Biosolids-Borne Trace Organics

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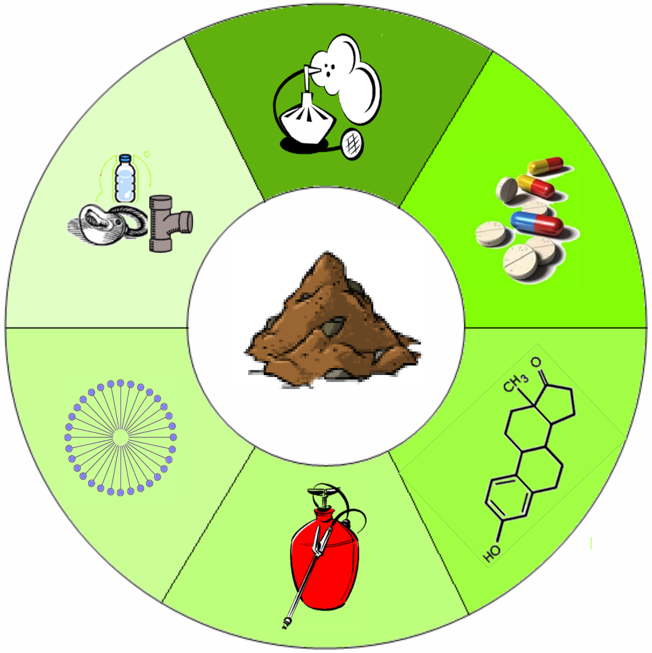
TAC Presentation

Nov 29, 2018



Common Organic Contaminant "Lingo"

Chemical Group	Grouping Method
EDC (Endocrine Disrupting Chemical)	toxicological mode of action or endpoint
PBT (Persistent, Bioaccumulative Toxic) **POP** (Persistent Organic Pollutant)	environmental properties
OWC (Organic Wastewater Contaminant)	location of occurrence
PPCP (Pharmaceuticals and Personal Care Product)	type of intended usage
Priority Pollutant	regulation
ECC (Emerging Compound of Concern)	novelty, fad, timeliness, or new concern
Xenobiotics	foreign versus endogenous
HPV (High Production Volume) chemical	quantity (manufactured/imported in US ≥1 million pounds/year)
POHO (Pollutant Of Human Origin)	source or origin

- additional categories (e.g., trace organics, microconstituent)
- use depends on context, author, audience, date of publication

Objectives

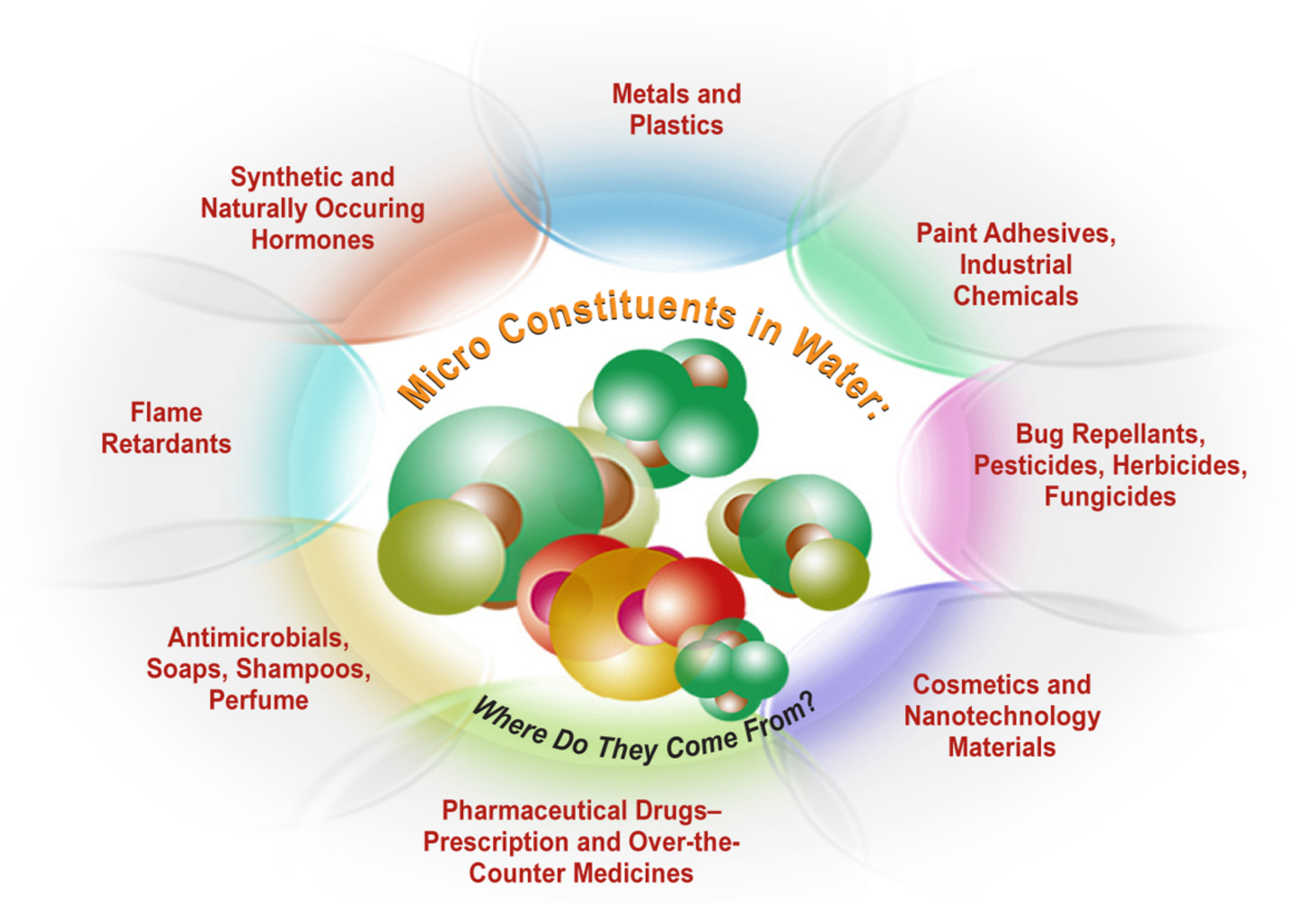
- Identify biosolids-borne trace organic contaminants, sources, typical concentrations, and potential impacts

- Review the basic principles of organic compound reactions/fates in soil/plant systems

- Identify potential impacts of biosolids-borne trace organics on the environment and humans and research needs

Focusing on Source Control

Micro Constituents in Water: Where Do They Come From?



