What is the fate and significance of PPCPs and EDCs following the application of biosolids to soils?

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- Ontario Municipalities

- ERApharm

Presentation outline

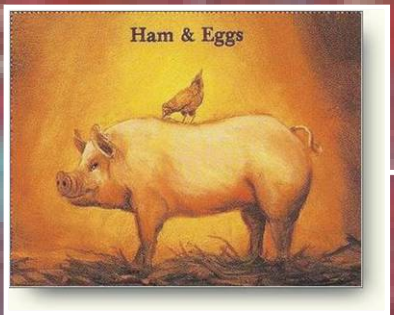
- Introduction- general comments on protection of water quality from contaminants carried in fecal fertilizers.
- Pharmaceuticals and hormonal substances:
  - State of “big picture”
  - Evidence of environmental risk?
- Are PPCPs/EDCs in biosolids?
- Environmental behaviour of some EDCs and PPCPs
  - Persistence characteristics in soils
  - Transport characteristics from land receiving biosolids
- General conclusions

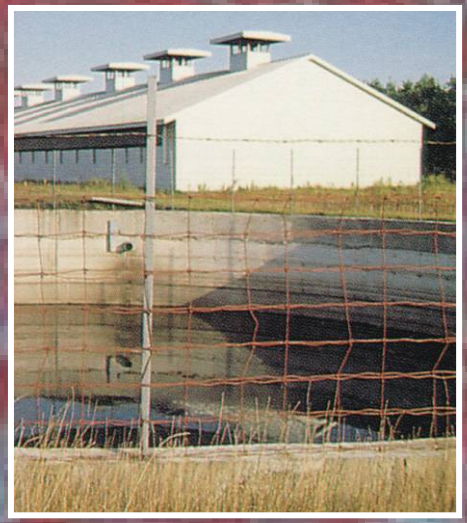
Risk from:

- Microorganisms.
- Endocrine-disrupting chemicals.
- Pharmaceuticals.
- Nutrients

- Livestock and poultry wastes
- Human wastes (municipal biosolids.)

Exposure:Opportunities for managing risk





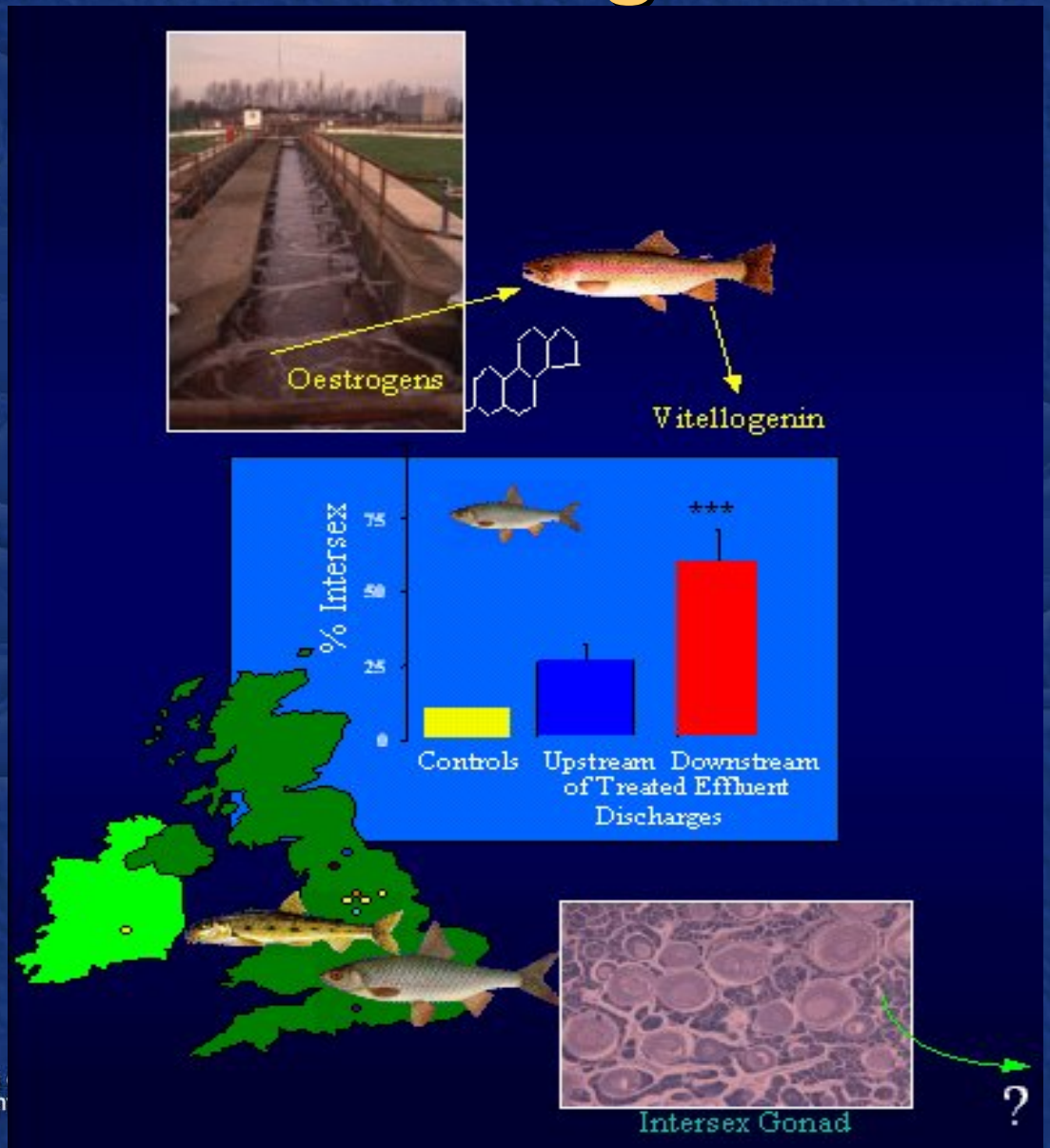

This is not a BMP

‘Emerging’ organic contaminants

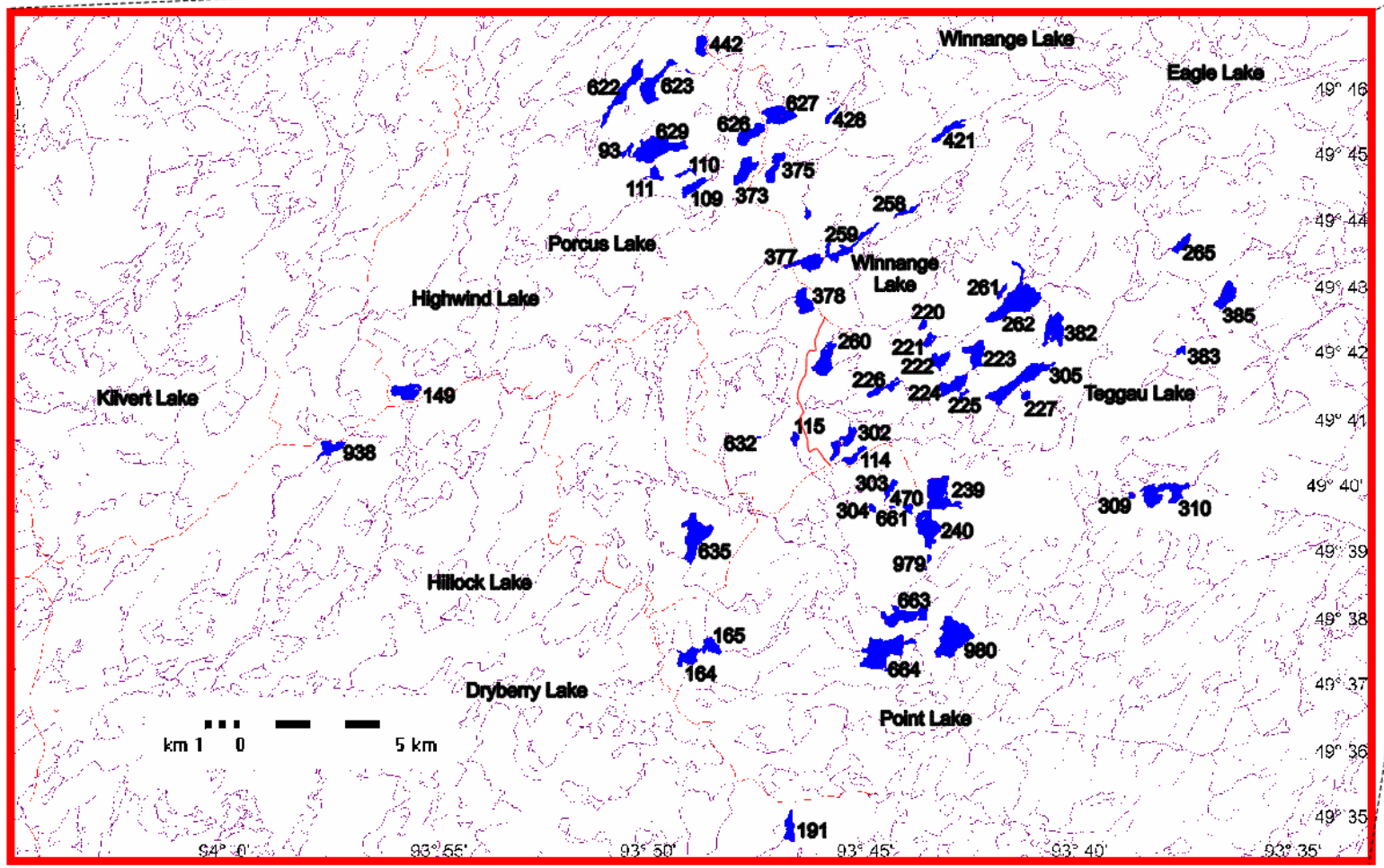
- Exposure
  - Some pharmaceutically- or endocrine-active substances are now found in the environment, but at very low concentrations.
  - Some of these substances are not removed during the sewage treatment process, and some may/do partition preferentially in biosolids.
- Impacts
  - The human health significance of these chemicals is unknown.
    - Reproductive cancers, early onset of puberty.
  - There are examples of environmental impacts, eg. intersex in fish downstream of STPs.
  - It is characteristic of (some) EDCs/PPCPs that short exposure at crucial developmental times, or chronic exposure at very low concentrations, may be problematic.
    - Challenges regulatory acute/chronic toxicology tests and endpoints.
- Overall,
  - the issue of these chemicals as ‘emerging contaminants’ is at a ‘definition of problem’ stage.

Is there any evidence that PPCPs or EDCs in the environment are harmful?

Reproductive abnormalities in fish exposed to sewage outflows



58 Designated Research Lakes and their Watersheds Detailed Monitoring since 1969

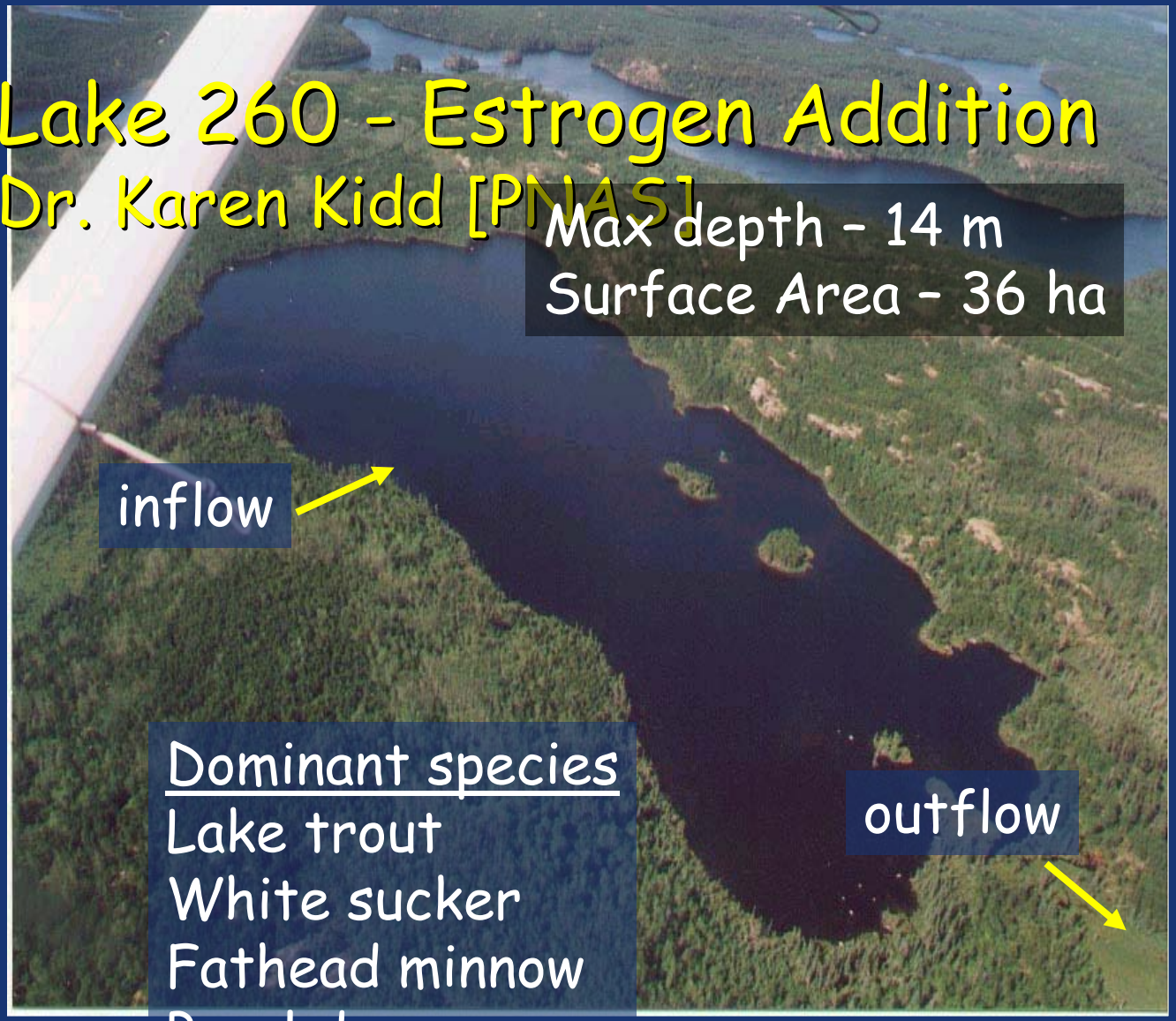


Experimental Lakes Area

Boreal Shield of northwestern Ontario

Lake 260 - Estrogen Addition

Dr. Karen Kidd [PNAS]



