Biosolids and Soil

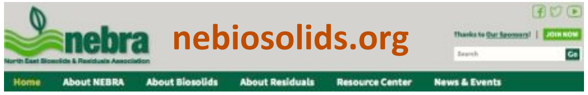
Remarkable Media for Managing Microconstituents

Ned Beecher • North East Biosolids & Residuals Association (NEBRA)

Presented to NEWEA Microconstituents Conference
Sept. 29, 2014 • Bentley University, Waltham, MA

Microconstituents (MCs) in biosolids

- Biosolids use
- Historic context
- Research spreads to biosolids:
  - Presence
  - Fate
  - Impacts
- Varieties of analytes
  - Antibiotics to pharmaceuticals to dibenzo-p-dioxins
- Bioassays
- What does it mean for biosolids managers?
- Biosolids & soils: Remarkable media for managing MCs!



Lewiston-Auburn WPCA biosolids composting facility

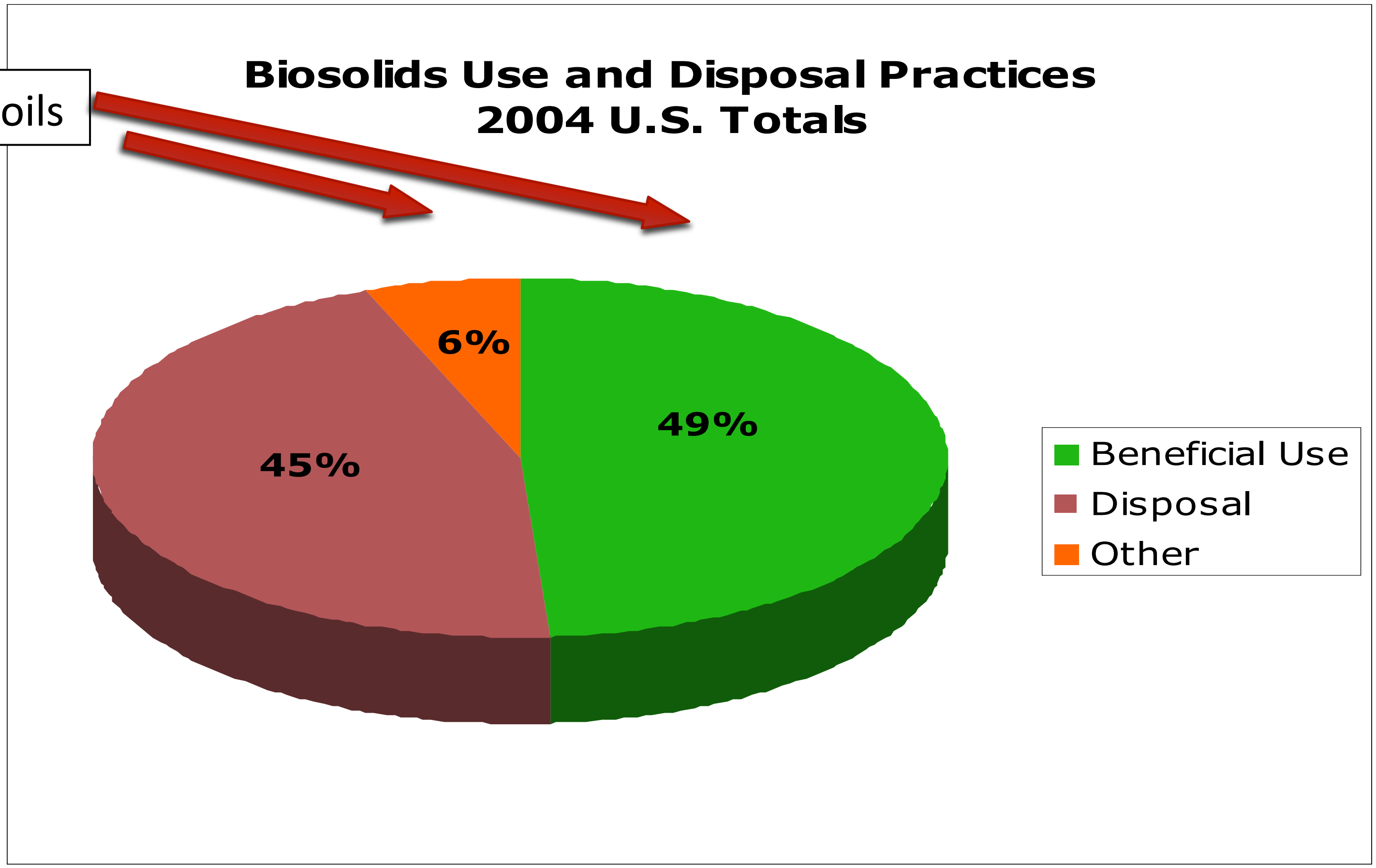
Biosolids Use

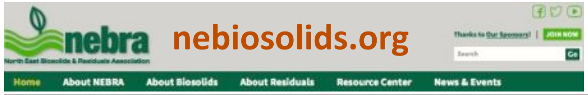
Biosolids improve soils and address environmental challenges.

USA total wastewater solids:

7,180,000 dry U. S. tons/year (~35.9 million wet tons)

55% is used on soils





Biosolids use: Agriculture

Moorhead, MN: Feed corn grown with liquid injected, Class B, anaerobically-digested biosolids, July 2012

- Bulk material markets: animal feed crops (corn, hay), grains (wheat, hops), soy, other commodity crops
- Prices:
  - Class B - $0 - $30 / wet ton
  - Class A – up to $60 / ton
- Trend: increasing demand; waiting lists in some areas

Agriculture:
Denver, CO

In the drier west, biosolids improve the water-holding capacity of the soil.

