Groundwater Contamination Dynamics

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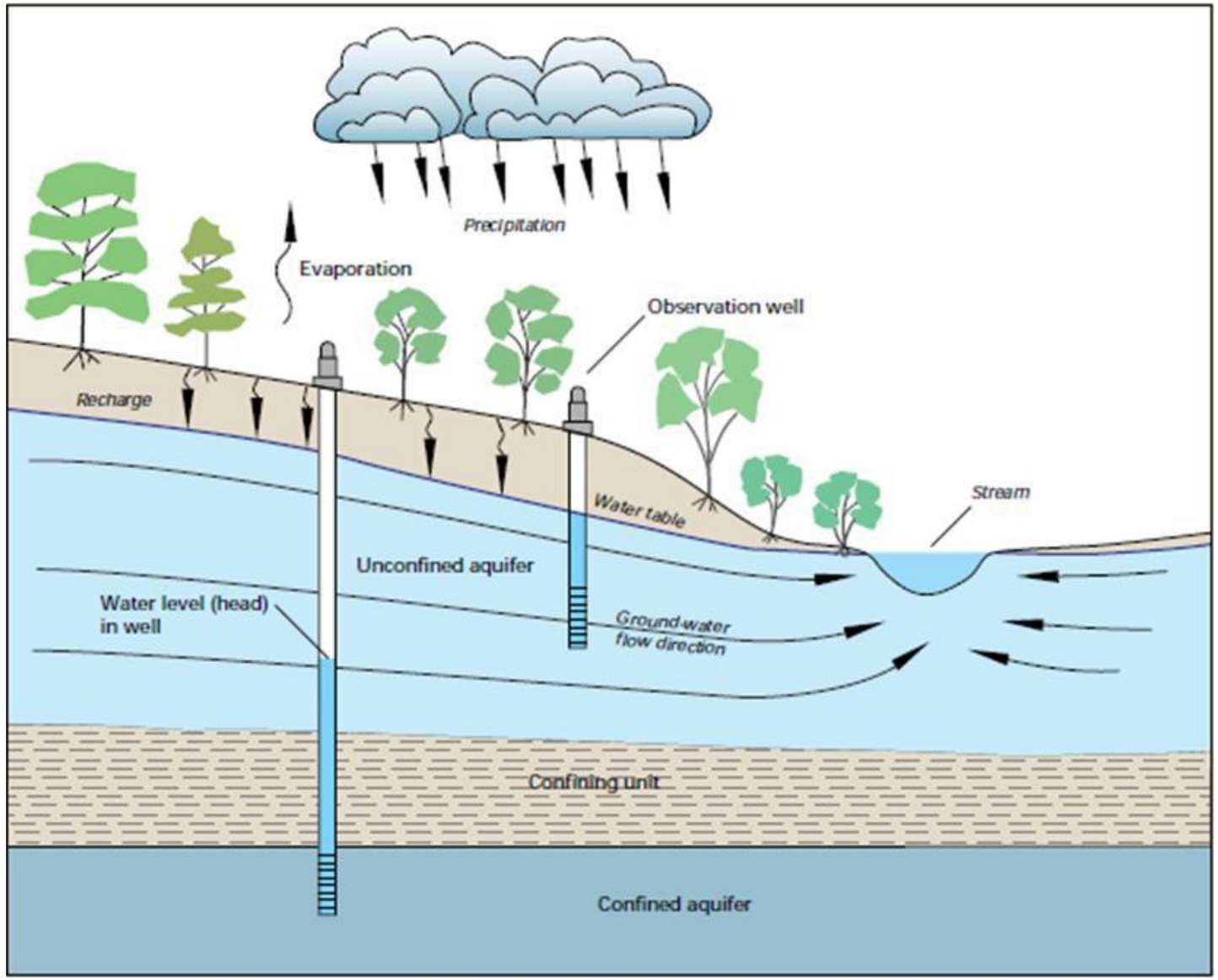
Content credit to Lange Jorstead (Geosyntec/ALGA)

Agenda

- Groundwater flow fundamentals
- Groundwater contaminant sources and types
- Contaminant transport in groundwater

The Groundwater Cycle



Definitions

- Piezometric – pressure – level to which water rises in a well (generic term)
- Potentiometric – under pressure – confined
- Water Table – atmospheric pressure - unconfined
- **Unconfined** – water table at atmospheric pressure
- **Confined** – potentiometric surface above top of aquifer
  - Artesian
  - Semi confined (time/space) or Leaky
- Perched – discontinuous above regional aquifer (unconfined)
- Leaky – a poorly confined aquifer - 'leakage' of groundwater through an aquitard

Groundwater Flow – you can't know where groundwater contamination is going if you don't know where groundwater is going!

