Micro-constituents in Soils

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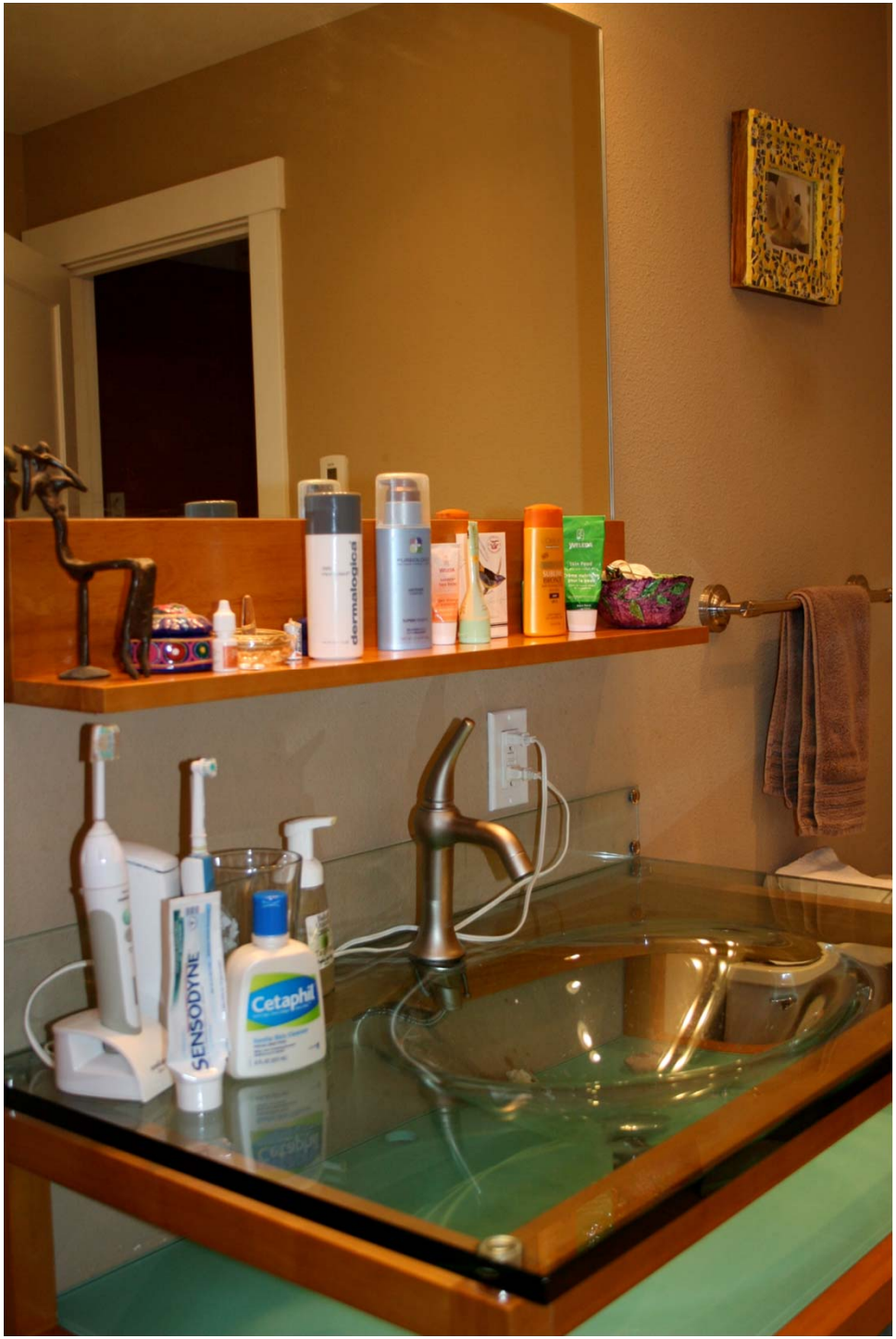
We've been concerned about organics

- Dioxins/Furans
- Polyclorinated Biphenols
- Pesticides

These are not compounds that you will find on the bathroom shelf
And they are considered highly toxic



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

Basic categories:

phthalate esters

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

plastic toys

pvc pipe

detergents/surfactants

paint

pharmaceuticals

printer ink

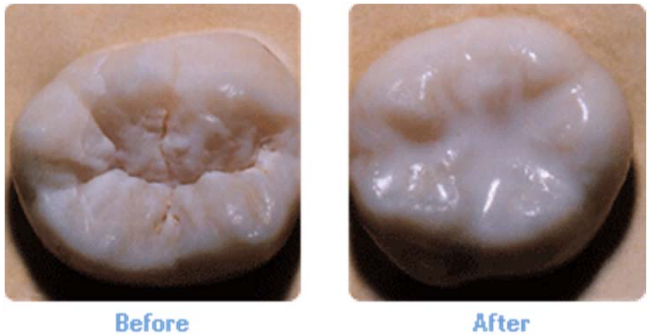
bisphenol A

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

nonylphenol ethoxylates

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

cleaning products

paint

pesticides

cosmetics

fragrance materials

include >2100 compounds, ubiquitous in consumer products

perfume/cologne

shampoo

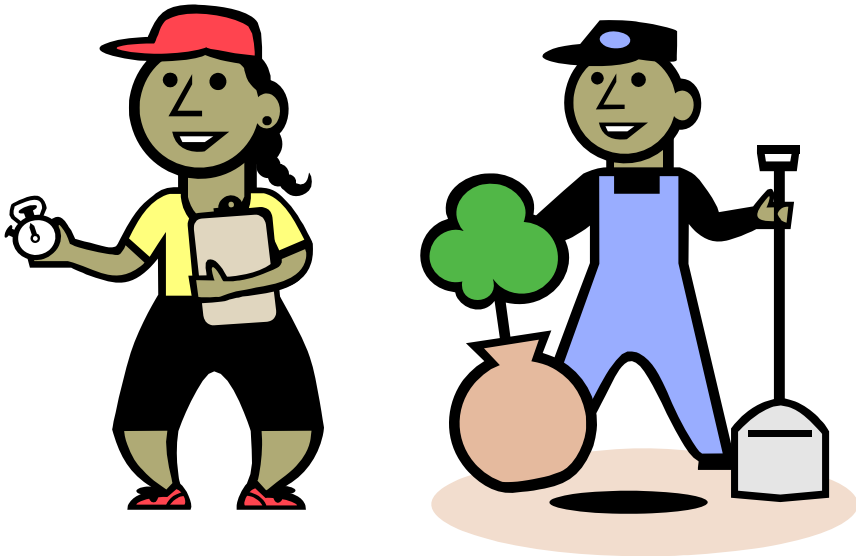
pesticide

soap

toothpaste

cleaning products

estrogens
natural and synthetic



people

birth control pills

Other

consumer goods

caffeine

pesticides

deet

microbial biocides

triclosan

triclocarban

pharmaceuticals

uv blockers (sunscreens)

oxybenzone

octyl methoxycinnamate

Why people are concerned?

- These are products that you recognize
- Direct use of products by people is clear exposure pathway
- Perhaps press and uncertainty- chronic exposure

ABC News: Consumer News: Phthalates Banned From Child Toys - Windows Internet Explorer

http://abcnews.go.com/WN/story?id=5474936&page=1

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ABC News: Consumer News: Phthalates Banned ...

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Consumer News: Phthalates Banned From Child Toys

Links to Resources on How to Make Your Home Toxin-Free

July 29, 2008

WORLD NEWS with Charles Gibson

3 comments

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Congress today approved a nationwide ban on phthalates, a group of harmful chemicals, from children's products after some studies linked them to a variety of long-term health issues.

Phthalates, commonly added to plastic products to make them soft and pliable, are found in a variety of children's products, like teething rings, rubber ducks and soft books, as well as common household items, like vinyl shower curtains, nail

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.

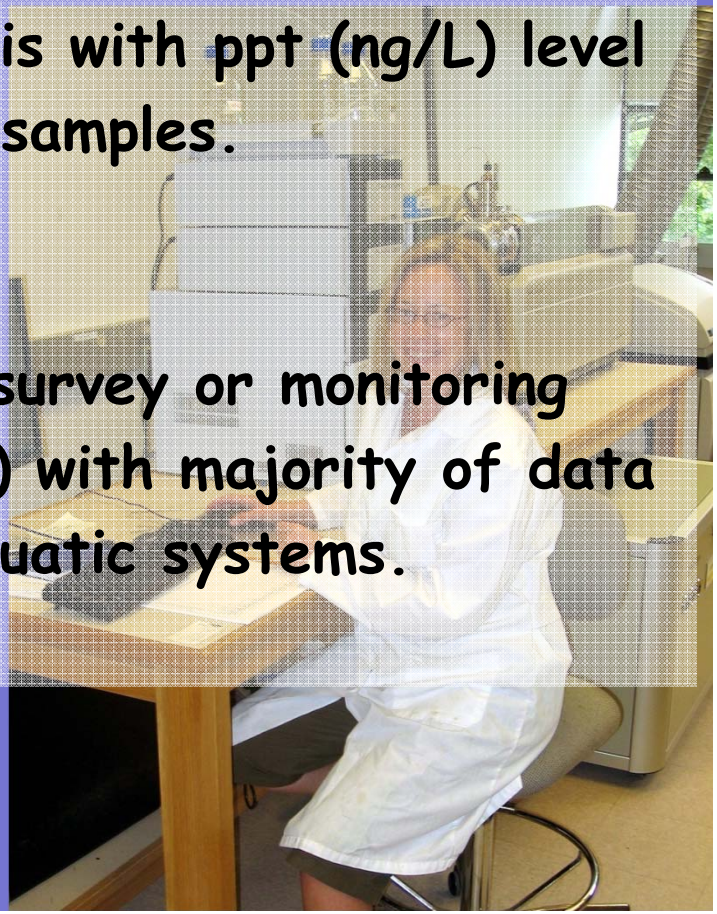
More than 92 percent of Americans have BPA in their urine, and scientists have linked it — though not conclusively — to everything from breast cancer to obesity, from attention deficit disorder to genital abnormalities in boys and girls alike.