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Agriculture - Waco, TX

Pasture, 1 year after application of bulk Class B, anaerobically-digested biosolids, December, 2012

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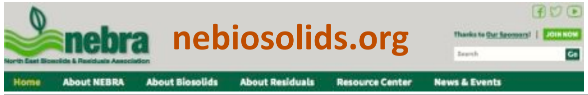
Agriculture

Central Valley, CA

Virginia



Biosolids use: Forestry

Photos courtesy of King County, WA
http://dnr.metrokc.gov/WTD/biosolids/

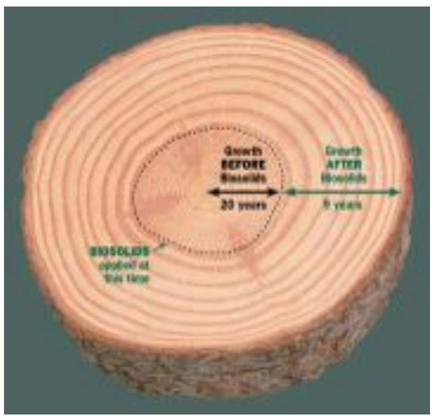


Photo courtesy of Philadelphia Water Dept.

- Only in some areas
- Speeds up harvest cycle in actively managed stands
- Price:
  - Class B $0 - minimal

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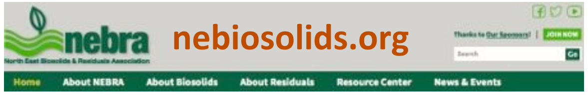
Biosolids use: Horticulture / Landscaping / Turf

Biosolids compost use on my home garden – raspberries, May 2014

- Class A bulk material markets: potting mixes (e.g. Tagro), golf courses (e.g. Milorganite), parks, lawns, growing turfgrass (e.g. in RI), sports fields (hi-spec turf)
- Prices:
  - Class A bulk – up to $60 / ton
  - Class A bagged/retail – up to $450 / ton
- Trend: increasing demand for the quality, consistent products



Horticulture / Landscaping / Turf

Billerica, MA biosolids compost applied on a green, mid-1990s.

Merrimack, NH biosolids compost helps keep this central MA golf course green.

Biosolids compost supports the growth of wildflowers along a NH interstate highway, 1999.