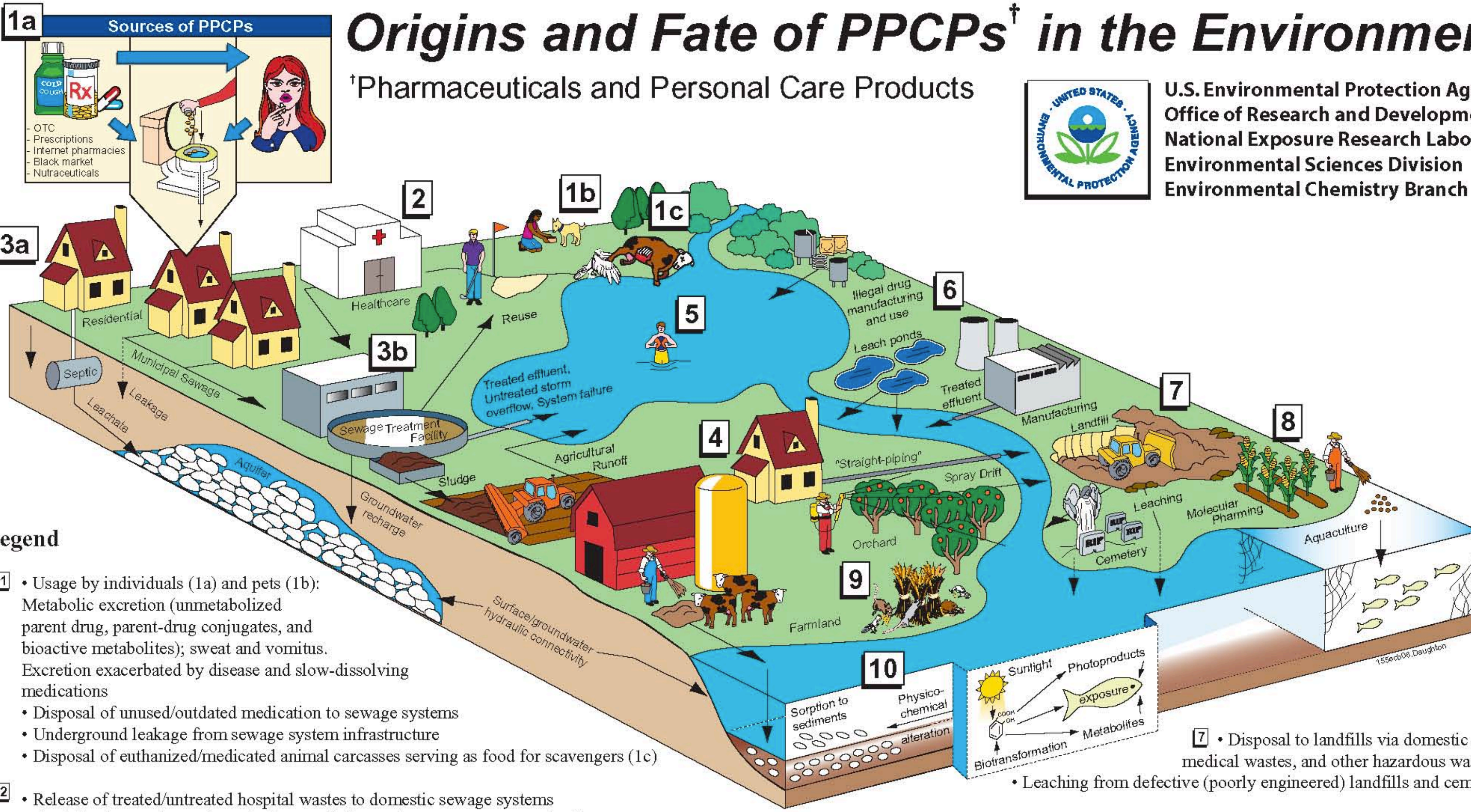
Courtesy of CH2M Hill

…applying science & technology to protect water quality

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



Legend

1 • Usage by individuals (1a) and pets (1b): Metabolic excretion (unmetabolized parent drug, parent-drug conjugates, and bioactive metabolites); sweat and vomitus. Excretion exacerbated by disease and slow-dissolving medications
• Disposal of unused/outdated medication to sewage systems
• Underground leakage from sewage system infrastructure
• Disposal of euthanized/medicated animal carcasses serving as food for scavengers (1c)

2 • Release of treated/untreated hospital wastes to domestic sewage systems (weighted toward acutely toxic drugs and diagnostic agents, as opposed to long-term medications); also disposal by pharmacies, physicians, humanitarian drug surplus

3 • Release to private septic/leach fields (3a)
• Treated effluent from domestic sewage treatment plants discharged to surface waters, re-injected into aquifers (recharge), recycled/reused (irrigation or domestic uses) (3b)
• Overflow of untreated sewage from storm events and system failures directly to surface waters (3b)

4 • Transfer of sewage solids ("biosolids") to land (e.g., soil amendment/fertilization)
• "Straight-piping" from homes (untreated sewage discharged directly to surface waters)
• Release from agriculture: spray drift from tree crops (e.g., antibiotics)
• Dung from medicated domestic animals (e.g., feed) - CAFOs (confined animal feeding operations)

5 • Direct release to open waters via washing/bathing/swimming

6 • Discharge of regulated/controlled industrial manufacturing waste streams
• Disposal/release from clandestine drug labs and illicit drug usage

7 • Disposal to landfills via domestic refuse, medical wastes, and other hazardous wastes
• Leaching from defective (poorly engineered) landfills and cemeteries

8 • Release to open waters from aquaculture (medicated feed and resulting excreta)
• Future potential for release from molecular pharming (production of therapeutics in crops)

9 • Release of drugs that serve double duty as pest control agents: examples: 4-aminopyridine, experimental multiple sclerosis drug → used as avicide; warfarin, anticoagulant → rat poison; azacholesterol, antilipidemics → avian/rodent reproductive inhibitors; certain antibiotics → used for orchard pathogens; acetaminophen, analgesic → brown tree snake control; caffeine, stimulant → *coqui* frog control

10 Ultimate environmental transport/fate:
• most PPCPs eventually transported from terrestrial domain to aqueous domain
• phototransformation (both direct and indirect reactions via UV light)
• physicochemical alteration, degradation, and ultimate mineralization
• volatilization (mainly certain anesthetics, fragrances)
• some uptake by plants
• respirable particulates containing sorbed drugs (e.g., medicated-feed dusts)

