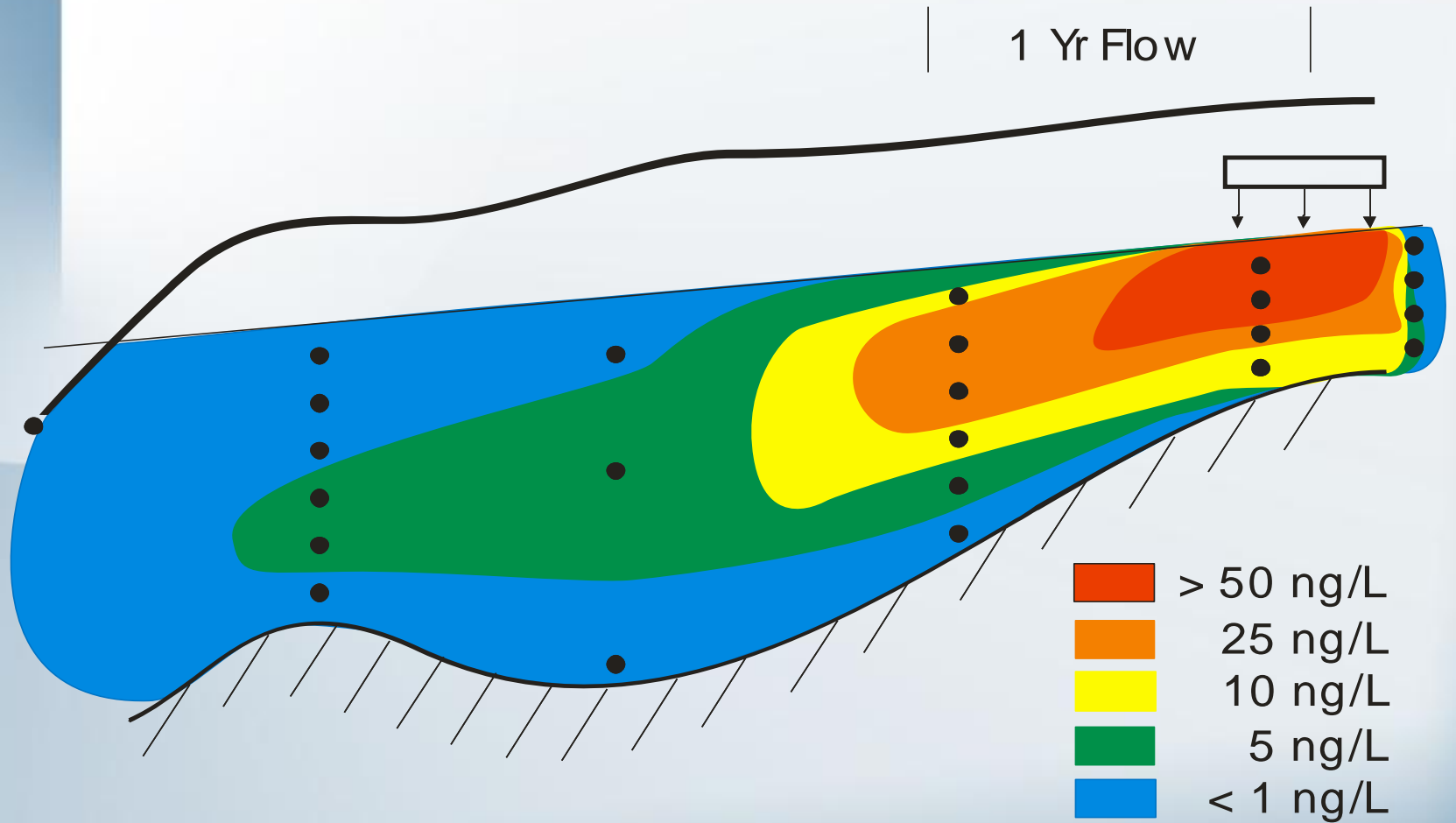
Site 1 – Nitrate



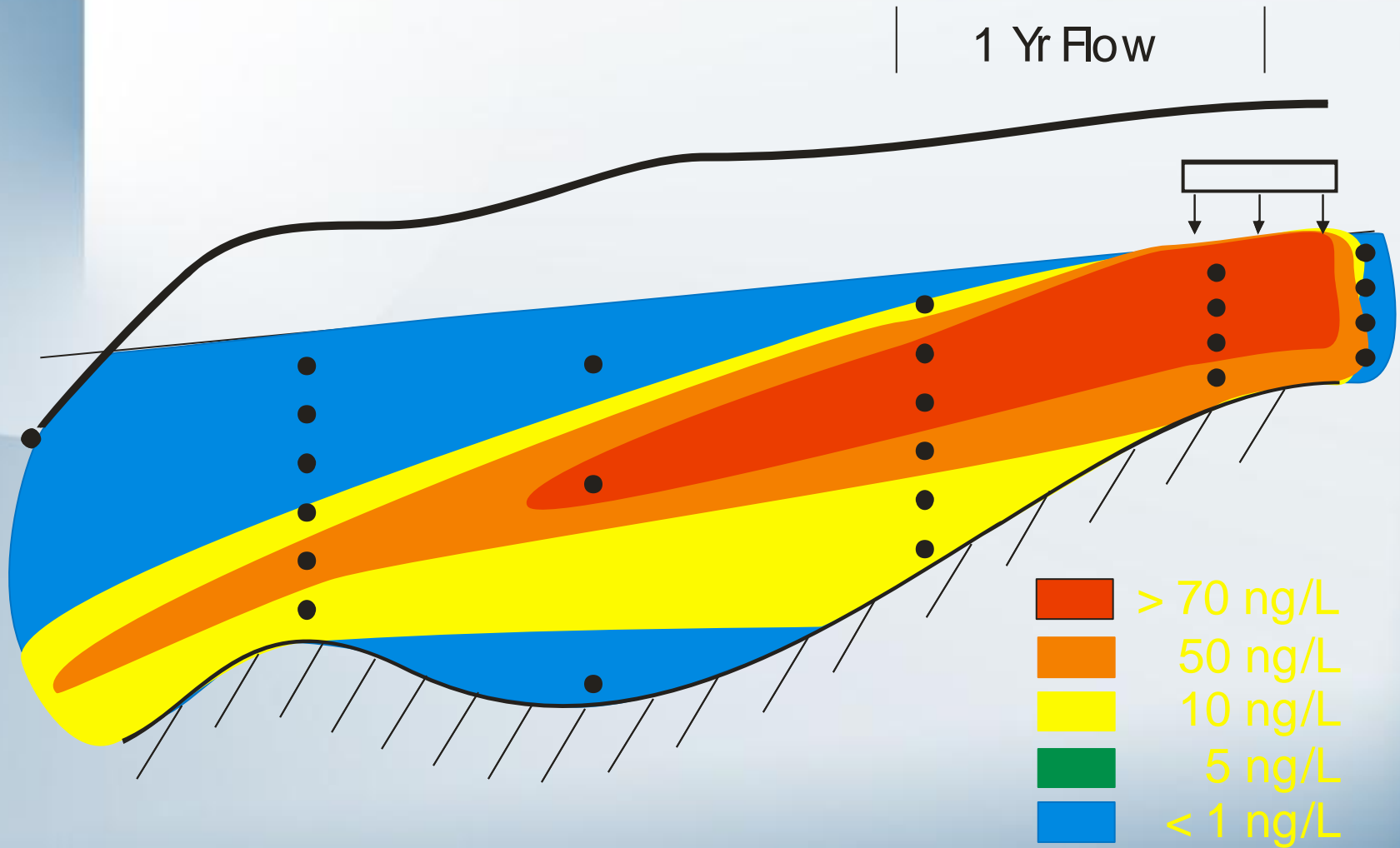