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Horticulture / Landscaping / Turf

before

after

Mid-1980s - photos courtesy of Eliot Epstein, Ph.D., and Orgro

Biosolids Use: Topsoil Blending

Topsoil blending with paper mill residuals and biosolids, central MA, 2006

- Bulk biosolids given or sold to topsoil blenders
- Prices: vary, often $0
- A way to use less processed material
- Topsoils used for reclamation, landfill cover, highway embankments, construction sites
- Trend: steady use

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Reclamation of Disturbed Sites

Spectacle Island in Boston Harbor was reclaimed with biosolids compost and other recycled organics, 2004.

- Bulk material market
- Used to restore healthy soil ecosystem and either native vegetation or cropland
- Prices: vary, often $0
  - Uses a lot of biosolids
- Trend: increasing use, because of huge benefits – biosolids use is best practice for this kind of reclamation

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Reclamation of Disturbed Sites

Pennsylvania mine
before

Same Pennsylvania mine
after

Photos courtesy Bill Toffey, MABA

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Reclamation of Disturbed Sites

Bunker Hill, ID mine
Superfund site

before

Bunker Hill, ID mine 2 years after reclamation with a blend of biosolids, wood ash, and logging debris.

Photos courtesy Rufus Chaney, USDA

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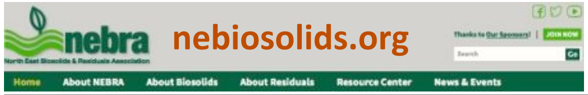
Energy - incineration with energy recovery

Does not utilize the nutrients & organic matter; requires some net energy input.

Cement kiln (Wikipedia photo). Some MWRA biosolids pellets are fuel in a MD cement kiln.

New Haven incinerator, operated by Synagro, with energy recovery.



Biosolids Use: Energy

Anaerobic digestion (followed by use or disposal)

Greater Lawrence San. Dist., Andover, MA

Nashua, NH

Essex Junction WWTF

60 kW CHP Application

Project Profile

Project Overview

Quick Facts

VT

- A biosolids treatment process that results in biosolids to be used or discarded.
- Trend: Huge interest & activity now, across the continent.

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Biosolids Use: Landfill Closure / Methane Mitigation

Slide courtesy of Sylvis, Vancouver, BC

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Home About NEBRA About Biosolids About Residuals Resource Center News & Events

Biosolids Use:
Landfill Leachate Treatment

Slide courtesy of Sylvis, Vancouver, BC

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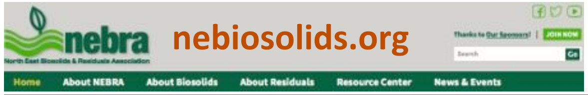
Biosolids Use:
Carbon Sequestration Plantations