Christian G. Daughton, U.S. EPA-Las Vegas

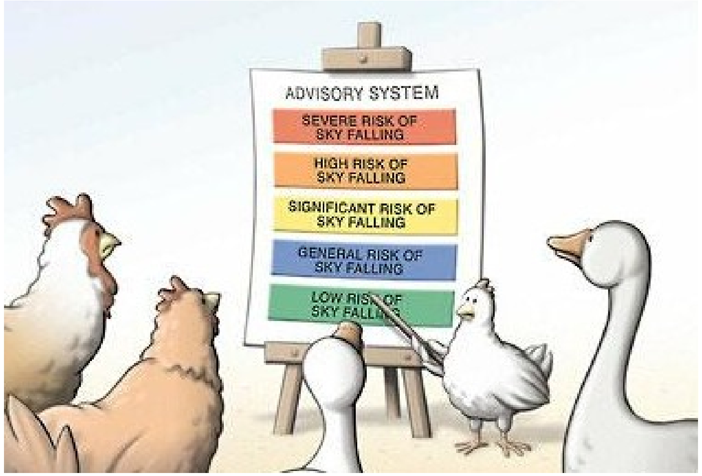
March 2006
(original February 2001)

http://epa.gov/nerlesd1/chemistry/pharma/images/drawing.pdf
from: http://epa.gov/nerlesd1/chemistry/pharma/

Attitudes Towards Trace Organics in Biosolids

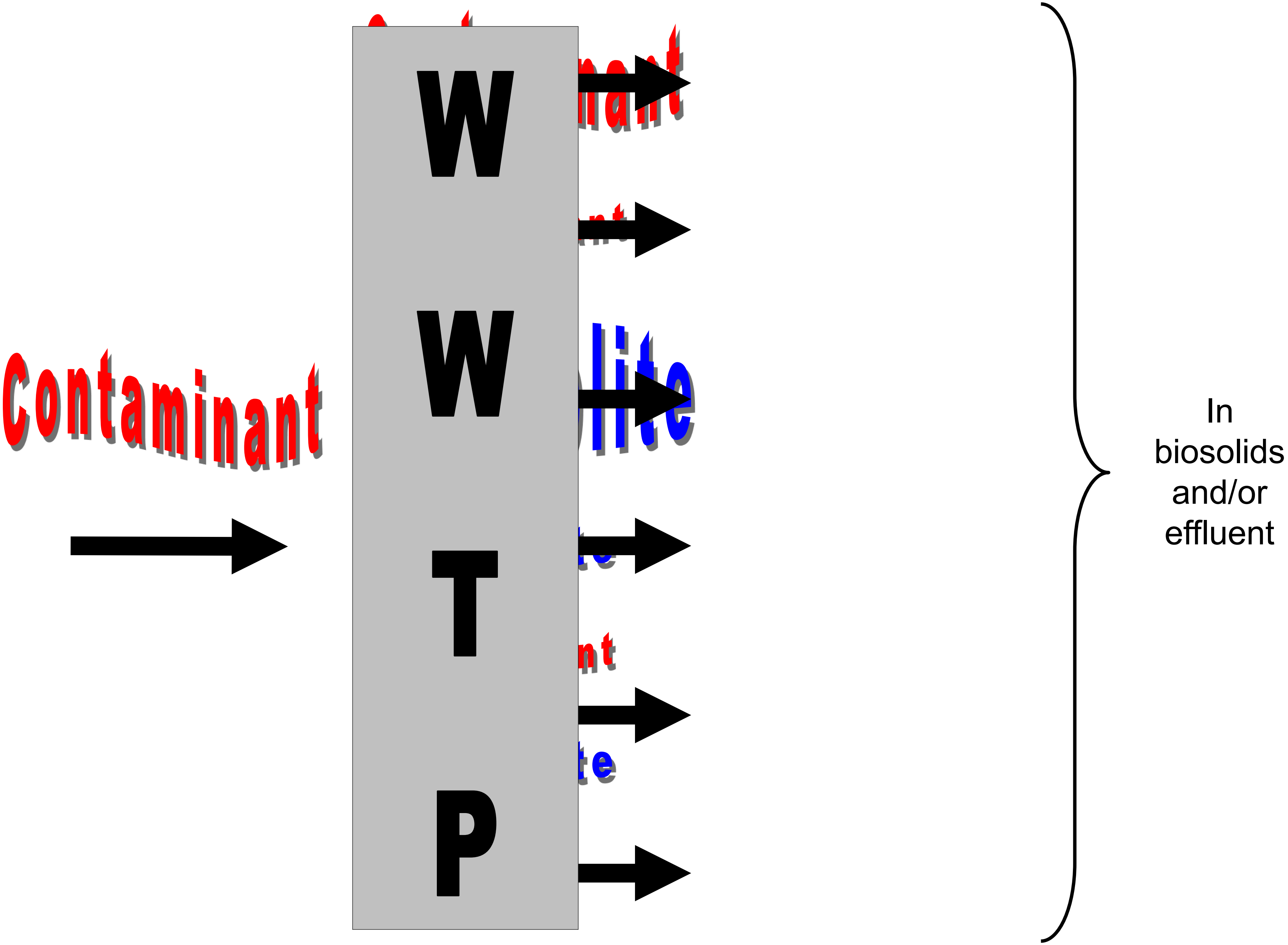
It's all a bunch of hype!

- "pollutant du jour" syndrome
- WWTPs are very efficient and will degrade organics
- availability in biosolids is so low, and the concentration in biosolids-amended soil is so low, that there's nothing to worry about

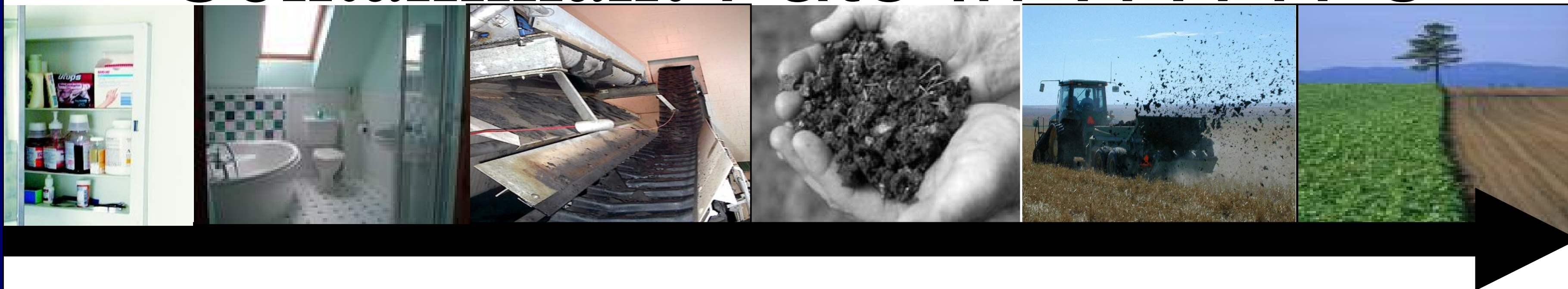


The sky is falling!

