







#### Today's Speakers

- Ed Topp, Agriculture and Agri-Food Canada
   Pharmaceuticals and personal care products [PPCPs] in biosolids
- Jeffrey L. Ullman, University of Utah
  Antibiotics in Environmental Systems
- Kuldip Kumar, Metropolitan Water Reclamation District of Greater Chicago
  - Land Application of Biosolids: Human Health Risk Assessment Related to Emerging Contaminants





#### **Presentation outline**

- Overview of 'emerging contaminants'
- Quantities and types of PPCPs in biosolids
- Fate of PPCPs following land application
- Conclusions

## *"Emerging organic contaminants"*Varied terms- "microconstituents", "micropollutants", "contaminants of emerging concern", etc Can include... Endocrine-active chemicals. Pharmaceuticals Personal care products [fragrances, microbiocides..] Nanomaterials [inorganic, organic] Polybrominated flame retardants Perfluorinated chemicals [non-stick and surface-protective coatings] Plasticizers

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• Etc..







## Overall general conclusion from the surveys

• PPCPs are ubiquitous in biosolids

PPCPs detected in biosolid (ng/g)						
	[Sabourin et al. STOTEN 431 (2012) 233-236]					
Triclocarban	6030	Amlodipine	120	Atorvastatin	15.1	
Ciprofloxacin	5870	Norverapamil	94.7	Cotinine	14.8	
Triclosan	4680	Carbamazepine	94.3	Codeine	14.6	
Norfloxacin	1750	Fluoxetine	89.8	Naproxen	14	
Ofloxacin	1068	Valsartan	76.5	Hydrocodone	11	
Diphenhydramine	781	Verapamil	70.2	Diltiazem	10.1	
Sertraline	497	Clarithromycin	67.4	Enrofloxacin	10.1	
Miconazole	477	Norfluoxetine	59.6	Gemfibrosil	7.89	
Amitriptyline	448	Anhydrotetracycline	55.8	DEET	6.89	
4-Epitetracycline	386	Doxycycline	42.4	Erythromycin-H <sub>2</sub> O	4.06	
Tetracycline	341	Cimetidine	42.1	Ranitidine	3.26	
Azithromycin	213	Digoxigenin	38.1	Propoxyphene	2.9	
Ibuprofen	167	Propranolol	35.4	Atenolol	2.88	
Triamfarene	153	Anhydrochlortetracycline	32.9	Benztropine	2.46	
Amphetamine	147	10-OH-amitriptyline	23.3	Desmethyldiltiazem	2.05	
Paroxetine	130	Thiabendazole	16.5	Diazepam	0.845	

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## Greenhouse studies reveal the potential for crop uptake

Environ. Sci. Technol. 2010, 44, 6157–6161

Uptake of Pharmaceutical and Personal Care Products by Soybean Plants from Soils Applied with Biosolids and Irrigated with Contaminated Water

CHENXI WU,\*.<sup>†</sup> ALISON L. SPONGBERG,<sup>†</sup> JASON D. WITTER,<sup>†</sup> MIN FANG,<sup>†</sup> AND KEVIN P. CZAJKOWSKI<sup>‡</sup> Department of Environmental Sciences, and Department of Geography and Planning, University of Toledo,

Toledo, Ohio 43606

Received April 8, 2010. Revised manuscript received June 25, 2010. Accepted July 12, 2010.

isms and humans (1-3). One enter the environment is throu cities, where the abundance wastewater is commonly treat plants (WWTPs) before dischar a result, much of the previou understanding the fate and wastewater treatment and in r removal efficiency of PPCPs has specific and affected by the operating conditions. During PPCPs have limited biodegrada removal from the water phase, a sludge instead of breaking dow able amounts of PPCPs rema treated sewage sludges (comm residuals have been found at levels in effluent and up to m and as a result discharge of contamination of receiving wa









## Factors that will influence transport potential

- Soil texture, eg. heavy soil and macropores.
- Tillage incorporation and macropore disruption.
- Antecedent moisture, rainfall, water holding capacity.











