

Identification and Ecotoxicity of Pharmaceuticals in the Surface Waters of the Upper Mississippi and Lower Illinois Rivers

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Overview

- The need to evaluate pharmaceuticals and EDCs in major rivers in the midwest
- Overall scope of the project
- Sampling, extraction, & analysis
- Toxicity testing
- Ending Comments

Pharmaceuticals in the Water

- Estimated 30-90% excreted as active ingredient¹
- Discharged into surface waters at similar rates as pesticides²
- Studies have found that they are prevalent in waters^{3,4}

¹ Halling-Sorensen, B., S.N. Nielsen, P.F. Lanzky, F. Ingerslev, H.C.H. Lutzhoft, and S.E. Jorgensen. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment - A review. *Chemosphere*, 36:357-394.

² Daughton, C.G. and T.A. Ternes. 1999. Pharmaceuticals and personal care products in the environment: Agents of subtle change? *Environ. Health Perspect.*, 107:907-938.

³ Kolpin, D.W., Furlong, E. T.; Meyer, M. T.; Thurman, E. M.; Zaugg, S. D.; Barber, L.B. and H.T. Buxton. 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: A national reconnaissance. *Environ. Sci. Technol.*, 36:1202-1211.

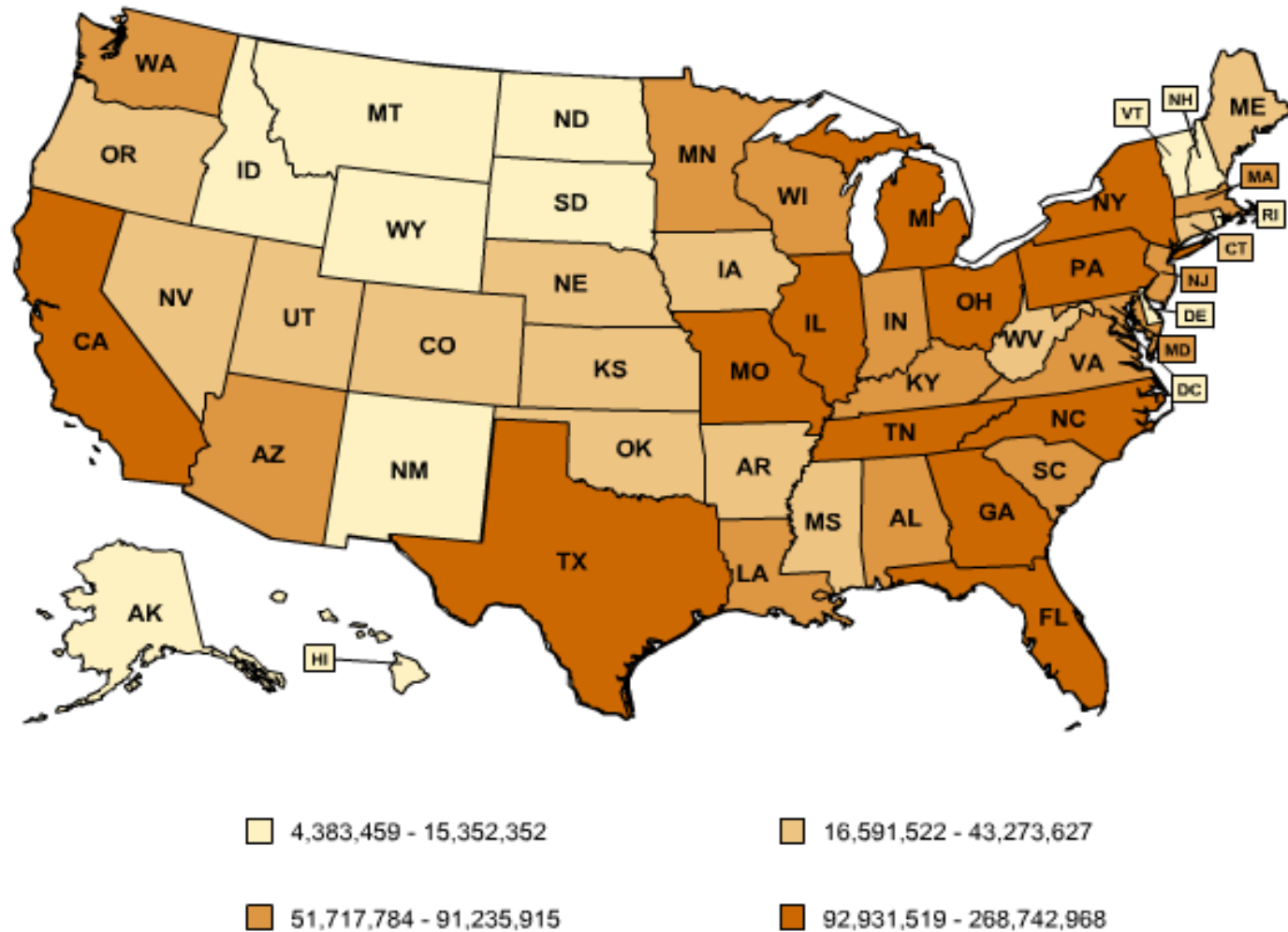
⁴ B. Halford. 2008. Pharmaceuticals have been finding their way into our environment for a long time, but just what are they doing there? *C&E News*. 86 (8), 13-17.