- we're awash in evermore dangerous chemicals
- unknown toxicity, mutagenicity, carcinogenicity


Contaminant
W
W
T
P
In
biosolids
and/or
effluent

Contaminant Fate In WWTPs



- Even when removal is efficient, sufficient chemical can exit in effluent to:
  - Affect aquatic organisms
    - Low concentrations do not mean “no effect”
  - Contaminate* surface and ground waters
  - Contaminate* drinking water supplies
- Organics may accumulate in biosolids
  - Removal from aqueous phase does not mean degradation
  - Subsequent availability of biosolids-borne organics in land-applied biosolids is THE question

Analyte	Use	# Detects (total=84)	Concentration Range Dry-Weight (ug/kg)
Flame Retardants			
BDE-47 (Tetra)	Reduces flammability	84	73 – 5,000
BDE-99 (Penta)		84	64 – 4,000
BDE-153 (Hexa)		84	9 – 410
BDE-209 (Deca)		83	150 – 17,000
Pharmaceuticals			
Azithromycin	Antibiotic	80	8 – 5,205
Diphenhydramine	Antihistimine (OTC)	84	37 – 5,730
Caffeine	Psychoactive stimulant	39	65 – 1,100
Carbamazepine	Anticonvulsant	80	9 – 6,030
Cimetidine	Ant-acid	74	4 – 8,330
Ciprofloxacin	Antibiotic - strong	84	75 – 40,800
Fluoxetine	Antidepressant	79	10 – 3,130
Ibuprofen	Anti-inflammatory	54	99 – 11,900
Miconazole	Antifungal	80	7 – 9,210
Tetracycline	Antibiotic	81	38 – 5,270
Triclocarban	Antimicrobial	84	187 – 441,000
Triclosan	Antibacterial	79	334 – 133,000

Analyte	Use	# Detects (total=84)	Concentration Range Dry-Weight (ug/kg)
Steroids / Hormones			
Campesterol	Plant sterol	84	2,840 – 524,000
Cholestanol	Cholesterol derivative	84	3,860 – 4,590,000
Coprostanol	Cholesterol degradate	84	7,720 – 43,700,000
Epicoprostanol	Pheromone	83	868 – 1,030,000
17 alpha-Estradiol		5	48
17α-Ethynyl Estradiol	Widely prescribed estrogen	0	NA
β-Stigmastanol	Plant steroid	83	3,400 – 1,330,000
Stigmasterol	Plant steroid	76	455 – 56,500
Testosterone	Steroid hormone	17	30 – 2,040
PAHs, Semi-Volatile Organic Compounds			
Bis (2-ethylhexyl) phthalate	Plasticizer (not a PAH)	84	657 – 310,000
4-Chloroaniline	Aniline derivative	63	51 – 5,900
Fluoranthene	Intermediate	77	45 – 12,000
Pyrene	Intermediate	72	44 – 14,000

Common Concentrations

Some Organic Contaminants in Biosolids

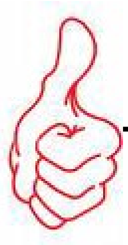
Compound	Concentration (mg kg^{-1})	Log Kow	Solubility (mg L^{-1})	Vapor Pressure (mmHg)
Antimicrobial Compounds				
triclosan	16	4.53	10	6.45×10^{-7}
Human Drugs				
carbamazepine	0.14	2.45	17.7	1.84×10^{-7}
Fragrances				
d-limonene	0.63	4.57	13.8	1.98
indole	20	2.14	3560	1.22×10^{-2}
Sex and Steroidal Hormones				
3b-coprostanol	4400	8.82	0.000203	5.47×10^{-10}
cholesterol	1100	8.74	0.095	7.79×10^{-10}
Plasticizers				
bis(2-ethylhexyl)phthalate	20 - 160	3.98	0.40	6.45×10^{-6}
diethylhexyl phthalate	11	7.88	0.27	1.42×10^{-7}
Polycyclic aromatic hydrocarbons				
anthracene	0.14	4.5	0.0434	6.53×10^{-6}
phenanthrene	0.34	4.52	1.15	1.21×10^{-4}
Others				
1,4-dichlorobenzene	5	3.52	79	1
phenol	2 - 55	1.5	82800	0.35
bisphenol A	5	3.32	120	3.91×10^{-7}
PCBs (Actual concentration – 95th %) Total toxic equivalent basis (TEQ)– 95th percentile	0.21 0.0000131	4.5 – > 8.0	0.000004 – 7.48	7.6×10^{-10} – 0.08
Penta dibrominated diphenyl ethers PBDEs (Sum)	<0.008 – 4.89	5.74 – 8.27	0.01 - 0.13	2.12×10^{-9} – 1.94×10^{-3}
Polychlorinated dibenzodioxins and Dibenzofurans (total TEQ)	0.0000333	6.8	0.0000193	7.4×10^{-4}

* Modified from Xia, 2005; Kinney, 2006; Kester, 2005; TNSSS, 2009

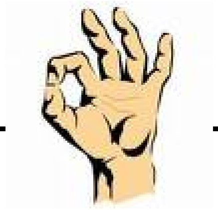
What are Perfluorochemicals (PFCs)?

Courtesy of Chris Higgins, Colorado School of Mines

- Family of man-made chemical structures that resist heat, oil, stains, grease and water
- PFC-based precursors and products are used in a variety of consumer products
- Relatively mobile in the environment
- Persistent, Bioaccumulative, and Toxic (PBT)
- Widely detected in wildlife and humans



The "Correct" Attitude



- Likely that fate of biosolids-borne trace organics is compound/biosolids/management specific
- Expected risks for many compounds are likely small, but not necessarily trivial, and the science for many compounds is incomplete
- Unknown risks require assessment by those who appreciate the uniqueness of biosolids-amended systems
- Don't bury your head to concern or hazard!

Predicting the fate of trace organics is difficult, but *not* hopeless

- Why difficult?
  - Complex compounds and metabolites
  - Low to very low concentrations
  - Analytical difficulties
  - Unknown chemical properties and biological effects
- Why not hopeless?
  - Previous experience with similar compounds, e.g. pesticides, priority pollutants
  - Basic chemical principles expected to apply
  - Previous risk assessments for other biosolids-borne organics, e.g. PCBs, dioxins

Principles of Trace Organic Behavior in Biosolids-Amended Soils

- Retention/Release/Partitioning
- Degradation
- Volatilization
- Photolysis
- Plant uptake and metabolism
- Leaching and runoff