Site 1 – Caffeine



Site 1 – Ibuprofen



Site 1 - Clofibric Acid

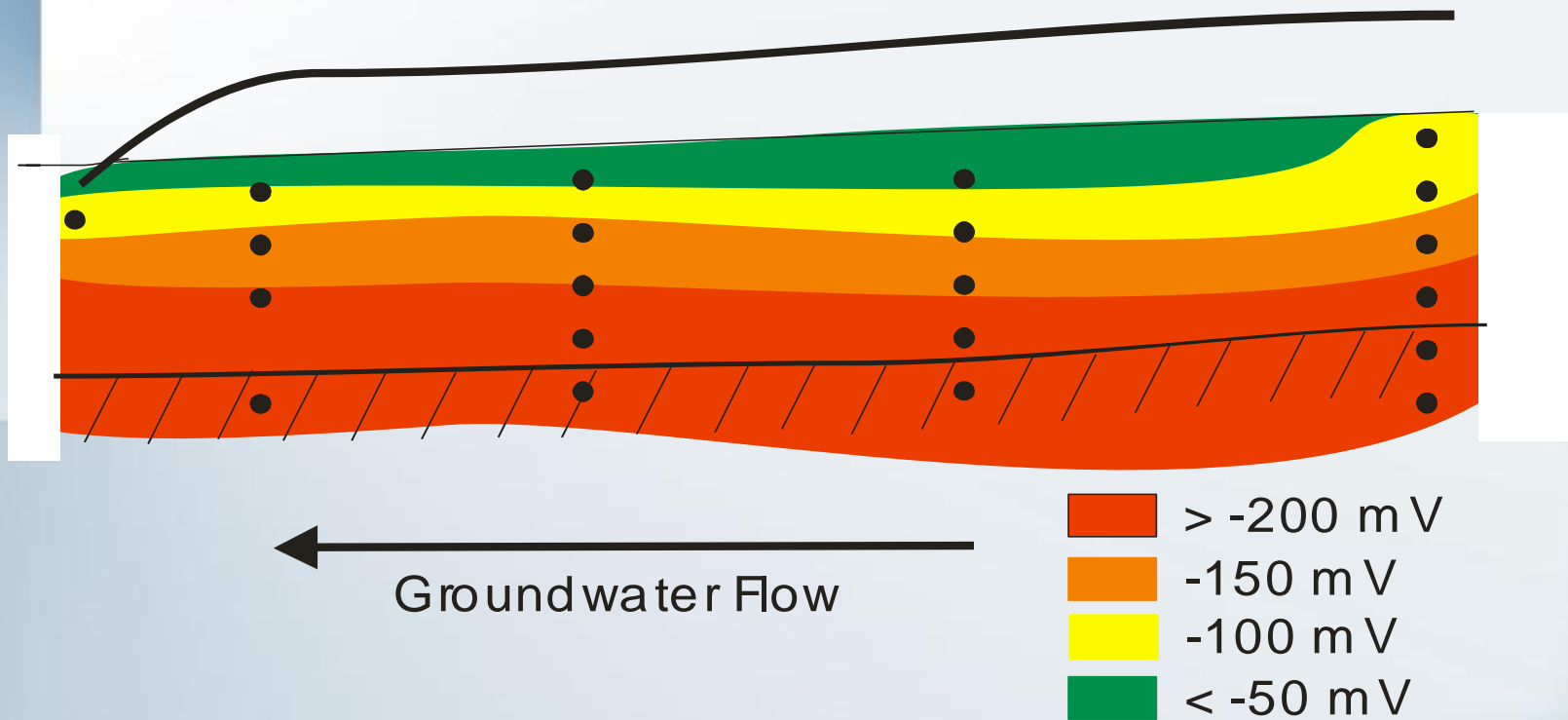