PPCPs detected	n groundwater 24-days post biosolids application	•
Chemical	Concentration (ng/l)	
Analgesics		
Ibuprofen	10	
<b>Microbiocides</b>		
Triclosan	19	
Triclocarban	12	
Antidepressants		
O-desmethylv	nlafaxine 13	
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### Management options to mitigate exposure concerns

- Application method, rate and timing; maximize contact with soil and minimize the opportunity for surface runoff or preferential flow to drainage tiles or subsurface water.
- A delay [of <u>></u> 1 year] between biosolids application and crop harvest will mitigate risk of crop uptake.

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• Pre-application biosolid treatment can reduce PPCP loading rates.

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#### Antibiotic Removal by WWTPs

			Concentration (ng/L)	
Sample description	Treatment step	Carbamazepine	Sulfamethoxazole	Trimethoprim
Raw municipal wastewater		291	4,850	246
Secondary activated sludge treatment effluent	2°	323 (-11.0%) <sup>a</sup>	901 (81.4%) <sup>a</sup>	211 (14.2%) <sup>a</sup>
Chlorinated-dechlorinated secondary effluent	$2^{\circ} + \text{dis.}$	314 (2.7%) <sup>a</sup>	119 (86.8%) <sup>a</sup>	98 (53.6%) <sup>a</sup>
Conventional sedimentation effluent	3°	340 (-5.3%)	746 (17.2%)	269 (-27.5%)
Microsand ballasted sedimentation effluent	3°	318 (-1.5%)	514 (43.0%)	216 (-2.3%)
Magnetite ballasted sedimentation effluent	3°	310 (-4.0%)	479 (46.8%)	234 (-10.9%)
Continuous backwash upflow sand filtration effluent after conventional sedimentation	3°	335 (-3.7%)	649 (28.0%)	239 (-13.3%)
Duel-media granular filtration effluent after microsand sedimentation	3°	302 (6.5%)	753 (16.4%)	160 (24.2%)
Duel-media granular filtration effluent after magnetite sedimentation	3°	316 (2.2%)	506 (43.8%)	218 (-3.3%)
Ultrafiltration effluent after microsand sedimentation	3°	335 (-3.7%)	792 (12.1%)	255 (-20.9%)
Ultrafiltration effluent after magnetite sedimentation	3°	313 (3.1%)	482 (46.5%)	243 (-15.2%)

Note: The tertiary treatment systems were designed for enhanced phosphorus removal. Percent removal from secondary effluent to tertiary treatment is shown in parenthesis.

<sup>a</sup>Percent removal from raw wastewater to secondary effluent.

Mitchell, S.M and J.L. Ullman. 2016. Removal of phosphorus, BOD, and pharmaceuticals by rapid rate sand filtration and ultrafiltration systems. Journal of Environmental Engineering doi:10.1061/(ASCE)EE.1943-7870.0001137











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per mg antibiotic).			
Biochar <sup>a</sup>	Ceftiofur removal (%)	Florfenicol removal (%)	
Dairy fiber, 600 Pinewood, 550-600 (0.7 mm)	>99.98 *	>99.98 *	
Pinewood, >550 with steam Pinewood, 650	>99.98	>99.98	
Hickory wood, 600 Binewood, 550, 600 (2 mm)	>99.98 *	99.90 * 90.01	
Brazilian pepper, 600	>99.98	99.86 *	
Bamboo, 600 Hickory wood, 450	99.97 99.6 *	99.80 99.66 *	
Mixed wood, 480-590 Poplar wood, 600	>99.98 * >99.98 *	99.60 * 98.72 *	
Pinewood, 600 Dairy fiber, 450	99.94 * >99.98 *	98.51 * 96.25	
Cherry pit, 600 Mixed wood, 700	97.65 99.98	95.95 94.77	
Pine bark, 600 Dairy fiber, 350	99.97 * 98.56	93.09 90.81	
Bamboo, 450	99.96 *	88.85	
Poplar wood, 350	99.57	80.35	
Poplar wood, 450 Pinewood, 450	99.87 97.95	75.01 72.57	
Peanut hull, 600 Pine bark, 450	99.59 * 99.26	68.04 61.12	Mitcholl S.M. M. Subbish I.I. Illimon C
Pinewood, 350 Brazilian pepper, 450	90.68 92.60	60.74 41.39	Frear and D.R. Call. 2015. Evaluation of 27
Pine bark, 350 Control, no biochar	58.16 -0.07	33.89 -0.17	different biochars for potential sequestration of antibiotic residues in food animal product
<sup>a</sup> Numbers following biochar feeds during production	stock type indicate p	yrolysis temperature	environments. Journal of Environmental
*P>0.05 for the bioassay results (s	ee Fig. 2 and Fig. 3	).	Chemical Engineering 5: 102-109.