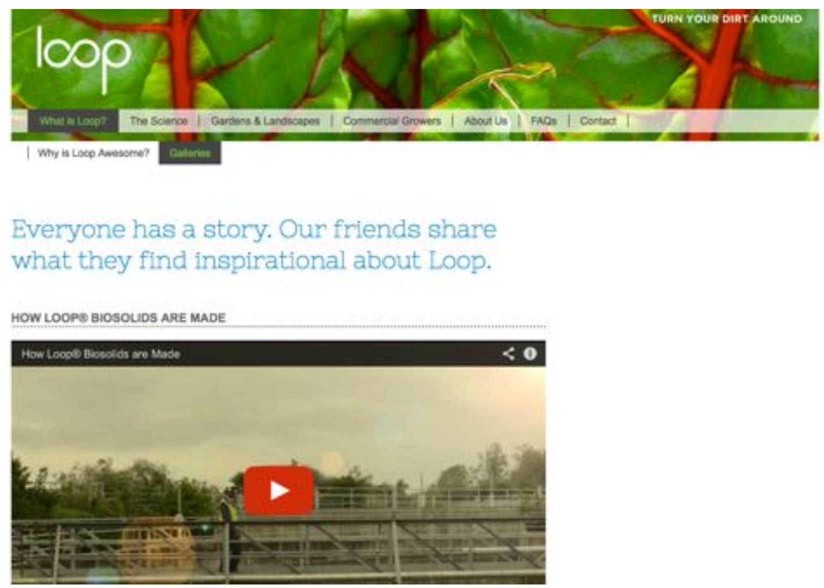
Slide courtesy of Sylvis, Vancouver, BC



General biosolids resources

http://www.endless-films.com/site/?portfolio=biosolids

http://www.loopforyoursoil.com




Water Environment Federation

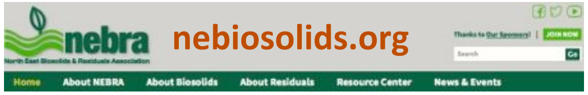
Q&A/Fact Sheet

Land Application and Composting of Biosolids

What are biosolids?

What are some of the benefits of biosolids land application?

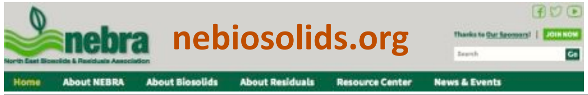
http://www.nebiosolids.org/uploads/pdf/
WEFLandApAndCompostFactSheet-Apr10.pdf



Gordon Price, Dalhousie Univ., NS – this region's sole current biosolids microconstituents researcher

Microconstituents research spreads to biosolids…

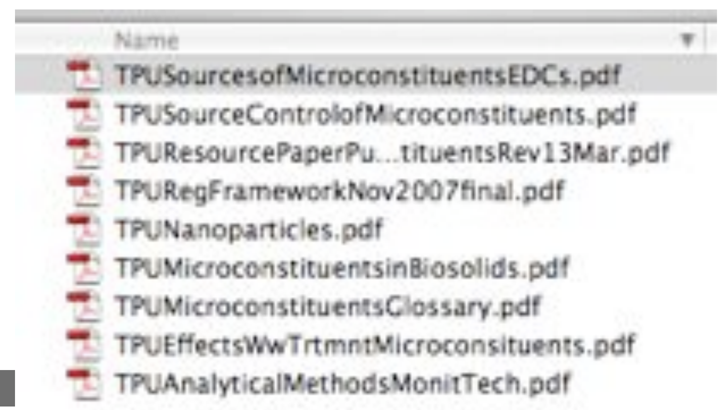
presence, fate, impacts



Historic context

- Trace chemicals in biosolids are not new
- 30 years of research (e.g. PCBs, priority pollutants)
- EPA dioxin risk assessment – early 2000s
- 2006-08: WEF Microconstituents CoP TPUs
- March 2008: AP news
- 2008 / 2011: NEBRA Info

Scroll down at http://www.nebiosolids.org/index.php?page=science for NEBRA coverage of topic.



Research spreads to biosolids: Presence

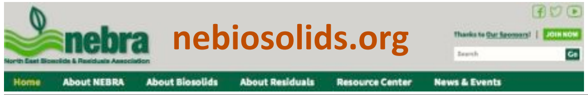
- Xia et al., 2005 (state-of-science of land application conference, U. Florida): "Although PPCPs, such as fragrances, flame retardats, surfactants, and their metabolites, have been detected in biosolids, there is limited information on the occurrence of many other PPCPs in biosolids. This lack of information is largely due to analytical limitations because of the complexity of the biosolids matrix."
- Harrison et al., 2006: literature review reporting 516 trace organic chemicals measured in biosolids
- Heidler et al. / Halden 2006: TCC up to 50 mg/kg in biosolids
- Kinney et al. 2006: USGS analyses of presence (http://toxics.usgs.gov/highlights/biosolids.html)
- Heidler and Halden 2007: TSS partitions to solids (MN has banned sale of TSS-containing products effective January 1, 2017)
- 2009: EPA Targeted Sewage Sludge Survey included microconstituents

Xia et al., 2005: The most common drugs

Table 2. The most commonly used prescription and over-the-counter pharmaceuticals in the United States.

