Pharmaceuticals and Contaminants of Emerging Concern in Domestic Wastewater and their Effects on Septic Systems

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outline

• The world of contaminants
  • Categories & how to prioritize
  • Properties that tell us about their likely removal

• What do we know about occurrence and removal
  • PPCPs and other household compounds, including PFAS
  • Onsite treatment systems
  • Comparison to centralized municipal systems

• Can any of these impact treatment performance?
The Universe of Chemicals

• Elements and their aqueous forms
  • 91 elements with $t_{1/2} > 100$ years
  • Each may have as many as 10 isotopes, 11 oxidation states, and many oxo-hydroxyl complexes

• Chemical compounds and ions – most are organic
  • 18.4 M in NIH’s PubChem database (9.8 M in Beilstein)
    • ~100,000 new ones each year
  • 800,000 are in active use today
  • 85,000 are or have been readily available in commerce
  • 8,000 currently in high production

At 20 min/compound, lecture ends at 3:50 AM on April 26, 2716
Organic Compounds: Types?

- **Natural Compounds**
  - Fulvics
  - Proteins, carbohydrates, etc
    - cyanotoxins
- **Domestic WW Organics**
- **Industrial Synthetic Organics**
  - Plasticizers: phthalates
  - solvents: tetrachloroethylene
  - waxes: chlorinated parafins
  - others: PCB’s
- **Hydrocarbons & oil derivatives**
  - includes products of combustion: PAH’s
- **Agricultural Chemicals**
  - pesticides: DDT, kepone, mirex
- **Pharmaceuticals, etc**
  - Anti-epileptics
  - Beta-blockers
  - X-ray contrast media
  - antibiotics
- **Home & Personal Care Products**
  - triclosan
  - Musks, flame retardants
- **Endocrine Disrupters**
  - Steroidal estrogens
- **Natural process byproducts**
  - Conjugated pharmaceuticals
- **Engineered process byproducts**
  - disinfection byproducts, etc

Covered with NOM-Day 1 and case studies Day 3
Figure 4. Third evaluation. Matrix plot of the nine remaining chemicals (point estimates for both exposure and toxicity). Those circled are the three designated high priority for further evaluation based on proximity to the yellow zone.
Figure 7. Exposure-toxicity intersection formed from mixing two probability distributions showing isoprob contours.
II. Anthropogenic Substances: EDCs & PPCPs

- **Endocrine Disrupting Compounds (EDCs)**
  - **Estrogens**: regulate and sustain female sexual development and reproductive function
  - **Androgen**: male sex hormones
  - **Mimics**: estrogenic and androgenic compounds
  - Also anti-estrogenic and anti-androgenic

- **Pharmaceuticals and Personal Care Products (PPCPs)**
  - Non-steroidal anti-inflammatory
  - Anti-epileptic
  - Antibiotics
  - Anti-anxiety
  - Antioxidants
  - Pain reliever
  - Anti-cholesterol
  - Sun Screen
Origins and Fate of PPCPs in the Environment

Pharmaceuticals and Personal Care Products

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Environmental Chemistry Branch
What are OWCs, EDCs and PPCPs and Why the Interest?

• **EDC**- Endocrine Disrupting Compounds
  • EDCs are a class of compounds which alter the hormonal system of an organism.
  • Eg: DDT, 17-alpha Ethinylestradiol, Bisphenol A, etc.

• **PPCP**- Pharmaceuticals and Personal Care Products
  • Any products used for personal health or cosmetic reasons
  • Includes prescription and non-prescription drugs, veterinary drugs, fragrances and cosmetics

• **OWC** – Organic wastewater compounds
  • All of the above and more

• **Why study them?**
  • Direct impacts on human health
    • Maybe not the most important?
    • Impacts of mixture are uncertain
  • Public perception
    • Becoming a very sensitive issue
  • Direct impacts on ecological health
    • Well documented: feminization of fish, etc.
  • Tracers of wastewater contamination
  • Indicators & promoters of antibiotic resistance
  • Precursors to more Hazardous DBPs
Fluorinated hydrocarbons: nomenclature

• Poly- and Perfluoroalkyl substances (PFAS)
  • **Per** means all hydrogens are substituted with fluorine atoms
  • **Poly** means more than one fluorine atom, but some hydrogens too