Why Now?

- Recent advances in analytical chemistry have enabled study of chemicals that were previously undetected in the environment.
- The advent of LC-MS, especially LC-tandem MS has revolutionized the environmental analysis with ppt (ng/L) level detection of polar compounds in water samples.

Trillions (ppt) < Billions (ppb) < Millions (ppm)

- Recent studies are largely focused on survey or monitoring (chemical occurrence/exposure effects) with majority of data on occurrence and effects based on aquatic systems.



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 [c,f]	4900 IC_{50} *Hydra attenuata* regeneration. (Quinn et al., 2008)
Acetaminophen	0.233	ND-9.000 [c]	20100 LC_{50} 48h acute exposure *Daphnia magna*. (Han et al., 2006)
Ibuprofen	0.073	ND-24.6 [c-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* (Fraysse and Garric, 2005)
Triclocarban	Below LOQ	0.17[h]	17.000 72h IC_{50} *Pseudokirchneriella subcapitata* (Yang et al., 2008)
Gemfibrozil	0.129	ND-0.7[1ij]	900 IC_{50} *Hydra attenuata* regeneration (Quinn et al., 2008)

In fact- many of these compounds have been around for a long time: Bisphenol A (BPA)

- Ubiquitous in the environment
- Estrogenic effect known since 1936
- Levels in biosolids – 0.03-36 µg/g; House dust – 0.2-17 µg/g
  (Rudel et al., 2003, ES&T 37:4583-4553)
- Degrades relatively easily in soil (half-life ranges from 1-10 days) – not mobile in biosolids-amended soil.

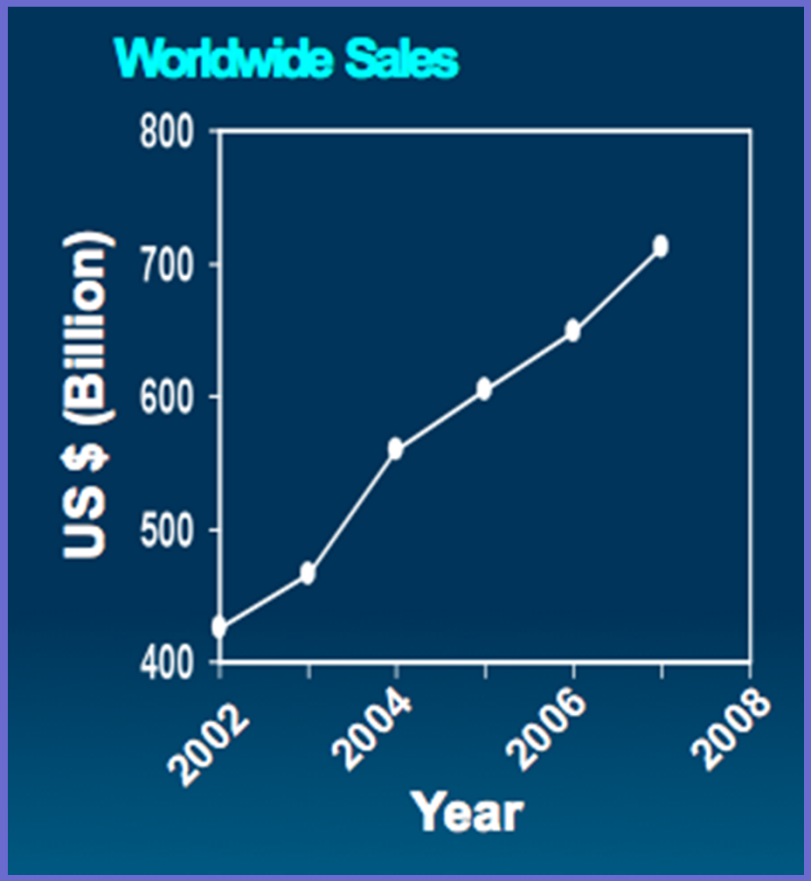
Plastic bottles and hot liquids – A bad combo

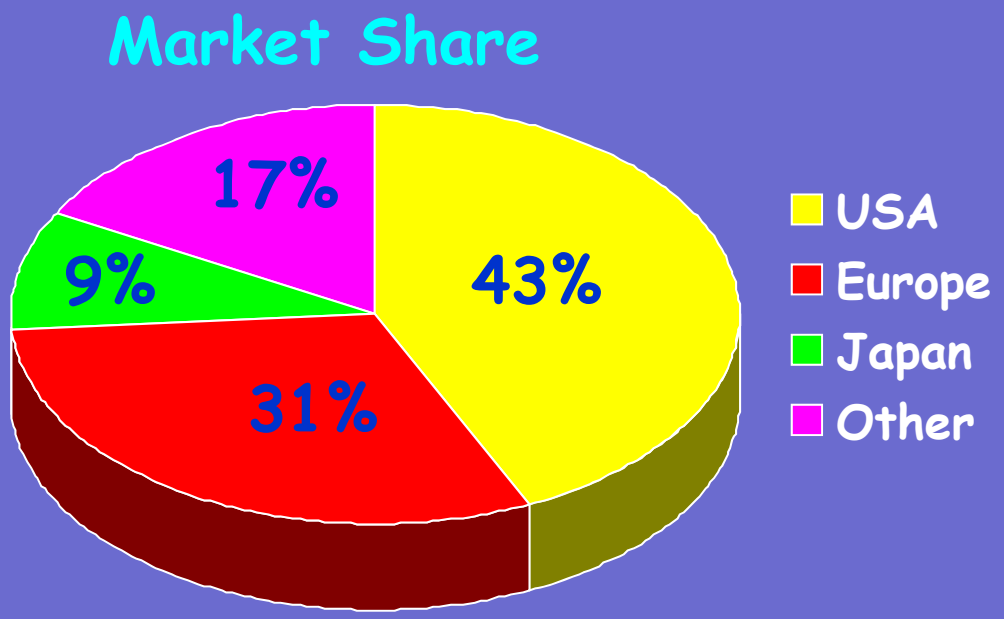
Antimicrobials TCC, TCS Surfactants 4-NP

- Introduced TCC in **1957**, TCS in 1964
- No benefits from use to consumer
- Alkylphenol ethoxylates used in detergents, spermicidal lubricant; as emulsifiers in pesticides, paints; etc.
- Degradation product 4-NP has estrogenic effect
- Estrogenic effect of NP is known since **1938**

TCC 5% by weight

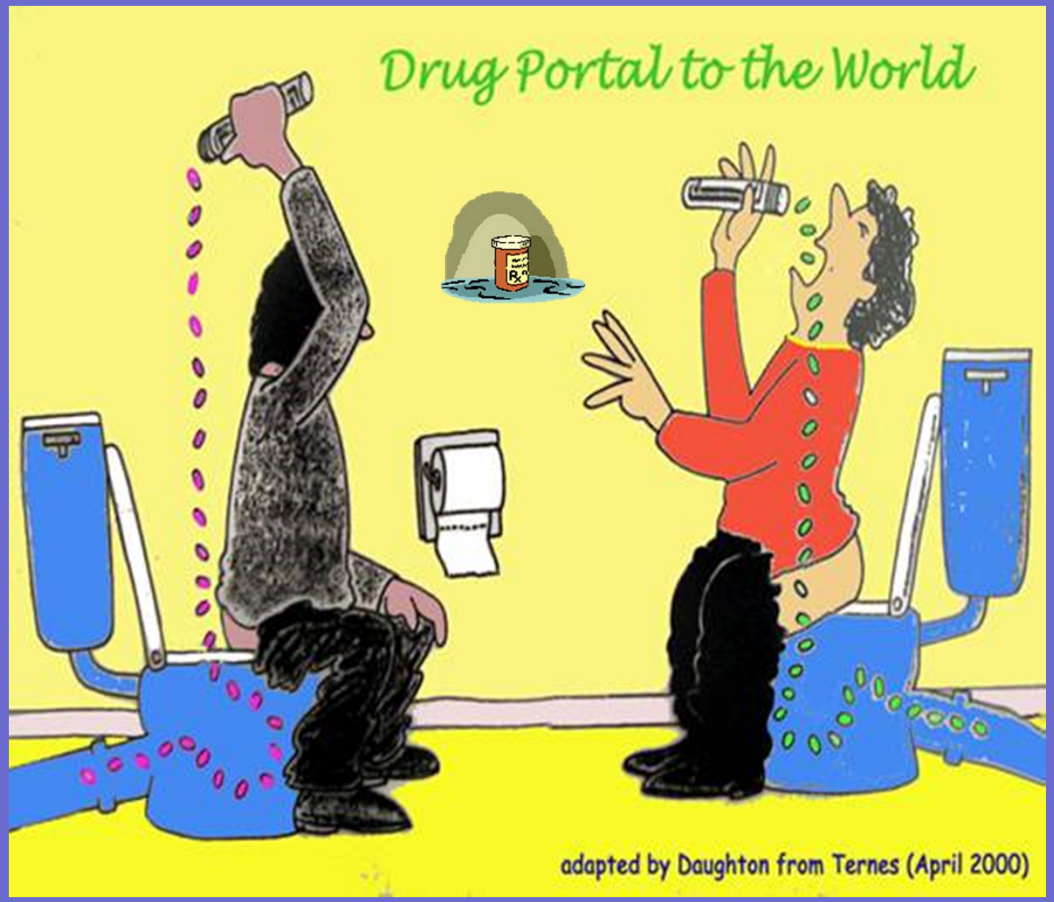
And the same consumers who are so afraid: Pharmaceutical Production and Use





Source: Statistics 2008, VFA

VFA is the trade organization of research-based pharmaceutical companies in Germany



"The red are for the illness, the blues are for the side effects of the red and the greens are for the side effects of the blue."

Even though we know concentrations are higher inside the house let's look at the data for what happens outside the house in the soil-plant environment

Concentrations in organics?

