Groundwater Impact Project:
Monitoring for Pharmaceuticals and Personal Care Products from a Wastewater Lagoon and Land Application Site

by
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Engineering Thesis Study
Overview

- Quick Background
  - How pharmaceuticals get into our environment
  - The concerns
- Review project investigating pharmaceuticals from a wastewater treatment site.
Contaminants of Concern

- Trace chemicals are found in waters around the world.
- Insufficient data on 87,000 chemicals.
- 2000 new chemicals introduced yearly.
The Concern

- Carcinogenic
- Promote antimicrobial resistance
- Biologically active
Pharmaceuticals and Personal Care Products (PPCPs)

- Products used by individuals for health or cosmetic reasons
- Prescription and over the counter medicines, shampoos, sunscreens, fragrances...
Pharmaceuticals and Personal Care Products (PPCPs) are introduced to the environment when:

- Pass out of the body.
- Washed off the body.
- Placed in the trash.
- Drugs are flushed down the toilet.
Pathways for PPCPs residues

Pharmaceuticals and Personal Care Products: medicines, soaps, fragrances, sunscreens, shampoos

Excretion or disposal (Hospital effluent) → Wastewater collection system → Sewage Treatment → Surface Water

Excretion (private household) → Wastewater collection system → Sewage Sludge → Ground Water

Solid waste disposal (unused medicine) → Waste disposal site → Soil

Drinking Water
Sewage systems are not equipped for PPCP removal

Picture of one of fourteen New York City Wastewater Treatment Facilities
Concern

- How does a drug optimized for a human target act on other species?

- Similar targets could govern different processes in different species.

Example: Serotonin re-uptake inhibitors i.e. Prozac, Zoloft, Luvox, and Paxil.

- Humans: regulates sleep, appetite, mood.
- Frogs: Thyroid signaling.
- Clams: regulates reproductive processes.
PPCP Project

- Could a small community in Idaho that uses wastewater lagoons be producing measurable PPCP’s in its sewage?

- And if so, could the PPCP’s be getting into the groundwater?
What is a Facultative Lagoon?

- A pond that holds wastewater.
- Frequently used in small communities.
- More than 7000 in use in the United States.
Wastewater is treated via physical, biological, and chemical processes.
Facultative lagoon treatment of PPCP’s?

Drinking water Treatment

Wastewater Treatment

River
Project Site

- Series of treatment lagoons
- Land application to 260 acres.
- Site permitted since 1989.
Lagoons

- 9 lagoons collect, treat and store wastewater.
- Lagoons leak or seep.
Can water from the lagoon be reaching groundwater wells?
Groundwater Flow is South to Southeast

Lagoons

Land Application Site

Groundwater flow
Aquifers

Soils

Fractured Basalt

Perched aquifer

Confining layer rock is leaky

Regional Aquifer

Flow direction
Lagoon Seepage

- lagoon
- Perched aquifer
- Confining “leaky” layer rock
- Regional Aquifer

Flow direction

Soils
Fractured Basalt

Flow direction
Lagoon Seepage

Lagoon

Perched aquifer

Confining “leaky” layer rock

Regional Aquifer

Flow direction
Idaho Wastewater Rules
IDAPA 58.01.16.493

- Lagoons constructed after April 21, 2007 must leak less than \( \frac{1}{8} \) inch per day (3400 gallons per acre per day).

- Existing lagoons constructed before that date may leak up to \( \frac{1}{4} \) inch per day (6800 gallons per acre per day).
This system leaks approximately 250 Million Gallons.
Meets state requirements.
Are pharmaceuticals (PPCPs) traveling with the water that is seeping?
Sample Sites

Headworks
Storage Lagoon
Shallow Wells

Groundwater Flow
Sample Sites

Seven Private Domestic Wells
Similar to procedures for using EPA Method 1669 (i.e., “clean hands/dirty hands” procedures) for Sampling Ambient Water for Trace Metals.
PPCPs list