• Perfluoroalkyl acids (PFAAs)
  • Perfluorocarboxylic Acids
    • C4 to C12 compounds measured
    • C8 was in CCL3: PFOA
  • Perfluorosulfonic Acids
    • C4 to C10 compounds measured
    • C8 was in CCL3: PFOS
  • Many others, e.g.,
    • Perflurosulfonamides
    • Perflorosulfonamidoacetic acids

More on PFAS at the end
Estimating Source Terms

• Use-based calculations (e.g., Sedlak)
  • Get national or regional use data
  • Estimate non-metabolized/adsorbed fraction
  • Estimate removal across conventional WWT

• Real WW effluent monitoring
  • Highly variable based on date, time, location, processes, climate, etc
Seasonal Variation in the Occurrence and Removal of Pharmaceuticals and Personal Care Products in Different Biological Wastewater Treatment Processes

Qian Sui, Jun Huang, Shubo Deng, Weiwei Chen, and Gang Yu*

School of Environment, THU – VEOLIA Joint Research Center for Advanced Environmental Technology, Tsinghua University, Beijing 100084, China

Supporting Information

ABSTRACT: The occurrence of 12 pharmaceuticals and personal care products (PPCPs) in two wastewater treatment plants in Beijing was studied monthly over the course of one year. The removal of PPCPs by three biological treatment processes including conventional activated sludge (CAS), biological nutrient removal (BNR), and membrane bioreactor (MBR) was compared during different seasons. Seasonal variations of PPCPs in the wastewater influent were discrepant, while in the wastewater effluent, most PPCPs had lower concentrations in the summer than in the winter. For the easily biodegradable PPCPs, the performance of MBR was demonstrated to be more stable than CAS or BNR especially during winter months. Diclofenac, trimethoprim, metoprolol, and gemfibrozil could be moderately removed by MBR, while their removal by CAS and BNR was much lower or even negligible. Nevertheless, no removal was achieved regardless of the season or the treatment processes for the recalcitrant PPCPs. Studies on the contribution of each tank of the MBR process to the total removal of four biodegradable PPCPs indicated the anoxic tank was the most important unit, whereas membrane filtration made a negligible contribution to their elimination.
Seasonal Variability

- BF → Bezafibrate
- CBZ → Carbamazapine
- CF → Caffeine
- CP → Chloramphenicol
- DEET → N,N-diethyl-m-toluamide
- DF → Diclofenac
- GF → Gemfibrozil
- MTP → Metoprolol
- SP → Sulpiride
- TP → Trimethoprim

Seasonal variation in the concentrations of some PPCPs in the wastewater influents (a–d) and effluents (e–h). The symbols represent the mean concentration, and error bars represent the maximum and minimum concentration in CAS, MBR, and BNR processes.

Qian Sui; Jun Huang; Shubo Deng; Weiwei Chen; Gang Yu; Environ. Sci. Technol. 2011, 45, 3341-3348.
Comparison of the overall removal efficiencies by:
• Conventional Activated Sludge (CAS)
• Biological Nutrient Removal (BNR), and
• Membrane Bioreactor (MBR) processes.

Qian Sui; Jun Huang; Shubo Deng; Weiwei Chen; Gang Yu;
Seasonal variability for removal

Seasonal variation in the removal efficiencies of PPCPs during the whole year: comparison among MBR and other two biological treatment processes.

Qian Sui; Jun Huang; Shubo Deng; Weiwei Chen; Gang Yu; Environ. Sci. Technol. 2011, 45, 3341-3348.
Removal efficiencies of PPCPs in each tank of A/A/O-MBR process: (a) BF, (b) CF, (c) DEET, (d) TP. *** means that the removal efficiency of aerobic tank and membrane filtration could not be calculated because the CF concentrations were <LOQ after anoxic tank in the first sampling.