Pharmaceuticals in the Water

- Some have even found seasonal relationship⁵
- Widespread and in the midwest.....

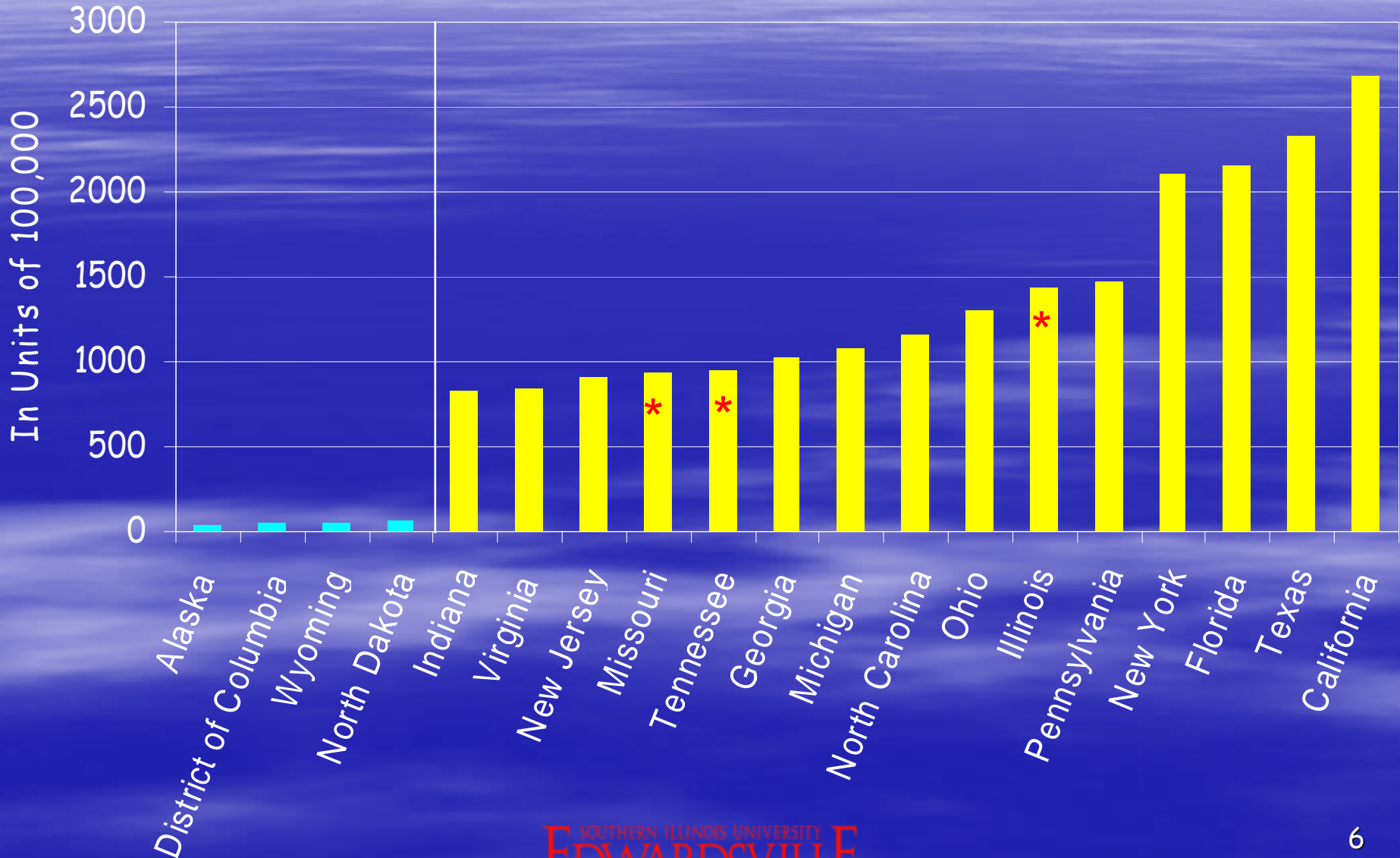
⁵ Niina, M.V., N.M., Tuhkanen, T. and L. Kronberg. 2005. Seasonal Variation in the Occurrence of Pharmaceuticals in Effluents from a Sewage Treatment Plant and in the Recipient Water. *Environ. Sci. Technol.* 39, 8220-8226.