- **Acetaminophen** – analgesic, antipyretic
- **Caffeine** – CNS stimulant
- **Carbamazepine** – anticonvulsant
- **Esterone** – steroid
- **Esteradiol, 17B** – steroid
- **Ethyl Estradiol** – steroid
- **Fluoxetine** – antidepressant
- **Gemfibrozil** – HDL drug
- **Ibuprofen** – nonsteroidal anti-inflammatory
- **Iopromide** – contrast agent
- **Progestrone** – steroid
- **Sulfamethoxazole** – antibiotic
- **Testosterone** – steroid
- **Triclosan** – antiseptic
- **Trimethoprim** – Bacteriostatic antibiotic
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<th>Analytes</th>
<th>Headworks</th>
<th>Detection Limit</th>
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Acetaminophen
Caffeine
Mood stabilizing Drug
Estrogens
Xray Contrast Media
Antibacterial
Lagoon Seepage

- Lagoon
- Perched aquifer
- Confining “leaky” layer rock
- Regional Aquifer

Well

Flow direction

Chemicals in groundwater:
- Acetaminophen
- Caffeine
- Carbamazepine
- Estrogens
- X-ray Contrast Media
- Sulfamethoxazole
Carbamazepine found in lagoon, shallow well, and deeper wells in similar concentrations.

Bar graph showing concentrations of Carbamazepine in different samples:
- Headworks
- Pond 8
- MW2
- Sample 11
- Sample 12
Carbamazepine

- anticonvulsant, antineuralgic, antimanic,
- antidiuretic, antipsychotic.

Potential Indicator for wastewater

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C_{15}H_{12}N_{2}O

Log Kow: 2.45
Carbamazepine

- Rainbow Trout: Very low doses changed oxidative metabolism in liver cells.

Sulfamethoxazole found in lagoons, shallow well, and deeper wells with carbamazepine
Anti-Bacterial: Sulfamethoxazole

- Used primarily in combination with other medicines, known as Bactrim or Septra.

- WW treatment may expose bacteria and create strains that are anti-biotic resistant.
Wastewater ponds are often duck ponds. Waterfowl migrate.
How Resistance Spreads

(Right) Intrinsic antibiotic resistance is a fact of bacterium life. Antibiotics do not induce resistance. Instead, they select for those few resistant bacteria in any given population, which then reproduce and create an increasingly resistant population through successive generations.

From “The Landscape of Antibiotic Resistance,” Environmental Health Perspectives Volume 117 Number 6 June 2009
Estrogens: Found in: shampoos, foods, drugs

In addition to reproductive development it effects:

**Body Structure**: accelerate growth, metabolism, reduce bone resorption.

**Protein synthesis**: increase liver production of certain proteins.

**Blood**: Increase platelet adhesiveness, increase HDL and decrease LDL.

**Fluid Balance**: influence sodium and water retention, increase cortisol.

**GI Tract**: reduce bowel motility and increase cholesterol in the bile.

**Cancer**: breast cancers may be hormone sensitive.
Estrogen conjugated with hydrophilic side chain.

Sewer

First lagoon

Storage lagoon

No Estrogens

Treatment

Side chain is detached

Estrogens

Estrogen

Side Chain

Chain

Estrogen

Estrogen

Side Chain

Side Chain
**Estrogens**

- Esterone - steroid
- Esteradiol, 17B - steroid
- Ethyl Estradiol – steroid

- Estrogen molecules *conjugate* with hydrophilic side groups.
- Conjugates are *easily cleaved* during treatment which can reform the original pharmaceutical.

**WW treatment may increase relevant environmental concentrations.**
Rainbow Trout: Estrogenic compounds may be more potent and may create issues with liver cell stress and viability. It's suspected of creating increased female/male ratios, sexual immaturity, and intersex issues.

Total Nitrogen

TN (Total Nitrogen) = TKN + nitrate + nitrite = organic nitrogen + ammonia + nitrate + nitrite.

TKN = organic nitrogen + ammonia.

