Case Studies

Resuspension of River Sediment Containing Benzo(a)Pyrene

- Another coal gasification plant which operated for 60 years was located next to the Watford River (used for cooling water)
- River sediments contain Benzo(a)Pyrene, another PAH which is quite toxic

River Sediment Containing Benzo(a)Pyrene

- Approximately 60 m of river in front of power plant contain BaP in sediments
- Upstream flood channel work caused erosion in this region of river, resuspending sediments
- Sediment load increased by 20 mg/L in vicinity of power plant

River Sediment Containing Benzo(a)Pyrene

- Over next 6 km of river, there was a net loss of 15 mg/L of suspended sediments
  - What is concentration of BaP in river downstream from site?
  - How much is dissolved in river?

River Sediment Containing Benzo(a)Pyrene

- Site information:
  - River velocity = 0.3 m/s
  - Settling velocity of sediments, \( v_{sed} = 1 \text{ m/day} \)
  - River depth, \( H = 1.5 \text{ m} \)
  - River volumetric water flow rate = 25 m\(^3\)/s
  - Suspended sediment conc., \( C_{ss} = 110 \text{ mg/L} \), upstream of plant

\[
\text{Sedimentation rate, } k_{sed} = v_{sed} C_{ss} / 0.5H
\]

Pollutant removal via sedimentation = \( k_{sed} C_{ss} \)
River Sediment Containing Benzo(a)Pyrene

- Site information:
  - fine sediment = 80% by mass
  - $f_{oc,f}$ (fine sediment) = 0.08
  - $f_{oc,c}$ (coarse sediment) = 0.03
  - concentration of BaP in river bed = 1,000 mg/kg
  - density of river bed sediments = 1,200 kg/m$^3$

- Physicochemical data:
  - $C_w^{sat}$ = 0.0038 mg/L
  - $P^{sat}$ = 7 x $10^{-12}$ atm
  - $K_H$ = 0.000018
  - $K_{ow}$ = 10$^{5.97}$ = 933,000

Volatilization is not significant and can be neglected.
Sorption will be a major process.
Desorption will occur, to a small extent (although this analysis doesn’t include the rate of desorption, this may be an important factor in determining the actual concentrations).

To calculate $K_d$, we consider both types of sediments:

$$K_d = 0.63 \times 10^{-3} \cdot K_{ow} \cdot [0.8 \cdot f_{oc,f} + 0.2 \cdot f_{oc,c}] \text{ m}^3/\text{kg}$$

= 38 m$^3$/kg

$$K_d = C_s/C_w \quad \Rightarrow \quad C_w \approx 0.0026 \text{ mg/L}$$

$R = 1 + (\rho_s \cdot K_d / q) = 45,601$

(most BaP travels sorbed in sediment)

In terms of reactions
hydrolysis doesn’t occur
no known biodegradation rate (or it is very, very small)
Photolysis is the only possible mechanism
estimated at 0.068/day

In terms of the advection/dispersion equation, we have the following terms:

$$0 = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - F^*_{gas} - F^*_{solid} \pm F^*_{react} + (I - O)$$

where $F^*_{solid}$ = sorption of BaP to sediments
$F^*_{react}$ = photolysis of BaP
$I$ = input due to resuspension of sediments
$O$ = output due to redeposition of sediments
River Sediment Containing Benzo(a)Pyrene

- Actual total concentration of BaP leaving contaminated region was calculated by a numerical model to be 0.019 mg/L
- 0.016 mg/L sorbed
- 0.003 mg/L dissolved
- Concentration 6 km downstream drops to 0.016 mg/L

- Major removal mechanism from water column was deposition of resuspended solids
- Photolysis played a minor role in BaP removal in this case

UST Leak: Benzene in Ground Water

Gasoline leak: Benzene in GW

- Gasoline leaks from underground storage tanks are extremely common
- In this case, it was estimated that leak from UST at a gas station had been going on for about a year
- Leak started in 1985
- Water supply well was located ~100 m downgradient from the tank
Benzene represents about 1 to 3% of most gasolines, and is one of the principal concerns due to its carcinogenicity.

When will the maximum concentration of benzene reach the well?

What will be the maximum concentration?

Emergency drilling and testing near tank indicated that benzene concentration in ground water was 40 mg/L on average.

Leak was found and sealed, but the ground water plume was migrating towards the site boundary.