- Concentrations well documented in biosolids and reclaimed water
- Not the case in composts

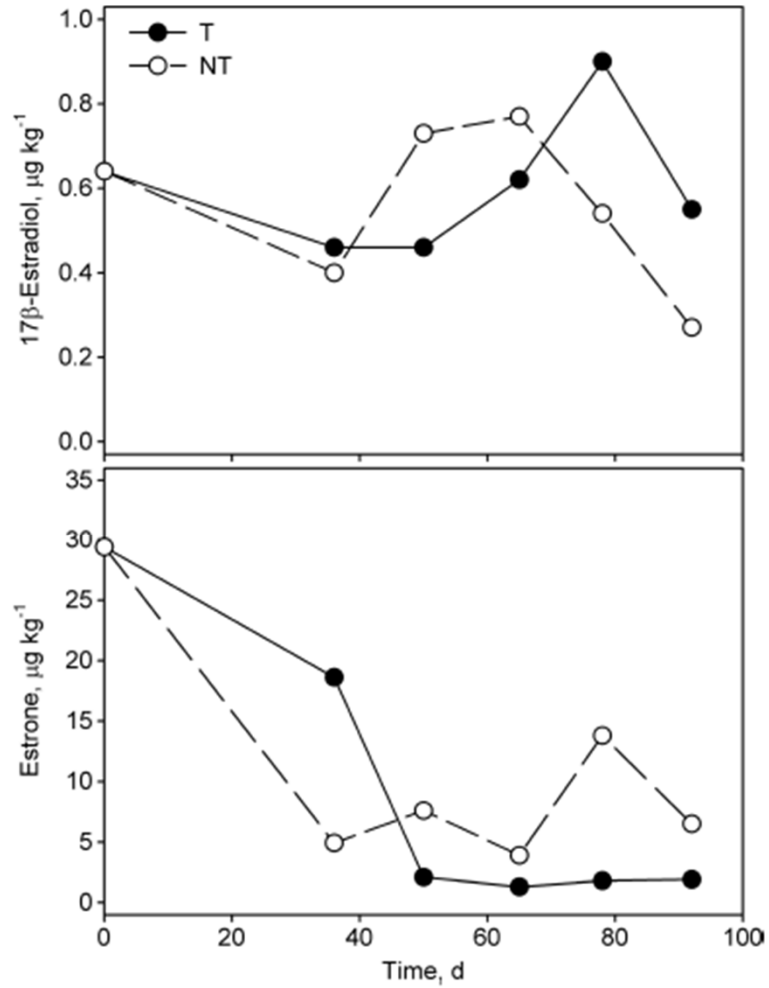


FIG. 4. Changes in dry weight basis 17β-estradiol and estrone concentrations in manure (NT) and composted (T) piles with time.

Derby et al., 2011

Patereau et al., 2012
Biosolids + greenwaste compost

- Phthalic acid esters + Nonylphenol ethoxylates 6-17 mg kg in feedstocks 8-13 in compost

- PAHs 900-3450 ug kg in feedstocks 1560 in compost

- Estrogens 10-21 ug kg in feedstocks BD in compost

Have a headache?
The recommended daily dose of Motrin is 1200-3200 mg per day
How much biosolids (Class A only) would you have to eat to get rid of your headache?

a)2 ounces

b)2 pounds

c)**2 tons**

Not ready to start a family?

How much biosolids has the the same amount of EE2 as 1 low dose birth control pill?

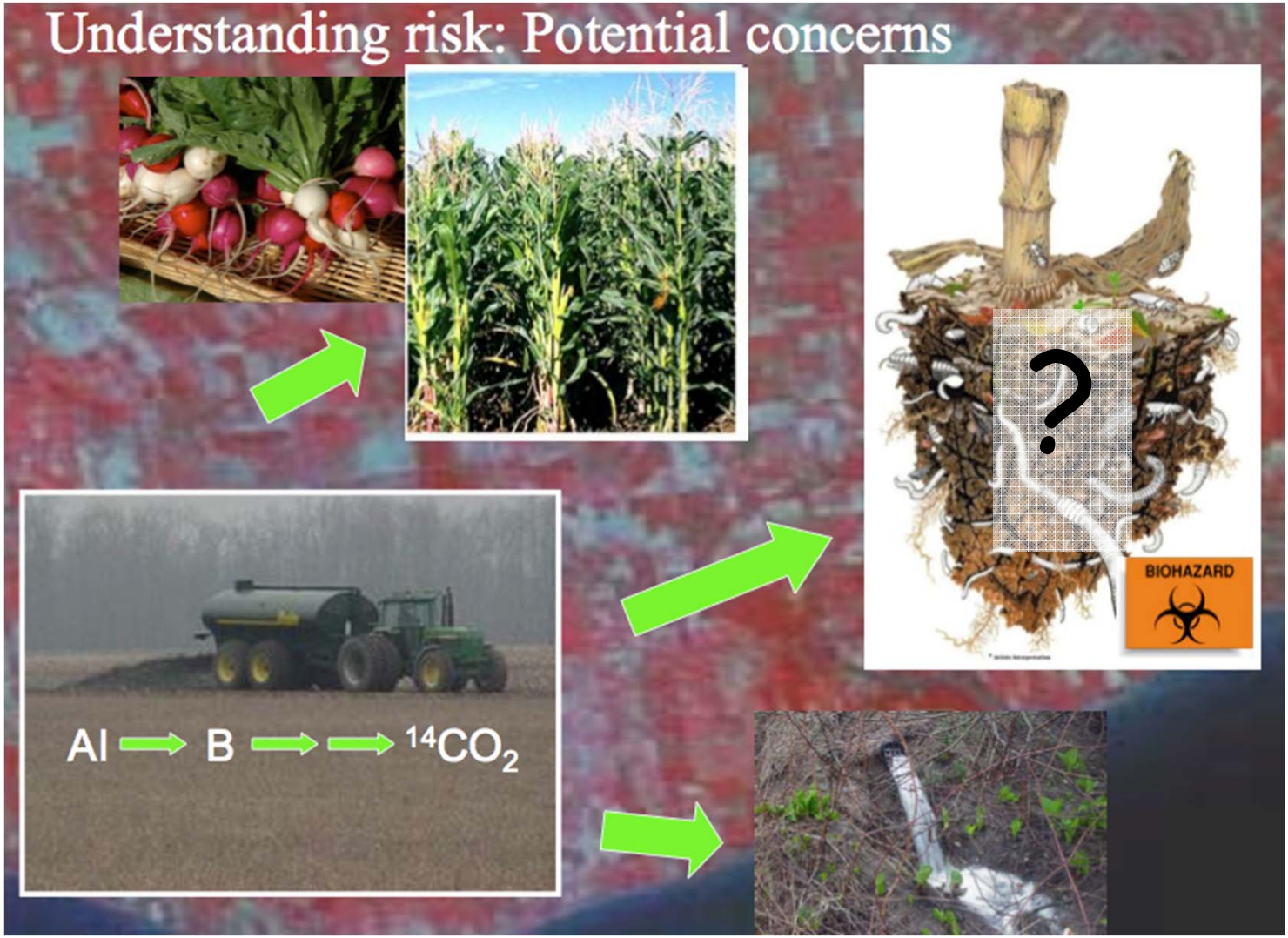
- EE2 in biosolids 4.6 ng g or 4.6 ug kg or 0.005 ppm
- EE2 in a low dose birth control pill 50 ug
- You need 10 kg biosolids to get same amount of EE2 as 1 birth control pill

A

B

C

Primary concerns



Movement to ground or surface water

- Rainfall simulation studies
  - Think shower before pressure control

  - Yang et al., 2012 2.5" per hour following biosolids application at 1,8 and 35 days

Tested for 17 hormones in runoff water

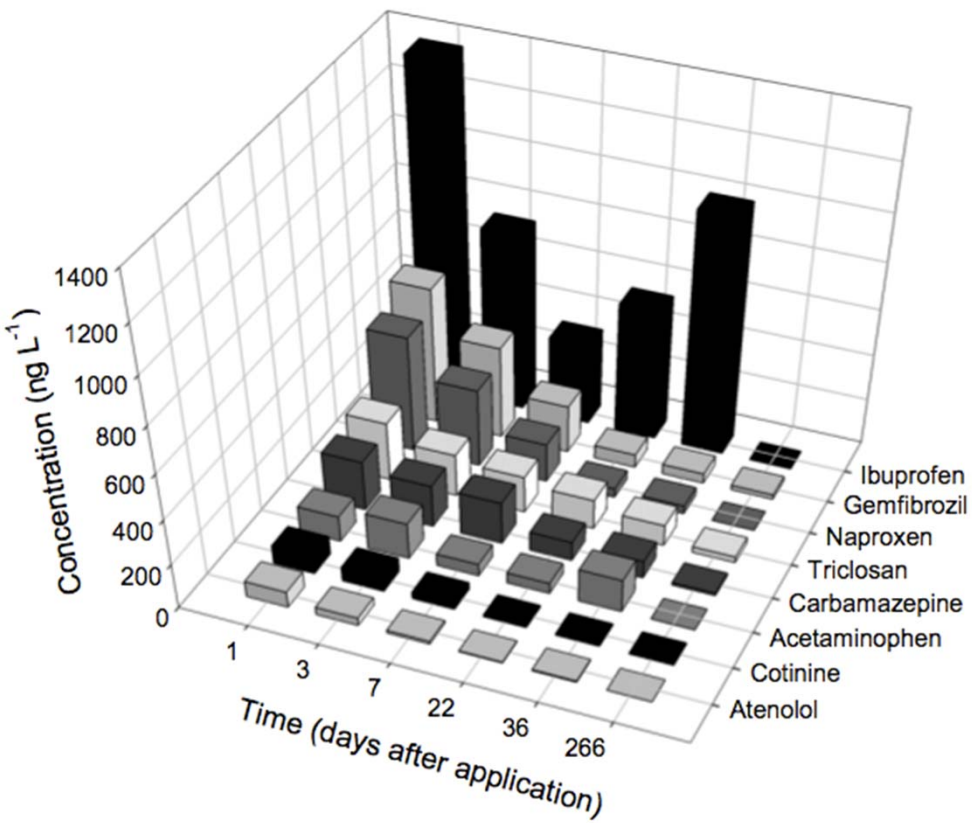
- Androstenedione
- In the biosolids- 22,000 parts per billion
- In the stormwater
  - Day 1 17-216 ppb
  - Day 8 Detected in all samples from 7 to 78 ppb
  - Day 35 detected in all of 6 samples from 17 to 38 ppb
- Hormones are microbially altered in soils so what starts out as testosterone turns into androstenedione before it turns into CO_2

