Pharmaceuticals in Groundwater: Fate, Transport, and Effects, Part I

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Overview

- Sources of Pharmaceuticals to Groundwater
- Detection/Monitoring
- Transport
- Potential Effects
- Mitigation Strategies
Routes to the Environment
Specific Sources to Groundwater

- Municipal wastewater
  - Sewage ponds/sewage farms
  - Artificial groundwater recharge
  - Irrigation
- Fertilization with liquid manure
- Manure lagoons
- Landfills
How are they detected?

- Levels range from ng/L to µg/L (ppt to ppb)
- 1-2 L samples
- pH adjustment
- Solid phase extraction (& derivatization)
- GC-MS or LC-MS/MS
What has been seen?

- **Source:** municipal wastewater
  - Clofibiric acid, lipid regulator
  - Carbamazepine, antiepileptic
  - Iopamidol, X-ray contrast
  - Sulfamethoxazole, antibiotic

- **Source:** wastewater for irrigation
  - Caffeine
  - Ibuprofen
  - Estrogens

Sacher et al, Vom Wasser, 2002, 99, 183
Scheytt, et al. ACS Symposium Series, 2001 v. 791
What has been seen?

- Source: lagoons/liquid manure
- Sulfa drugs
- Tetracyclines
What has been seen?

- **Source:** Landfill leachate
- **Sulfa drugs and analgesics**
  - Grunsted landfill, Denmark
  - In operation 1930-1977
- **22 different OWCs**
  - Landfill in Oklahoma
  - In operation 1920-1985
- **Suggests long term persistence/transport**

Barnes et al., *GWMR*, 2004 24, 119-126
Detection summary

- Wide range of compounds
  - Variety of structures
  - Variety of drug classes
- Maximum concentrations 1-10 ppb
- Antibiotics and estrogens of particular concern
Fate/ Transport

- Biodegradation is possible for some compounds, especially under aerobic conditions

- Sorption/Retardation
  - Pharmaceuticals don’t fit the “standard mold”
    - Acid/base chemistry, (multiple) pKₐ’s
    - Variety of substituents
    - Strong interactions with mineral surfaces
Fate/ Transport


\[ K_{ow} = 0.06 \]
\[ K_D = 1-100 \]
\[ R = 5-400 \]

\[ K_{ow} = 3 \]
\[ K_D = 0.1 \]
\[ R = 1.4 \]
Fate/ Transport

\[ K_{ow} = 0.12 \]
\[ K_D = 200-7000 \]
\[ R = 500-30,000 \]


**FIGURE 2.** Sorption of oxytetracycline to sodium-saturated montmorillonite (●) and kaolinite (○) clays at a total ionic strength of 10 mM. The solid line (−) denotes the best fit of eq 3 to the montmorillonite data, and the dashed line (−−) denotes a model fit that considers only cation species interactions with the clay.
Potential Effects

- Public perception
  - Reliability of groundwater resources
  - Water reuse
    - Artificial groundwater recharge
    - River bank filtration
    - “Toilet to tap”
    - Irrigation with (treated) wastewater
Antibiotic Resistance

You are the next class of drug-resistant bacteria. As humans continue to abuse and overuse antibiotics, your ranks will swell. So, go out there and mutate! And remember: that which does not kill us makes us stronger!!

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Resistance Genes in Groundwater

Up to six tetracycline resistance genes detected

Eight tetracycline resistance genes detected

One tetracycline resistance gene detected

Potential mitigation strategies

- Improved municipal wastewater treatment
  - Membranes
  - Add-on lagoons/wetlands (mixed success)
- Improved handling of manure
  - Lined ponds
  - Elevated temperature or time to allow degradation to occur before
- Answers will affect irrigation and groundwater recharge