Qian Sui; Jun Huang; Shubo Deng; Weiwei Chen; Gang Yu; Environ. Sci. Technol. 2011, 45, 3341-3348.
• 25 systems monitored

From: Glassmeyer, 2016
Occurrence: Treated Water

From: Glassmeyer, 2016
Figure 1 | Micro-pollutant (MP) fractions and processes, influencing MP removal in wastewater. Compiled based on studies by Criddle (1993); Alvarez-Cohen & Speitel (2001); Ternes & Joss (2006); Meiler et al. (2007); Monteith et al. (2008); Lindblom et al. (2009); Barret et al. (2010a); Plösz et al. (2011b,c). DCM: dissolved and colloidal matter.
Fate and Transport Modeling
Chemical Properties => Destiny

Chapra, 1991 [ASCE JEED 17(5)656]

- Fate in Aquatic systems
  - Relates to fate in treatment
- Aquatic assessment assuming:
  - $T_a = 283$ K
  - $M = 200$ g/mole
  - $U_w = 5$ mph
  - $v_s = 91$ m/yr
- Assimilation refers to general rate of removal

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![Diagram of fate and transport modeling with chemical properties leading to destiny. Regions include SEDIMENT ZONE (Assimilation depends on sediment recycle), WATER ZONE (Poor assimilation), AIR ZONE (Strong assimilation), with categories for oxidation, IX or biodegradation, coagulation or adsorption, stripping or adsorption, and solubility.](chart.png)
Summary: pesticides

- Modified from: Surface Water Quality Modeling, by Chapra, pg.735
Aromatic Carcinogens

• PCBs (Polychlorinated Biphenyls)
  • Arochlor mixtures

• PAHs (polynuclear aromatic hydrocarbons)

Chapra, 1991 [ASCE JEED 17(5)656]
Pesticides

- Broad spectrum of properties
Where are the PPCPs and OWCs?

• Not much data on volatilization, but we do have $K_{ow}$ values
• Most are probably in this region

![](chart.png)
Onsite Wastewater Treatment Systems

- Conventional
  - Septic Tank
  - Drainfield
- Alternative
  - Biofilters
  - Aerobic units
  - Special sorbents

Concentrations of OWCs in septic tank effluent, drainfield effluent, and WWTP effluent. Horizontal lines show censoring values for systems where the median value was below the censoring value.

Removals of OWCs

• Septic tank
  • Effluent similar to primary effluent in a conventional wastewater treatment plant
  • Mostly due to association to solids, grease, some anaerobic degradation

• Drainfields
  • Removal by sorption, aerobic biodegradation, and some volatilization
  • Some are very well removed (>99%)
    • Triclosan, Caffeine, acetaminophen
      • Presence of these indicates a failed septic system
  • Some are not removed at all
    • Example: certain artificial sweeteners, especially sucralose
      • Presence of these indicates zone of influence
Removal in Drainfields

• Drainfields viewed as analogous to activated sludge systems
• Median effluent concentrations are similar
  • Vary by < factor of 10 for 24 of 29 OWCs
  • A few were much lower in drainfield effluents
    • Trimethoprim (antibiotic)

OWC median removal efficiencies in onsite drainfields and in WWTPs. For median removal efficiencies above a censoring value, the range of possible values is plotted as a light blue line.
Modeling approach applied to OWCs

**Sorption**

![Sorption graph](attachment:graph_a.png)

**Biodegradation**

![Biodegradation graph](attachment:graph_b.png)

Fluorinated hydrocarbons: nomenclature

• Poly- and Perfluoroalkyl substances (PFAS)
  • Per means all hydrogens are substituted with fluorine atoms
  • Poly means more than one fluorine atom, but some hydrogens too

• Perfluoroalkyl acids (PFAAs)
  • Perfluorocarboxylic Acids
    • C4 to C12 compounds measured
    • C8 was in CCL3: PFOA
  • Perfluorosulfonic Acids
    • C4 to C10 compounds measured
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  • Many others, e.g.,
    • Perflurosulfonamides
    • Perflorosulfonamidoacetic acids
Tip of the PFAS-iceberg?

- Family tree of PFASs
  - most of the studies to date have focused on
    - Long-chain perfluoro carboxylic acids (PFCAs) which include PFOA
    - Long chain Perfluoro sulfonic acids (PFSAs), which include PFOS
    - Along with their major precursors.
  - New interest in GenX and others

Zhanyun Wang; Jamie C. DeWitt; Christopher P. Higgins; Ian T. Cousins; Environ. Sci. Technol. 2017, 51, 2508-2518
PFAS properties