Total Number of Retail Prescription Drugs Filled at Pharmacies, 2006

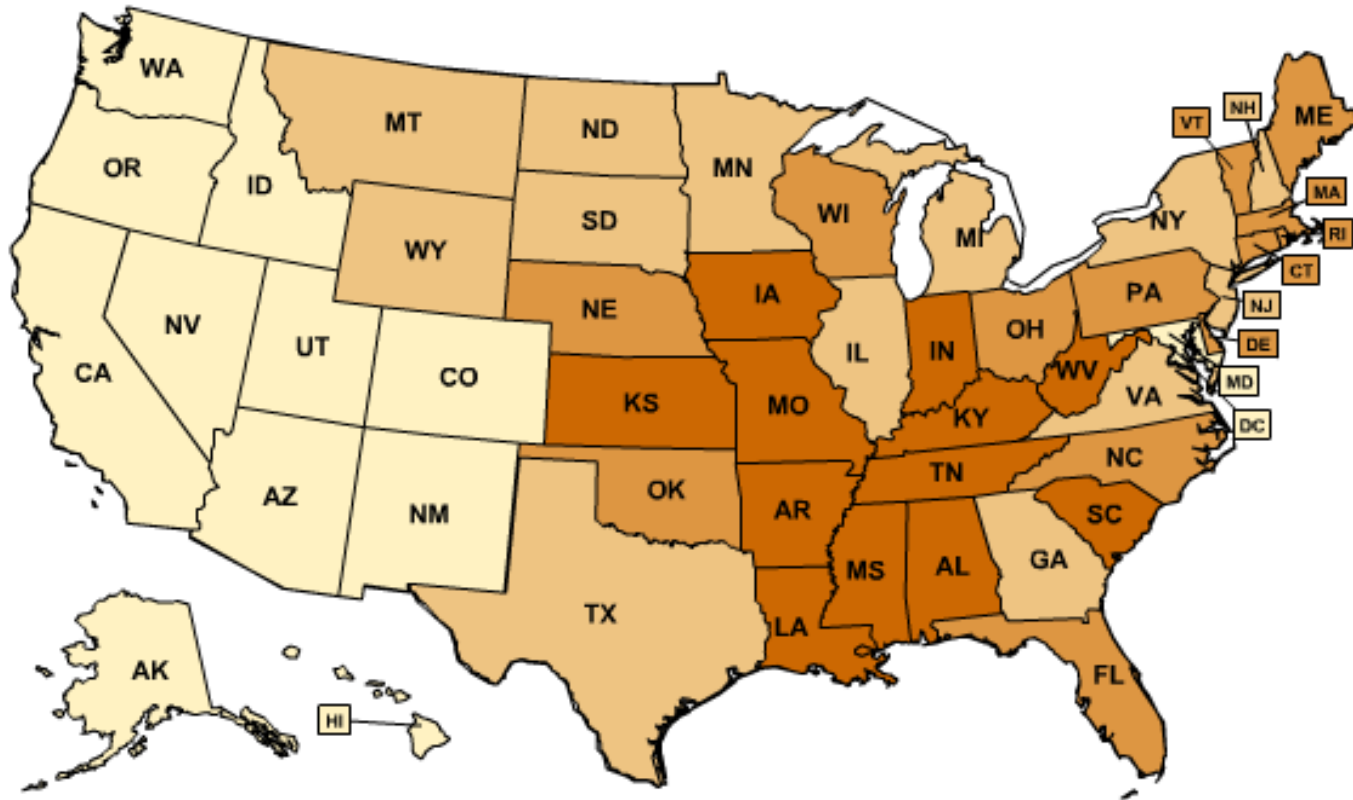


Total Number of Retail Prescription Drugs Filled at Pharmacies, 2006

(<http://www.statehealthfacts.org>)