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- City of Spokane Wastewater Management Department



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#### The Chemical Universe

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#### The KNOWN Universe

- As of October 2005, over 26 million organic and inorganic substances had been documented.
- (indexed by the American Chemical Society's Chemical Abstracts Service in their CAS Registry; excluding bio-sequences such as proteins and nucleotides)
- ~ 9 million were commercially available.
- Fewer than a quarter million (240,000) were inventoried or regulated by numerous government bodies worldwide -
  - representing less than 3% of those that are commercially available or less than 1% of the known universe of chemicals.



#### CWA & 40 CFR Part 503 Risk Assessment Included:

- Heavy Metals
- PCBs
- Furans/dioxins
- Benzo(a)pyrene
- Benzo(a)anthracene
- Phenanthrene
- Chlordane
- Aldrin/Dieldrin
- Toxaphene
- Malathion
- DDT/DDD/DDE
- Methylenebis(2-chloroaniline)

- Bis(2-ethyl hexyl)phthalates
- n-nitrosodimethylamine
- Vinyl Chloride
- Pentachlorophenol
- > Trichloroethylene
- Chloroform
- Heptachlor
- Carbon tetrachloride
- Benzene
- Hexachlorobenzene
- Hexachlorobutadiene







- 1993: Initial Hazard Assessment for 12 Organic Compounds
  - None was regulated
- 2001: Further screening for Dioxins and Dioxin like compounds
- 2003: Dioxins and Dioxins like compounds posed no significant risk to human health or the environment

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> Not to regulate in land applied biosolids



- Prosser and Sibley (2015) Based on Extensive Review on Plant Uptake of OCs Calculated HQs:
- Estimated Daily Intake (EDI) for OCs for Adult or Toddler
- EDIs compared to ADI (Acceptable Daily Intake)
- ADI Were calculated :
  - Drugs = Lowest Therapeutic Dose (LTD, mg/d)/1000
  - Drugs (Endocrine Disruptors) = LTD/10,000
  - > Other OCs = NOAEL/300

Calculated HQs for Various OCs				
OCs	Сгор	Adult HQ	Toddler HQ	
Atenolol	Tomato	0.01	0.02	
Carbamazepine	Collard	1.5* <sup>a</sup>	<b>3.7</b> *a	
Ciprofloxacin	Carrot	0.0001	0.0003	
Diphenhydramine	Tomato	0.03	0.07	
Naproxen	Corn	0.0001	0.0002	
Norfloxacin	Carrot	0.0002	0.0004	
Progestrone	Corn	0.01	0.04	
Salbutamol	Cabbage	1.5* <sup>b</sup>	3.8* <sup>b</sup>	
Testosterone	Tomato	0.08	0.2*c	
Triamterene	Carrot	0.0001	0.0002	
Triclocarban	Collard	0.002	0.005	
Triclosan	Radish	0.05	0.1* <sup>d</sup>	
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#### Quantitative Human Health Risk Analysis for OCs

Northwest Biosolids (2015) Conducted a quantitative exposure assessment for uses of biosolids using general risk assessment methodology by the USEPA. The following scenarios of exposure from dermal contact and ingestion were evaluated:

- Child exposed while playing in a home garden or lawn fertilized with Class A biosolids compost.
- Adult gardener exposed while working in a home garden fertilized with Class A biosolids compost.
- Occupational worker exposed while applying Class B biosolids to agricultural land.
- Adult hiker exposed while hiking in a forested area fertilized with Class B biosolids.