Active compound	CAS number	log K_{ow}†	Brand name	Use
		Prescription drugs (top 10 prescribed in the United States in 2002) (RxList, 2004)		
Hydrocodone	125-29-1	0.98–2.45	Hydrocodone w/APAP	analgesic, antitussive, antipyretic
Acetaminophen	103-90-2	1.18–1.53		
Atorvastatin	134523-00-5	0.12–3.67	Lipitor	lipid-lowering agent
Atenolol	29122-68-7	0.23–1.37	Atenolol	beta1-selective (cardioselective) adrenoreceptor blocking agent
Levothyroxine	51-48-9	0.16–2.11	Synthroid	thyroid hormones
Estrone	53-16-7	3.22–3.38	Premarin	estrogens (female hormones)
Equilin	474-86-2	3.03–3.29		
17α-Dihydroequilin	5965-19-5	4.21		
17α-Estradiol	57-91-0	3.45–3.62		
Equilenin	517-09-9	2.95–3.42		
17α-Dihydroequilenin	6639-99-2	3.12–3.55		
Azithromycin	83905-01-5	0.44–3.16	Zithromax	antibiotic
Furosemide	54-31-9	1.96–2.96	Furosemide	diuretic (treating hypertension, congestive heart failure, and edema)
Amoxicillin	26787-78-0	water soluble	Amoxicillin	gram-positive and gram-negative bactericide
Amlodipine	88150-42-9	0.26–3.38	Norvasc	treating high blood pressure and angina (diuretic)
Besylate	98-11-3	water soluble		
Hydrochlorothiazide	58-93-5	1.23–1.34	Hydrochloro-thiazide	diuretic and antihypertension
		Common over-the-counter drugs (Arthritis Foundation, 2004; RxList, 2004)		
Acetaminophen	103-90-2	1.18–1.56	Anacin, Excedrin, Panadol, Tylenol	analgesic, anti-inflammatory
Ibuprofen	15687-27-1	0.82–3.40	Advil, Motrin IB, Nuprin	anti-inflammatory, analgesic, antipyretic
Aspirin	50-78-2	1.39–2.02	Anacin, Ascriptin, Bayer, Bufferin, Ecotrin, Excedrin tablets	analgesic, anti-inflammatory
Dextromethorphan	125-71-3	0.63–3.65	Benylin cough syrup	relieves cough
Diphenhydramine	58-73-1	0.27–3.34	Benadryl	antihistamine, cold and cough medicine
Loratadine	79794-75-5	4.56–4.77	Claritin	antihistamine
Omeprazole	73590-58-6	1.39–2.35	Prilosec	treating heartburn

† Octanol–water partition coefficient.



Xia et al., 2005: Personal care products

Table 3. Common additives in some personal care products.