Site data:
- ground water velocity, v = 15 m/yr
- porosity, n = 0.25
- bulk density of soil, $\rho_s = 1700$ kg/m$^3$
- $D_x = 150$ m$^2$/yr
- $D_y = 15$ m$^2$/yr
- $f_{oc} = 0.003$

Physicochemical data:
- $C_{w, sat} = 1,787$ mg/L
- $K_H = 0.227$
- $K_{ow} = 10^{2.13} = 135$
- $\rho = 876.5$ kg/m$^3$

In terms of degradation
- Chemical degradation in subsurface is considered negligible for benzene, in the time frame considered
- Biodegradation occurs according to the following rate constant:

\[ k_r = 0.35/yr \]
Considering that sorption is very fast relative to water transport, then we used the modified advection/diffusion equation:

\[
\frac{\partial C}{\partial t} = \frac{v_a}{R} \frac{\partial C}{\partial x} + \frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R} \frac{\partial^2 C}{\partial y^2} - F_{\text{gas}} \frac{\partial C}{\partial t} + F_{\text{react}} + (I-O)
\]

Use two-dimensional numerical solution (dispersion is in x and y directions)
- Predicts maximum concentration at well will be 0.004 mg/L
- Maximum occurs 9 years after the beginning of the leak (1985).

Action Level = 1 ppb = 0.001 mg/L

Comparing processes:
Test #1: \( k_r = 0.35/yr > \frac{v^2}{D} = 0.20/yr \)
Test #2: \( k_r = 0.35/yr >> \frac{D}{L^2} = 0.015/yr \)
- If biodegradation is not included, maximum concentration at well would be 0.42 mg/L

Pesticides down the Rhine River
Case Studies

Pesticides down the Rhine River

- A fire broke out in a chemical warehouse located above Basel, Switzerland
- The fire burnt for about 12 h before it could be controlled
- Water from hoses ran into drains around warehouse and directly into Rhine River

Pesticides down the Rhine River

- 11 pesticides and other chemicals were stored at a facility:
  - organophosphorus pesticides:
    - disulfoton
    - thiometon
    - propetamphos
    - ethyl-parathion
    - etrimfos
    - fenitrothin
  - ethoxy-ethyl mercuric hydroxide
  - phenyl-mercuric acetate
  - oxadixyl

Pesticides down the Rhine River

- Chemicals entered river in two phases
  - dissolved
  - organic phase
- Organic phase was heavier than water and sank to bottom - some broke up in globules

Pesticides down the Rhine River

- About 40 to 80% of organic phase was later recovered by a vacuum operation around point of discharge
- Red dye was also present in warehouse, which colored organic and dissolved phases and made identification easier
Field measurements were taken at 4 locations as the plume passed:
- Maximiliansau (362 km below)
- Mainz-Wiesbaden (496 km)
- Bad Honnef (640 km)
- Lobith (865 km)

14 water supply plants dependent on Rhine were notified. There was no detection of contamination of drinking water. 75% of the pesticide load was disulfoton and thiometon, organophosphorus esters.

Esters hydrolyze rapidly in environment to form an acid and an alcohol or a mercaptan.

Neutral pH half-lives are:
- disulfoton, $t_{1/2} = 1.3$ days
- thiometon, $t_{1/2} = 8.0$ days

Biological activity may reduce these half-lives to 0.57-1.5 days.

Photolysis is possible, in particular due to the nitrate concentrations in the river, but is slower than hydrolysis, with half-lives of ~40 days.

Both pesticides are reasonably soluble:
- disulfoton, 25 mg/L
- thiometon, 200 mg/L

The total input of chemicals was estimated at 7,000 kg.
A small dam was constructed after fire was controlled to prevent further spillage into river.
Pesticides down the Rhine River

- Other site information:
  - Q = 1350 m³/s
  - h = 5 m
  - A = 1500 m²
  - Dₓ = 3.5 m²/day
  - Kᵋ = 0.2 m³/kg

Pesticides down the Rhine River

- Actual concentration pulse was much broader than modeled pulse due to:
  - slow dissolution of organic phase
  - dead zones in the river (locks, banks)
  - some chemical “short-circuited” along navigational channels

Pesticides down the Rhine River

- Total mass decreased with time:
  - 4,700 kg after 362 km
  - 3,700 kg after 496 km
  - 3,200 kg after 640 km
  - 1,400 kg after 865 km

  - Best fit for degradation constant was 0.2/day => t₁/₂ = 3.5 days

Pesticides down the Rhine River

- Effects of spill would have been much more long-lasting if the pesticides were more hydrophobic and persistent (e.g. DDT)

- Mercury compounds and oxadixyl were more persistent, but field concentrations were typically below detection limits
Most sensitive parameters in model were Q, A, I and kr.
A model that considers a changing flow channel cross-section would do better job fitting the data.
Determining the input function I is usually one of the hardest problems.

Samples of the sediment concentrations indicated levels up to 40 µg/kg, during an interval of 2 weeks.
Although sorption to the suspended sediments was fast, desorption back to the water column from the deposited sediments was slow, on the order of 2 months.