- High solubility, low volatility, low reactivity

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa</th>
<th>Vapor Pressure</th>
<th>Henry’s Law Const</th>
<th>Aqueous Solubility</th>
<th>Log $K_{oc}$ (L/Kg)</th>
<th>Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA $\text{C}<em>8\text{H}</em>{15}\text{O}_2$</td>
<td>1.3</td>
<td>0.1 kPa (20°C) 10 mm Hg (25°C)</td>
<td>5.0 mol dm$^{-3}$ atm$^{-1}$ log $H_e = -3.7$ (-9.4 @pH7)</td>
<td>4.1 g/L (22°C) 9.5 g/L (25°C)</td>
<td>2.06 $^{\text{HL}}$ (Log $K_{dm} = -1.54$)</td>
<td>Stable</td>
</tr>
<tr>
<td>PFOS $\text{C}<em>8\text{F}</em>{17}\text{SO}_3$</td>
<td></td>
<td>3.31 x 10$^4$ Pa at 20°C</td>
<td></td>
<td>570 mg/L</td>
<td>2.57 $^{\text{HL}}$ (Log $K_{dm} = -1.03$)</td>
<td>Stable</td>
</tr>
<tr>
<td>PFHxS $\text{C}<em>6\text{F}</em>{13}\text{SO}_3$</td>
<td></td>
<td>0.61 Pa (25°C)$^{\text{ES}}$</td>
<td></td>
<td>6.2 mg/L$^{\text{ES}}$ 22 mg/L$^{\text{ES}}$</td>
<td>3.5$^{\text{ES}}$ (Log $K_{dm} = -0.1$)</td>
<td>Stable</td>
</tr>
<tr>
<td>PFBS $\text{C}_4\text{F}_9\text{SO}_3$</td>
<td></td>
<td>0.29 mm Hg at 20°C</td>
<td></td>
<td>8900 mg/L$^{\text{ES}}$ 344mg/L$^{\text{ES}}$</td>
<td>2.2$^{\text{ES}}$ 1.9$^{\text{ES}}$ (Log $K_{dm} = -1.5$)</td>
<td>Stable</td>
</tr>
<tr>
<td>6:2 FTS $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{SO}_3$</td>
<td></td>
<td>0.115Pa(25°C)$^{\text{ES}}$ 0.00086 mm Hg (25°C)$^{\text{ES}}$</td>
<td></td>
<td>11 mg/L$^{\text{ES}}$ 2mg/L$^{\text{ES}}$</td>
<td>4.0$^{\text{ES}}$ (Log $K_{dm} = -0.4$)</td>
<td>Biodegradable</td>
</tr>
</tbody>
</table>

$K_{d} = K_{oc}f_{oc}$

$K_{d} = K_{oc}f_{oc}$

FTS=Fluorotelomersulfonic acid

Some data from: Michelle Crimi, Clarkson University

$K_{d} = K_{oc}f_{oc}$


ES = estimated from EPISuite (U.S. EPA [http://www.epa.gov/opptintr/exposure/pubs/episuite.htm])
Chemical Properties $\rightarrow$ Treatment

- Fate in Aquatic systems
  - Relates to fate in treatment
- Partitioning Parameters
  $f_{oc} = 0.05 \quad m = 5 \text{ g/m}^3$
  $K_d = K_{oc} f_{oc}$
- Aquatic assessment assuming:
  - $T_a = 283 \text{ K}$
  - $M = 200 \text{ g/mole}$
  - $U_w = 5 \text{ mph}$
  - $v_s = 91 \text{ m/yr}$
- Assimilation refers to general rate of removal

Chapra, 1991 [ASCE JEED 17(5)656]
Study of 6 WWTPs

Sorption to biosolids in WWT

- On “activated sludge and final sludge”
- Aeration basin solids and secondary settled solids?

Fluorotelamers in AS

- Degradation under anaerobic conditions

Formation of PFAS products

Some de-fluorination!

Impacts on WWT organisms

- Anecdotal evidence and growing literature
Only a problem at high Concentrations?

• Process performance
  • Decreasing rate of $\text{O}_2$ utilization
    • Ampicillin (20 mg/L)
  • Decreasing rate of nitrification
    • Ciprofloxacin (0.2 mg/L), Ampicillin (20 mg/L), tetracycline (5 mg/L)
  • Inhibition of denitrification
    • Chlorotetracycline
  • Poorer removal of orthophosphate
    • Chlorotetracycline (10 mg/L), erythromycin (5 mg/L)

• Shifting microbial ecology
  • Loss of accumulibacter, increase in competibacter
    • erythromycin (5 mg/L)

• Sludge behavior
  • Reduction in attached biomass and floc size
    • Ciprofloxacin (0.2 mg/L),
  • Sludge bulking
    • tetracycline (5 mg/L)

• Enzymatic impacts
  • Dehydrogenase inhibition
    • Ampicillin
  • Reductase
    • Chlorotetracycline

• Reactive Oxygen Species (ROS)
  • Increased production
Pharmaceuticals found in US drinking water

Trace quantities could endanger wildlife, humans

By Jeff Dennis
Associated Press

NEW YORK — An array of pharmaceuticals — including antibiotics, anti-inflammatories, mood stabilizers, and anticancer drugs — have been found in the drinking water supplies of at least 41 million Americans, an Associated Press investigation found.