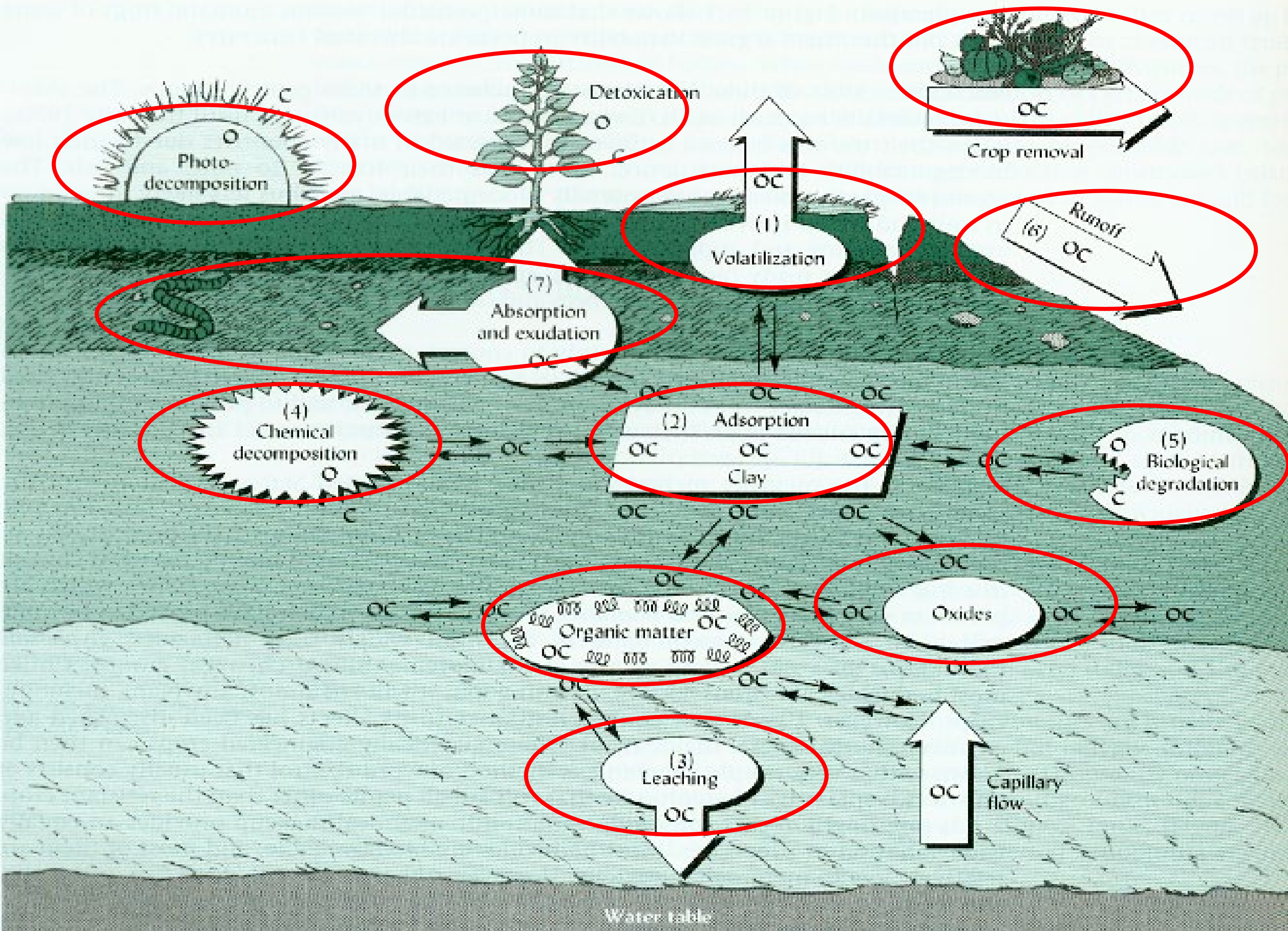


Photo-
decomposition
Detoxication
Crop removal
OC
(1)
Volatilization
Runoff
(6)
(7)
Absorption
and exudation
(4)
Chemical
decomposition
(2) Adsorption
Clay
(5)
Biological
degradation
Organic matter
Oxides
(3)
Leaching
Capillary
flow
Water table

“Hazardous Traits”

- High concentrations and detection frequency
  - Likely exposure risk
- Low log K_{ow} (<-2)
  - High solubility, minimal retention, leachable, high bioavailability
- High log K_{ow} (>5)
  - Strongly retained, bioaccumulative, persistent, particle runoff
- High $t_{1/2}$ (>2 months)
  - Persistent, long-term effects
- High Henry’s constant ($>10^{-5}$)
  - Volatile, easily transported in wind (world-wide)
- High BAF– contamination of vegetation and organisms

Applying Principles to Emerging Organics

- Models
  - Transport
  - Quantitative structure-activity relationship (QSAR)
  - Fugacity
- Inferences
  - Similarities in chemical structure, modes of action (MOAs)
  - Common sense
- Experience
  - Successes/failures of WWTPs and application programs
  - Part 503 risk assessment (PCBs and dioxins)

Knowns and Expectations

- Concentrations of many, **but not all**, trace organics in biosolids are low
- Amended soil concentrations can be ≤ 200-fold lower than in biosolids
  - 10,000 lbs (5 T/A) of biosolids diluted in ~ 2,000,000 lbs of soil
- “PBTs” expected to be strongly retained by biosolids
- Some trace organics in biosolids may be slow to degrade, but likely have limited bio- and environmental availability
- Soluble trace organics are expected to be more of a problem in the safe disposition of **effluents** than of the biosolids
- Lessons (e.g., risk assessments) learned with better-studied chemicals with similar properties are probably extendable to trace organics

Unknowns and Potential Surprises

- Even low concentrations of trace organics could affect organisms in ways we haven't considered
  - Antibiotic resistance in humans/animals
  - Changes in soil microbes and reactions they mediate
  - Chronic hormone exposure
  - Cumulative and synergistic effects of various chemicals
  - ?

- Risks due to prolonged human and environmental exposure at low concentrations largely unknown

- Effects of various biosolids preparation processes on chemical structure, behavior, persistence, bioavailability unknown?

- And ?

WERF 2010 "State of the Science Review"

- Compile occurrence data
  - Access quality and completeness
- Identify what has been done
  - Access quality, completeness and applicability
- Identify what needs to be done
  - Identify "target" chemicals/classes
  - Data gap analysis
  - Meaningful risk assessment needs

Selection of Target Compounds

- Focus gap analysis on frequently detected, high concentration, or “data poor” microconstituents
- Exclude (initially)
  - Detection frequency (TNSSS) < 10%
  - Max Mean/Median < 1 mg/kg
    - Included if known to be potentially problematic
      - BFRs, PFCs
  - Priority pollutants, PAHs, pesticides, etc.
  - Chemicals/classes regulated elsewhere
  - Chemicals previously considered by EPA
- Still *many* TOrCs to choose from . . .