Study Design

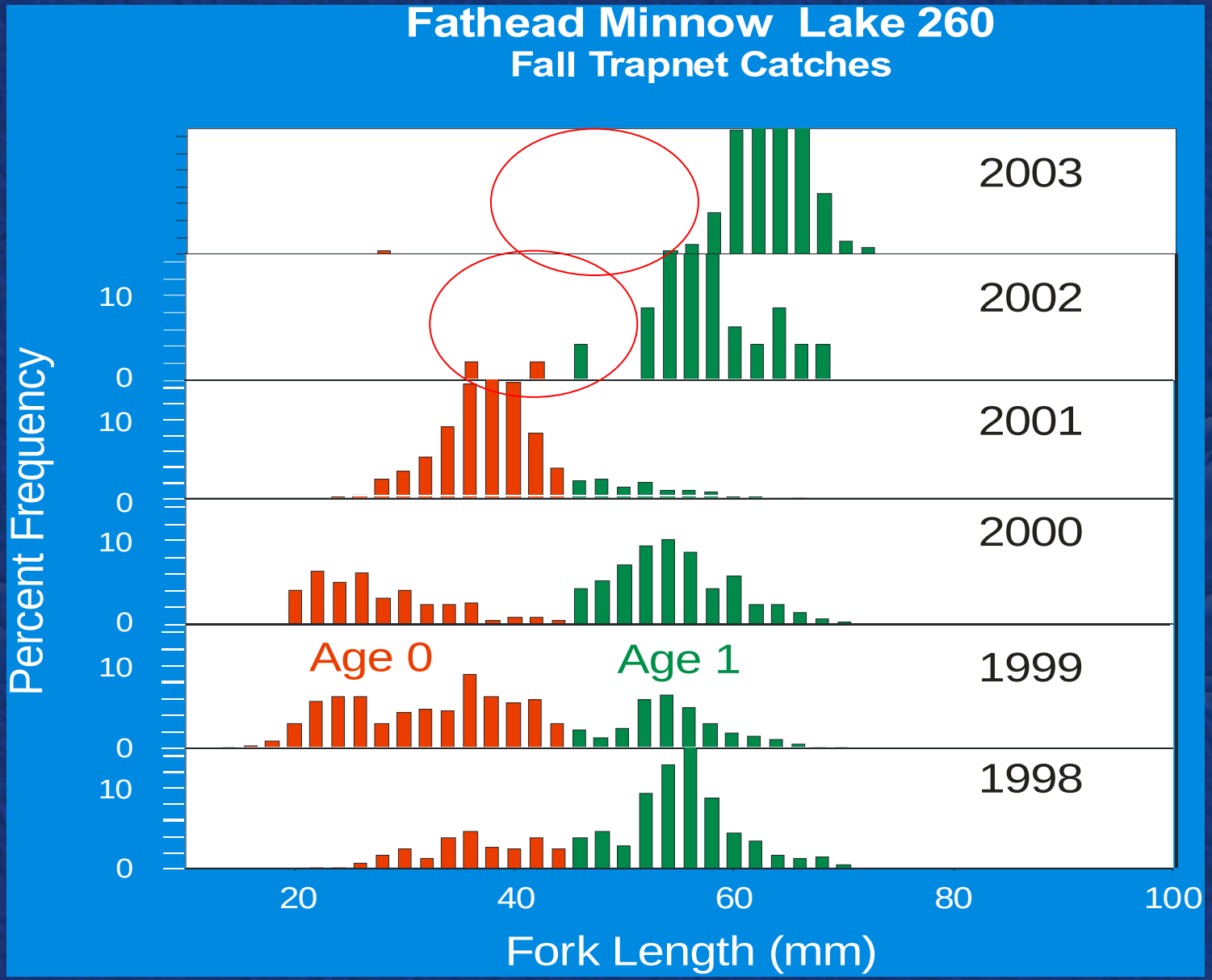
recovery?

effects on individuals & populations

ethynylestradiol additions – 5 ng/L

baseline data

1999 2000 2001 2002 2003 2004


Fathead Minnow Lake 260
Fall Trapnet Catches
Percent Frequency
2003
2002
2001
2000
1999
1998
Age 0
Age 1
10
0
20
40
60
80
100
Fork Length (mm)

EDC/PPCP exposure and impacts: Risk from agricultural use of organic materials

- Are EDCs/PPCPs present in materials that are applied to land?
- What are their dissipation kinetics and pathways?
- How is dissipation influenced by key rate-controlling parameters?
- What are their transport characteristics in commercial application context?

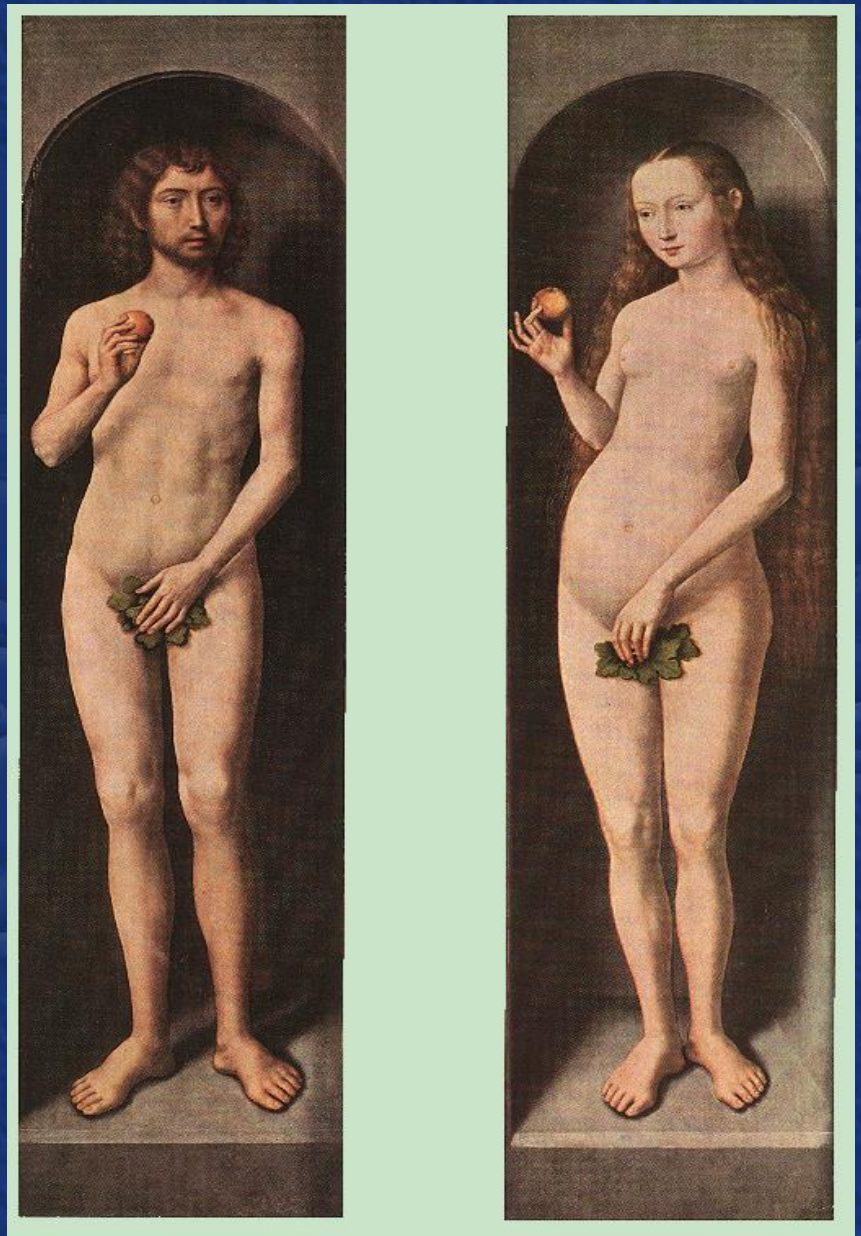
Selected PPCP concentrations (µg/ Kg OC) in biosolids (range and median; n=9)

Kinney et al. ES&T 40:7207-7215.

- Carbamazepine 51-1200, 64
- Diphenhydramine 32-22000, 340
- Fluoxetine 140-4700, 370
- Triclosan 1170-32900, 10200

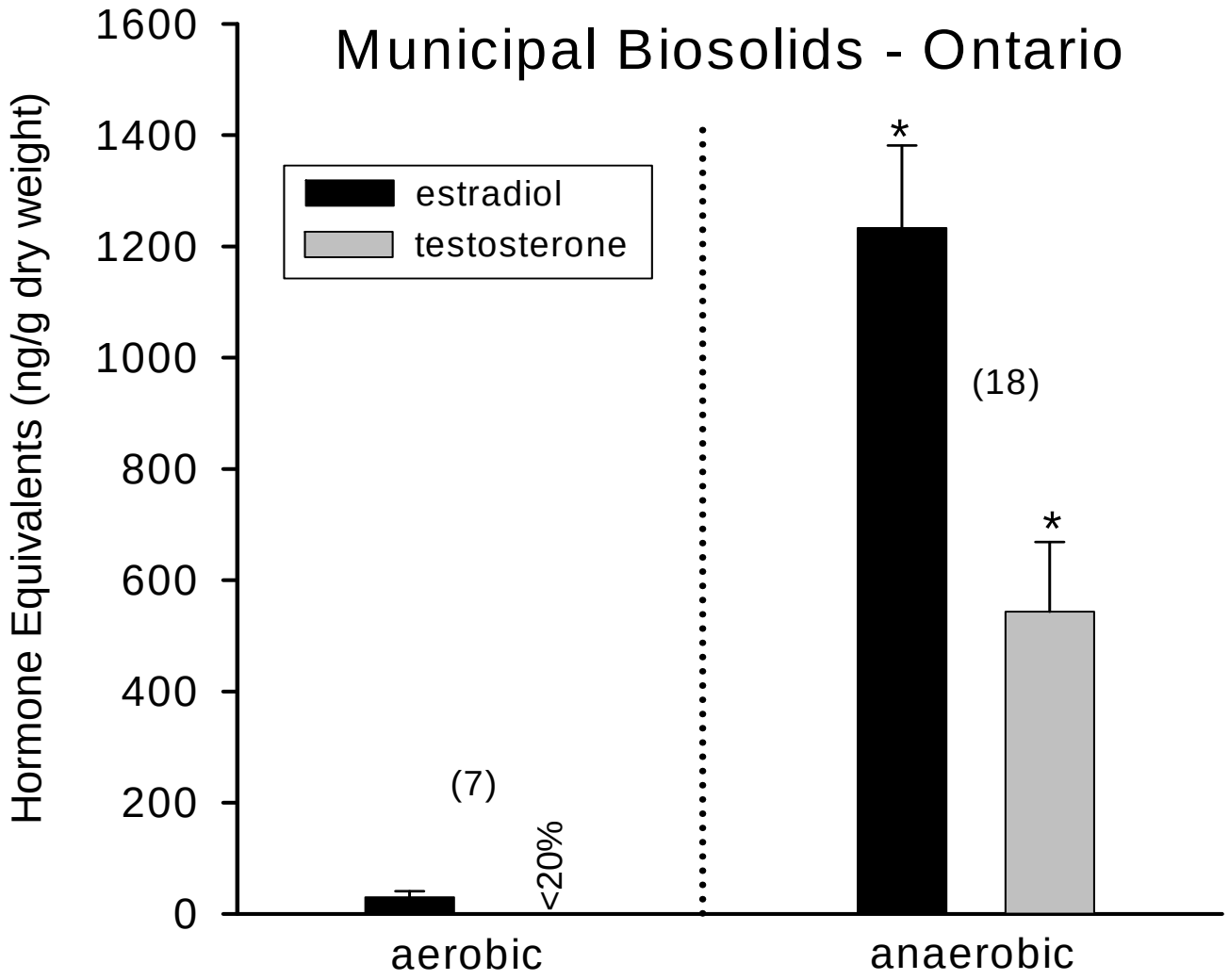
Vive la difference

Estrogens

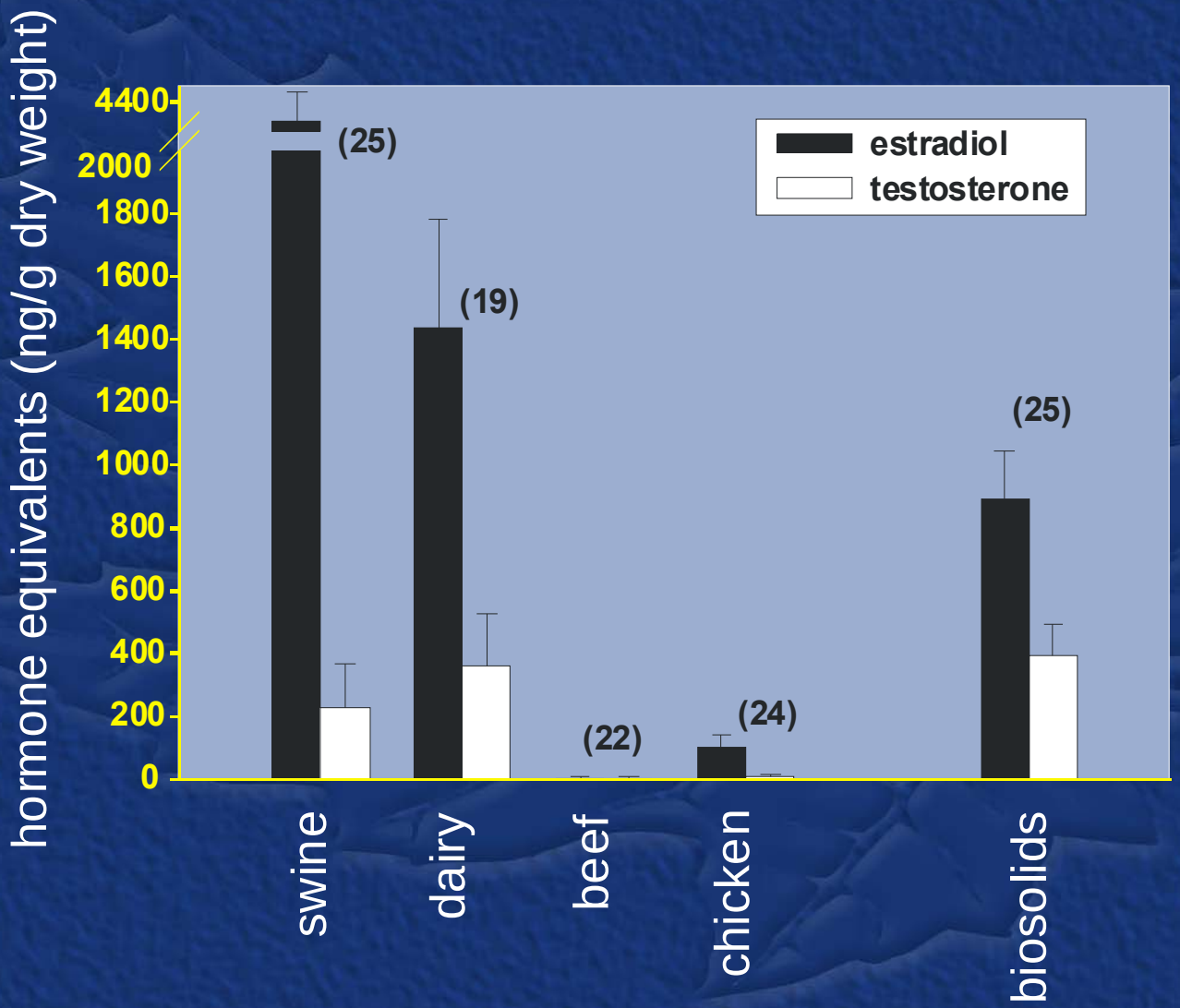


Androgens

Hormonal activity in Biosolids



Hormone Activities: Manures and Municipal Biosolids



Summary

- Are EDCs/PPCPs present in materials that are applied to land?