- What controls groundwater flow?
  - Recharge and Discharge – must understand regional as well as local hydrogeologic regime!!!
  - Darcy's Law: An empirical equation which describes the observed relationship between Groundwater Flow (Discharge), Porous Media (Hydraulic Conductivity) and Gradient (Water Levels) in an aquifer
    - $Q = KiA$ or $q=Ki$ or $v=Ki/n_e$
    - **i** – hydraulic gradient or change in water level divided by distance
  - Understanding groundwater flow requires understanding the hydraulic gradient which requires water level contours!

Hydraulic Gradient – Influences on groundwater flow

- Recharge and Discharge
  - Natural (ie rainfall) and Manmade (drains, pumping wells, etc)
- For a given groundwater flux, hydraulic conductivity is inversely proportional to hydraulic gradient:
  - Increase in K results in decrease in gradient.
- Hydraulic Conductivity is a function of lithology:
  - Anisotropy
  - Homogeneity
- Variations over time – seasonal, tidal, barometric

CSM Cross Section Example

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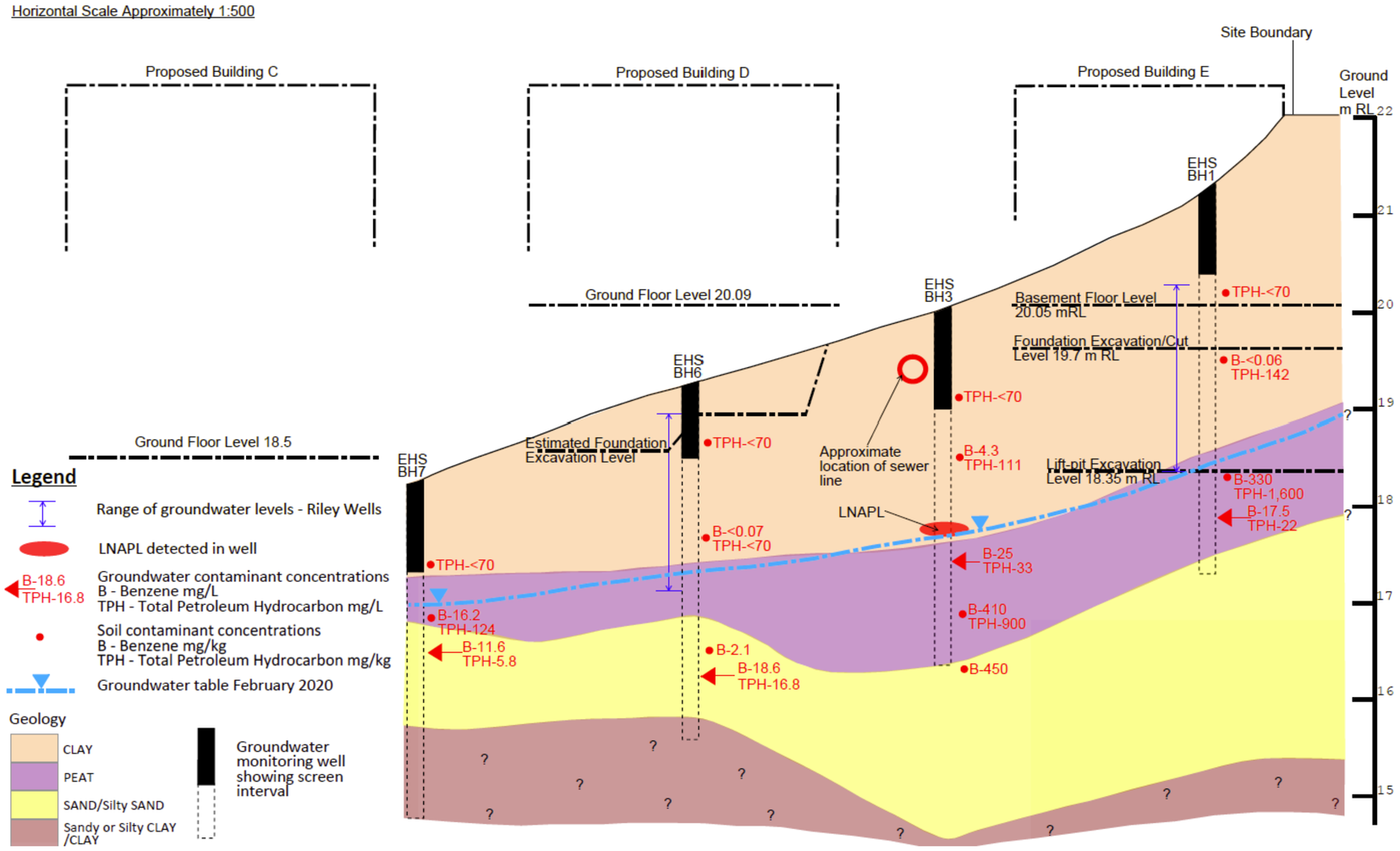