Initially Targeted Compounds

- 40+ chemicals/chemical classes
  - PPCPs
  - Steroidal chemicals
  - BFRs
  - PFCs
  - Plasticizers
  - Surfactants
- Additional candidates to be added/removed depending on toxicological significance

Data Gaps Identified

- Occurrence data: some need verification/validation
  - i.e., PFCs and PFC precursors
- Sorption/mobility data: abundant, but few specific to biosolids-amended soils
  - Unique matrix effects
- Persistence data: high quality data sparse (few pertinent to biosolids-amended soils)

Data Gaps Identified

- Bioavailability/bioaccumulation: limited
- Ecological toxicity: sparse
- Microbial effects: minimal/limited (scope)
- Long-term field studies: rare/non-existent
- Risk assessments: limited applicability
- Studies that focus on delivery of microconstituents <u>in biosolids</u>: rare
- Report: "Trace Organic Chemicals in Biosolids-Amended Soils" 2010. SRSK5T09

Our Progress Since

Brown, S., D. Devin-Clark, M. Doubrava, and G.A. O'Connor. 2009. Fate of 4-nonylphenol in a biosolids amended soil. Chemosphere 75: 540-554.

Snyder, E.H. et al., 2010. Measured physicochemical characteristics and biosolids concentrations of the antimicrobial triclocarban (TCC). Sci. Total Environ. 408: 2726-2732.

Snyder, E.H. et al., 2010. Fate of ^{14}C-triclocarban in biosolids amended soils. Sci. Total Environ. 408: 2667-2673.

Snyder, E.H. et al., 2011. Toxicity and bioaccumulation of biosolids-borne triclocarban. Chemosphere 82:460-467.

Waria, M. et al., 2011. Biodegradation of triclosan (TCS) in biosolids-amended soils. Environ. Toxicol. Chem. 30: 2488-2496.

Pannu, M.W. and G.A. O'Connor. 2012. Toxicity and bioaccumulation of biosolids-borne triclosan in food crops. Environ Toxicol & Chem 31: 2130-2137.

Pannu, M.W. et al. 2012. Toxicity and bioaccumulation of biosolids-borne triclosan in terrestrial organisms. Environ Toxicol & Chem 31:646-653.

Snyder, E.H. and G.A. O'Connor. 2013. Risk assessment of land-applied biosolids-borne triclocarban (TCC). Sci Total Environ. 442: 437-444.

Sidhu, H., C. et al., 2015. Endocrine disrupting chemicals in reclaimed water and residential ponds and exposure potential for dislodgeable residues in turf irrigated with reclaimed water. Arch Environ Contam Toxicol. 69: 81-88.

Sidhu, H.S. et al., 2019. Plant toxicity and accumulation of biosolids-borne ciprofloxacin and azithromycin. Sci. Tot. Environ. 648: 1219-1226.

Sidhu, H.S. et al., 2019. Bioavailability of biosolids-borne ciprofloxacin and azithromycin to terrestrial organisms: microbial toxicity and earthworm responses. Sci. Tot. Environ. 650: 18-26.

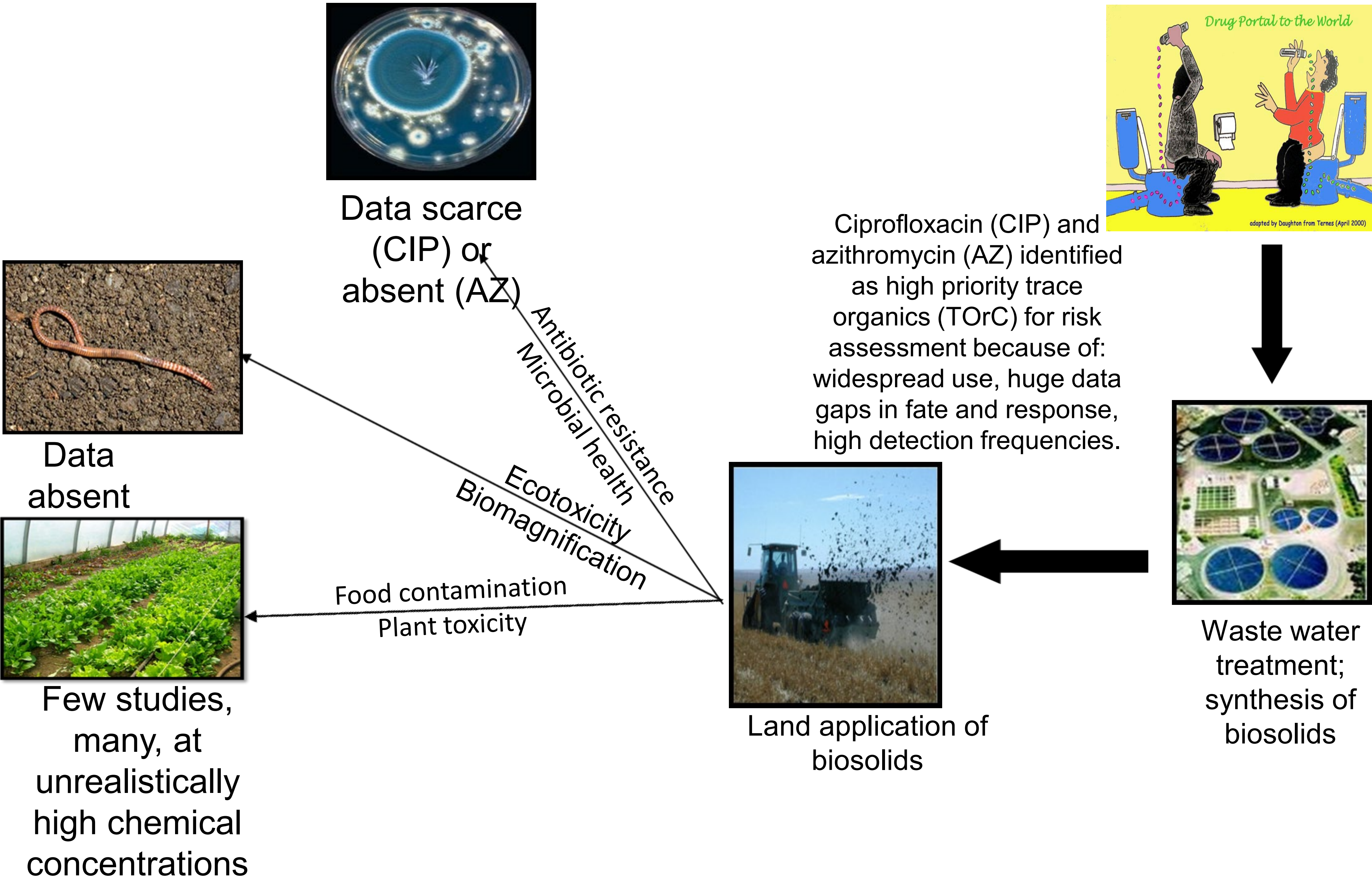
Sidhu, H.S., et al., 2019. Retention-release of ciprofloxacin and azithromycin in biosolids and biosolids-amended soils. Sci. Tot. Environ. 650: 173- 183.