Site 2

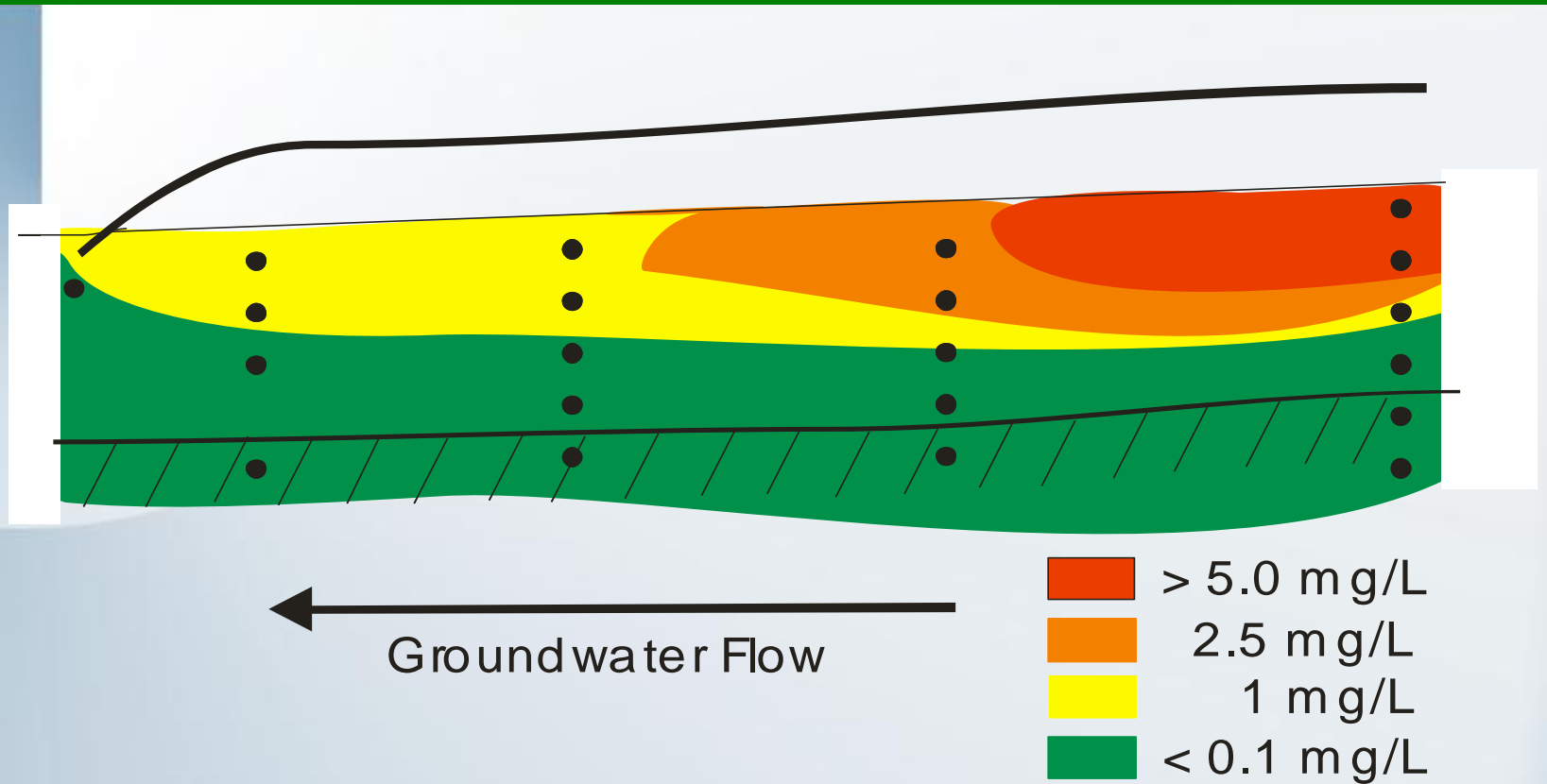
- Southern Canada
- Communal Septic
 - Campground
 - ~0.5 metres vadoze zone
- Geology
 - Sandy overburden
 - Shale Bedrock
- Hydrogeology
 - ~10 m/yr