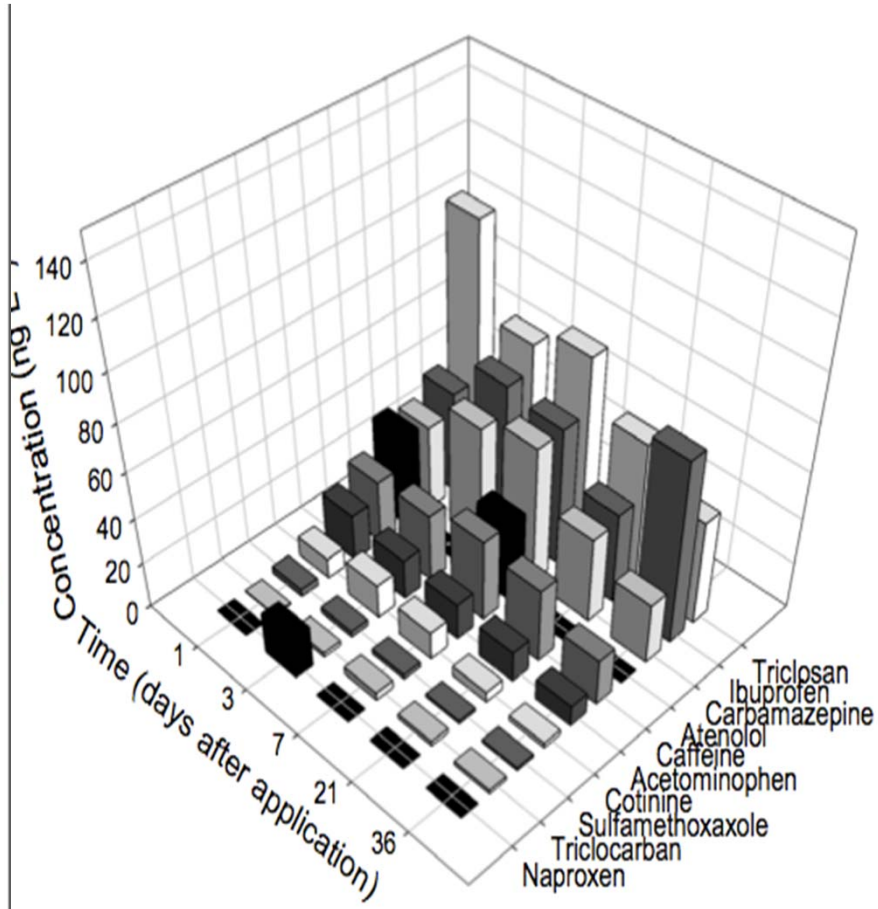
Additional studies

- Guidice and Young, 2011
  - Measured range of EDCs and activity in simulated rainfall. Only triclosan was detected at a level that might be a risk to aquatic organisms
- Sabourin et al., 2009
  - Measured pharmaceuticals and personal care products in simulated runoff. 'Maximal concentrations of all analytes were below toxic concentrations using a variety of endpoints available in the literature '

Runoff potential -Ed Topp

Slurry

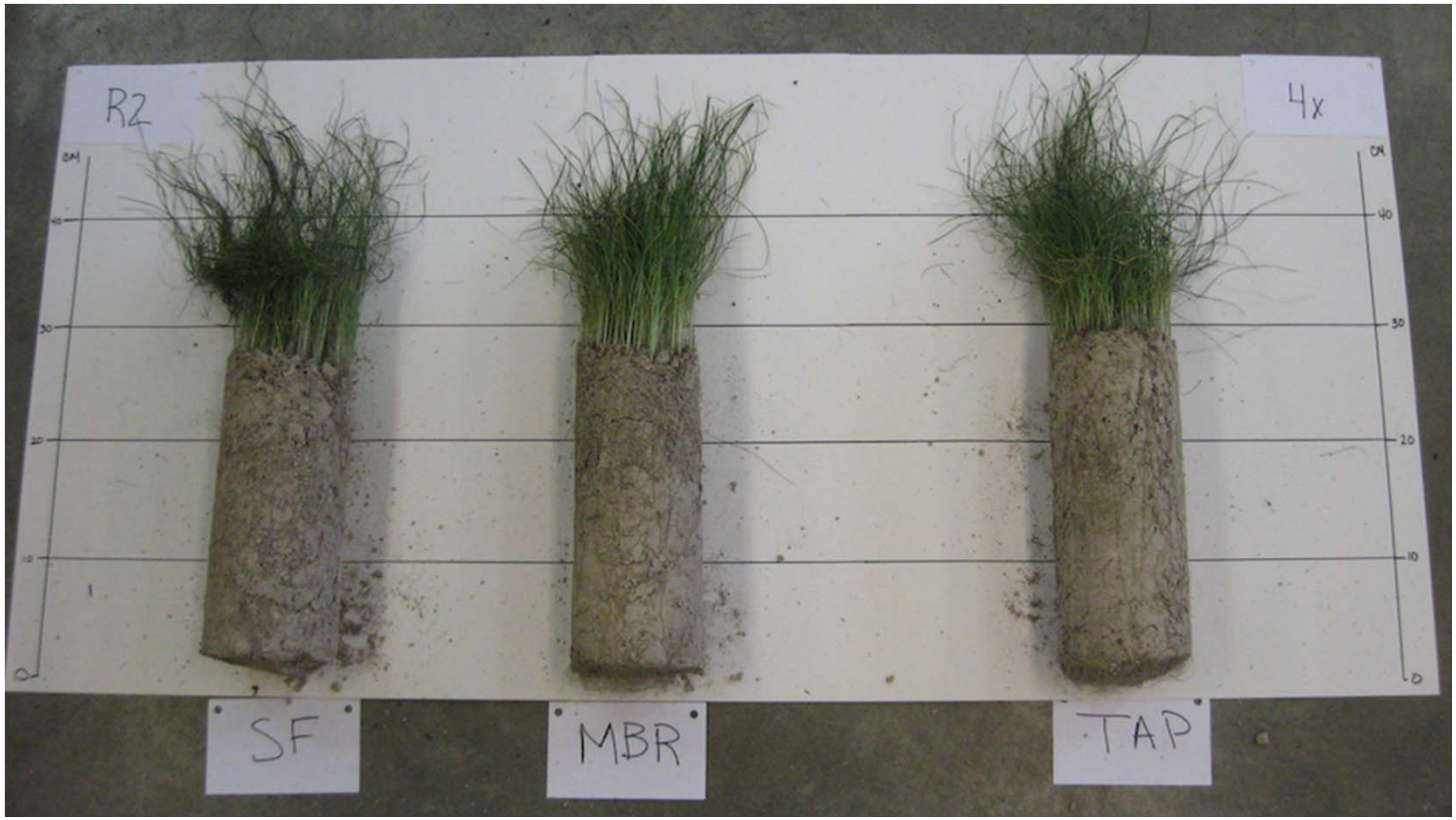




Cake

Rebecca Singer

- Tested leachate from columns irrigated with reclaimed water



YES Assay

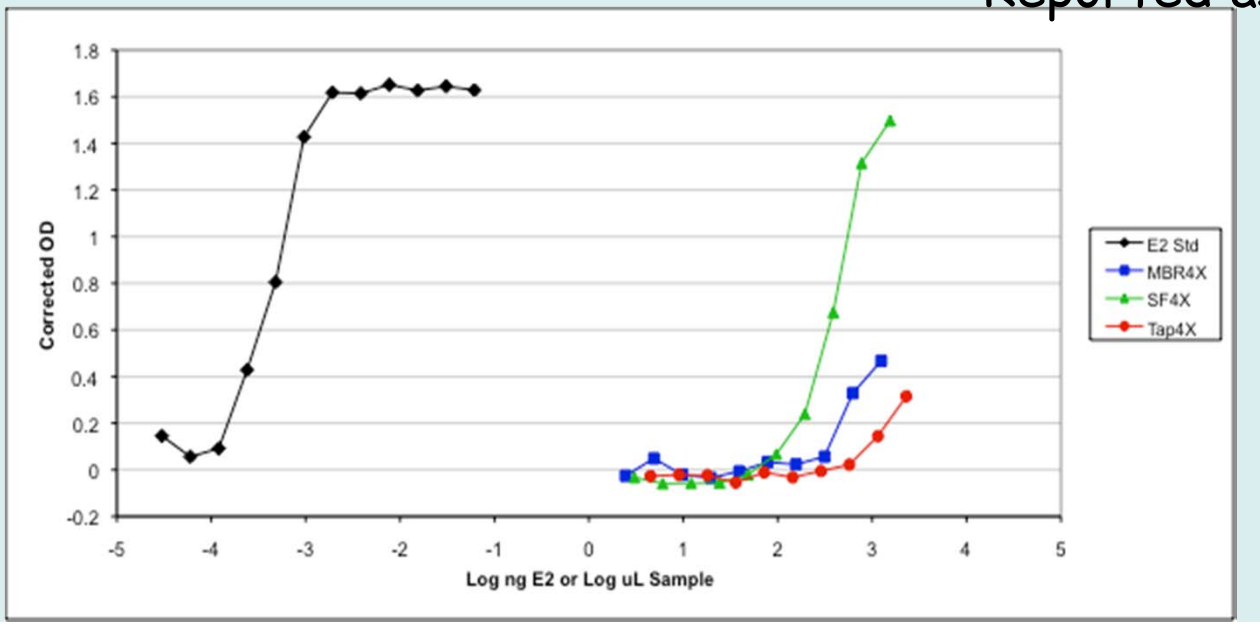
Using Estradiol as a point of reference, the half maximal effective concentration (EC_{50}) was calculated