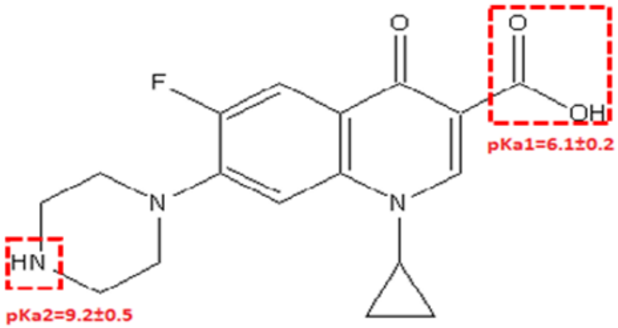
Sidhu, H.S., et al., 2019. Risk assessment of biosolids-borne ciprofloxacin and azithromycin. Sc. Tot. Environ. 651: 3151-3160.

Sidhu, H.S., et al., 2019. Ciprofloxacin and azithromycin resistance in biosolids and biosolids-amended soil (In prep).

Risks from Biosolids-borne Ciprofloxacin (CIP) and Azithromycin (AZ)

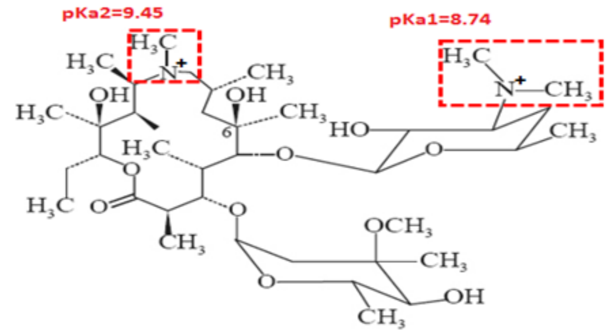
Harman Sidhu


Drug Portal to the World
adapted by Daughton from Ternes (April 2000)
Ciprofloxacin (CIP) and azithromycin (AZ) identified as high priority trace organics (TOrC) for risk assessment because of: widespread use, huge data gaps in fate and response, high detection frequencies.
Waste water treatment; synthesis of biosolids
Land application of biosolids
Antibiotic resistance
Microbial health
Ecotoxicity
Biomagnification
Food contamination
Plant toxicity
Data scarce (CIP) or absent (AZ)
Data absent
Few studies, many, at unrealistically high chemical concentrations



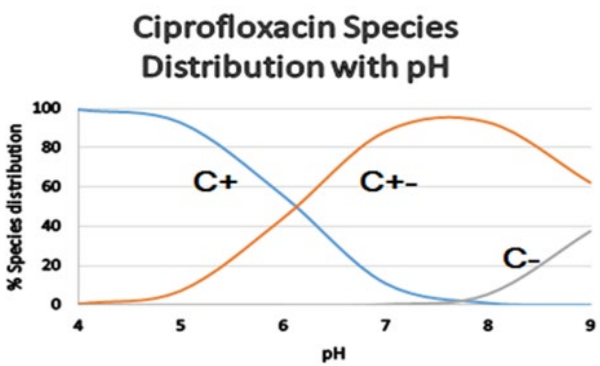
Ciprofloxacin

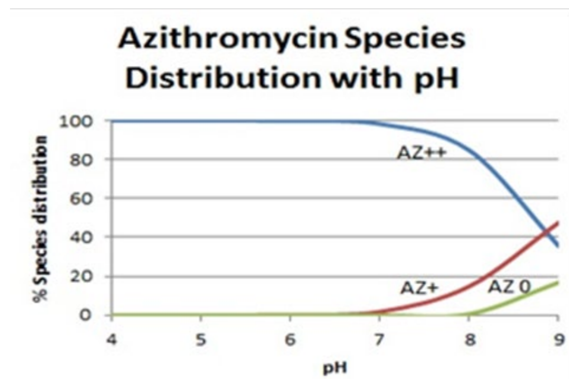
(M.W. = 332.3 g/mol)



Azithromycin

(M.W. = 749.5 g/mol)





Hypothesis

Limited bioaccessibility of the strongly sorbed biosolids-borne CIP and AZ minimizes risks to human and environmental health.

Objectives

Ultimate Objective:

To conduct human and ecological health risk assessment of biosolids-borne CIP and AZ.

Intermediate Objectives:

#1. To assess retention-release behavior of CIP and AZ

#2. To assess plant responses to biosolids-borne CIP and AZ.

#3. To assess microbial responses to biosolids-borne CIP and AZ.

#4. To assess earthworm responses to biosolids-borne CIP and AZ.

Concentrations of Biosolids-Borne CIP and AZ

USEPA targeted national sewage sludge surveys (TNSSS) reports

Concentration	CIP	AZ
Average (mg/kg)	10.5 ± 17.7	0.83 ± 2.3
Median (mg/kg)	5.4	0.25
95th percentile (mg/kg)	36.1	3.2

Nine geographically and synthetically diverse biosolids surveyed and analyzed by AXYS (BC, Canada).

Concentrations of Biosolids-Borne CIP and AZ

Chemical	Biosolids	Quantification limit (mg/kg)	Concentration found (mg/kg)
CIP	1 Class A	0.018	3.57
	2 Class A	0.066	3.28
	3 Class A	0.019 ± 0.006	0.954 ± 0.04
	4 Class A	0.021	3.51
	5 Class B	0.016	4.64
	6 Class B	0.014	5.90
	7 Class B	0.023	4.81
	7 Heat dried	0.025	0.815
	7 Compost	0.212	Below reporting limit
AZ	1 Class A	0.017	0.435
	2 Class A	0.009	0.694
	3 Class A	0.004 ± 0.009	0.06 ± 0.04
	4 Class A	0.004	0.990
	5 Class B	0.006	0.205
	6 Class B	0.005	0.268
	7 Class B	0.004	0.217
	7 Heat dried	0.008	0.012
	7 Compost	0.004	Below reporting limit

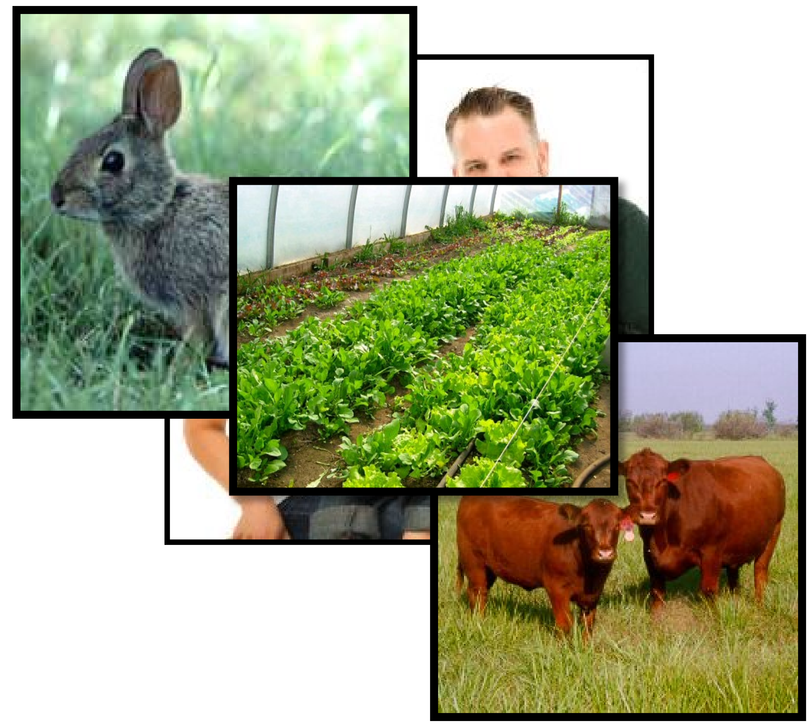
Ultimate Objective: Risk assessment of biosolids-borne CIP and AZ

- **Integrated risk a** mework.

