Micro-constituents in Biosolids

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We've talked about organics in biosolids before

- Dioxins/Furans
- Polyclorinated Biphenols
- Pesticides

These are not compounds that you will find on the bathroom shelf

In contrast-
Just about all of the new organics that people are concerned about are found in common household products

So why the fuss?

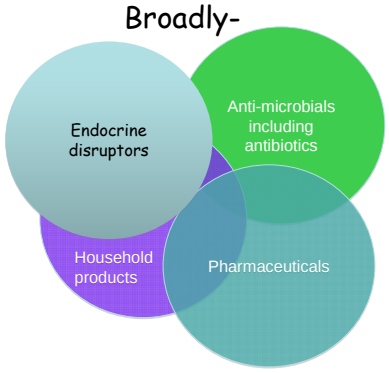
Why people are concerned?

- As near as I can figure:
- We are beginning to recognize long-term negative effects of using certain common chemicals that had been considered innocuous
- Information for some in aquatic systems shows potential for harm
- Some compounds designed to kill things
- Dearth of information on behavior in a soil system

Hopefully- I'll cover

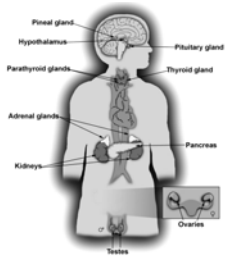
- Classes of compounds
- How they are used
- Quantity in biosolids
- Why we care
- Fate in the environment

Broadly-



Let's start with: endocrine disruptors

the endocrine system



regulates body growth, metabolism, behavior, sexual development and function

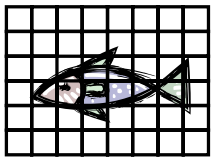
secretion of hormones by ductless endocrine glands into the bloodstream

hormones transported to receptors where they trigger responses

AGONISTS mimic hormones, bind to receptors producing same response
ANTAGONISTS block hormones, prevent binding to receptors and responses

Figure taken from eMedicineHealth.com The Endocrine System. 2005. Website http://www.emedicinehealth.com/images/4453/4453-13250-37539-37611.jpg

1990s - male trout in cages by WWTF outfalls developed eggs in their testes



laboratory studies showed synthetic estrogen could cause increased production of protein responsible for egg production (vitellogenin) as low as 1 ng/L

predicted no-effect concentration to fish for synthetic estrogen of 0.35 ng/L (350 **pico**grams/L)

1 ng/L equivalent to:
a single penny in $10,000,000,000

OP-ED COLUMNIST

Chemicals in Our Food, and Bodies

By NICHOLAS D. KRISTOF
Published: November 7, 2009

Your body is probably home to a chemical called bisphenol A, or BPA. It's a synthetic estrogen that United States factories now use in everything from plastics to epoxies — to the tune of six pounds per American per year. That's a lot of estrogen.

More than 92 percent of Americans have BPA in their urine, and scientists have linked it — though not conclusively — to everything from breast cancer to obesity, from attention deficit disorder to genital abnormalities in boys and girls alike.

what are some known EDCs, and what are their fates in WWTFs

?

possible mechanisms of removal

SIGNIFICANT	NOT SIGNIFICANT
sorption to biosolids •dependent on solid-water distribution coefficient (k_d)	**volatilization** •low Henry's constants (k_H)
biodegradation •aerobic •anoxic •anaerobic	**chemical** transformations •hydrolysis, acid-base •photocatalytic •precipitation

phthalate esters

plasticizers – used in wide range of products from PVC to cosmetics


plastic toys


pvc pipe


detergents/surfactants


paint

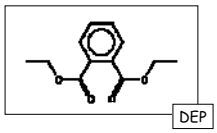

pharmaceuticals

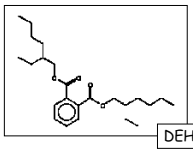

printer ink

phthalate esters

not covalently bound in plastic, readily leach

1-13 carbon alkyl chains


DEP


DEHP

•ballpark: µg/L in influent, <10% in effluent
•amount in biosolids varies with length of alkyl chain (10-70%)