E2: Slope =1.0

Sample:
Slope > 1.0 = high estrogenic response
Slope < 1.0 = low estrogenic response

REP_{50} (relative estrogenic potency)
$REP_{50}=EC_{50}$ standard/EC_{50} sample

Reported as: (ng/L) %potency



EDCs- Water type

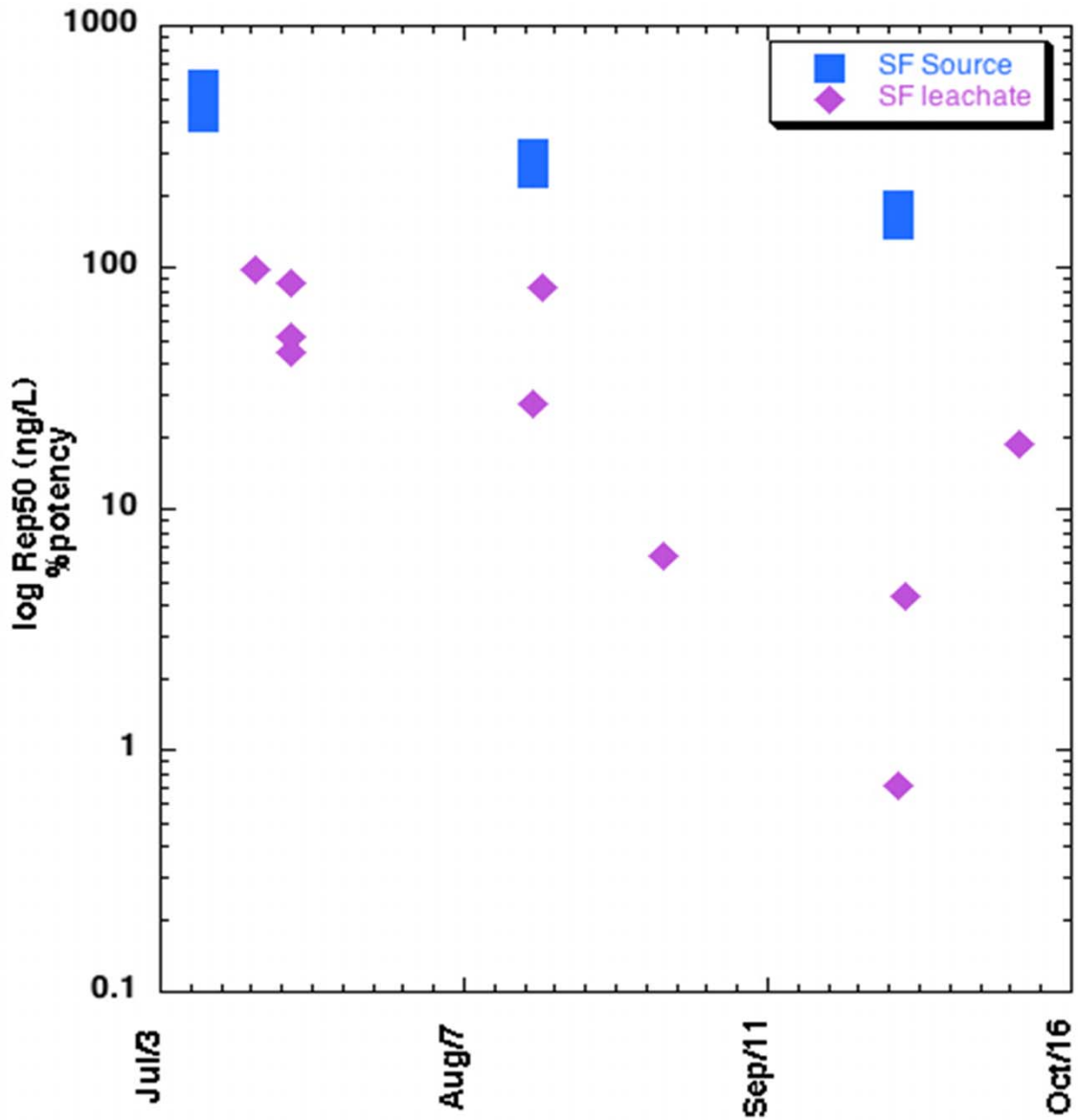
Source Water	n	Rep_{50} (ng/L) %potency
Control	9	.02 +/-.03
MBR	9	0.11 +/- .05
SF	9	307 +/- 147

Agriculture Soil SF Wat

Log Rep_{50} (ng/L)

- SF Source water had very high EDC activity
- SF Leachate was significantly lower than SF Source *Reduced by 86% (Trend across both soils)

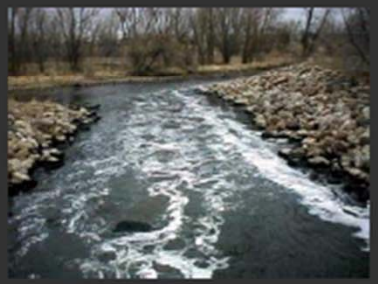
Soil appears to reduce EDC potency in water



Toxicity to soil microbes?

ANTIMICROBIALS AND OTHER TRACE ORGANICS IN BIOSOLIDS: EFFECTS ON SOIL MICROBIAL PROCESSES AND POTENTIAL FOR ENDOCRINE DISRUPTION

Thomas Young, Temitope Ogunyoku, Ben Giudice, Kate Scow, Inmyoung Park, Nannan Zhang
University of California, Davis