- Yes, but the concentrations vary widely.
- Biosolids can be managed to reduce content.

- Sex hormone activity can be comparable with some other agricultural “fecal fertilizers”.

EDC/PPCP exposure and impacts: Risk from agricultural use of organic materials

- Are EDCs/PPCPs present in materials that are applied to land?
- What are their dissipation kinetics and pathways?
- How is dissipation influenced by key rate-controlling parameters?
- What are their transport characteristics in commercial application context?

Persistence in soils

- Texture
- Temperature
- Moisture
- Concentration
- Transformation products
- Carrier effects

Laboratory elucidation of dissipation kinetics and pathways

of so
the

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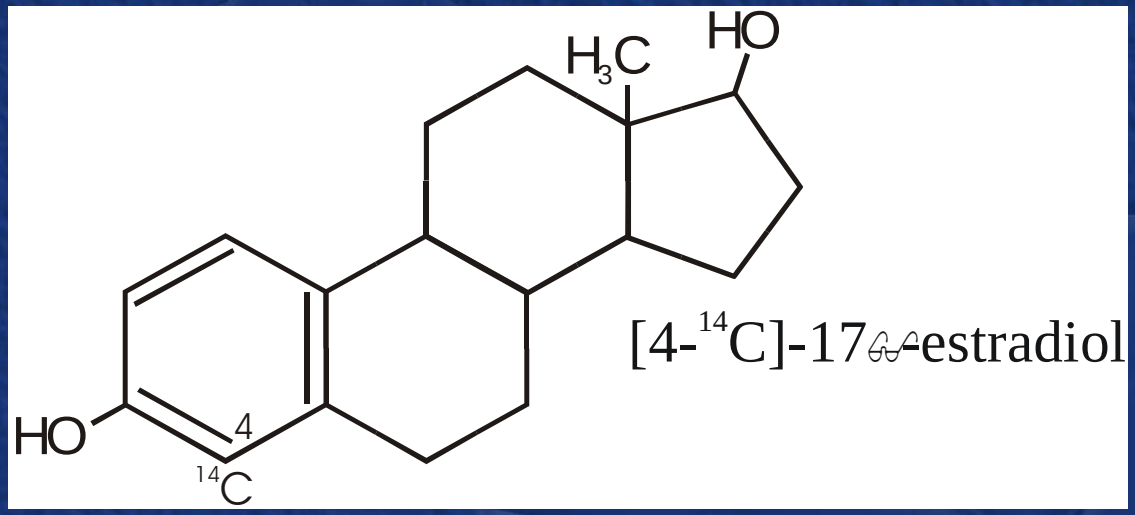
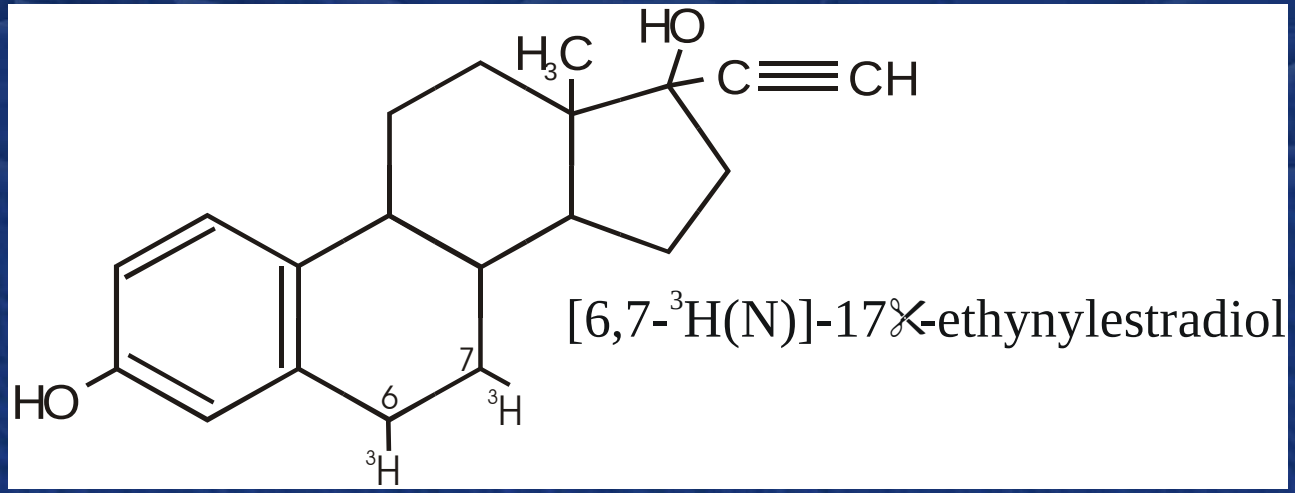
Radiolabeled substrates