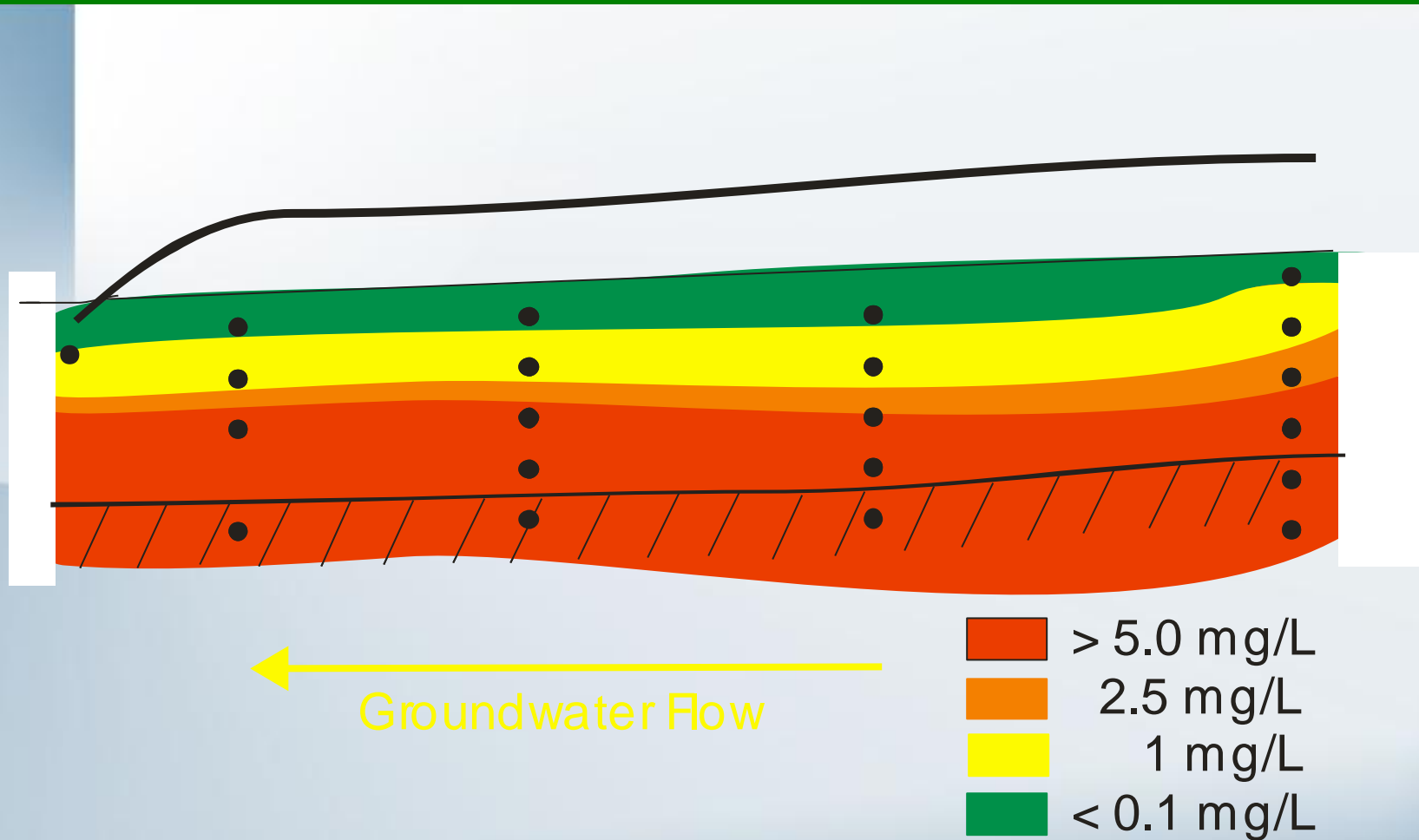
Site 2 - Eh



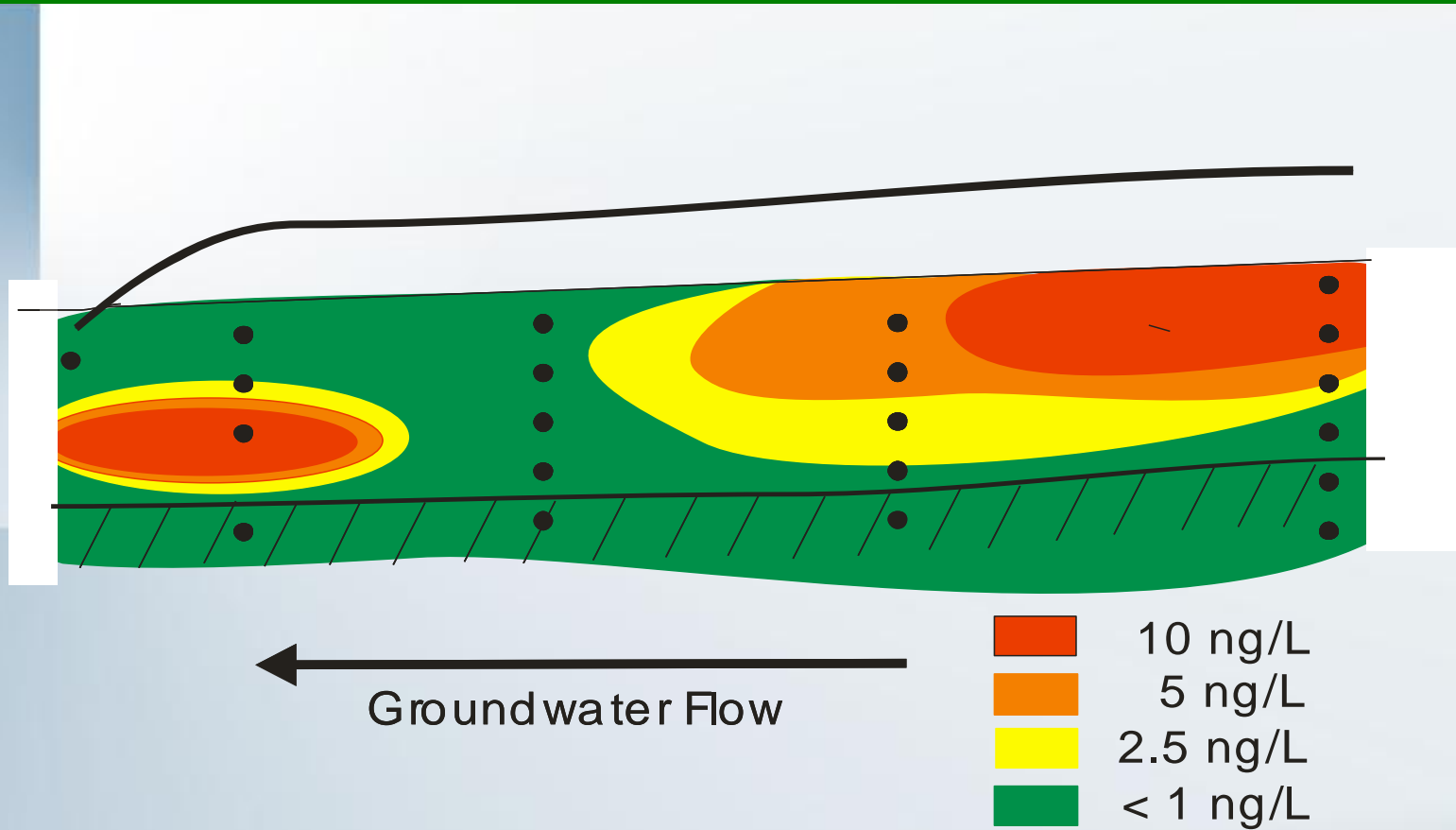
Site 2 - Nitrate



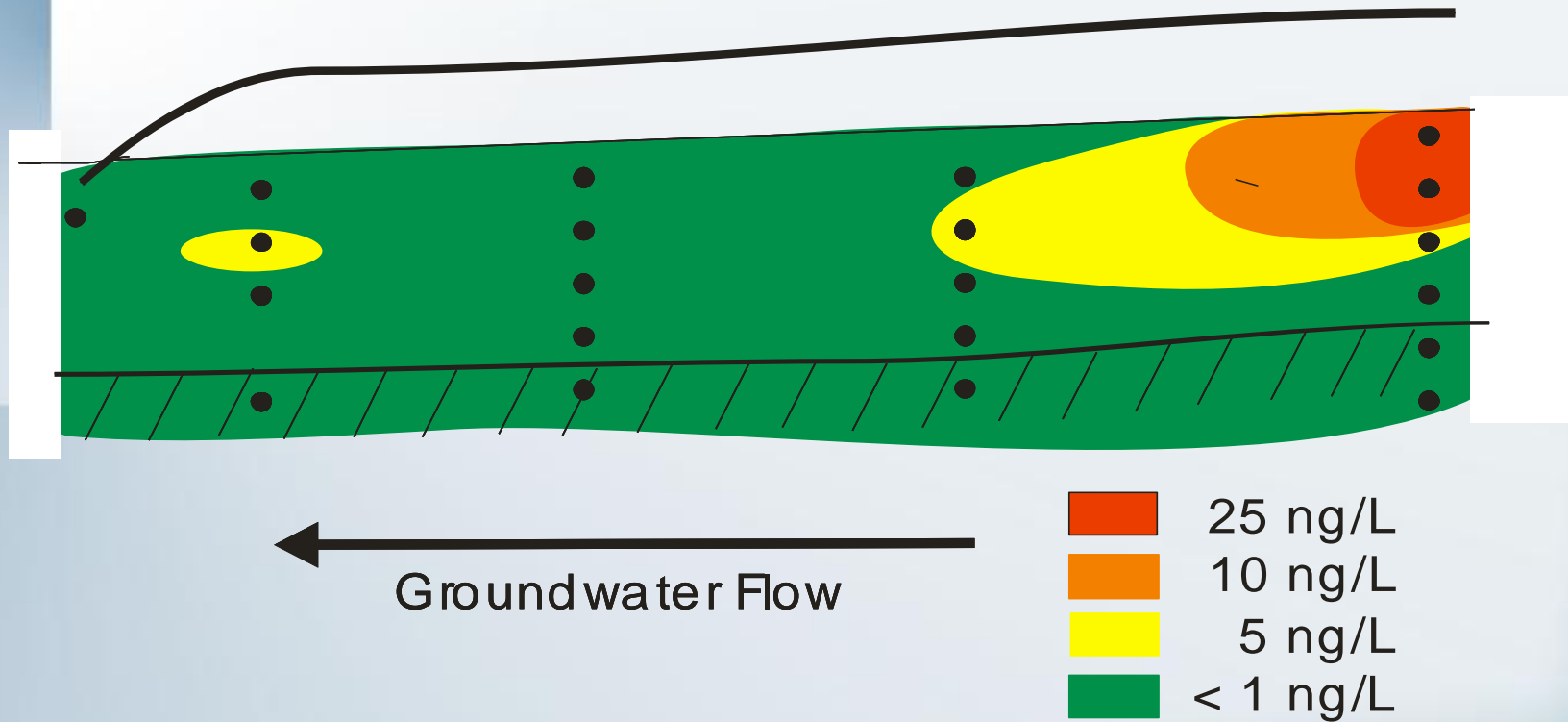