August 2012

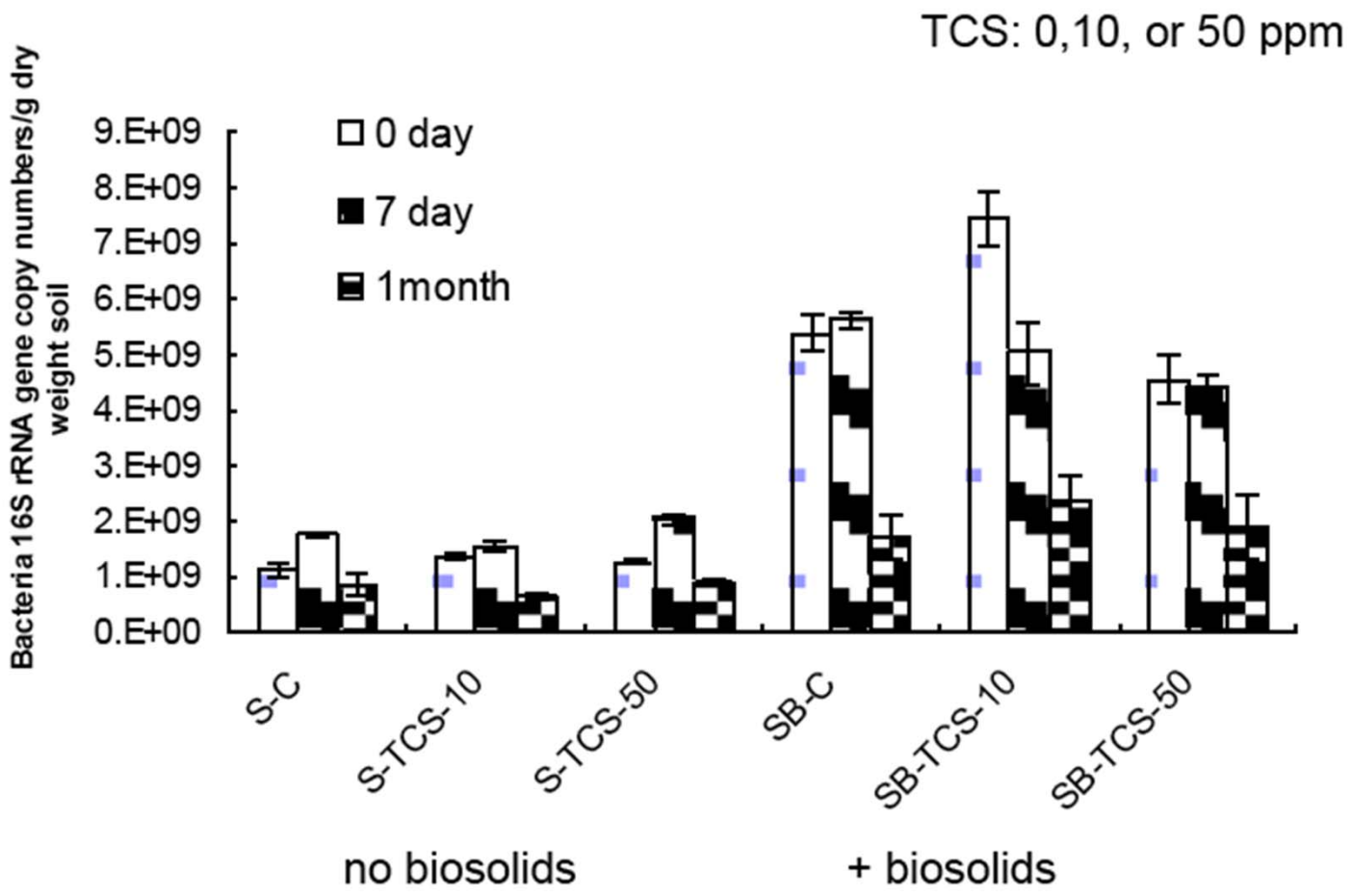
BioFest 2012

TCS Ecosystem Effects

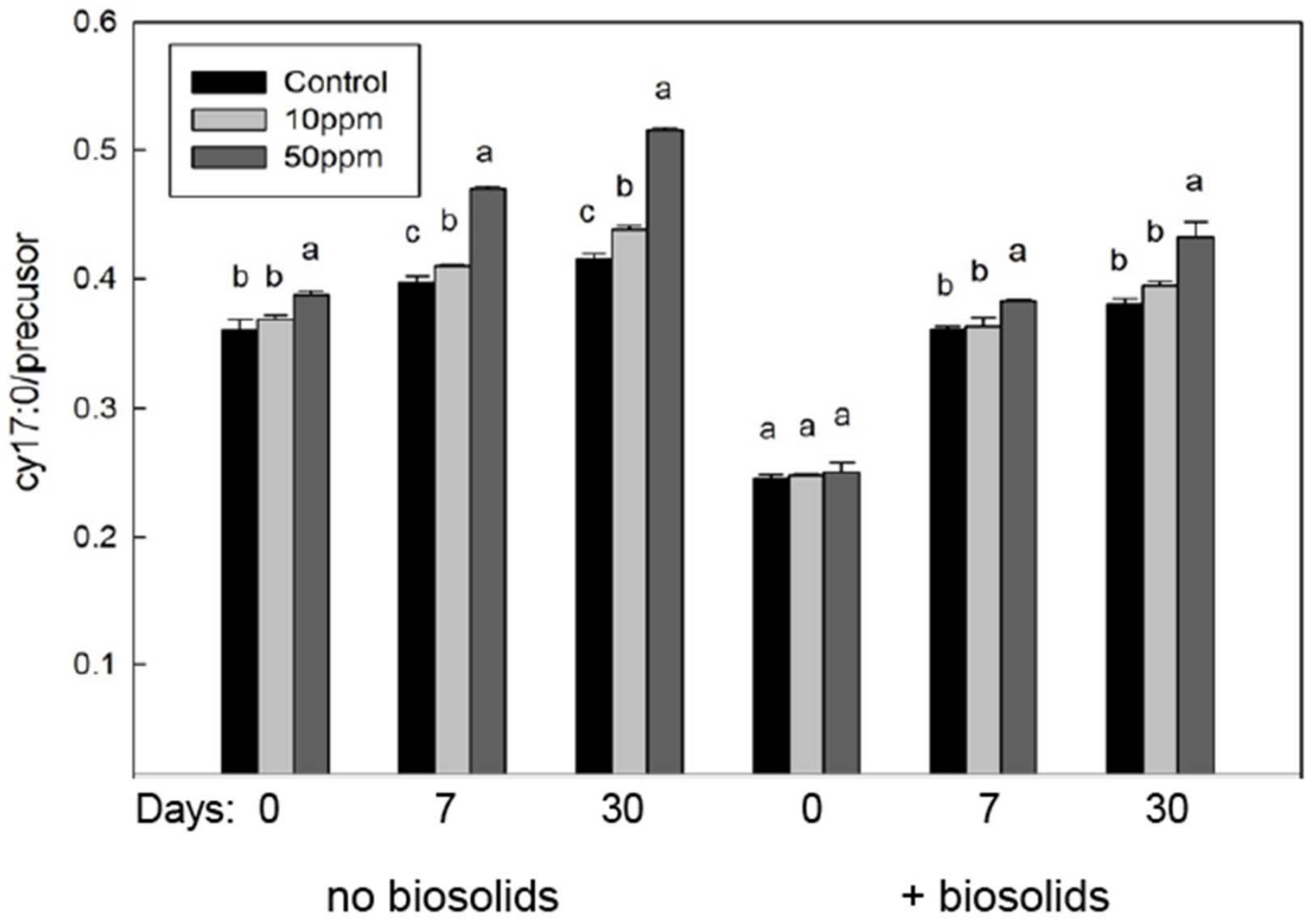
OBJECTIVES:

- Determine effects of TCS on soil microbial community structure
- Assess whether TCS addition interferes with particular soil microbial functions, particularly nitrogen cycling

Biosolids increase total bacterial biomass, TCS impacts are negligible



TCS addition increases biomarkers of stress



Summary of ecosystem effects findings

- TCS decreased ammonia oxidation (activity and populations) and increased microbial stress
- Biosolid addition had a larger effect on monitored parameters than TCS did
- Presence of biosolids mediated effects relative to soils spiked with similar levels of TCS, presumably by reducing bioavailability of TCS

Plant uptake?

Wu et al. parts I and II

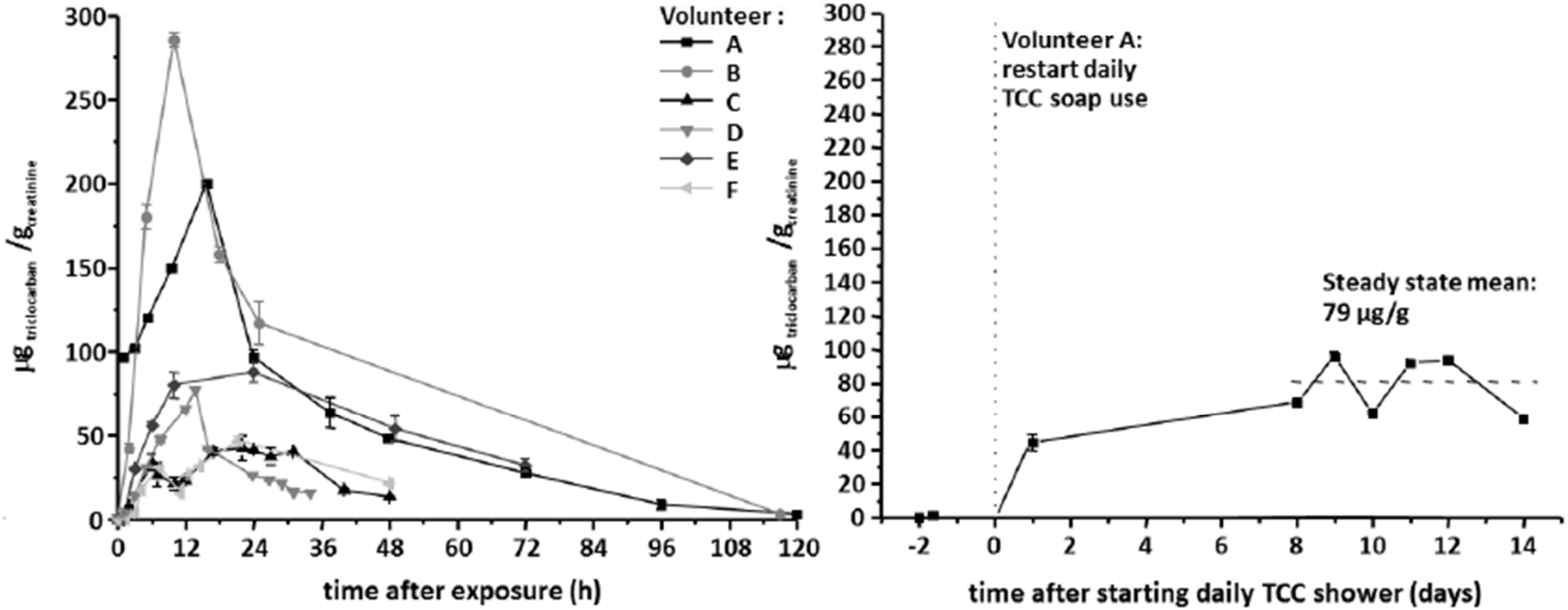
- Wu part I
  - Spiked concentrations in biosolids to 0.7 mg kg not counting residual biosolids concentration
  - Say biosolids had 100 ppm X, when you apply it to soil that gets diluted about 200 fold.
  - So concentrations of TCC and TCS 2x
  - Other compounds 10-100x

Wu et al. parts I and II

- Soybean had between 2.5 and 12.6 ng g (ppb) TCS or TCC

Better not wash your hands after eating….

Products cause most human exposure

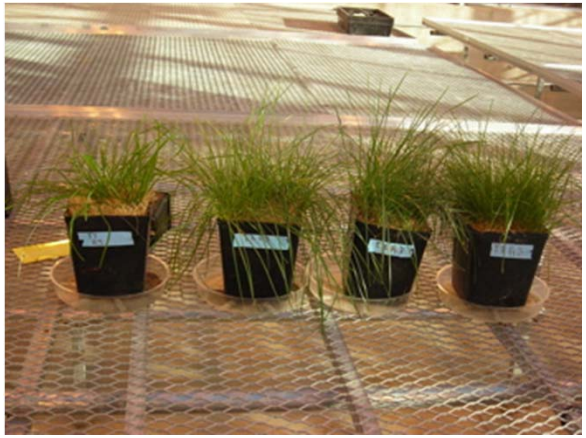


Schebb et al., Environ. Sci. Technol., 2011, 45, 3109-3115

Dana Devin Clarke-Turf grass

Treatments- water source x fertilization

- **Control (Tap water + 100%Fert)**
- **Reclaimed water (RW) only**
- **RW + 50% Fertilizer**
- **RW + 100% Fertilizer**
- **Biosolids (Tap water only)**

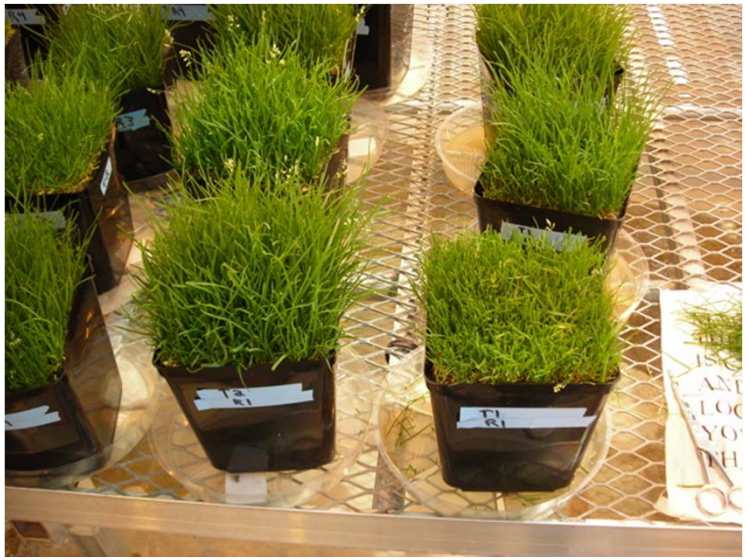


Estrogens in the biosolids

Compound	Biosolid 1 (ng/g)	Biosolid 2 (ng/g)	Average
E1	153.2	150.4	151.8
E2	10.8	10.4	10.6
EE2	4.6	5	4.8