Groundwater Contaminant Sources and Types

Organic Contaminants

Contaminant Types	Typical Source(s)
▪ Petroleum hydrocarbons ▪ TRH, BTEX, PAHs	Leaking underground storage tanks (USTs) a.k.a. underground petroleum storage systems (UPSS)
▪ Chlorinated solvents ▪ PCE, TCE, DCE, VC	Metal fabrication/degreasing, auto mechanics, electronics manufacturing, waste disposal sites
▪ Coal Tar ▪ TRH, BTEX, PAHs, phenols	Gasworks, "older" bitumen, industrial applications (sealant application)
▪ Pesticides ▪ OCP, OPP	Agriculture, commercial/residential applications
▪ PFAS ▪ PFOS, PFOA, PFHxS	Fire fighting foams (Defence bases, airports, fire training grounds, bulk fuel facilities), chrome plating facilities, landfills/STPs, *many more*!

Inorganic Contaminants

Contaminant Types	Typical Source(s)
▪ Metals and metalloids ▪ Arsenic, chromium, mercury, lead	Acid mine drainage, acid sulfate soils, industrial facilities, waste management sites, electroplating
▪ Nutrients ▪ Nitrate, ammonia, phosphate	Landfills, fertilizer application, explosives residue, sewage treatment plants, animal waste
▪ Cyanide ▪ Free, weak- and strong- acid dissociable	Gasworks, gold mines, aluminium smelters
▪ Radionuclides ▪ Radon, uranium, tritium	Nuclear waste, nuclear research facilities, naturally occurring
▪ Salts ▪ Major and minor ions	Acid mine drainage, seawater intrusion, groundwater "mining"

Light Non-aqueous Phase Liquids (LNPAL)

- LNAPL-Light non-Aqueous Phase Liquids (free product, SPH, PSH)
  - Specific gravity less than water –forms a liquid phase over groundwater in monitoring wells
  - Petrol, diesel, motor oils
  - Occurs at the interface of the unsaturated and saturated zones (smear zone) of an unconfined aquifer

Dense Non-aqueous Phase Liquids (DNAPL)

- DNAPL-Dense non-Aqueous Phase Liquids
  - Specific gravity greater than water –forms a liquid phase below groundwater in monitoring wells
  - Chlorinated solvents, coal tar, metallic mercury
  - Occurs at the base of the and saturated zone of an unconfined aquifer

ɔ ɘraph 3: DNAPL product sample. Lighter aqueous phase has suspended sediment resulting in a milky texture.

Contaminant Transport in Groundwater

Groundwater Contamination – what is it?

- RMA Section 2 defines a 'contaminant' as 'any substance, energy, or heat that changes the physical, chemical, or biological condition of the environment'.
- By inference, contaminated groundwater is groundwater that contains a "contaminant'.

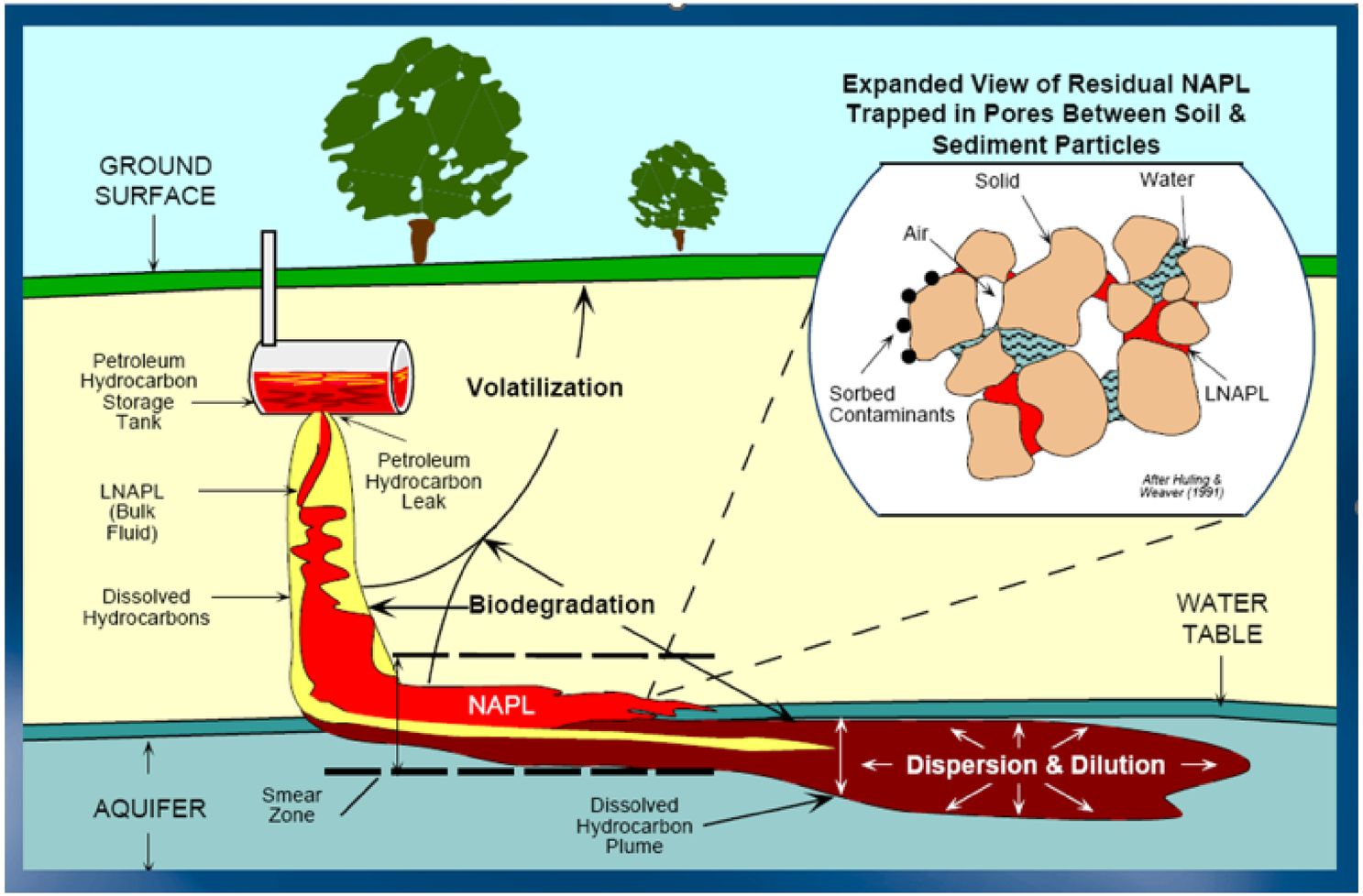
Contaminant Transport – What is a groundwater plume and how does it form?