  -Involves highl posure pathways.

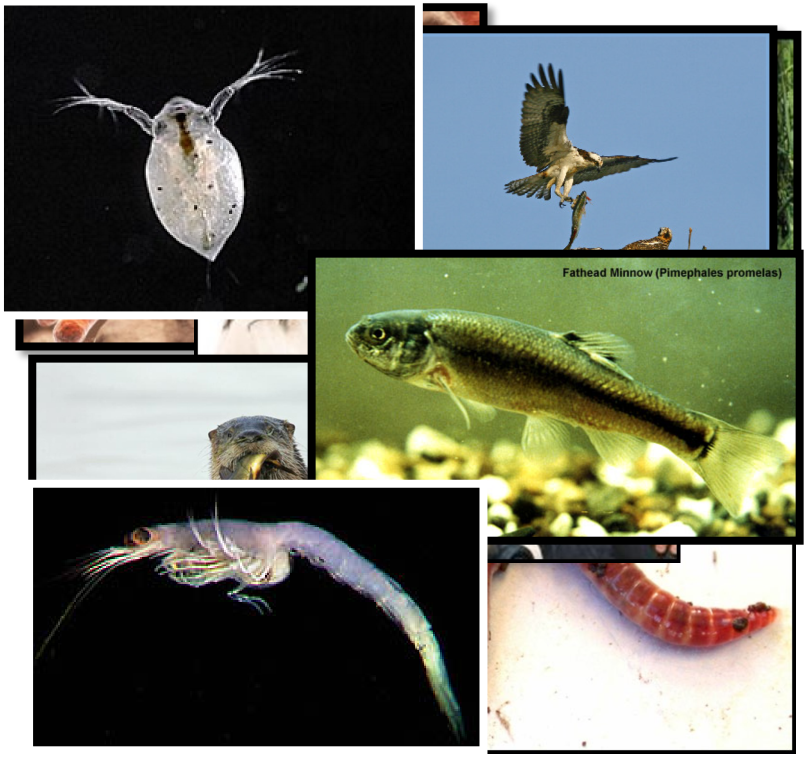
Exposure pathways

Pathway	HEI
1. Biosolids→soil→plant→human	
2. Biosolids→soil→plant→human	
3. Biosolids→soil→human	
4. Biosolids→soil→plant→animal→human	
5. Biosolids→soil→animal→human	
6. Biosolids→soil→plant→animal	
7. Biosolids→soil→animal	
8. Biosolids→soil→plant	



Exposure pathways

Pathway	HEI
9. Biosolids→soil→soil organism	
10. Biosolids→soil→soil organism→predator	
11. Biosolids→soil→airborne dust→human	
12. Biosolids→soil→surface water→human	
13. Biosolids→soil→air→human	
14. Biosolids→soil→groundwater→human	
15. Biosolids→soil→surface water→animal	
16. Biosolids→soil→surface water→aquatic organism	



Ultimate Objective: Risk assessment of biosolids-borne CIP and AZ

Three exposure scenarios:

a) **BAR_1**: A one-time cropland application (at the rate of $\boxed{\text{100 Mg/ha}}$) of biosolids that contain 95th percentile chemical concentrations found in USA biosolids (USEPA, 2009).

b) **BAR_2**: Annual land application of biosolids containing average chemical concentration (USEPA, 2009) at the rate of 20 Mg/ha for 40 y.

c) **BAR_3**: Annual land application of biosolids containing 95th percentile chemicals concentrations (USEPA, 2009) at the rate of 20 Mg/ha for 40 y.

Ultimate Objective: Risk assessment of biosolids-borne CIP and AZ

Tiered approach.

Tier I: (screening level): Employed high-end parameters (e.g., BAF and BCF values, 100% bioavailability, no chemical degradation).

Tier II: Bioavailability reduced to 50% and a conservative 10-y chemical half-life used.

Tier III: Bioavailability reduced to 30%.

Conservative

Realistic

Hazard quotient (HQ) approach.

$$HQ = \frac{exposure\ concentration}{reference\ dose}$$

HQ < 1 [Negligible risk]

Example exposure concentration calculation

Biosolids-amended soil $\xrightarrow{soil\ concentration\ x\ BAF}$ plant $\xrightarrow{chemical\ in\ plant\ x\ amount\ consumed}$ humans

Risk Assessment Results

After **Tier III** assessment, pathways of concern:

<u>biosolids→soil→soil organism→predators</u> (both CIP and AZ)

HQ values ≤ 2.1 (CIP) and ≤ 1.3 (AZ).

<u>biosolids→soil→plants</u> (CIP)

HQ value = 1.5;

but only in the <u>unrealistic</u> BAR_3 scenario.

Biosolids-borne CIP and AZ pose **negligible human and ecological health risks** under real world based biosolids management scenarios.

Preliminary Pollutant Limits

<u>Ceiling Concentration Limit:</u>

95 mg CIP and 26 mg AZ per kg biosolids.

MAXIMUM CHEMICAL CONCENTRATION IN BIOSOLIDS

MAXIMUM ALLOWED CUMULATIVE CHEMICAL CONCENTRATION

<u>Cumulative Pollutant Loading Rate (CPLR) Limit:</u>

5.9 mg CIP and 1.1 mg AZ per kg amended soil.

<u>Pollutant Concentration Limit:</u>

12 mg CIP and 2.2 mg AZ per kg biosolids.

NO PERMIT REQUIRED

Conclusions and Future Work

- Biosolids-borne CIP and AZ p mental risks from the 16 exposure pathways under cc cenarios.
- Even severely contaminated erm, pose minimal risks.
- Negligible human and ecolo biosolids.

- Biosolids-borne antibiotic resistance development – a potential 17th pathway.
- Long-term field investigations using various biosolids and quantitative frameworks required to address environmental impacts of biosolids-borne antibiotic resistance.