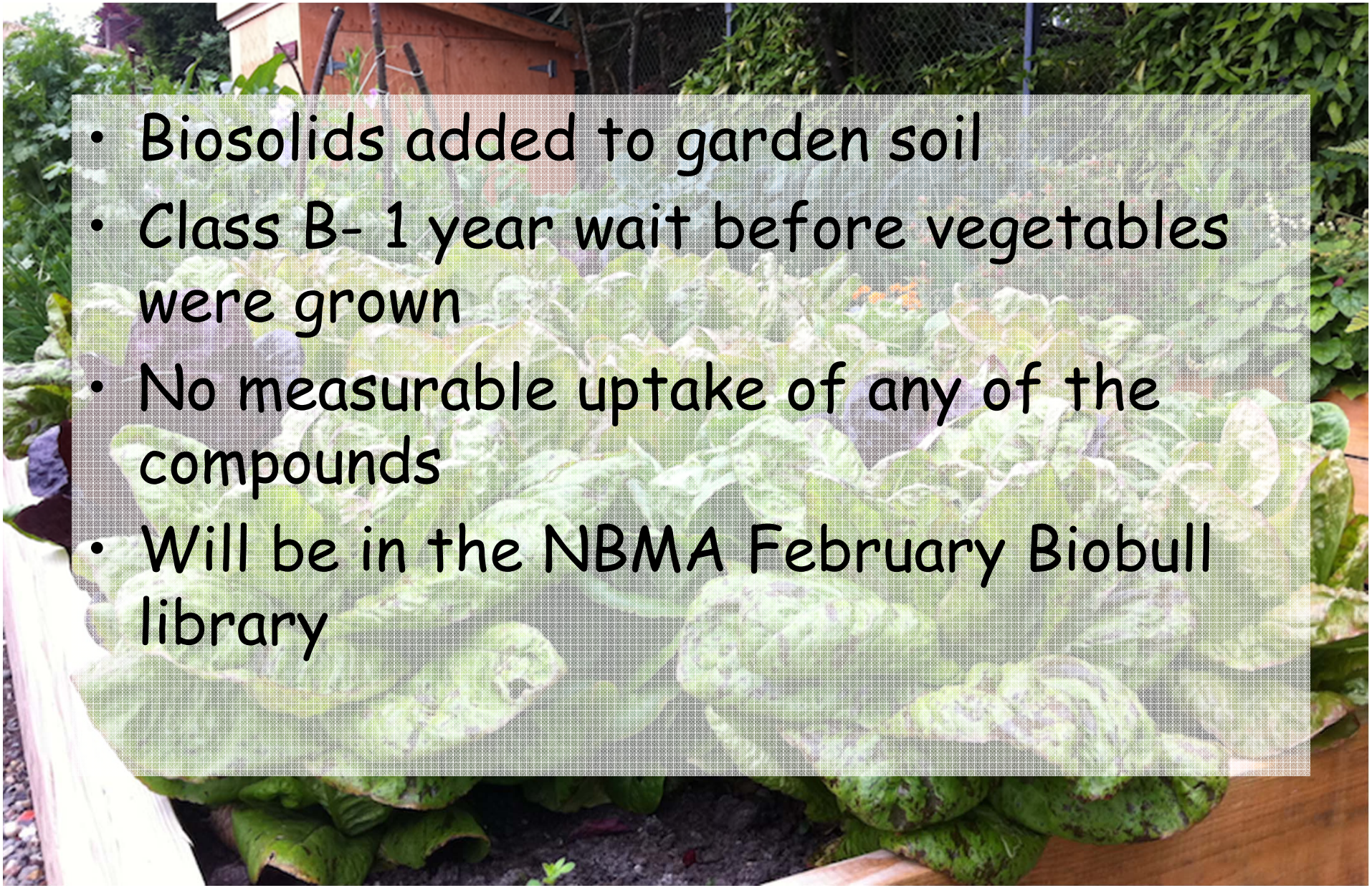
No estrogens were detected on plant surface or in the plant tissue

	E1 (µg/kg)	Avg. Recovery +/- st. error	E2 (µg/kg)	Avg. Recovery +/- st. error	EE2 (µg/Kg))	Avg. Recovery +/- st. error
Biosolids	< MDL	101 +/- 0.5	< MDL	102 +/- 0.6	< MDL	95+/-0.6



New Study- Ed Topp et al

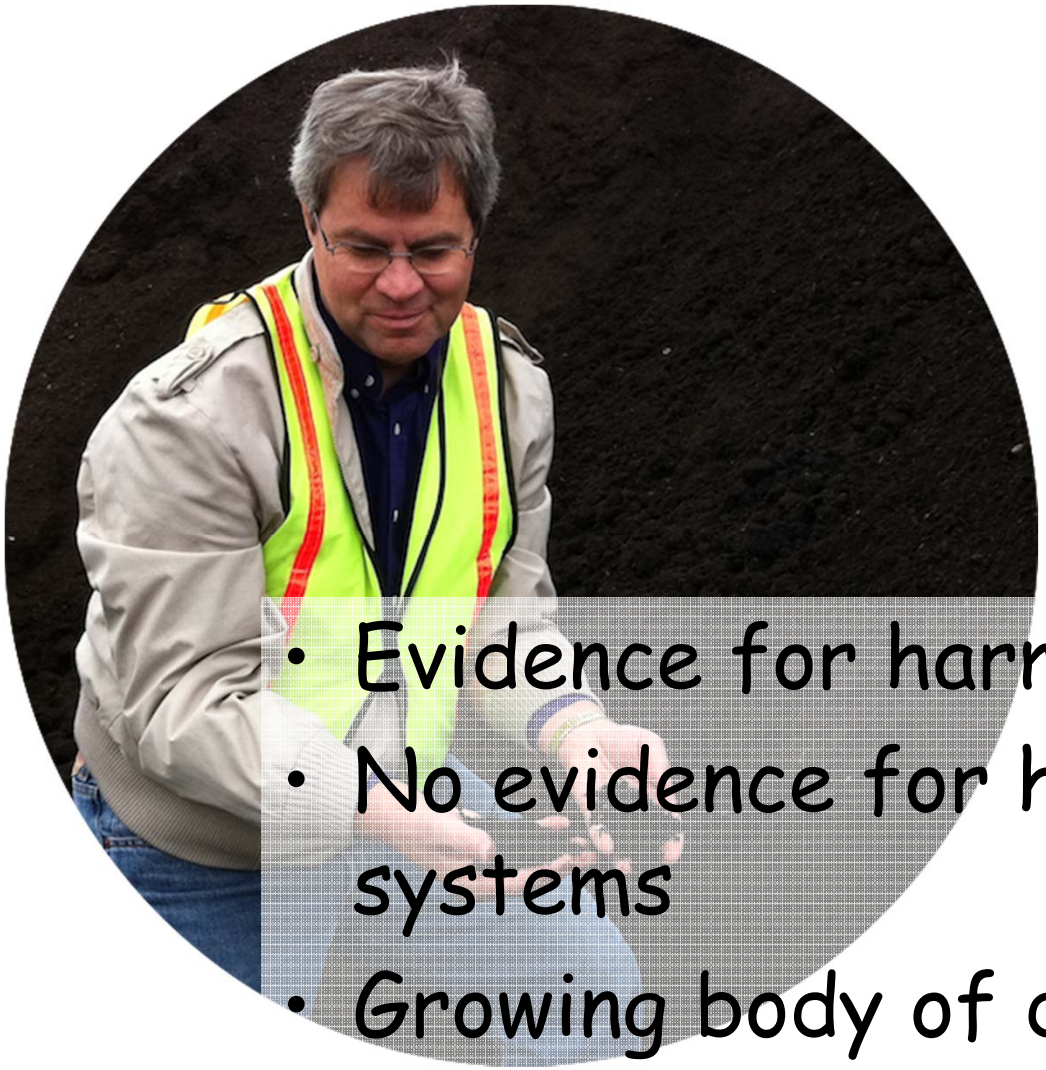
>100 different compounds



- Biosolids added to garden soil
- Class B- 1 year wait before vegetables were grown
- No measurable uptake of any of the compounds
- Will be in the NBMA February Biobull library