A volume of groundwater containing dissolved contamination

In simple terms:

- Contamination is present in soil in contact with groundwater
- Groundwater flows through / interacts with the contamination
- Contamination dissolves into groundwater
- Dissolved contamination flows with groundwater, subject to processes that act to limit the “migration” of the contaminant in the aquifer

Contaminant Transport – What is a groundwater plume and how does it form?



Partitioning

- Contaminant propensity to bind with soil or dissolve in groundwater (Kd)
- Propensity to absorb to organic compounds in the aquifer (Kow)
- Propensity for contaminant to volatilise from groundwater form soil gas (K_H)

Partitioning - Solid/Liquid Distribution Coefficient Kd

- Solid/Liquid Distribution Coefficient Kd = Cs/Cw (L/Kg)
- Ratio of sorbed concentration is soil to concentration in groundwater
- It predicts mobility:
  - High Kd means a contaminant binds strongly to soil and moves slowly with groundwater
  - Low Kd indicates high mobility in groundwater.
- Varies based on pH, clay content, organic matter, and contaminant type.
- Used to compute a retardation factor (Rf), which estimates how much slower a contaminant plume travels compared to the actual groundwater flow
- Used principally for assessing retardation of metals, polar organic compounds

Partitioning - Octanol-Water Partition Coefficient Kow

- Octanol-Water Partition Coefficient Kow
- Ratio of the chemical concentration in octanol vs water at equilibrium (no units- often expressed as Log Kow)
- Kow Indicates hydrophobicity of specific compounds
  - higher values (Kow >1) indicates chemical preferentially to partition into organic matter than dissolve in groundwater.
- Used principally for assessing retardation of metals, non-polar organic compounds such as BTEX
- Log Kow Benzene 2.13 (Non-polar)
- Log Kow Pyrene 4.88 -5.18 (Non-polar) - relatively high partitioning to organic matter
- Log Kow Ethanol 0.31-0.35 (Polar) - relatively low partitioning to organicmatter

Partitioning – Henrys Law Constant K_H

- Henrys Law Constant K_H - Partitioning of compounds between soil gas and groundwater
- Ratio of a compound's concentration in air (or soil gas) to its concentration in groundwater at equilibrium K_H = Csg/Cgw m3/mol
- Lower K_H values indicate less partitioning into the vapour phase

- K_H for Benzene order of magnitude greater than for Naphthalene

Contaminant Fate & Transport – what happens to groundwater contaminants in an Aquifer?

Natural processes act on contaminants in groundwater to limit how far they can move.