Additive compound	CAS number	log K_{ow}†	Characteristics
		Fragrances	
Musk ketone	81-14-1	3.48	Distribution of the use of synthetic musks in personal care products: candles, air fresheners, and aroma therapy = 41%, perfumes, cosmetics, and toiletries = 25%, soaps, shampoos, and detergents = 34% (Fragranced Products Information Network, 2004).
Musk xylene	81-15-2	3.46	
Galaxolide (HHCB)	1222-05-5	4.60	
Tonalide (AHTN)	21145-77-7	4.84	
Phantolide (AHMI)	15323-35-0	4.53	
Traseolide (ATII)	68857-95-4	4.72	
Celestolide (ADBI)	13171-00-1	4.37	
Cashmeran (DPMI)	33704-61-9	4.84	
		Flame retardants	
Tetrabromobisphenol A	79-94-7	4.39–5.34	Used as additive in flexible polyurethane foam, in textile coatings, coatings for furniture, and in plastics for electrical and electronic equipment, wire, and cable insulation and electrical connectors, automobiles, and construction and building materials (Bromine Science and Environmental Forum, 2004). The current estimated worldwide growth for flame retardants is 4% per year. Distribution of the 1.14 million Mg global consumption of flame retardants in 1998: Al-, Mg-, and N-based = 56%, Br-based = 23%, P-based = 15%, Cl-based = 6% (Clariant, 2004). Worldwide market demand for PBDEs in 2001 was 67 440 Mg, 83% of which was in the Americas (Hites, 2004).
Polybrominated diphenylether (commercial available PBDEs primarily consist of penta-, octa-, deca-PBDE)		log K_{ow} > 5.74, log K_{ow} = 0.621(Br) + 4.12 (Braekevelt et al., 2003)	
Polybrominated biphenyl		>4.0	
Pentabromochlorocyclohexane	87-84-3	4.01	
Hexabromocyclododecane	25637-99-4	4.98	
Pentabromotoluene	87-83-2	4.57	
Tetrabromophthalic anhydride	632-79-1	3.17	
Tris(2,3-dibromopropyl)phosphate	126-72-7	>4.0	
		Disinfectants, antiseptics, and pesticides	
Triclosan (2,4,4′-trichloro-2′-hydroxy diphenyl ether)	3380-34-5	2.39–4.54	Bactericide added in detergents, dishwashing detergents, laundry soaps, deodorants, cosmetics, lotions, creams, toothpastes and mouthwashes, footwear, and plastic wear. It interferes with an enzyme crucial to the growth of bacteria (Bhargava and Leonard, 1996).
Biphenylol	90-43-7	2.67–2.98	Bactericide and virucide added in dishwashing detergents, soaps, general surface disinfectants in hospitals, nursing homes, veterinary hospitals, commercial laundries, barbershops, and food processing plants. It is used to sterilize hospital and veterinary equipment (National Library of Medicine Specialized Information Services, 2004).
Chlorophene	120-32-1	3.37–3.78	Bactericide and fungicide added in disinfectant solutions and soaps (National Library of Medicine Specialized Information Services, 2004).
DEET (N,N-diethyltoluamide)	134-62-3	2.44	Pesticide added in insect repellant (National Library of Medicine Specialized Information Services, 2004).
Butylparaben (alkyl-p-hydroxy-benzoates)	94-26-8	1.49–3.26	Fungicide added in cosmetics, toiletries, and food (National Library of Medicine Specialized Information Services, 2004).
		Surfactants	
Alkylphenol polyethoxylates (usually branched nonyl or octyl; ethoxylate units = 1–20)		>4.5	Nonionic surfactants added in detergents (National Library of Medicine Specialized Information Services, 2004).
Sodium dodecylbenzenesulfonate	25155-30-0	water soluble	Ionic surfactants added in detergents (National Library of Medicine Specialized Information Services, 2004).
Benzalkonium chloride	8001-54-5	water soluble	Ionic surfactants added in detergents, preservative and disinfectant in contact lens solutions (National Library of Medicine Specialized Information Services, 2004).

† Octanol–water partition coefficient.

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Harrison et al., 2006: …yes, microconstituents are in biosolids…

Table 3: Concentration of organic chemicals reported in biosolids (Modified from Harrison *et al.* 2006). ND = non detect.

Legacy Contaminants	Category	Range mg/kg dry wt
dieldrin	pesticide	ND-64.7
toxaphene	pesticide	51
bisphenol-A	phenols	0.00010-32.100
phthalates	phthalate acid ester/plasticizers	ND-58.300
dioxins and furans (polychlorinated dibenzo)	polychlorinated biphenyls, naphthalenes, dioxins and furans	ND-1.7
PCB congeners	polychlorinated biphenyls, naphthalenes, dioxins and furans	ND-765
anthracene	polynuclear aromatic hydrocarbons acenaphthene	ND-44
benzopyrene congeners	polynuclear aromatic hydrocarbons acenaphthene	ND-24.7
naphthalene	polynuclear aromatic hydrocarbons biphenyl	ND-6610
total PAH	polynuclear aromatic hydrocarbons biphenyl	ND-199
coprostanol	sterols, stanols and estrogens	216.9
alkylbenzene sulfonates	surfactants	<1-30,200

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Kinney et al., 2006:
…yes, microconstituents are in biosolids…

Table 4: Carbon Normalized Concentrations, Organic Carbon (µg/kg), of Organic Wastewater Contaminants Detected in all Nine Biosolids (Modified from Kinney *et al.* 2006)