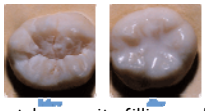
bisphenol A

monomer of polycarbonate plastics
adhesives, building materials, canned food liners, dental sealants, water bottles…


drinking water bottles

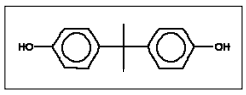

adhesives


canned food liner


dental composite fillings and sealants


CDs/DVDs

bisphenol A



•biodegradation mainly aerobic
•ballpark: µg/L in influent, ~70% biodegraded
•majority not biodegraded will be with biosolids

some chlorinated and biodegradation products are MORE estrogenic than BPA

nonylphenol ethoxylates

non-ionic surfactants - detergents, pesticides, plastics, paint, liners,…

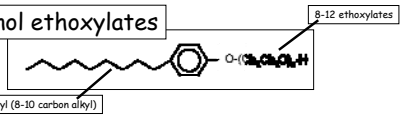

cleaning products


paint


pesticides

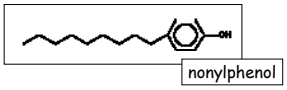

cosmetics

nonylphenol ethoxylates

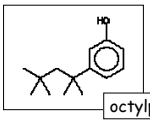


•commercial mixture (technical nonylphenol) is >100 isomers

- ballpark: μg/L in influent, ~70% biodegraded
- majority not biodegraded will be with biosolids



nonylphenol



octylphenol

some breakdown products are more persistent & have greater estrogenic activity

fragrance materials

include >2100 compounds, ubiquitous in consumer products

perfume/cologne

shampoo

pesticide

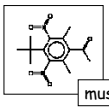
soap

toothpaste

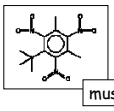
cleaning products

fragrance materials

nitromusks replaced natural musk ~50 years ago

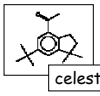


musk ketone

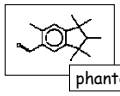


musk xylene

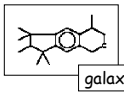
polycyclic musks less toxic, but more persistent



celestolide



phantolide



galaxolide

ballpark: ng/L-μg/L in influent, majority sorbs to biosolids
musks are recalcitrant, <<50% biodegraded

estrogens

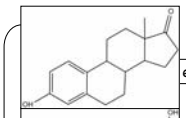
natural and synthetic

people

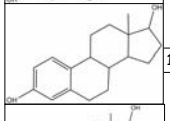
birth control pills

hormones

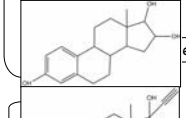
ballpark: ng/L in influent



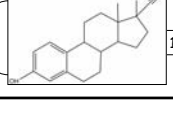
estrone (E1)



17β-estradiol (E2)



estriol (E3)



17α-ethinylestradiol (EE2)

natural estrogens

synthetic estrogen

other?

consumer goods

caffeine

pesticides

deet

microbial biocides

triclosan

triclocarban

pharmaceuticals

uv blockers (sunscreens)

oxybenzone

octyl methoxycinnamate

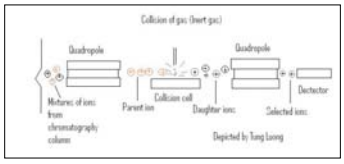
Concentration ranges

Analyte	Concentration Range Dry-Weight (mg/kg)
Phthalate esters	
Bis (2-ethylhexyl) phthalate	0.66-310*
Bisphenol A	0.1-10 0.47+
Nonylphenol	2.2-1520 58.7(Australia)
Polycyclic musks	5-50
Estrogens	
17B Estradiol	NA* NA(Australia)

How to measure?

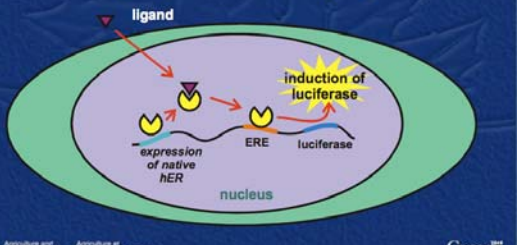
I. Concentration
- LC-MS-MS
- $$$
- Often BD in soil matrix

I. biological activity



In Vitro Estrogen Receptor Binding Assays:

- recombinant estrogen-responsive cell line stably transfected with an estrogen responsive luciferase reporter plasmid