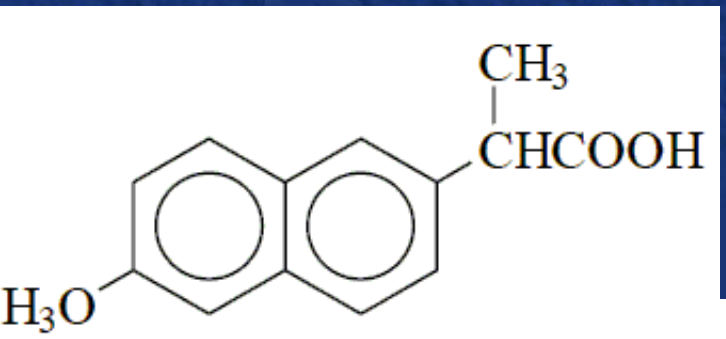


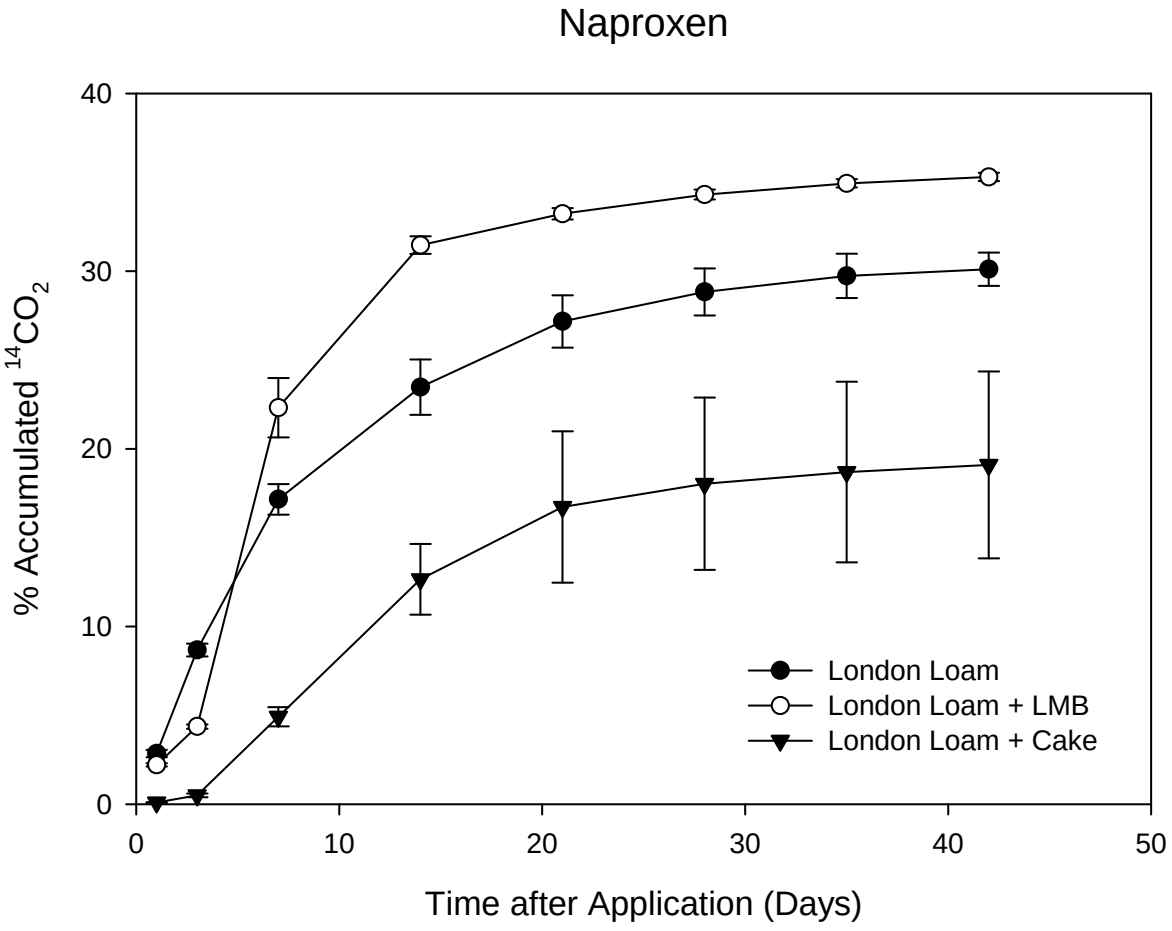
[4-^{14}C]-17α-estradiol



[6,7-^{3}H(N)]-17α-ethynylestradiol

Naproxen is labile, varies with matrix





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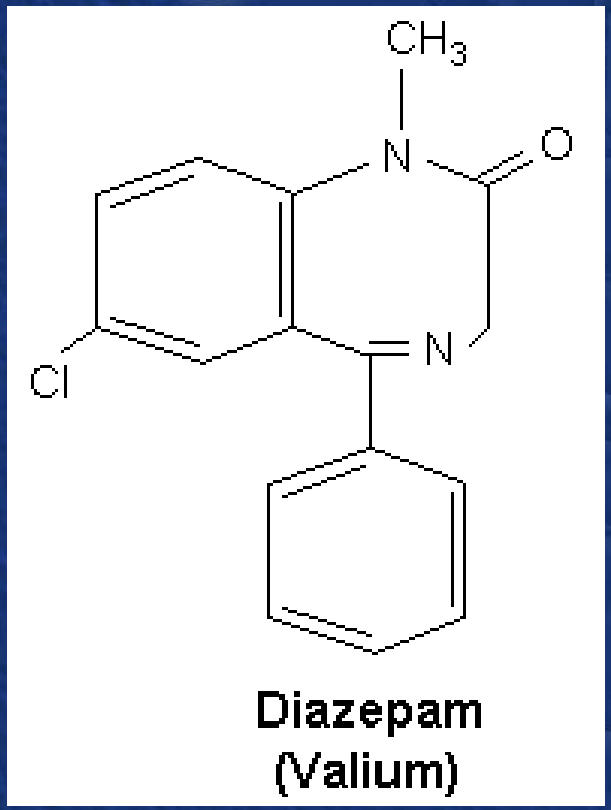
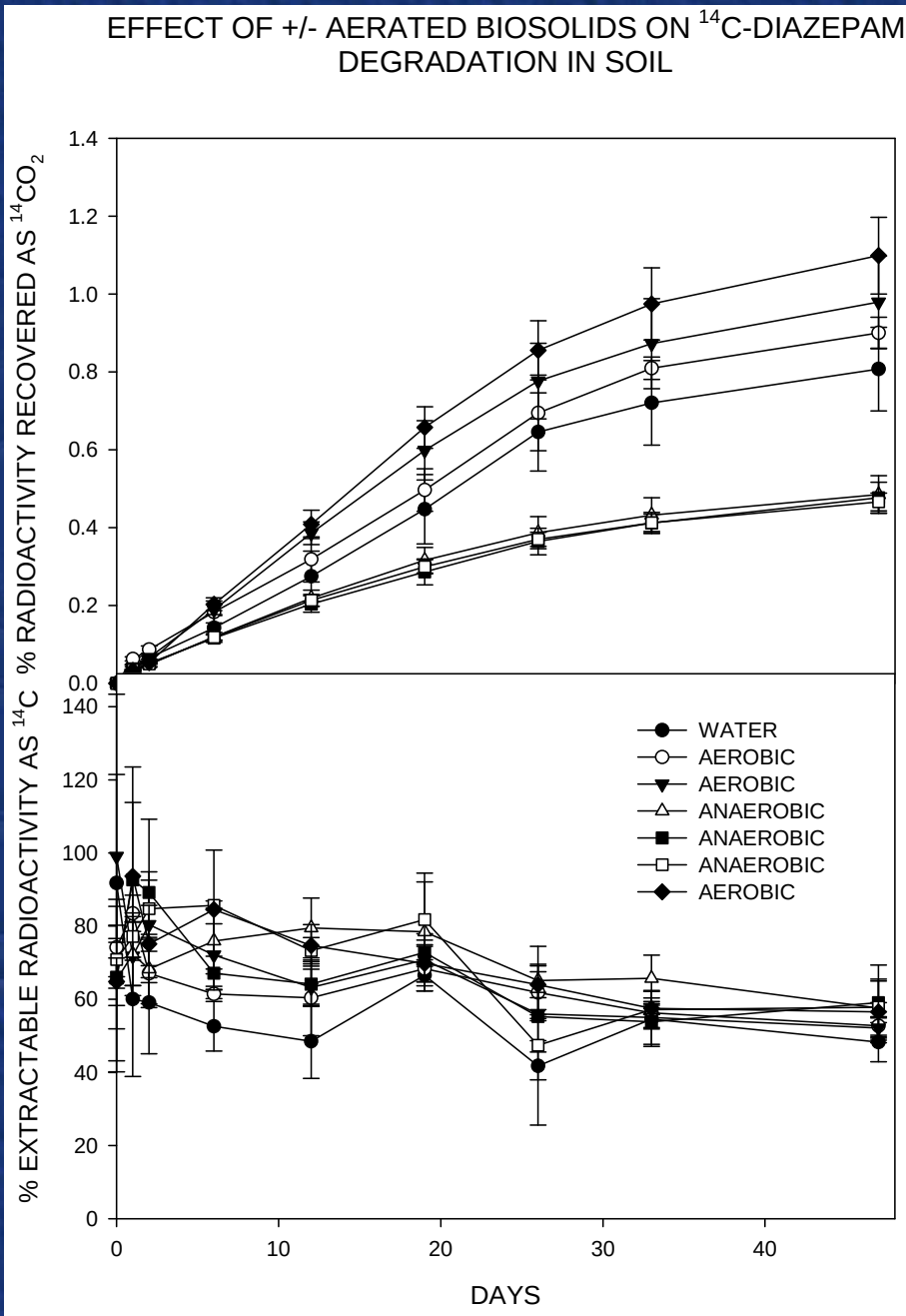
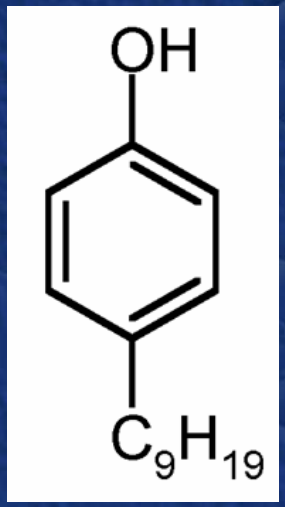
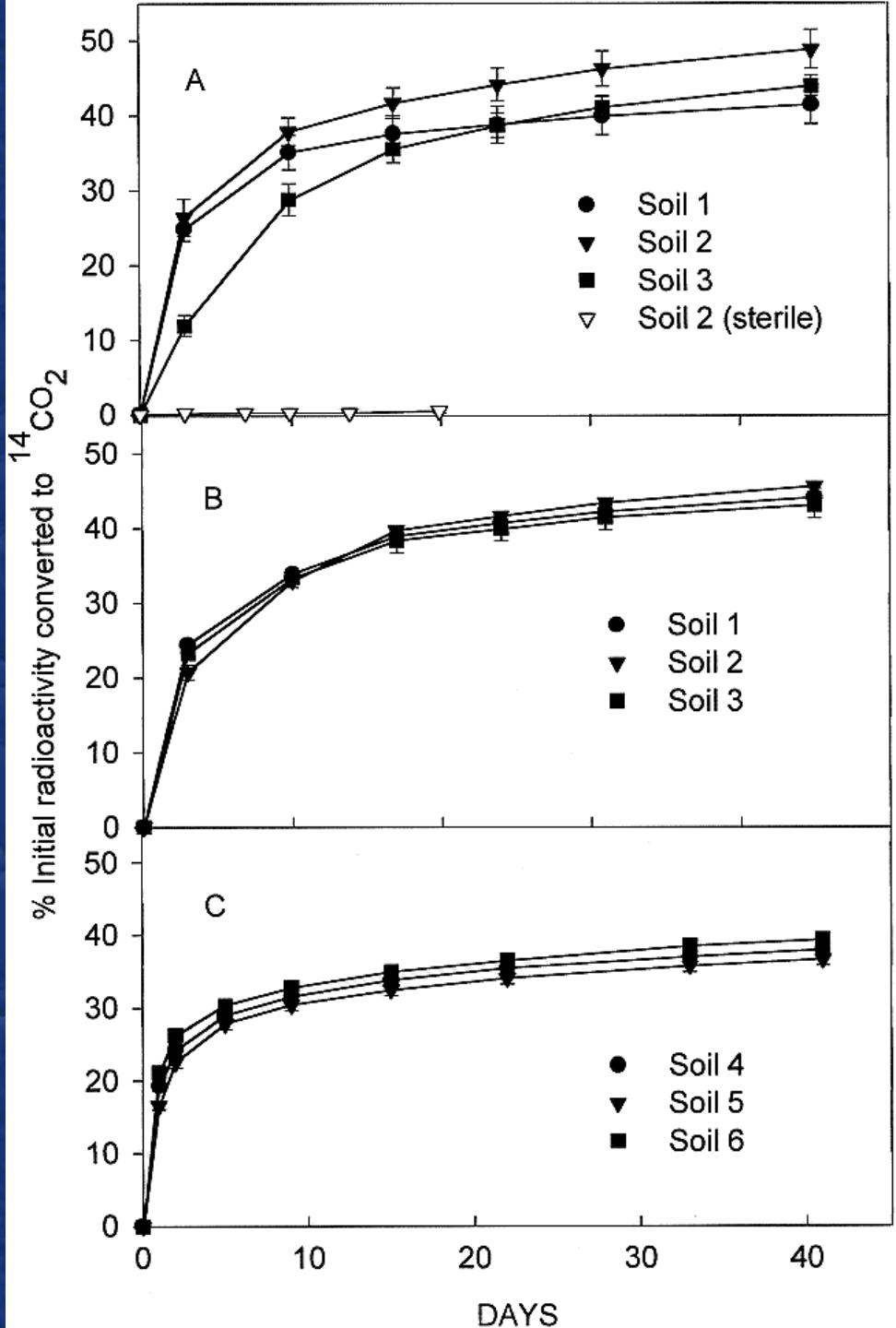
Valium is very persistent



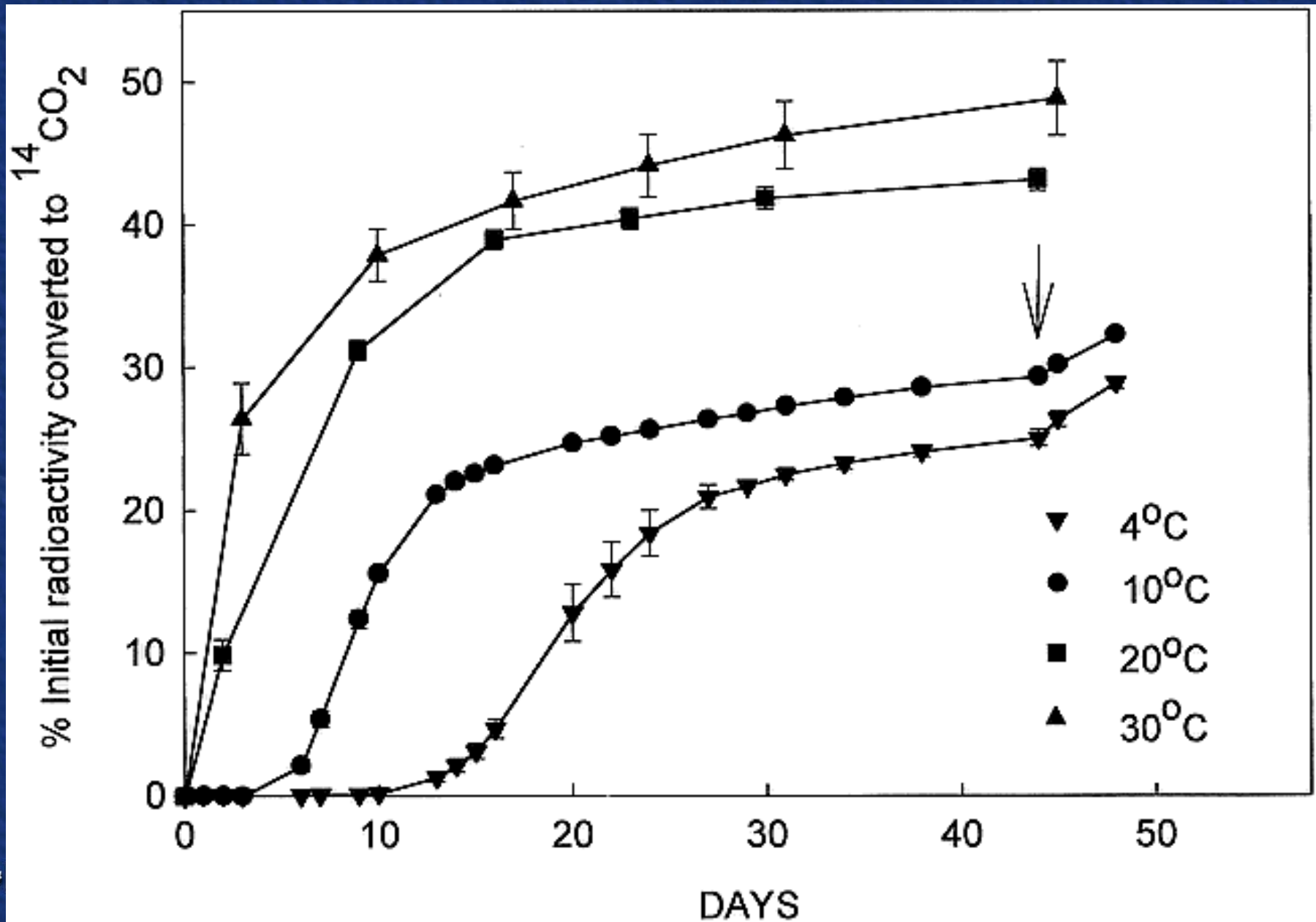


Mineralization of [^{14}C]4-NP by various soils

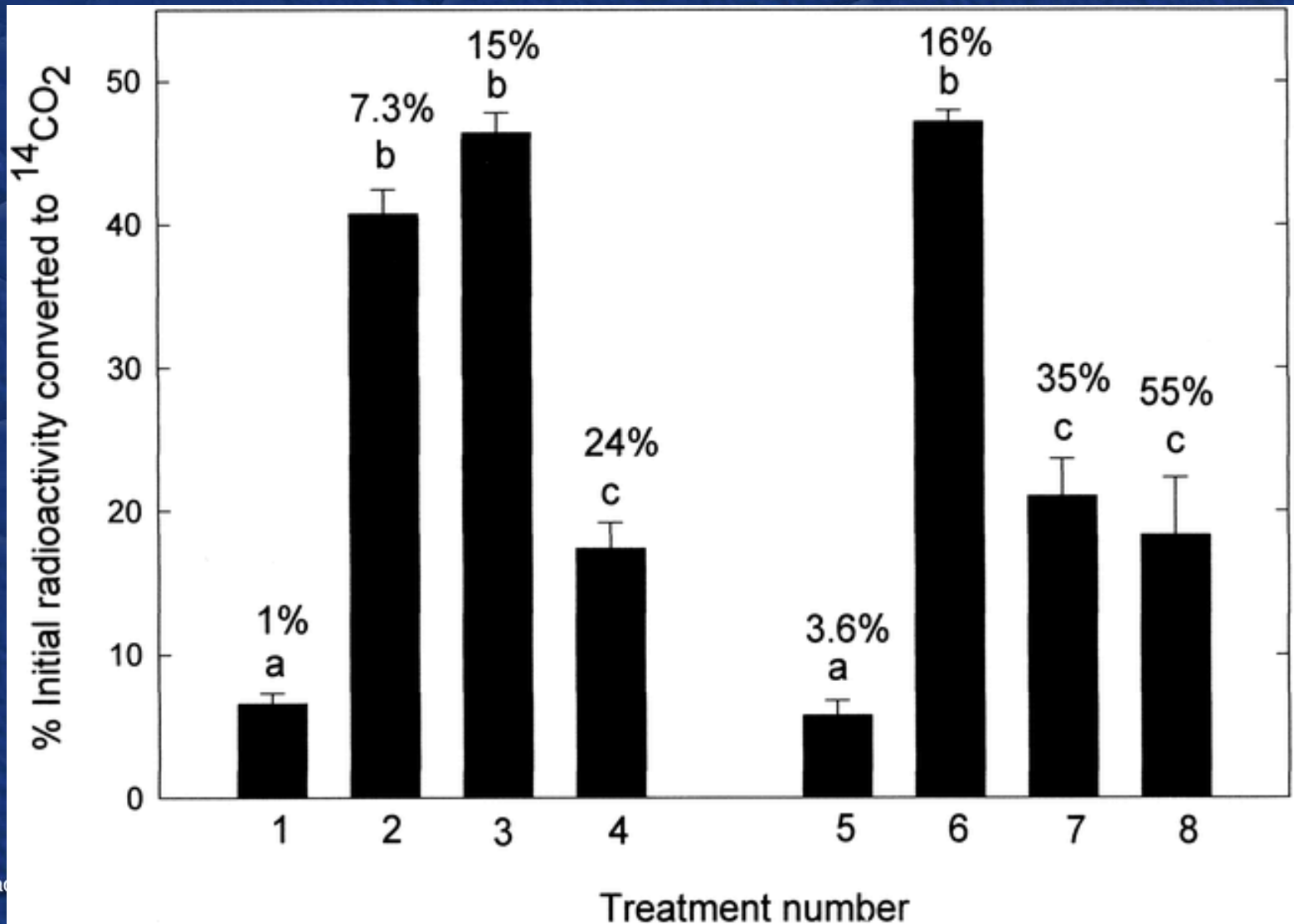




Effect of temperature on ^{14}C-4NP mineralization



Effect of moisture on ^{14}C-NP mineralization



Summary

- Dissipation
- These chemicals vary widely in their persistence in soil, need to consider on a case by case basis.
  - Low temperature and redox can limit degradation.

EDC/PPCP exposure and impacts: Risk from agricultural use of organic materials

- Are EDCs/PPCPs present in materials that are applied to land?
- What are their dissipation kinetics and pathways?
- How is dissipation influenced by key rate-controlling parameters?
- What are their transport characteristics in commercial application context?