These are:

- Physical
- Chemical
- Biological

They cause contaminants to:

- Slow down and spread out
- Stick to the aquifer
- Volatilise into soil gas
- Precipitate / chemically transform
- Biologically degrade

Processes Affecting Contaminant Migration

Physical

- Recharge, dilution
- diffusion, advection, dispersion
- dissolution (from NAPL), volatilization

Chemical

- sorption, ion exchange, dissolution/precipitation, neutralisation (pH changes
- oxidation-reduction, complexation, surface reactions
- radioactive decay

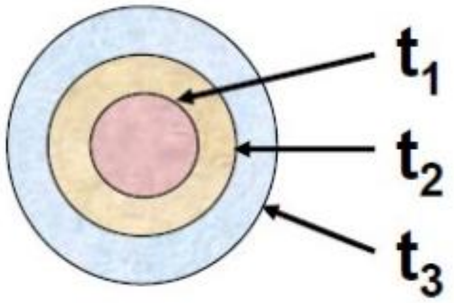
Biological

- biodegradation, transformation, cell synthesis, respiration

Physical Mechanisms Affecting Movement

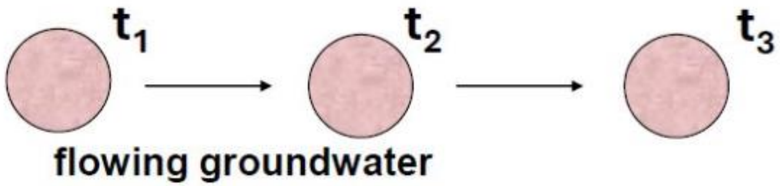
Diffusion

- Transport due to a chemical concentration gradient



Advection

- Movement of solute due to flow of groundwater



Physical Mechanisms of Movement

Mechanical Dispersion

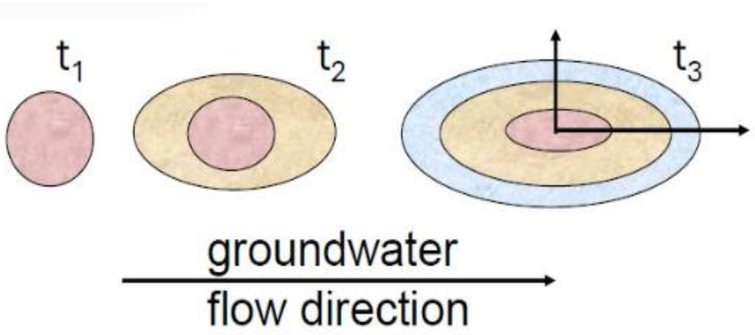
- Hydraulic mixing processes due to variations in velocity

Contaminant travels along a convoluted path

Result → longitudinal and transverse spreading of the plume

Advection and Dispersion

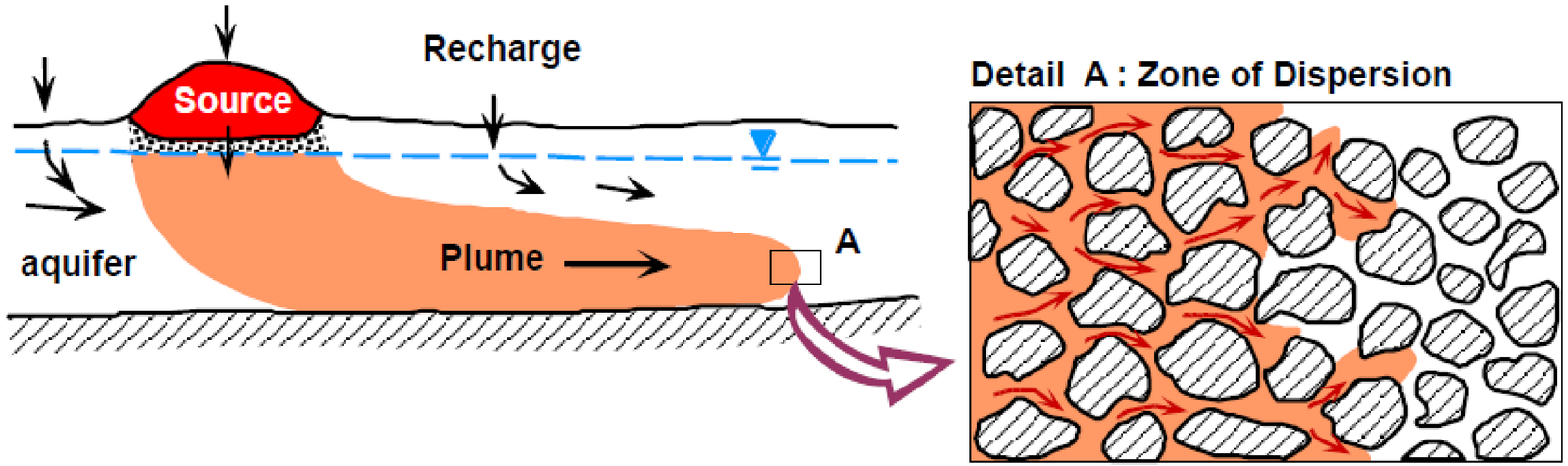
- Movement and spreading due to different pathways through a porous medium