![Graph showing Total Nitrogen levels for different locations on 11/14/2007.](image)
Sulfamethoxazole and carbamazepine found in shallow well and deeper wells where nitrate levels were at ambient levels.
Groundwater Flow

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Deeper wells

- Carbamazepine: 80 ng/L
- Sulfamethoxazole: 3.1 ng/L

Shallow well

- Acetaminophen: 21 ng/L
- Caffeine: 12 ng/L
- Carbamazepine: 77 ng/L
- Esterone: 120 ng/L
- Ethyl Estradiol: 9 ng/L
- Iopromide: 6.8 ng/L
- Sulfamethoxazole: 1.1 ng/L

Headworks

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Storage lagoon

- Acetaminophen: 21 ng/L
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Wastewater Treatment will create two paths:
Liquid and Solids

- Sewage In
- Effluent Out
- Chemical reactions
- Biosolids/Sludge
- Seepage
- Lagoon
Biosolids

In Idaho 60% of municipal solids are reclaimed by land application.
55 of 87 chemicals were detected in at least one of the samples collected, (45 chemicals found in a single sample).

25 of 87 chemicals were found in every sample. This includes: an antimicrobial disinfectant (triclosan), a musk fragrance (tonalide), an antihistamine (diphenhydramine), and an antiepileptic drug (carbamazepine).

The biosolids were more similar than different.
- Produced by a variety of treatment processes.
- Served vastly different sized cities and towns.
- The types of contaminants and their relation to each other did not vary greatly between the biosolids tested.

Victor Hugo wrote in his book Les Miserables, “…the history of men is reflected in the history of sewers…”
In 2004, 2.6 billion people in the world did not have basic sanitation. Wastewater treatment often doesn’t happen.

- In the Northeast Pacific 98% of domestic wastewater is discharged without treatment.
- In the Caribbean 90% is discharged without treatment.

Picture Source: UNEP, David Tapia Munoz, Topham Picturepoint
Wastewater Reuse

- Eliminates the need for discharge to surface water.
- Can be the primary source of irrigation water for nutrient utilization by crops.
Wastewater Reuse

Can be a source of aquifer recharge.
Global Sustainability, Reuse and Recycling of Wastewater and Biosolids

- Population and density create water challenges
  - Affordable and Sustainable

- Water quality goals need to be health based
  - Detection ≠ safe
  - Non-detect ≠ risk

Diagrams show intersections of Society, Economy, and Environment.
Risk = Toxicity x Exposure

There are no systematic studies demonstrating that much lower than therapeutic doses will cause direct harm in exposed humans, however:

- Hypersensitivity
- Indirect health effects (i.e. antibiotic resistance)
- Incomplete data for reliable benchmarks for chronic low dose exposure
- Multiple chemical low dose exposure
- Indirect effects from harm to other species in the environment
An early water regulation:

“No one shall with malice pollute the waters where they issue publicly. Should anyone pollute them, his fine shall be ten thousand sesterti.”

(approx. $600)

Source: Sextus Julian Frontinus, Water Commissioner of the City of Rome, 97 CE
Thoughts

- **100% probability of chronic low dose exposure** over your lifetime, to a mixture of chemicals that are unknown endocrine disruptors.

- **Unknown Effects**
  - From the organism to the population.
  - From acute to chronic exposure.
  - To understanding of the processes and consequences of system disruption.
  - From single chemical to multi-chemical exposure and dose understanding.

- **Mitigation: Probability + Impact**
  - Can you reduce the impact of Drugs (endocrine disruptors) or carcinogens?
  - Can you reduce the probability of exposure?
Pharmaceuticals and Personal Care Products (PPCPs) are introduced to the environment when:

- Pass out of the body.
- Washed off the body.
- Placed in the trash.
- Drugs are flushed down the toilet.
PPCP  Project Summary

➢ Don’t Flush Drugs Down the Toilet!
Chemicals change us.

a dash of triclosan,

a pinch of caffeine,

mix in some anti-depressants,

....a little fire retardant....

only a bit of atrazine...

and estrogens and.....