Retail Prescription Drugs Filled at Pharmacies (Annual per Capita), 2006



6.5 - 9.6

9.9 - 11.3

11.4 - 13.1

13.2 - 17.2

Overall scope of the project

- Sampling, extraction, and analysis of selected pharmaceuticals, veterinary antibiotics and endocrine disrupting compounds (EDCs) from surface waters
 - Along the Mississippi River (MR) & the Illinois River (IR)
 - In tributaries to both rivers
- Use results to determine chemicals to use in aquatic toxicity tests
 - Individually
 - In mixtures at concentrations found in surface waters

Sampling

- Identification of sampling sites
- Weekly or biweekly sampling
- Periodic hourly sampling (24-48hr)
 - ISCO automated samplers

Use the results to go into the toxicity assays

Sampling Locations

- Alongside river
 - Above and below convergence
- Tributaries
 - Downstream feedlots
- Water Treatment facilities
 - Pre- and post

Some of the Compounds of Interest (~33%)

17-a-ethynylestradiol

5,5-diphenylhydantoin

Acetaminophen

Amoxicillin trihydrate

b-estradiol

Ciprofloxacin

Coumestrol

Diltiazem HCl

Estrone

Fluoxetine HCl

Gemfibrosil

Genistin

Ibuprofen

Irgasan

Levofloxacin

Lexapro

Lipitor

Naproxen

Nexium

Ranitidine HCl

Sertraline HCl

Singulair

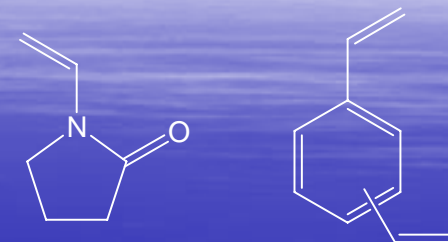
Sulfamethoxazole

Synthroid

Trimethoprim

Extraction

- 1 L samples
- Solid phase extractions
 - In development
 - 1L H₂O samples (varying pH depending on analyte)
 - ^{6,7} Oasis HLB (hydrophilic lipophilic balance) (50-500mg)
 - N-vinylpyrrolidone and divinylbenzene
 - Pretreatment w/5mL each of MTBE, MeOH, H₂O, then sample, dry, and elute w/90:10 MeOH:MTBE
 - Analytes & Matrix interferences



⁶ Vanderford, B.J., Pearson, R.A., Rexing, D.J., and S.A. Snyder. 2003. Analysis of Endocrine Disruptors, Pharmaceuticals, and Personal Care Products in Water Using Liquid Chromatography/Tandem Mass Spectrometry. *Anal. Chem.* 75(22); 6265-6274.

⁷ W.W. Buchberger. 2007. Novel analytical procedures for screening of drug residues in water, waste water, sediment and sludge. *Analytica Chimica Acta.* 593. 129-139.

Analysis

- LC-MS/MS
 - Varian 310 (triple quadrupole)
 - ESI ionization source (pos & neg)
 - Current detection limits range between 500 ng/L down to 50 ng/L (ppt)

LC-MS/MS Parameters (for some analytes)

| Pharmaceuticals | Precursor Ion | Daughter Ion | ESI |
|------------------------|---------------|--------------|-----|
| Acetaminophen | 150.9 | 109.9 | + |
| Gemfibrozil | 396.1 | 317.9 | - |
| Ibuprofen | 293.7 | 249.6 | - |
| Naproxen | 415.2 | 178.1 | - |
| Sulfamethoxazole | 310.3 | 148.1 | + |
| Fluoxetine | 249.1 | 120.7 | + |
| Diclofenac Sodium | 205.0 | 160.7 | - |
| Amoxicillin Trihydrate | 172.9 | 157.6 | - |
| Trimethoprim | 250.1 | 156.0 | + |
| Diltiazem HCl | 291.1 | 230.1 | + |

Toxicity Testing

- Individual compounds
- Combinations
- Seasonality⁵ (if concentrations vary)

⁵ Niina, M.V., N.M., Tuhkanen, T. and L. Kronberg. 2005. Seasonal Variation in the Occurrence of Pharmaceuticals in Effluents from a Sewage Treatment Plant and in the Recipient Water. *Environ. Sci. Technol.* 39, 8220-8226.

Toxicity Testing

- Organism: *Daphnia magna*
 - Static renewal
 - 96hr toxicity tests
 - Pulsed exposures
 - Based on 24-48 hour sampling
- Endpoints
 - Mortality
 - Reproduction
 - Molting

Ending Notes

- Very early in the process
- There are a lot of ecotoxicological questions that need to be answered
 - Bioavailability to organisms
 - Aquatic toxicity (lethality)
 - Sublethal effects
- Down the road.....biomonitoring

Comments/Questions