Site 2 - Iron



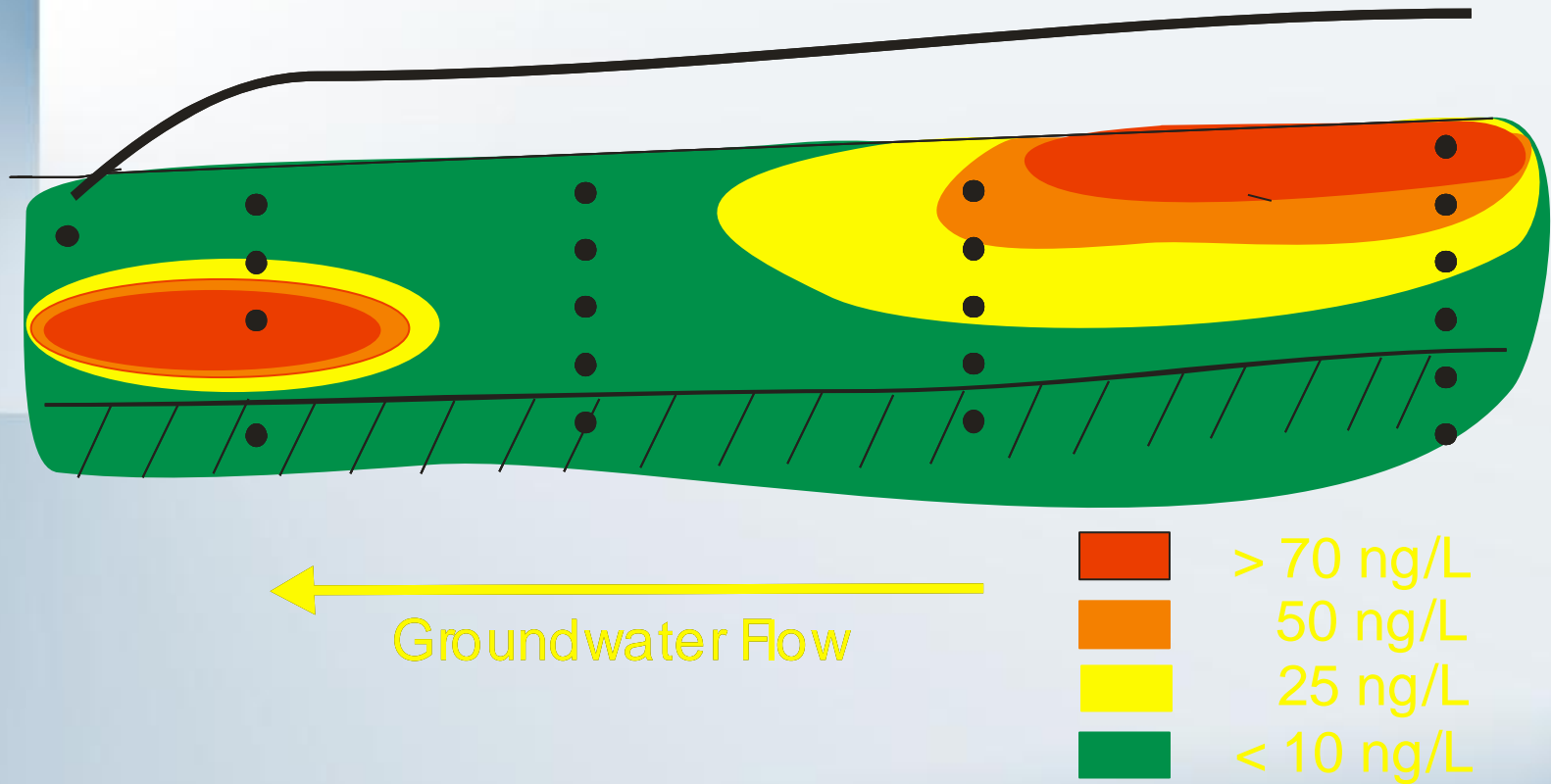
Site 2 - Caffeine



Site 2 - Ibuprofen



Site 2 – Clofibric Acid



Summary

Compound	Aerobic	Anaerobic
Caffeine	R ~ 1.0	R ~1.0
Ibuprofen	R ~ 2.5	R ~4.0
Clofibric acid	R ~1.0	R ~1.5

Questions

*“Water is H₂O
Hydrogen two parts
Oxygen one
But there is also a third thing
That makes it water
And nobody knows what that is.”*

D.H. Lawrence