Solute spreads out more longitudinally than laterally

Hydrodynamic Dispersion

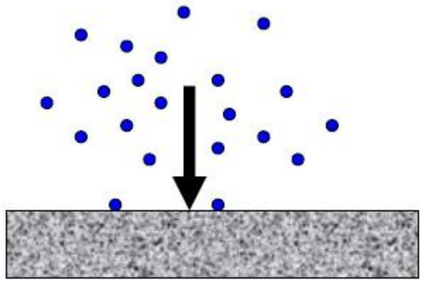
- Natural spreading of the solute mass, both in the direction of flow and perpendicular to the direction of flow



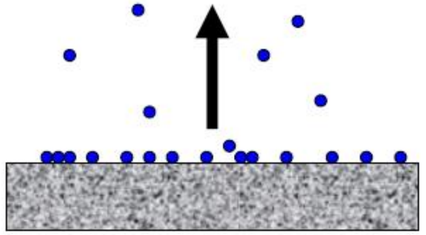
Chemical Mechanisms Affecting Movement

Sorption (absorption and adsorption)

- Process by which contaminants are removed from solution by interaction with aquifer matrix
- Contaminants “stick” to the aquifer (soak in or adhere to the surface)
- Leads to slowing down of the migration of dissolved chemicals relative to groundwater flow



solute SORBS when concentration in water is higher than at equilibrium



solute DESORBS when concentration in water is lower than at equilibrium

Chemical Mechanisms Affecting Movement

Oxidation-Reduction (Redox) Reactions

- Redox reactions occur when microbes (bugs) in soil eat organic carbon and use oxygen and oxygen-containing elements to gain energy from the carbon consumed, reducing the amount of oxygen in the aquifer
- This affects the valence state of metals affecting their solubility and concentrations in groundwater
- e.g., Ferric iron predominates in anaerobic environments and is more soluble than Ferrous iron which tends to precipitate as insoluble iron hydroxides under aerobic conidiations (seen in iron pans)

Biological Processing Affecting Contaminant Migration - Biodegradation – we love bugs!

Bacteria are everywhere

- There are 10^5 to 10^7 microorganisms in every gram of soil

Bacteria need to eat and breathe

- They eat organic carbon
- They “breathe” oxygen and oxygen-containing chemicals

Bacteria can biologically degrade (eat and breathe) organic contaminants

- The process creates “redox zones” – areas of “oxidising” and “reducing” conditions in the aquifer, which can influence how chemicals behave

Why do we care about redox reactions and zones?

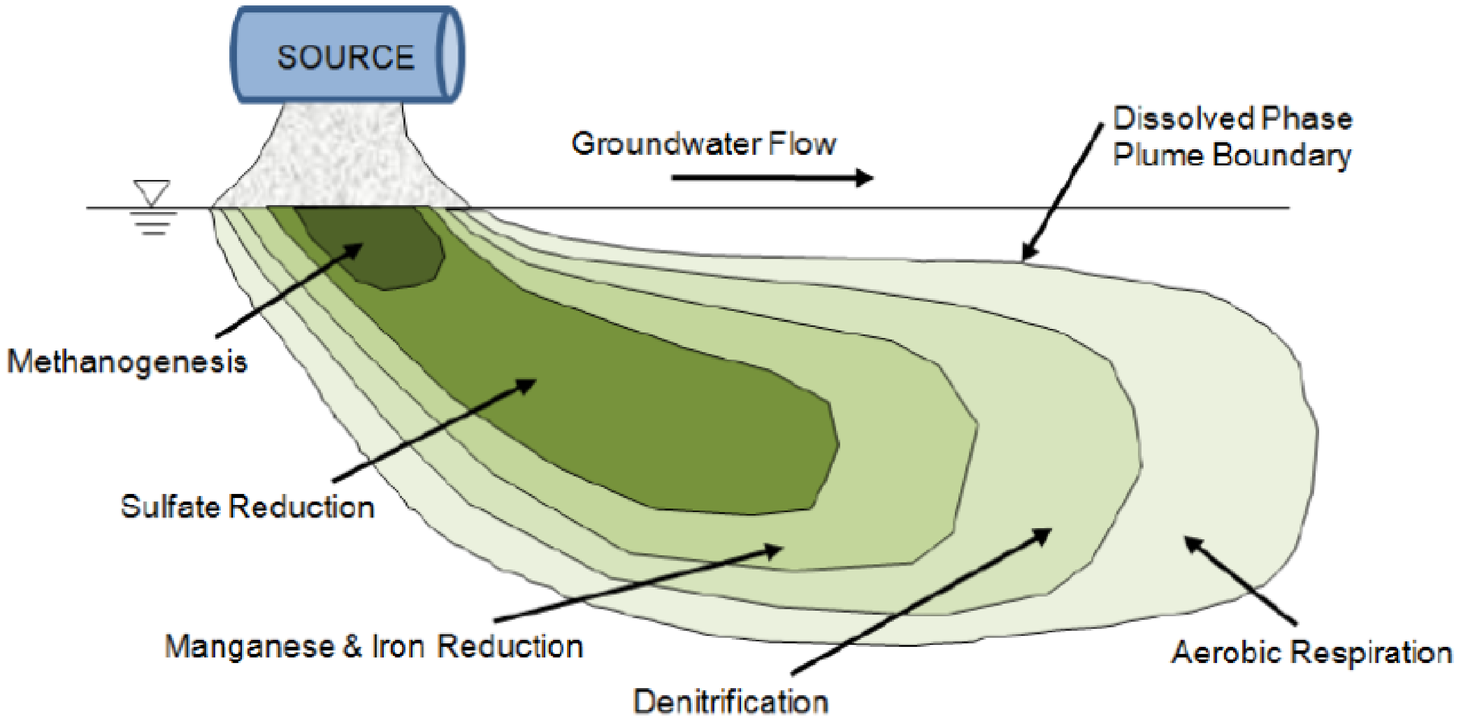
Some contaminants only degrade in oxidizing conditions, and some only in reducing conditions