Organic Wastewater Contaminants	Use	Log K_{ow}	Median of all Biosolids (µg/kg)
carbamazapine	antiepileptic	2.45	68
diphenhydramine	antihistamine	3.27	340
fluoxetine	antidepressant	4.05	370
d-limonene	fragrance	4.57	630
tonalide (AHTN)	fragrance	5.70	11,600
galaxolide (HHCB)	fragrance	5.90	3,900
indole	fragrance	2.14	19,600
4-tert-octylphenol	detergent metabolite	5.28	4,030
para-nonylphenol-total	detergent metabolite	5.92	261,000
nonylphenol, diethoxy-total	detergent metabolite	4.21	7,010
bisphenol A	fire retardant	3.32	4,690
3-beta-coprostanol	steroid	8.82	126,000
cholesterol	steroid	8.74	209,000
beta-sitosterol	steroid	9.65	131,000
stigmastanol	steroid		174,00
phenol	disinfectant	1.50	2,180
triclosan	disinfectant	4.53	10,200
diethylhexyl phthalate	plasticizer	7.88	10,500
para-cresol	preservative	1.97	4,400
skatol	fecal indicator	2.60	2,510

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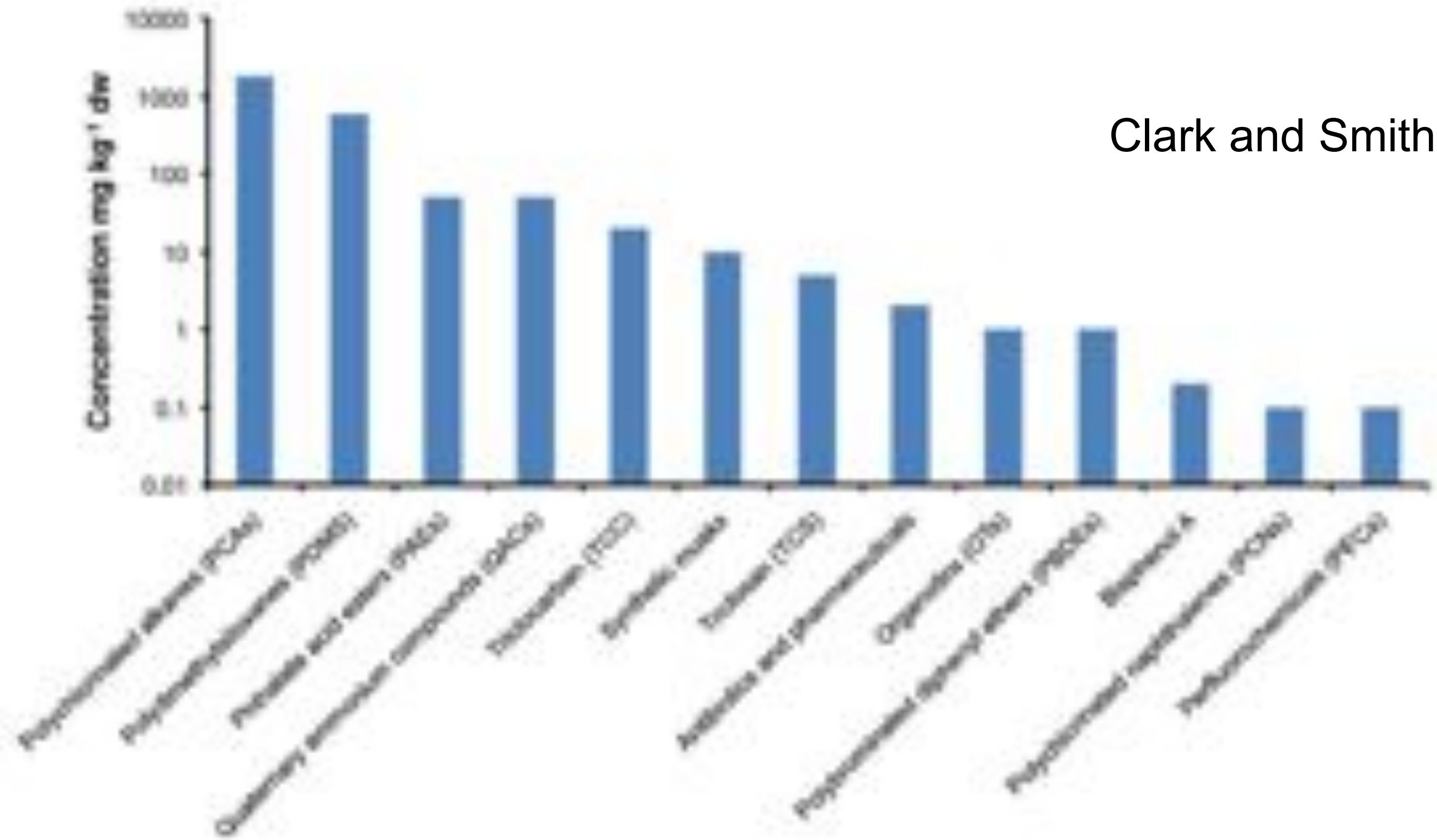
Concentrations of MCs in biosolids