The concentrations of these pharmaceuticals are tiny, measured in quantities of parts per billion or trillion, far below the levels of a medical dose. And utilities insist that their water is safe.

But the presence of so many prescription drugs — and over-the-counter medicines like acetaminophen and ibuprofen — is an ominous sign that much of our drinking water is being contaminated with an array of substances of long-term consequences to human health.

In the course of a five-month investigation, the AP discovered that drugs have been detected in the drinking water supplies of 25 major metropolitan areas from southern California to northern New Jersey, from Detroit to Louisville, Ky.

Water providers often dispute results of pharmaceutical screenings, unless pressed, the Associated Press found.

For example, the head of a group representing major California suppliers said the public “doesn’t know how to interpret the information” and might be unduly alarmed.

When people take pills, their bodies absorb some of the medication, but the rest of it passes through and is flushed down the toilet. The wastewater is treated before it is discharged into reservoirs, rivers, or lakes.

Then, some of the water is cleaned again at drinking water treatment plants and piped to consumers. But most treatments do not remove all drug residue.

While researchers do not yet understand the exact risks from decades of persistent exposure to random combinations of low levels of pharmaceuticals, recent studies, which have gone virtually unnoticed by the public, have found alarming effects on human cells and wildlife.

“We recognize it is a growing concern, and we’re taking it very seriously,” said Benjamin Grumbles, assistant administrator for water at the US Environmental Protection Agency.

The Associated Press reviewed hundreds of scientific reports, analyzed federal drinking water databases, visited environmental scold sites, and treatment plants and reviewed more than 250 officials, academics, and scientists. They also surveyed the nations 50 largest cities and a dozen other major water providers, as well as smaller community water providers in all 50 states.

Here are some of the key test results:

- Officials in Philadelphia said testing discovered 56 pharmaceuticals or byproducts in treated drinking water, including medicines for pain, infection, high cholesterol, asthma, epilepsy, mental illness, and heart problems. Slugs, three pharmaceuticals or byproducts were found in the city’s water supplies.

- Antidepressant and antiangiogenesis medicines were detected in a portion of the treated drinking water for 25.5 million people in southern California.

- Researchers at the US Geological Survey analyzed aPasqual Valley Water Commission’s drinking water treatment plant, which serves 650,000 people in northern New Jersey, Fairlands, Va., Montgomery County in Maryland; Omaha; Oklahoma City; Santa Clara, Calif.; and New York City.

- Of the 38 major metropolitan areas where tests were performed on drinking water supplies, only Albuquerque, Austin, Denver, and Virginia Beach, Va., said tests were negative.

EPA ADDRESSING THE ISSUE

The federal government doesn’t require any testing and hasn’t set safety limits for drugs in water.

Some providers assess only for one or two pharmaceuticals, leaving open the possibility that other are present.

Out of the 10 major water providers contacted, the drinking water for 26 was tested. Boston is among the 46 that haven’t been tested, along with Baltimore, Chicago, Houston, Miami, New York, and Phoenix.

The investigation also indicates that every drinking water test, the natural sources of so much of the nation’s water supply, are contaminated. Tests were conducted in the watersheds of 35 of 62 major providers surveyed by the Associated Press and pharmaceuticals were detected in 31.

Yet officials in six of those 38 metropolitan areas said they did not go on to test their drinking water for generic drugs, Fairlands, Va., Montgomery County in Maryland; Omaha; Oklahoma City; Santa Clara, Calif.; and New York City.

Of the 38 major metropolitan areas tested, drugs were detected in San Francisco’s drinking water.

The drinking water for Washington, D.C., and surrounding areas tested positive for six pharmaceuticals.

Calif. dunes lure off-road enthusiasts, smugglers

March 10, 2008; page 2