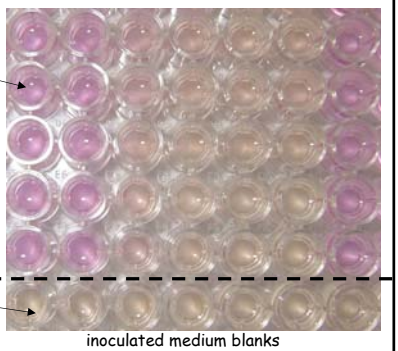


Agriculture and Agri-Food Canada | Agriculture et Agroalimentaire Canada

Canada

YEAST ESTROGEN SCREEN

positive response

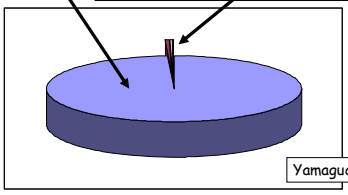


negative response

inoculated medium blanks

100 E2 (17β-estradiol)

0.38 BPA metabolite
(4-methyl-2,4-bis(4-hydroxyphenyl)pent-1-ene(MBP))
0.25 phenolic resin
(4-(1-adamantyl)phenol (AdP))
0.05 BPA metabolite
(4,4'-dihydroxy-α-methylstilbene (DHMS))
0.02 NP (nonylphenol)
0.001 BPA (bisphenol A)

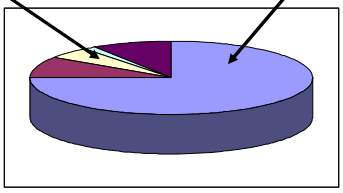


Yamaguchi et al. 2005

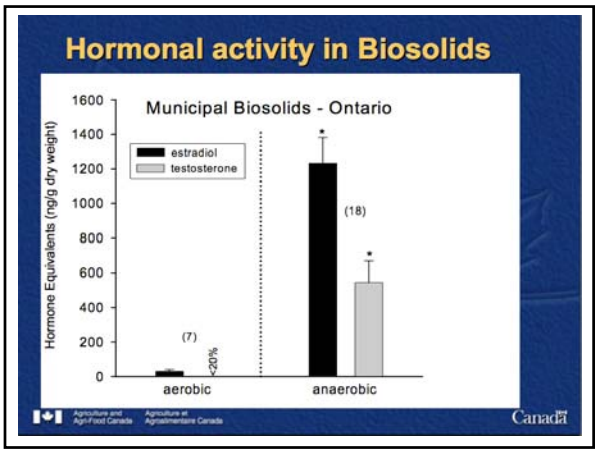
relative estrogenic potencies of pure chemicals……

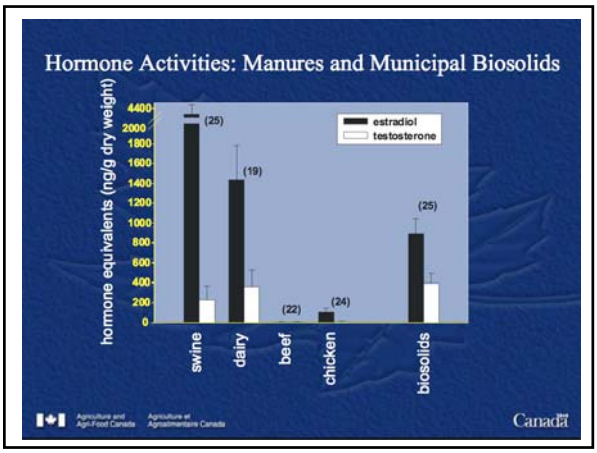
majority due to estrogens

xenoestrogens



…and then extrapolate using known influent and effluent concentrations





In soil

Water Environment Association of Ontario

- Hormones- short half life in soils, no plant uptake
- Nonylphenol- short half life in soils, no plant uptake
- Synthetic musks- no data
- Bisphenol A- human health via land application not a concern, no data on terrestrial toxicity or persistence
- Phthalates- slow to degrade – no evidence of potential hazard in terrestrial systems

So let's move on

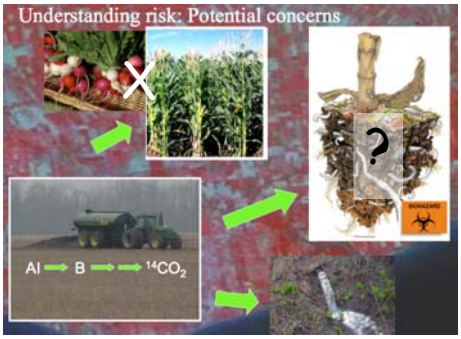
Pharmaceuticals detected in biosolid (ng/g)