Transport studies:
(semi)-commercial scale applications of slurry or dewatered biosolids
-tile drainage
-runoff

Classes of agents of interest

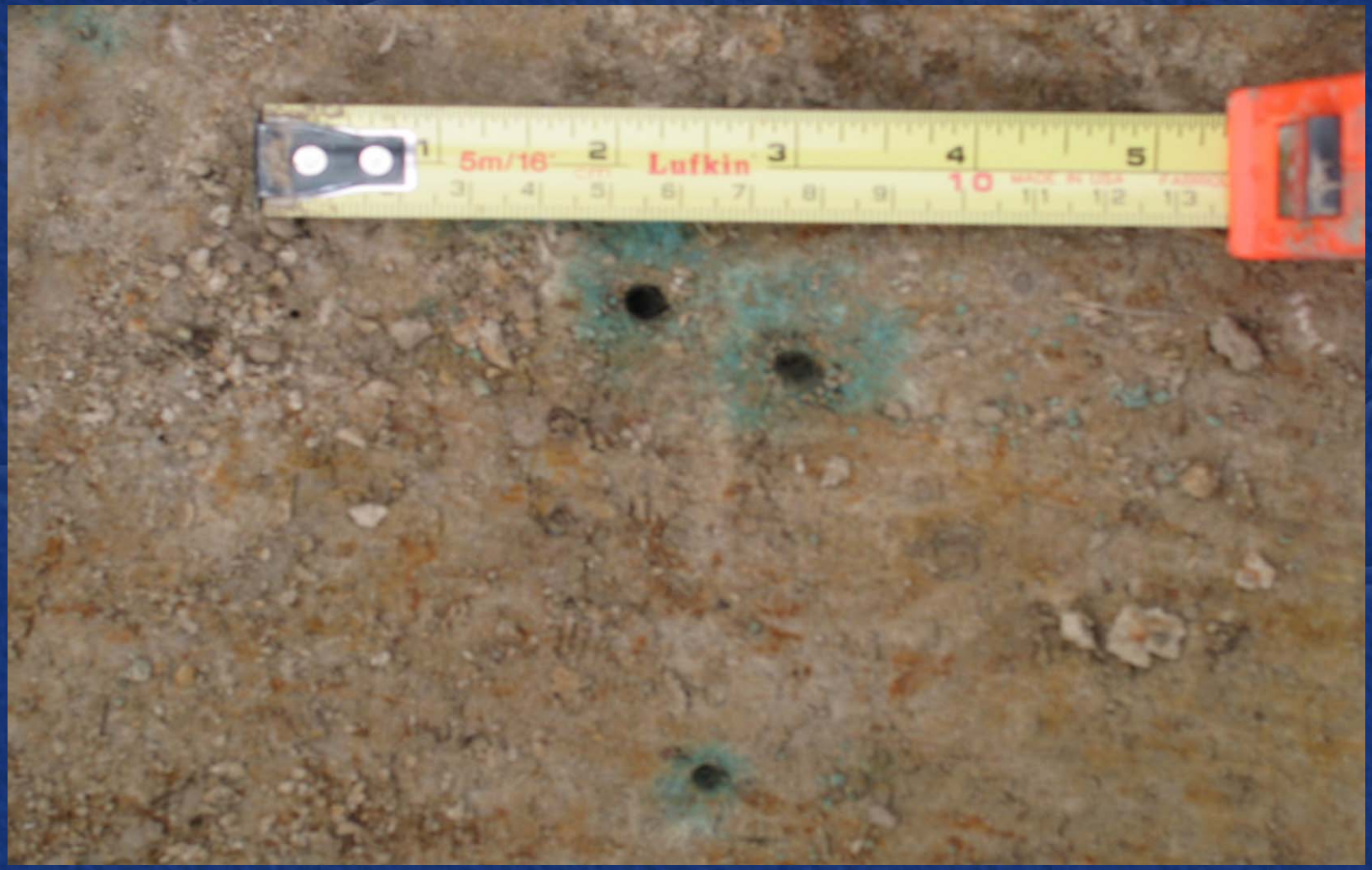
- Substances carried in human waste-municipal biosolids.
  - Pharmaceuticals, fragrances, antimicrobials, synthetic hormonal substances.

PPCPs under investigation in field studies

• Acetaminophen	Analgesic
• Naproxen	NSAID
• Ibuprofen	Analgesic
• Gemfibrozol	lipid regulator
• Atenolol	Beta-Blocker
• Cotinine	Nicotine met. Neutral
• Carbamazepine	Anticonvulsant Neutral
• Fluoxetine	SRI [prozac]
• Sulfapyridine	Sulfonamide
• Sulfamethoxazole	Sulfonamide
• Triclosan	Antibacterial

Transport Characteristics:Managing the application

Worm Channels a Common Macropore



Cracks in Structured Soil are a Common Macropore

Application over tile

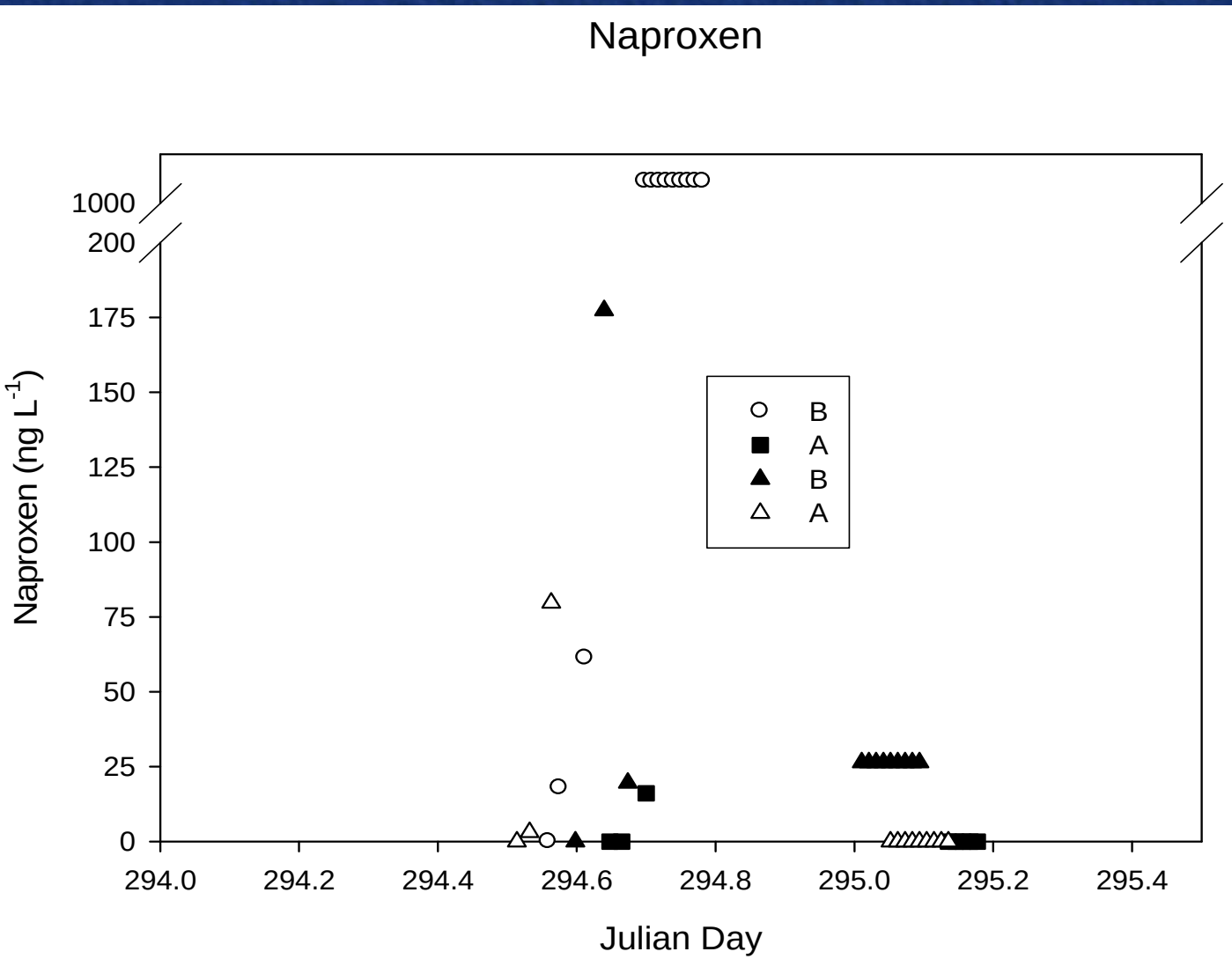
Tile sampling pit

Macropore flow to tiles

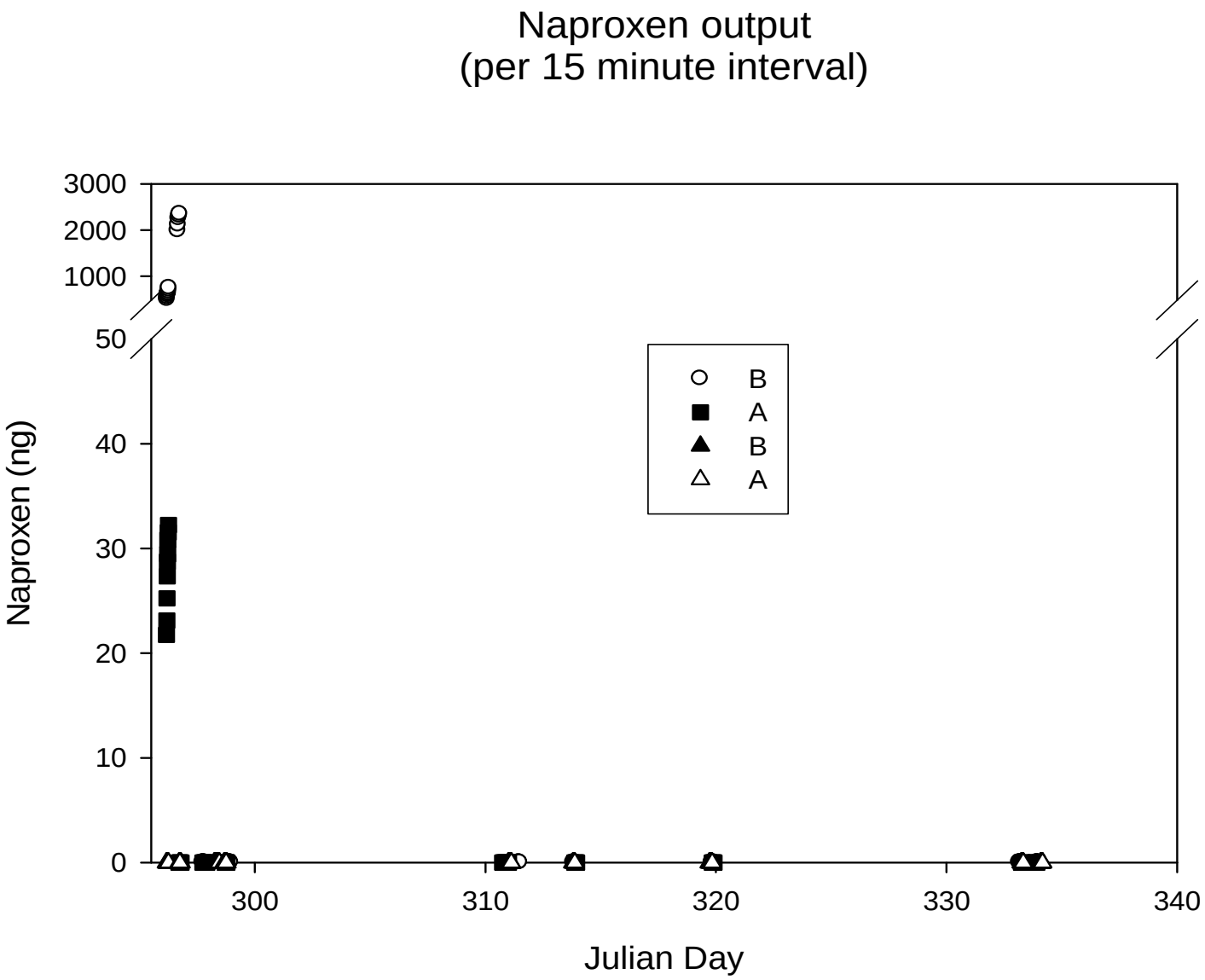
-Over 90% of flow to tile drains can result from macropores