(mg/kg) and resulting ex (from NW Biosolids, 201!	posure wit 5)	hout adverse ef	fects in years	
OCs	Represe- ntative	Exposure Without Adverse Effects YEARS		
	Conc.	Adult Gardner	Child Resident	
Acetaminophen	0.0015	143,000,000	4,494,000	
Fluoxetine	0.036	91,000	3,000	
17 -a ethinylestradiol	0.0011	3,000	98	
Bisphenol A	9.0	437,000	14,000	
Ibuprofen	0.35	94,000	3,000	
Deca-BDE	0.24	1,470,000	159,000	
Azithromycin	0.035	2,350,000	74,000	
Ciprofloxacin	0.93	35,000	1,000	
Erythromycin	0.0060	13,709,000	432,000	
Ofloxacin	0.66	100,000	3,000	
Sulphamethoxazole	0.001	131,000,000	4,148,000	
Triclosan	1.2	4,935,000	156,000	
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Representative concentrations of OCs in Class A compost biosolids

Representative concentrations of OCs in Class B biosolids (mg/kg) and resulting exposure without adverse effects in years (from NW Biosolids, 2015)

OCs	Represe- ntative	Exposure Without Adverse Effects YEARS		
	Conc.	Adult Hiker	Occupational	
Acetaminophen	0.29	4,334,000	292,000	
Fluoxetine	0.087	222,000	15,000	
17 -a ethinylestradiol	0.0011	18,000	1,000	
Bisphenol A	9.0	2,566,000	173,000	
Ibuprofen	0.35	552,000	37,000	
Deca-BDE	4.1	556,000	11,000	
Azithromycin	0.46	1,051,000	71,000	
Ciprofloxacin	3.4	58,000	4,000	
Erythromycin	0.020	24,171,000	1,630,000	
Ofloxacin	1.8	217,000	15,000	
Sulphamethoxazole	0.0056	137,000,000	9,265,000	
Triclosan	17	2,023,000	136,000	
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Class B biosolids (mg/kg) and number of years of exposure to reach an equivalent dose (from NW Biosolids, 2015)					
OCs	Therapeutic Dose or	Years of Exposure to Receive Equivalent Do Class A Compost Class B Biosolids			llent Dose llids
	Typical Daily	Adult	Child	Adult	Occup-
	Intake (mg)	Gardner	Resident	Hiker	ational
Acetaminophen (Analgesic)	1,000 2 Tylenols	90,143,000	50,514,000	2,740,000	147,000
17-aethinylestra- diol (Birth control)	0.01 Lo Loestrin	1,000	700	7,500	400
lbuprofen (NSAID)	200 1 Tablet Advil	77,000	43,000	454,000	24,000
Ciprofloxacin (Antibiotic)	250 Lowest Daily Dose	36,000	20,000	59,000	3,000
Erythromycin (Antibiotic)	1,000 Lowest Daily Dose	22,535,000	12,628,000	39,734,000	2,144,000
Triclosan (Anti-microbial)	87 Soap Single Use	10,000	5,000	4,000	200
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Representative and acceptable concentrations of MCs in Class A and

#### Other Recent Risk Assessments

#### Norwegian Risk Assessment - 2009

- Norwegian Food Authority evaluated
  - Six classes of organic pollutants
    - Phthalates, Octylphenols and ethoxylates, NP, NPEs
    - PCBs, PAHs
  - 14 pharmaceuticals (atorvastatin, carisoprodol, chlorprothixene, ciprofloxacin, dipyridamole, fexofenadine, gabapentin, levetiracetam, losartan, mesalazine, metoprolol, ranitidine, sotalol,tetracycline).

#### Conclusion

- Exposure risk from all pollutants evaluated
  - Well below PNEC
  - Promotion of antibiotic resistance in biosolids-amended soils unlikely

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#### **Other Recent Risk Assessments**

#### Danish Government Risk Assessment - 2012

#### Danish EPA evaluated

- Five classes of organic pollutants
  - BFRs, Musks, PFCs
  - Pharmaceuticals
  - PCBs
- Used margin of safety (MoS) to calculate quotient of predicted soil concentration and NOAEL
- Used MoS value of between 10 and 1000

#### Conclusion

No significant risk to soil dwelling organisms and soil quality in general



#### Take Home Messages

- Land application of biosolids is a beneficial practice and it does not result in human exposure to Emerging Contaminants.
- We can minimize exposure to Emerging Contaminants by becoming smart consumers and reducing indiscriminate use of chemicals in our daily lives.
- DEA released data on National Rx Take-Back Day (May, 2016)
  - PROUD to say that Illinois was at No. 5 and our efforts kept 24 tons of drugs out of our biosolids, waterways and landfills

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