- Important for understanding if natural processes are capable of managing groundwater contamination…
- …or if we need to “engineer” redox conditions suitable for contaminant biodegradation

The redox condition of the aquifer can cause other “redox sensitive” elements to dissolve, or precipitate (various metals, for example)

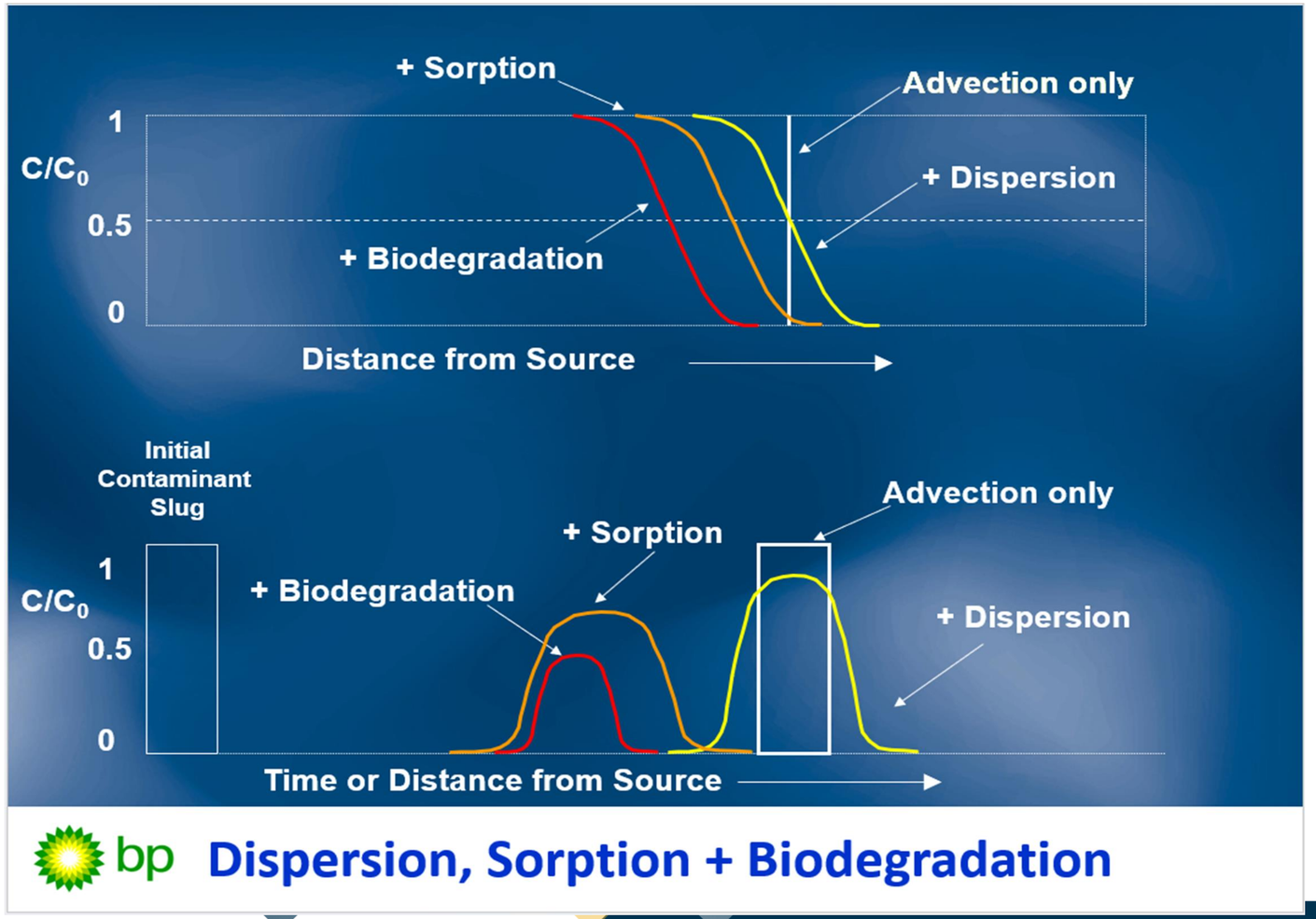
Redox reactions and redox zones

- Sequential redox reactions create “redox zones” in a plume

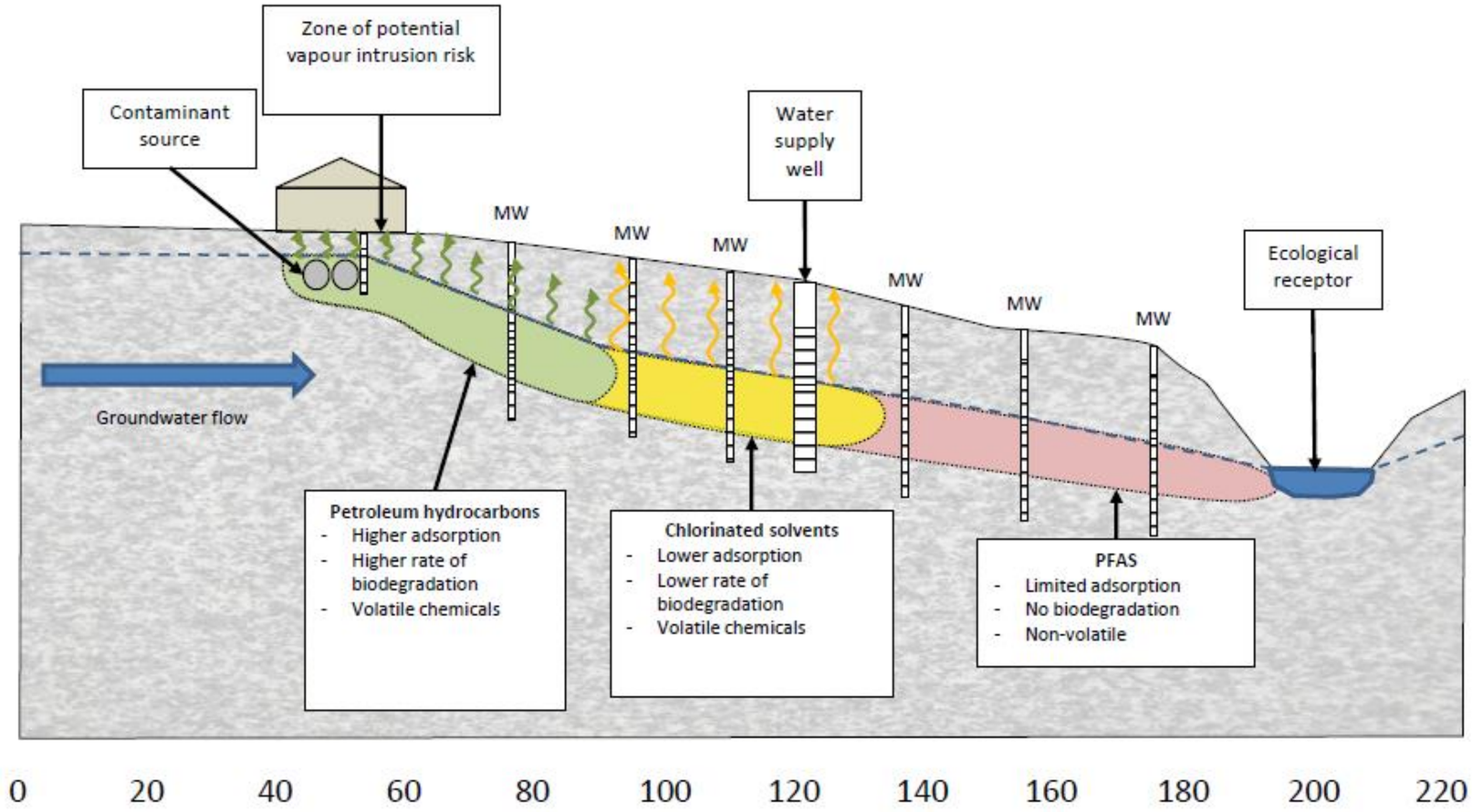


Physical, Chemical and Biological Effects on Organic Plume Migration

(From Andrew King BP Australia)



Migration of Different Contaminants



In Summary.....

- You need to know where groundwater is flowing, to know where groundwater contamination is going
- You need to know where groundwater contamination is going to understand what could be at risk
- Physical, chemical and biological processes affect the movement of contamination in groundwater
- Understanding these processes helps understand how far contamination will go, how fast, and if it will reach a sensitive receptor