[ ]s B>A

Concentration spike within minutes of application



All export associated with the first event



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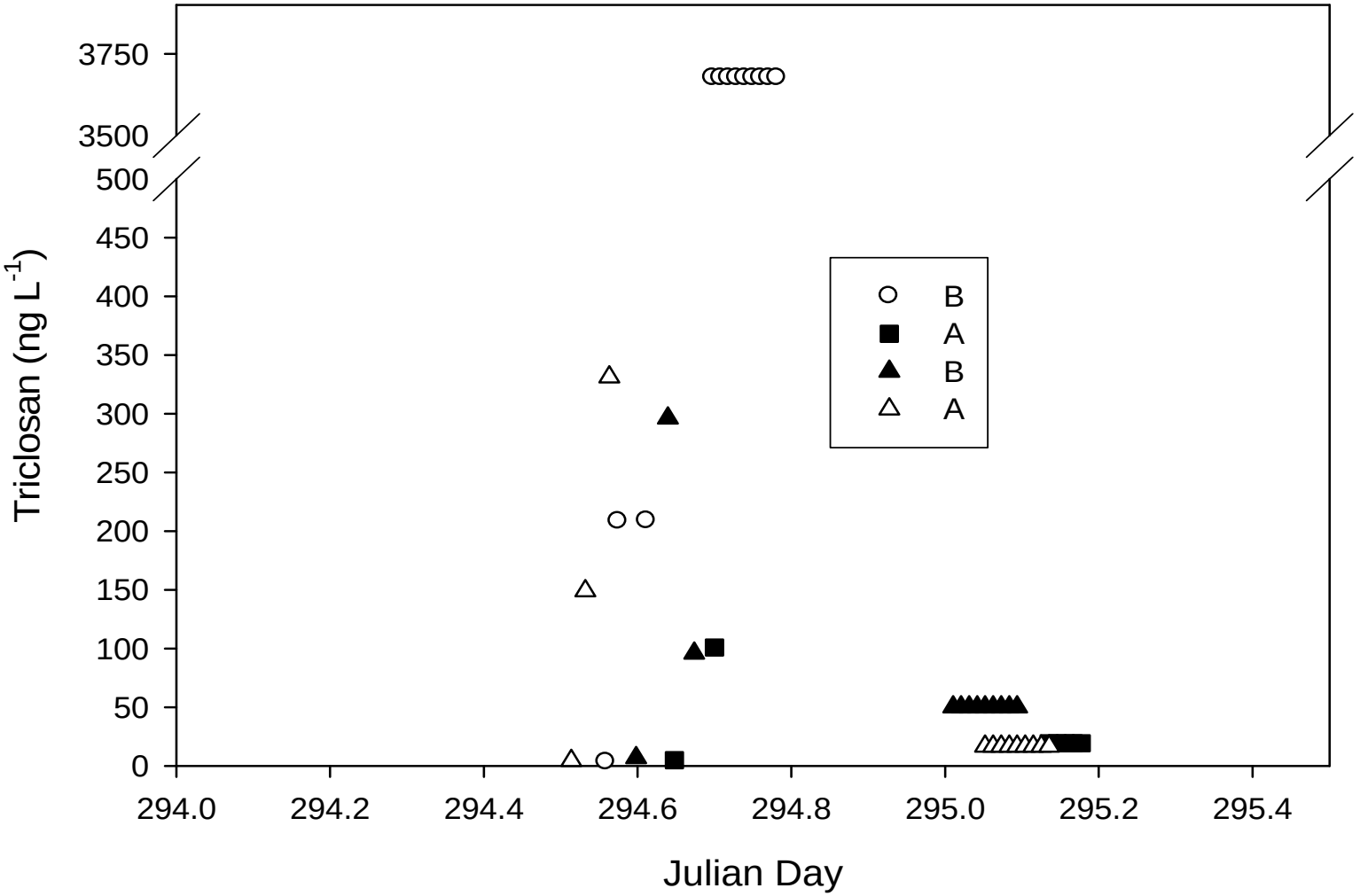
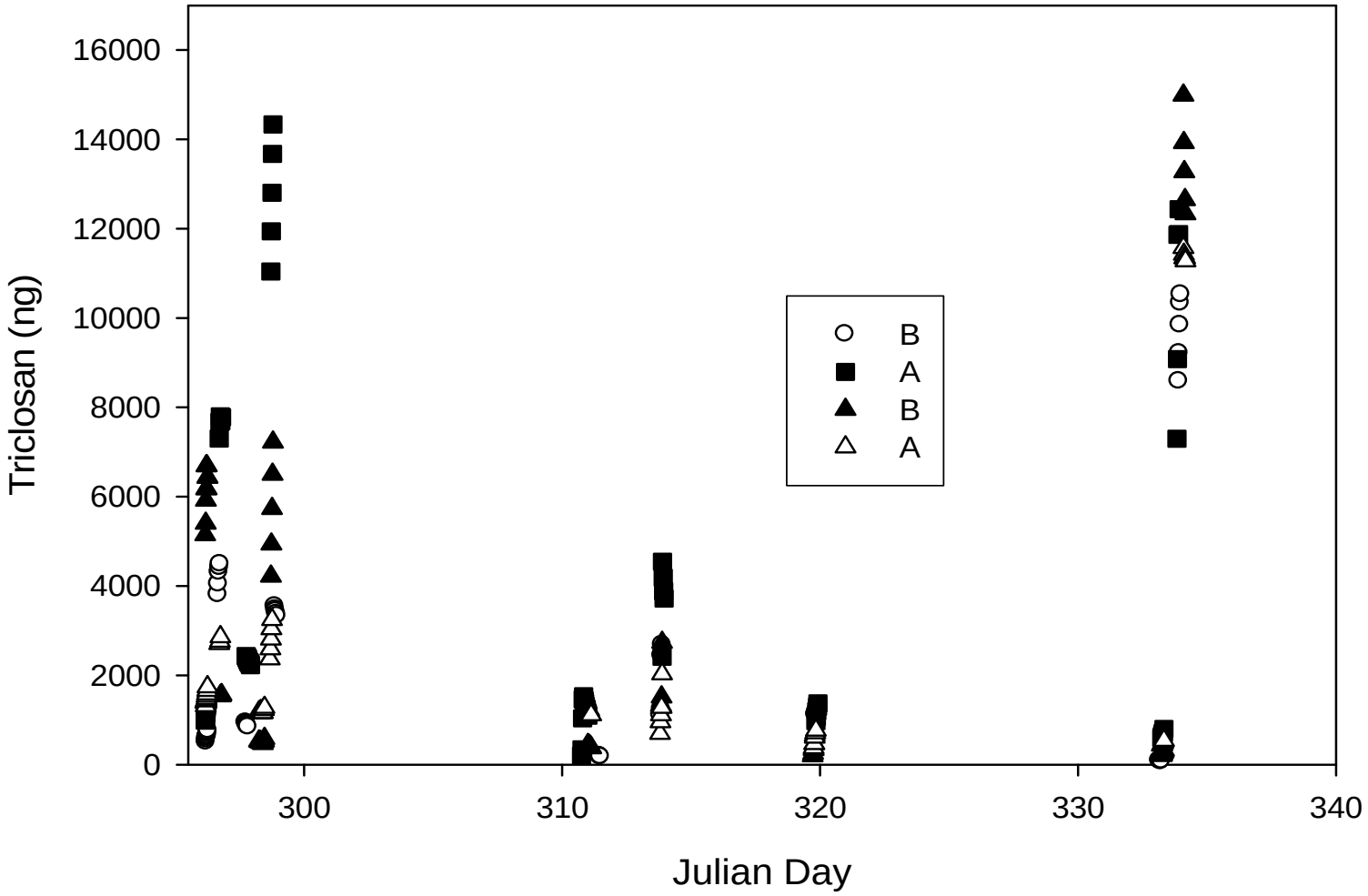
Triclosan


3750
3500
500
450
400
350
300
250
200
150
100
50
0
Triclosan (ng L-1)
294.0
294.2
294.4
294.6
294.8
295.0
295.2
295.4
Julian Day
B
A
B
A

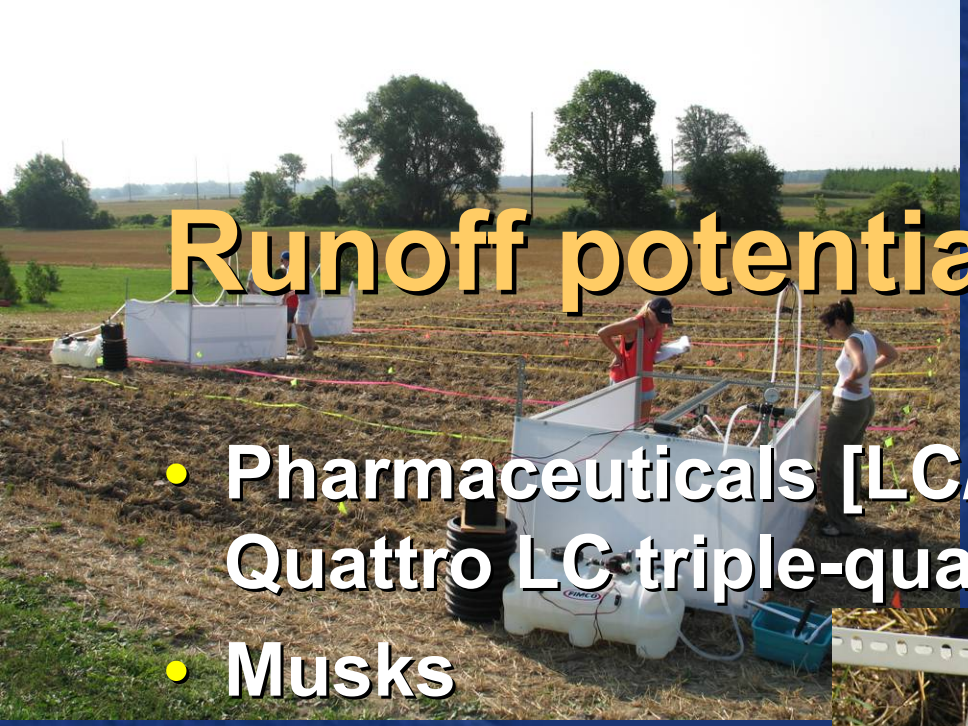
Triclosan output
(per 15 minute interval)



Max fluxes of PPCPs in tile drainage.

		T3(A)			T6(SS)		Study period export (A:SS)
PPCPs and RWT	**Linear regression equation and (R^2)**	**Study period mass flux (ng)**	**Study period PPCPs tile export as % of total applied[a]**	**Linear regression equation and (R^2)**	**Study period mass flux (ng)**	**Study period PPCPs tile export as % of total applied**	
Carbamazepine	Y=0.86x (0.73)	167962	0.9	Y=0.99x (0.98)	241269	1.3	0.69
Atenolol	Y=0.83x (0.84)	8781	0.7	Y=0.95x (0.94)	158539	13.4	0.05
Cotinine	Y=0.73x (0.37)	25996	0.9	Y=0.97x (0.96)	79484	2.6	0.35
Sulfamethoxazole	Y=0.73x (0.62)	2425	0.4	Y=0.99x (0.99)	94144	15.9	0.03
Triclosan	Y=0.77x (0.65)	644763	2.4	Y=0.91x (0.90)	655617	2.4	1.00
Acetaminophen	Y=0.80x (0.77)	42594	0.13	Y=0.99x (0.99)	665901	2.1	0.06
Naproxen	Y=0.72x (0.21)	2889	0.02	Y=0.99x (0.99)	123832	1.0	0.02
Ibuprofen	Y=0.72x (0.21)	31436	0.08	Y=0.99x (0.99)	567844	1.4	0.06
Gemfibrozil	Y=0.72x (0.21)	4564	0.04	Y=0.98x (0.97)	147930	1.2	0.03
Rhodamine WT	NA	614663	1.0	NA	327229	0.5	2.00

Runoff potential



- Pharmaceuticals [LC/MC/MS, Micromass Quattro LC triple-quadrupole MS]
- Musks
- PBDEs
- PFOS
- HMetals
- Bacteria
- P

5 key observations

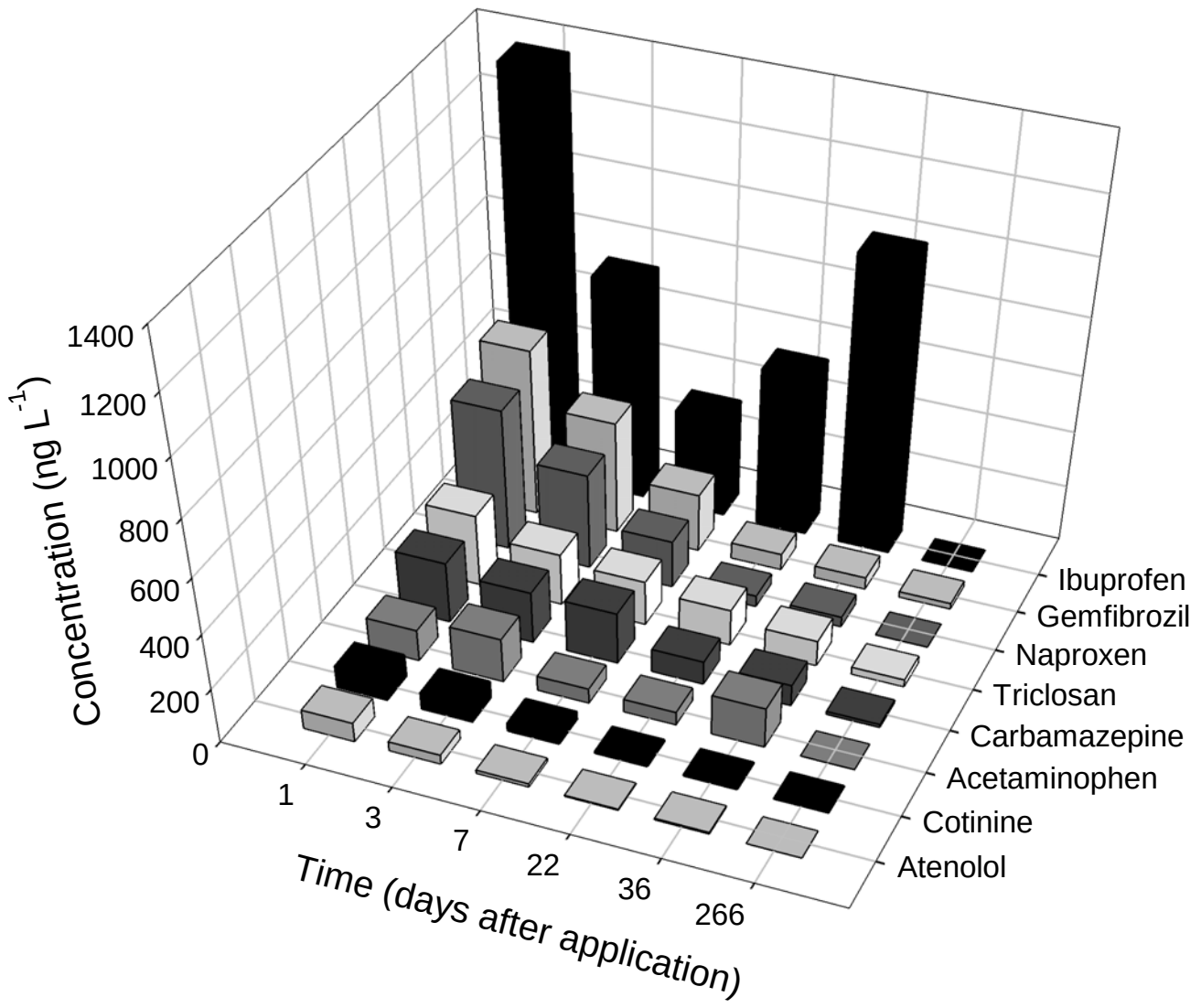
-runoff concentrations are in ppt or in case of ibuprofen ppb range

-Generally first order loss of materials post-application.