And- majority of these compounds degrade quickly in soils

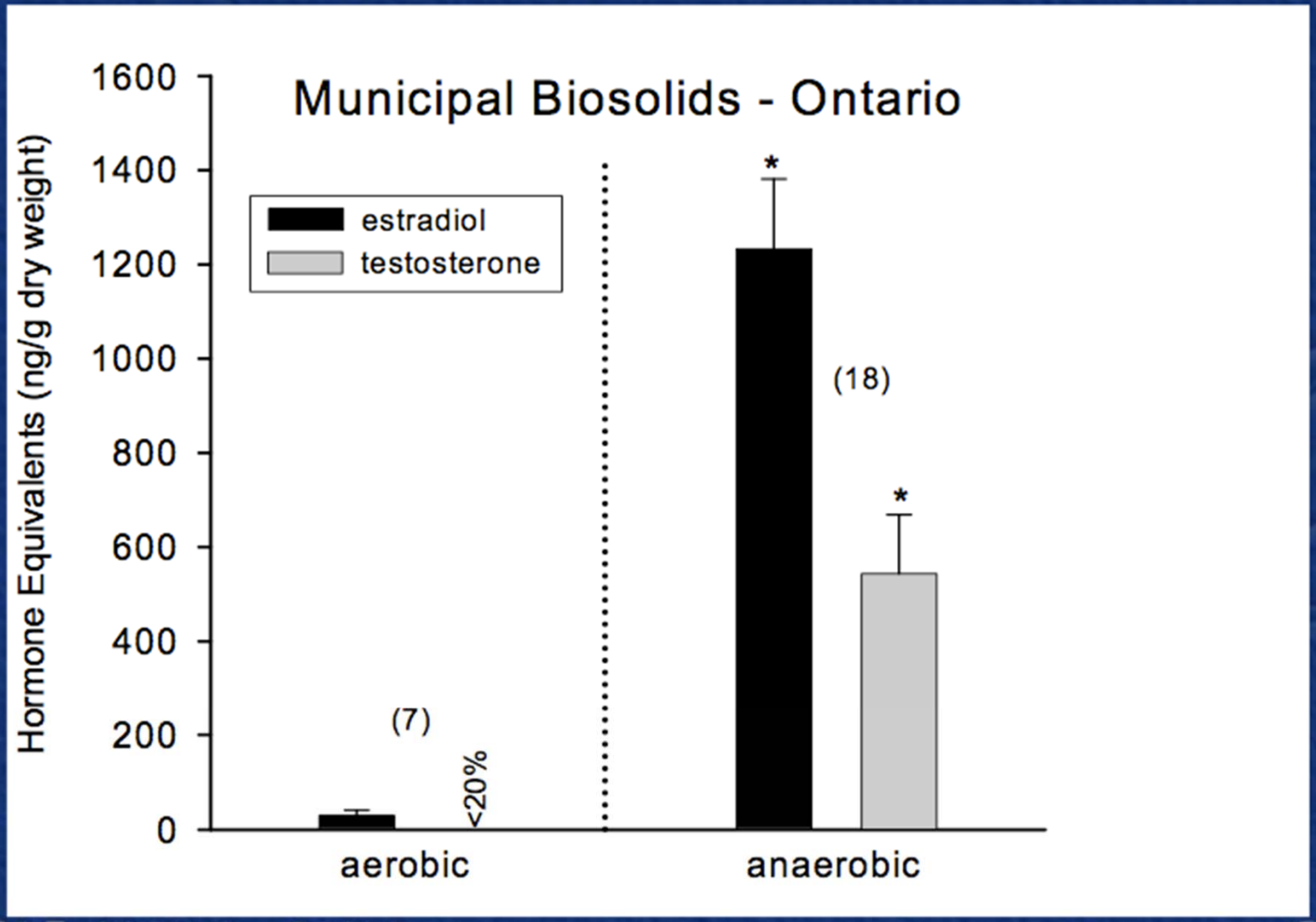
- Hormones - generally days
- 4 NP- weeks
- TCS- months
- TCC, carbamazapine and a few others persist over time



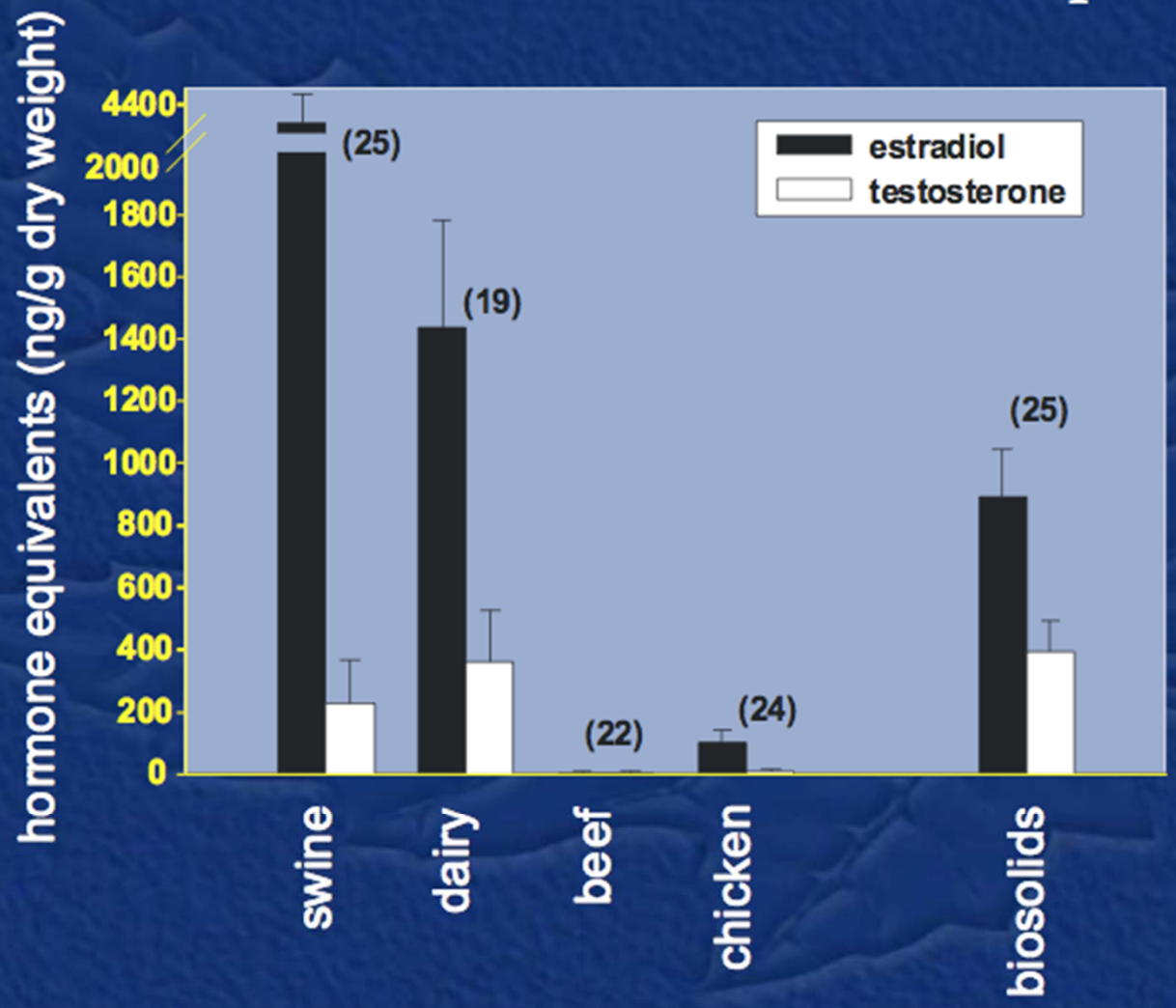
Conclusions

- Evidence for harm in aquatic systems
- No evidence for harm in terrestrial systems
- Growing body of data
- Read before you panic
- Concern because of subtlety of effects?

Hormonal activity in Biosolids



Hormone Activities: Manures and Municipal Biosolids



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

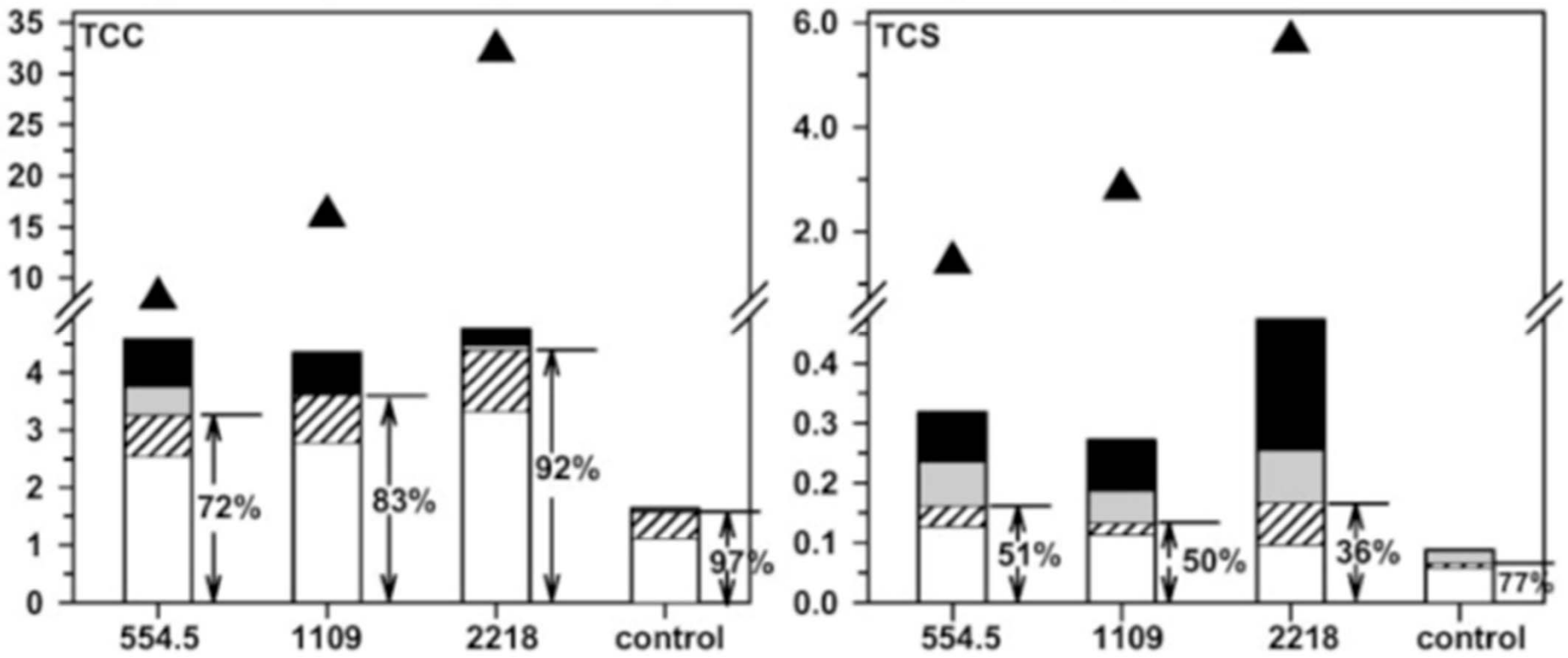
Biosolids relative to effluent

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

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

Allen Brisson-Smith for The New York Times

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

Phthalates – DEHP, DBP, …

- Plasticizer - plastics (PVC, etc.), cosmetics, medical products (bags, tubing, etc.)
- Ubiquitous in the environment
- Levels in biosolids – 0.1-200 µg/g

  House dust, DEHP = 16-7700 µg/g
  DBP = 3.9-1310 µg/g
- Degrades relatively easily in soil (half-life ranges from 20-25 days) – not expected to be stable and mobile in biosolids-amended soil

What's Up Down There!

Phthalates alter boys' genitals!
Reduce anogenital distance (AGD)

AGD = Distance between penile and anal openings

Why people are concerned?

- A lot of press
- 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