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_2O	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

Biosolids relative to effluent

Chemical	Max release via effluent	Release via biosolids
	kg	
Caffeine	206160	75
Carbamazepine	3763	17
Ibuprofen	40250	69
Triclosan	4420	2690
Triclocarban	268	640

Primary concerns

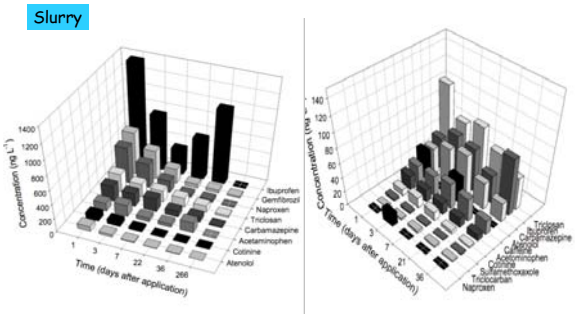


Aquatic is well defined risk

PPCP	Max tilewater Conc (μg L^{-1})	Concentrations in WWTP effluent (μg L^{-1})	Toxicological endpoints (μg L^{-1})
Naproxen	0.035	ND-0.855 [a,f]	4900 IC_{50} *Hydra attenuata* regeneration. (Quinn et al., 2008)
Acetaminophen	0.233	ND-9.000 [e]	20100 LC_{50} 48h acute exposure *Daphnia magna*. (Han et al., 2006)
Ibuprofen	0.073	ND-24.6 [e,g]	3840 IC_{50} *Hydra attenuata* regeneration. (Quinn et al., 2008)
Carbamazepine	0.050	ND-2.300 [c,e,g]	160 (μg/kg sediment) EC_{50} pupation of *Chironomus riparius* (Oetken et al., 2005)
Triclosan	0.235	0.043-2.700 [a,b,d]	1.200 (LOEC) *Scenedesmus subspicatus*. (Orvos et al. 2002) 0.5300 72h IC_{50} *Pseudokirchneriella subcapitata*. (Yang et al., 2008)
Atenolol	0.131	0.360 [g]	10000 (LOEC growth) *Pimephales promelas* embryo. Winter et al. 2008 33400 EC_{50} *Ceriodaphnia dubia* (Frayssе and Garric, 2005)
Triclocarban	Below LOQ	0.17[b]	17.000 72h IC_{50} *Pseudokirchneriella subcapitata* (Yang et al., 2008)
Gemfibrozil	0.129	ND-0.71[g]	900 IC_{50} *Hydra attenuata* regeneration (Quinn et al., 2008)

Runoff potential -Ed Topp

Slurry

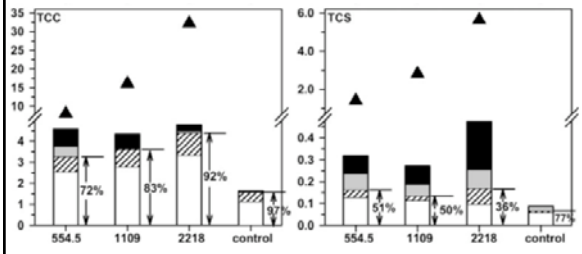


Cake

How about that toothpaste? Antimicrobials

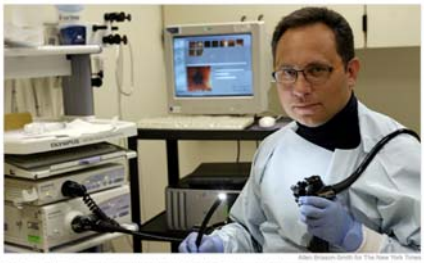
- Triclosan-
  - less persistent $T_{1/2}$ 18-108 d
- Triclocarban-
  - more persistent <4% degraded in 7.5 months
  - Bioavailability/extractability decreased significantly over time

Long-term study Xia et al., 2010



Future for antimicrobials and antibiotics?

How Microbes Defend and Define Us



Dr. Alexander Khoruts, a gastroenterologist at the University Minnesota, used bacteriotherapy to help cure a patient suffering from a gut infection.

By CARL ZIMMER

Published: July 12, 2010

Conclusions

- Evidence for harm in aquatic systems
- No evidence for harm in terrestrial systems
- Lack of data
- Concern because of subtlety of effects?