-but kinetics don't hold at low concentration end

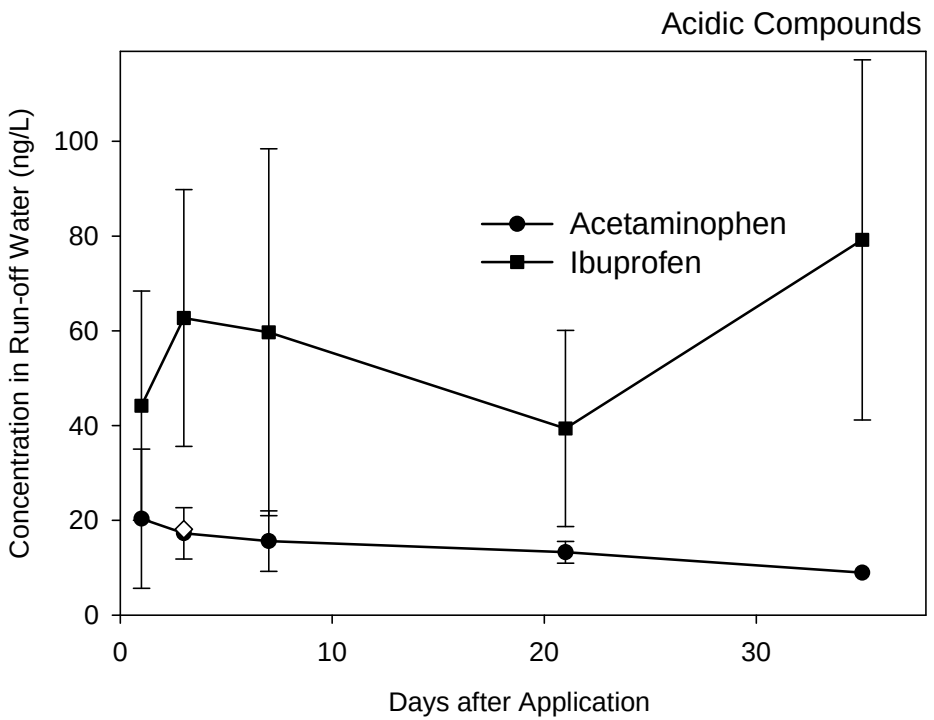
-Carbamazepine and triclosan detected after winter.

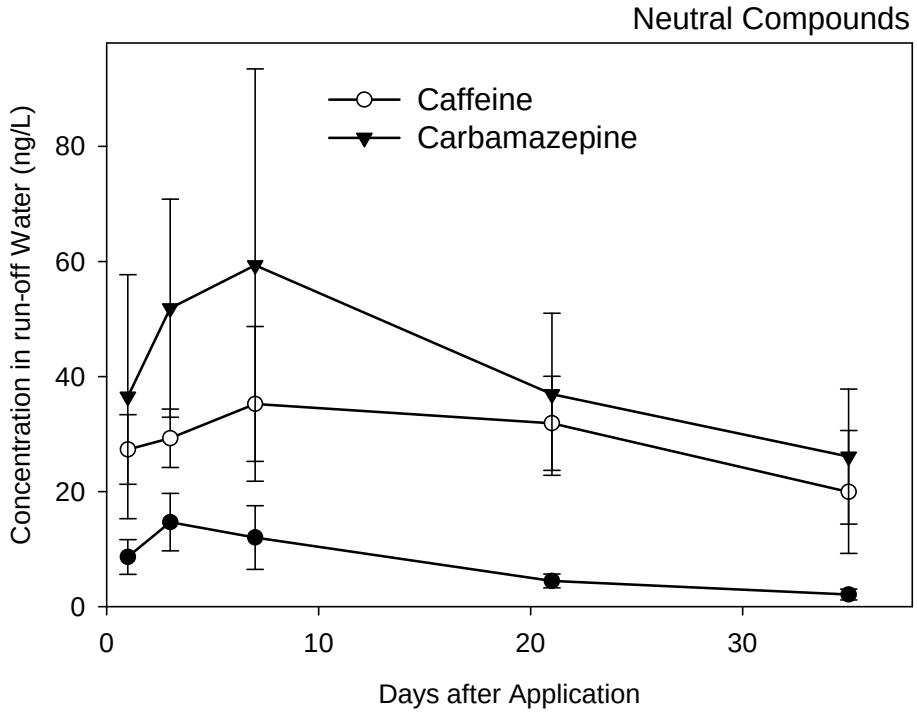
-acetaminophen and (especially) ibuprofen have unusual concave Kinetics.



PPCP concentrations in runoff from plots receiving dewatered

-Concentration not maximal at start
-Slow decline
-Ibuprofen behaviour?





Summary

- **Transport**

- **Slurry PPCP kinetics are close to first order.**
  - **Highest risk at time of application**
- **Dewatered biosolids, highest concentrations after a lag, slower decline in concentrations.**

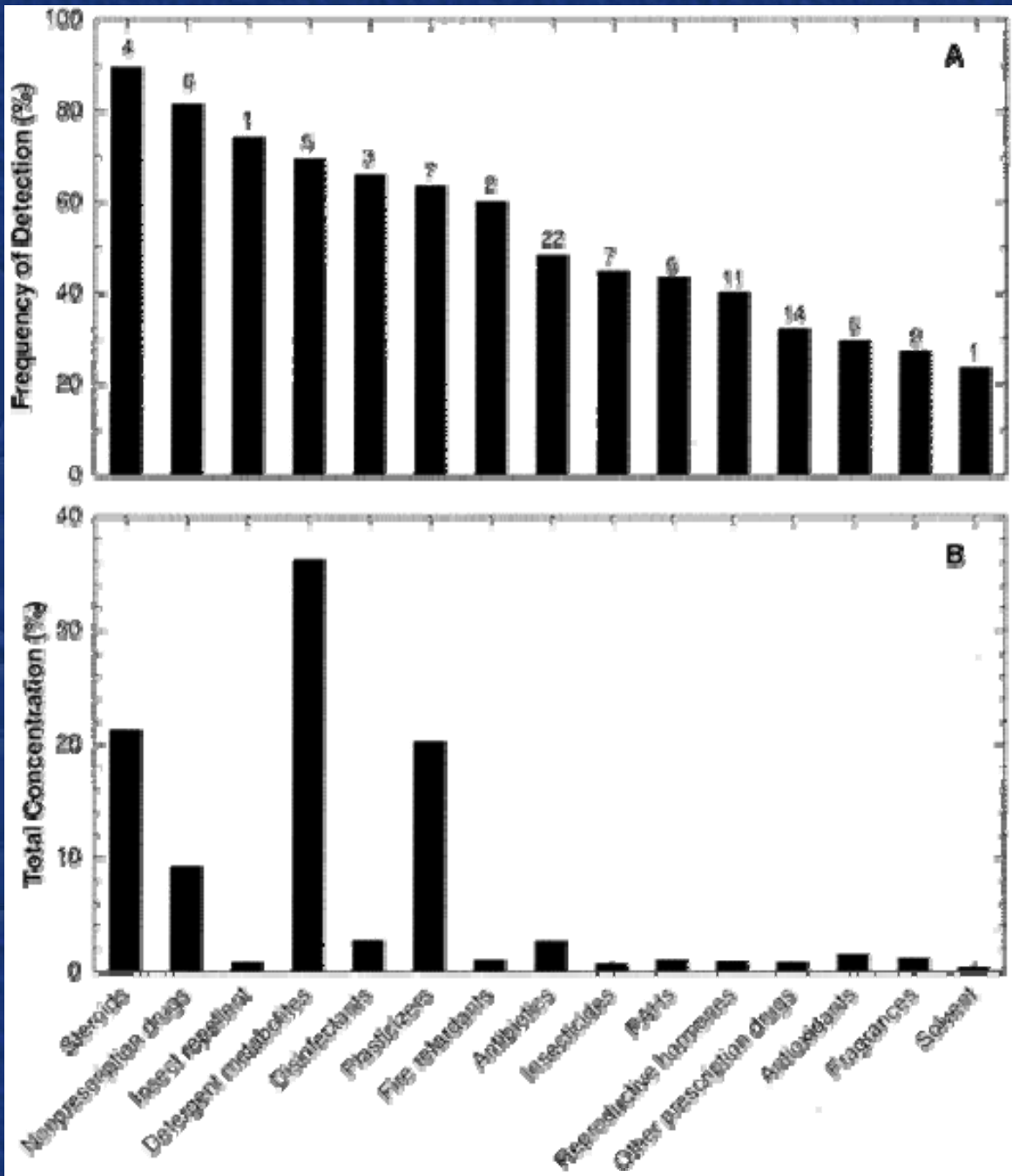
- **Differences in pattern and timing of PPCP movement, not clear yet what differences are with respect to mass flux.**

General Conclusions

- The PPCP/EDC composition of biosolids will vary according to treatment.
- These chemicals vary in their persistence, need to consider on a case by case basis.
  - Low temperature and redox can limit degradation.
- Transport characteristics from agricultural applications does happen, fluxes and rate control mechanisms remain to be defined.

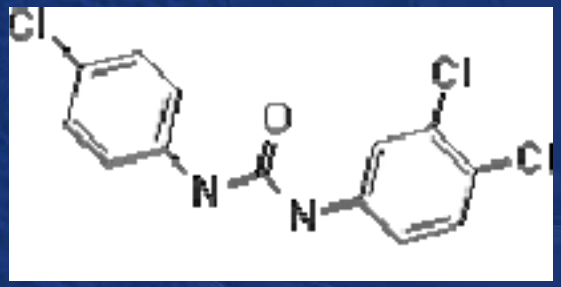
Are PPCPs and EDCs in the environment?

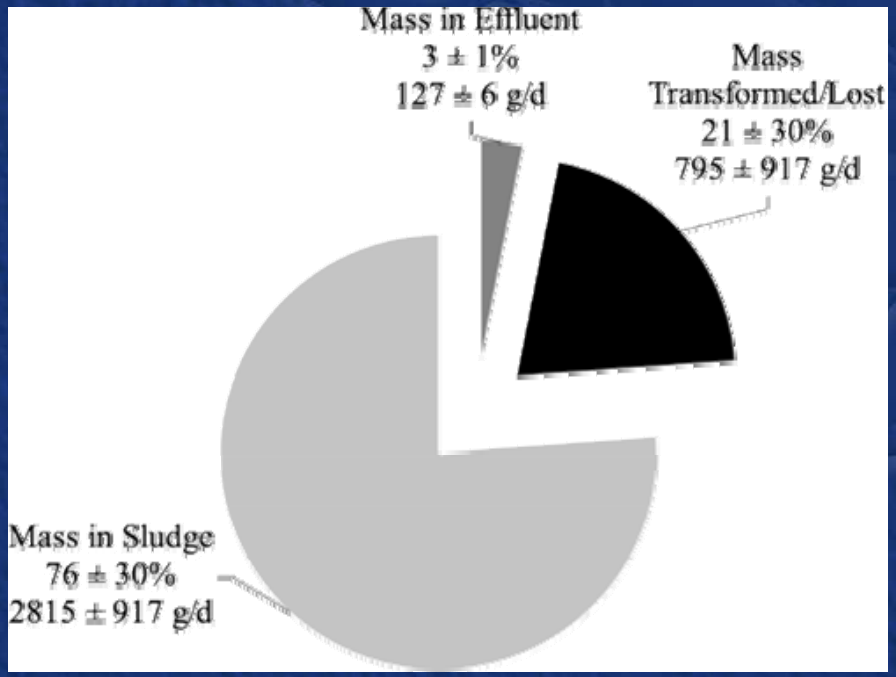
Kolpin et al. 2002 ES&T 36:1202-1211

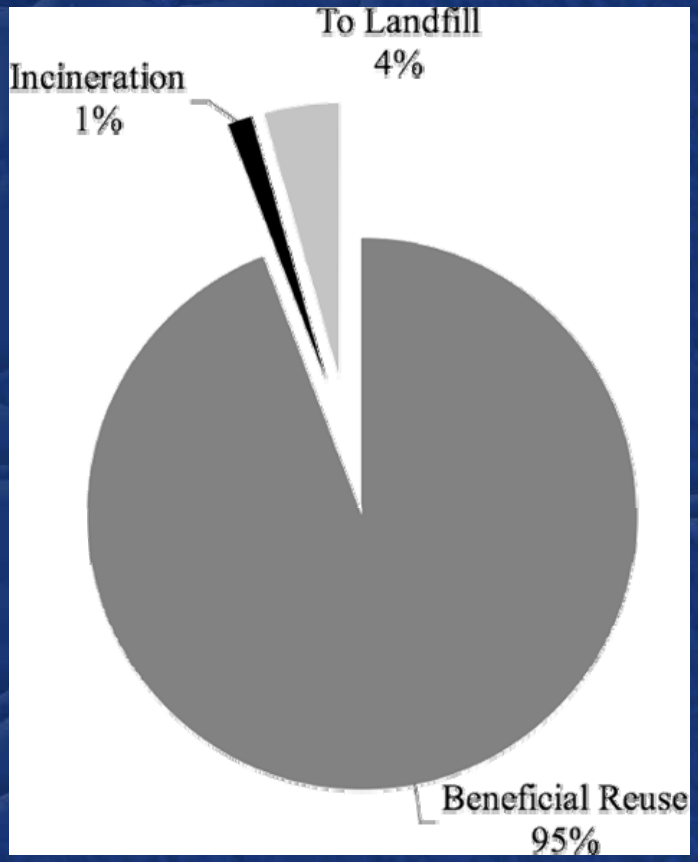


Fate of the topical antiseptic triclocarban during wastewater treatment

Heudler et al. 2006 Environ Sci. Technol. 40:3634-3639





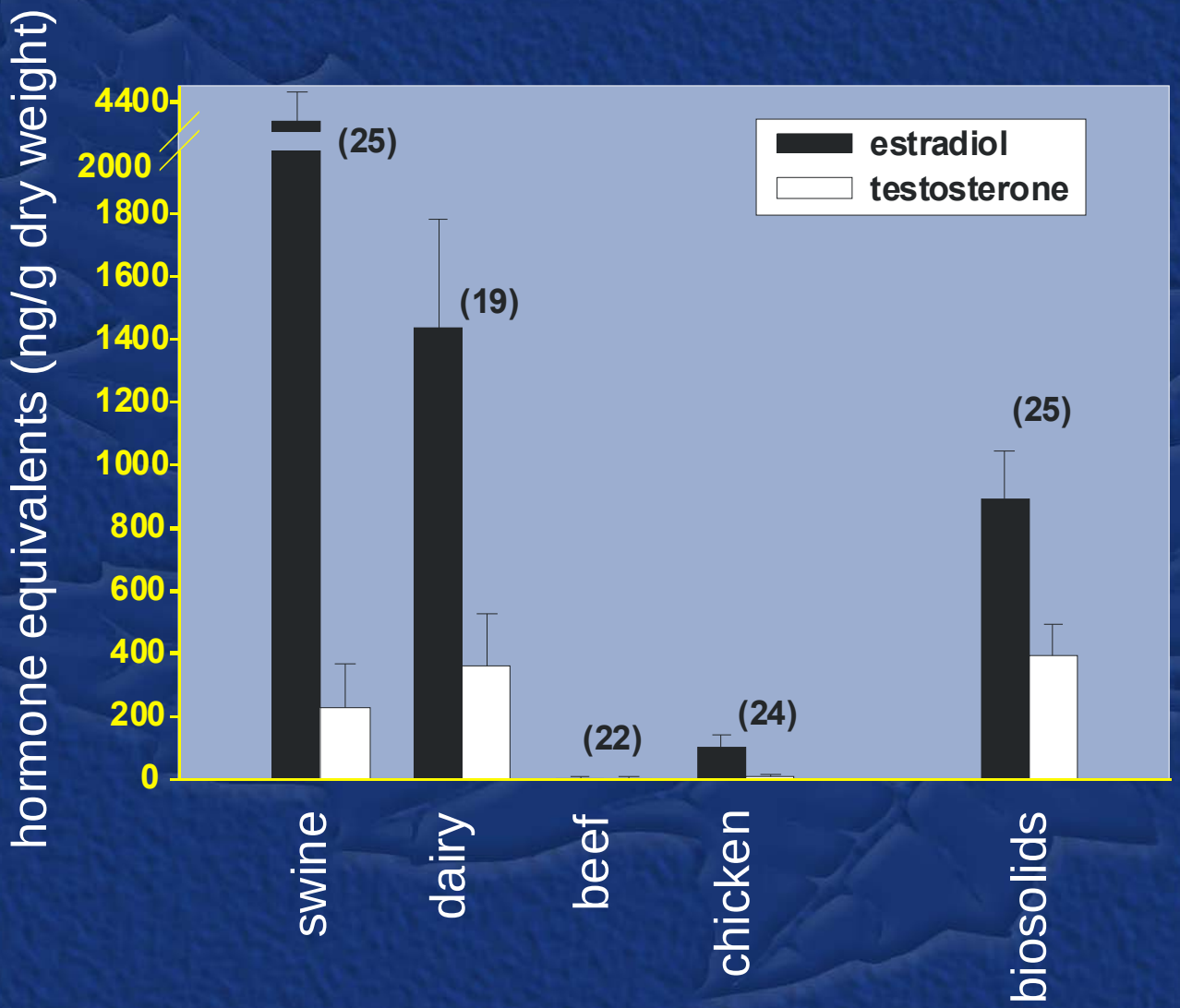


Summary of Pharmaceutical Concentrations in Water & Sediment Samples

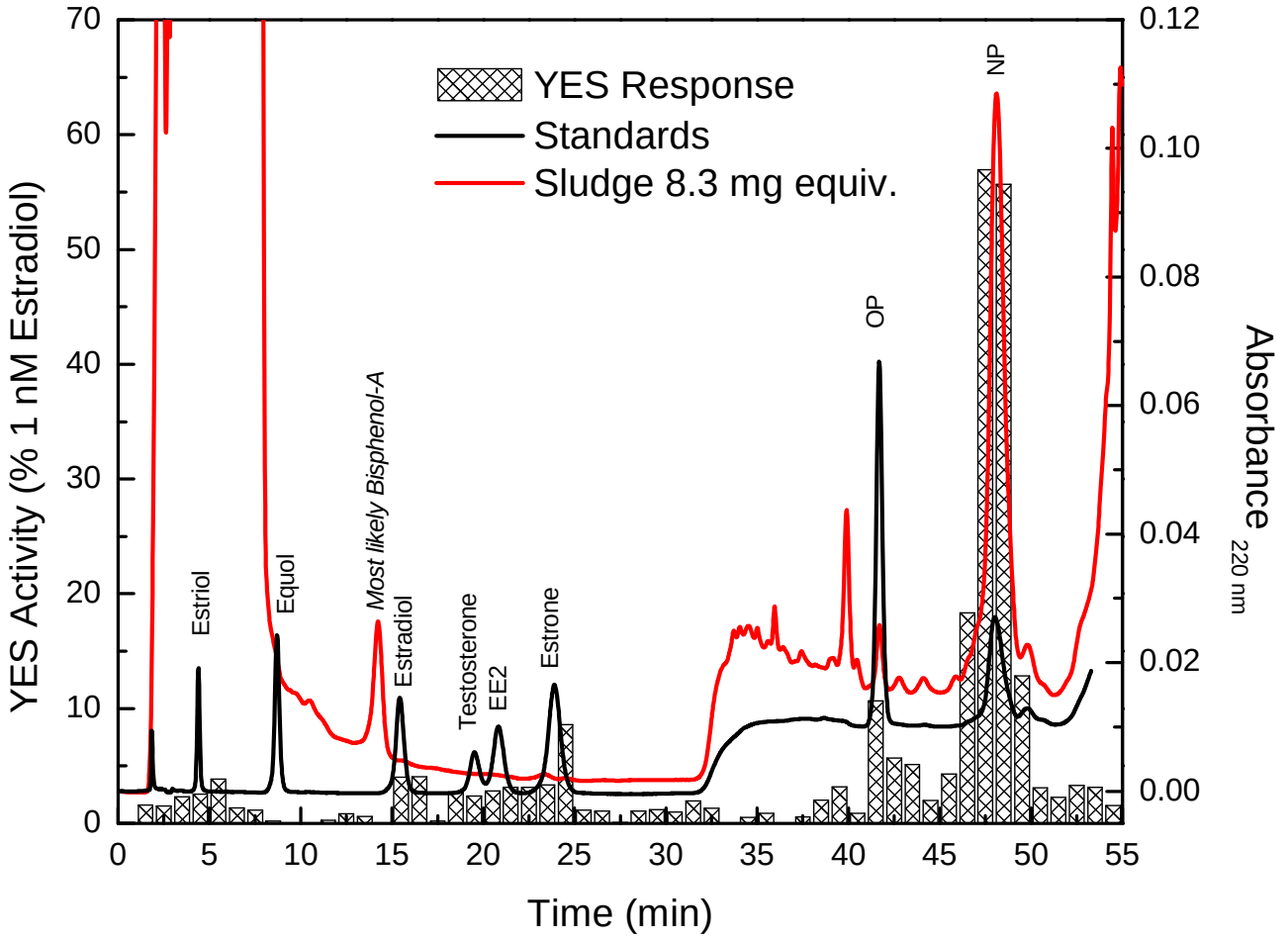
USGS

Compound	Number of detections in water (of 44)	Mean of detections in water, in µg/L	Number of detections in sediment (of 44)	Mean of detections in sediment, in µg/kg	Number of detections in biosolids (of 6)	Mean of detections in biosolids, in µg/kg
Metformin	3	0.1119	N/A	N/A	N/A	N/A
Cotinine	36	0.0332	15	0.51	5	21.04
Salbutamol	4	0.0282	0	0.00	1	29.68
Cimetidine	6	0.1122	15	2.45	3	44.98
Acetaminophen	16	0.0630	11	0.27	6	122.42
Ranitidine	4	0.1218	N/A	N/A	N/A	N/A
1,7-dimethylxanthine	7	0.7501	1	0.09	6	1333.34
Trimethoprim	10	0.1110	12	1.22	2	11.81
Diltiazem	9	0.0265	19	1.60	3	23.92
Fluoxetine	2	0.0019	28	1.84	6	37.38
Ibuprofen	0	N/A	N/A	N/A	N/A	N/A
Gemfibrozil	0	N/A	10	20.35	6	235.16
Paroxetine metabolite	0	N/A	N/A	N/A	N/A	N/A
Caffeine	24	0.4238	13	10.87	6	242.39
Sulfamethoxazole	16	0.1609	3	1.08	1	162.25
Dehydronifedipine	16	0.0088	28	1.79	3	16.75
Codeine	15	0.0700	3	0.70	3	10.12
Thiabendazole	1	0.0072	19	4.86	5	6.55
Diphenhydramine	12	0.0598	30	15.58	6	164.75
Erythromycin	0	N/A	16	5.87	2	5.00
Carbamazapine	26	0.0576	32	4.16	6	20.89
Miconazole	0	N/A	10	2.99	6	198.98
Warfarin	0	N/A	6	0.69	6	31.87

Hormone Activities: Manures and Municipal Biosolids



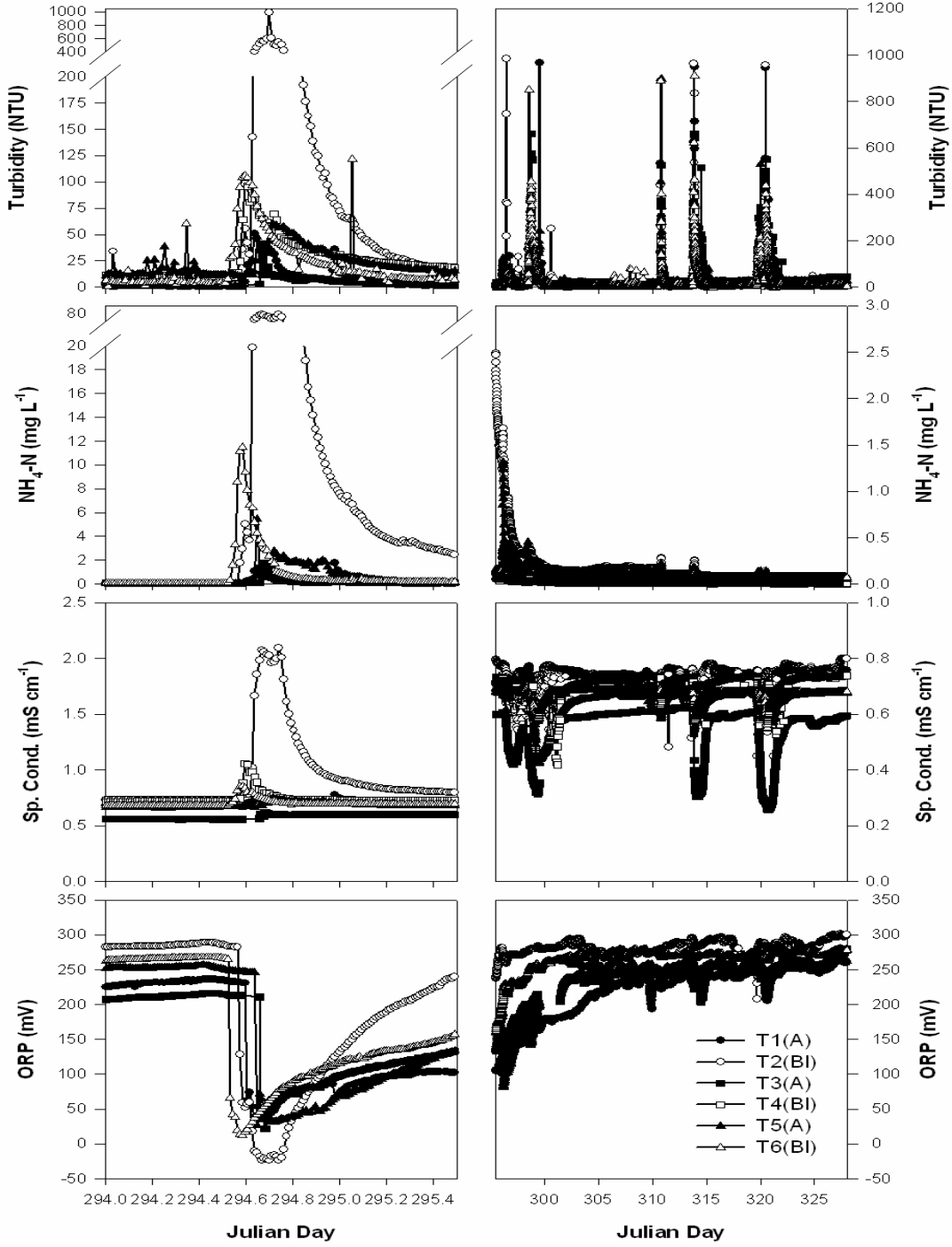
Identity of estrogenic substances in municipal biosolids



Rapid movement to tile at time of application.

Periodic movement to tile with subsequent rain events.

Turbidity, ammonium and bacteria [not shown here] indicate macropore flow.



Effects of PPCPs on zooplankton communities

- Laird, BD, et al. Chemos. 69:949-954. 2007
- Mixture of SSRIs fluoxetine, sertraline, fluvoxamine, 0-100 ug/l.
- 12,000l outdoor microcosms aquatic ecosystems, natural assemblage of microbiology, phyto- and zooplankton, 3 fish species.
- Abundance and species richness of rotifers, cladocerans, copepods. Acute (4d) and chronic (35d) exposures.
- Based on hazard and PEC [STP effluent], conclude no risk from this mixture.

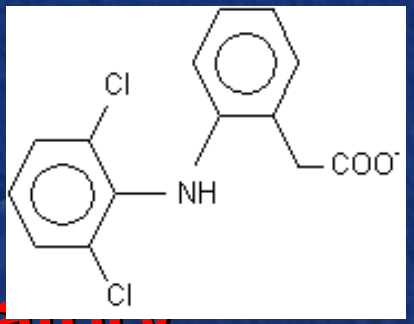
Effects of PPCPs on benthic invertebrates

- Dussault EB, et al. ET&C 27:425-432. 2008
- Atorvastatin, CBZ, TCS, EE2
- midge *Chironomus tentans* and the freshwater amphipod *Hyalella azteca*; exposure10d
  - Based on acute tox data and measured environmental [ ]s, conclude no risk from ATO and EE2, but TCS and CBZ may have, and merit further investigation.

Oriental White-Backed Vultures (*Gyps bengalensis*)

- >95% drop in populations in India, Pakistan and Nepal since early ’90s. Was very abundant, now endangered.
- Mortality associated with renal failure.
- Carrion feeder, especially the remains of domestic livestock- cattle.
  - Nature 2004 427:630-633

Diclofenac residues in medicated livestock at fault



- Diclofenac widely used
- as vet drug- analgesic, anti-inflammatory. Over the counter, hooved livestock [cattle, buffalo, goat]
- Non-steroidal anti-inflammatory drug (NSAID)
- Residues [~<ppm] in carrion poisoning vultures.
- Recovery program consists of withdrawing the drug

In Vitro Estrogen Receptor Binding Assays:

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