Clark and Smith, 2010

Fig. 1. Typical concentrations of selected 'emerging' organic contaminants in sewage sludge (mg kg^{-1} dw).

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Research spreads to biosolids: Fate

- Buyuksonmez and Sekeroglu, 2005: composting certainly degrades many microconstituents
- Lappen et al., 2008: worst-case field application scenario with spiking of PPCPs led to measured PPCPs in tile drainage
- Kinney et al. 2008: USGS study on fate: trace organics from biosolids & swine manure is found in worms (http://toxics.usgs.gov/highlights/earthworms.html)
- Gottschall et al., 2012, 2013: no significant impact on tile drainage water quality from biosolids land application
- Gottschall et al. 2012, Hale et al. 2012, Sauborin et al. 2012. These studies generally demonstrated low risk to human health from biosolids borne PPCPs, PBDEs, hormones and parabens, citing low rates of plant uptake and minimal impact on ground water quality

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Research spreads to biosolids: Fate

- Topp et al., 2009: "PPCPs are detected in tile drainage and in surface runoff, sometimes months after application. Maximum concentrations of PPCPs detected in effluent are generally lower following application of DMB* than application of LMB**. Incorporation of LMB eliminates the potential for loss via runoff. Application of LMB using an Aerway device reduces contamination via tile drainage, compared to surface applied and incorporated. The mass transport (fraction of chemical applied that is exported) varied widely. Maximum concentrations of PPCPs detected in effluents were generally far below toxic thresholds for a variety of endpoints drawn from the literature."

* dewatered municipal biosolids

**liquid municipal biosolids

Research spreads to biosolids: Impacts

- Hundal et al. 2009, Chicago: "The data suggest limited mobility of biosolids borne TCC, TCS, total PBDEs, and 4-NP in biosolids-amended soils. Although the concentrations of, TCC, TCS, 4-NP, and total PBDEs in soil were greater in the biosolids-amended plots than in the Control plots, the contaminants had no detrimental effects on the soil biota. Indeed, microbial community studies showed that the microbial populations were more diverse and much more biologically active in the biosolids-amended plots than in the control plots."

Research spreads to biosolids: Impacts


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

- Wu et al., 2010
  - Considerable media attention
  - Soybean plant uptake
  - Greenhouse study
  - Spiked samples
  - Past research on trace metals and chemicals shows similar over-estimation of effect when spiked samples of the pollutant are used

Context for the Wu et al. study

- Triclosan (TCS)
  - In toothpaste: 3,000 mg/kg
  - Wu et al. maximum measured concentration in plant (conservative scenario): 0.1 mg/kg
  - Typical land application calculated estimated soil concentration: 0.05 mg/kg
  - TCS (& TCC) decompose in soil at a moderate rate.
  - Young, (Univ. of CA, Davis): "increased nitrogen added with biosolids stimulates nitrogen cycling sufficiently to offset any detrimental impacts on the nitrogen cycling caused by Triclosan at realistic application concentrations."

Plant uptake: Sabourin et al. 2012

"Biosolids at application, and crop samples following harvest, were analyzed for 118 pharmaceuticals and transformation products, 17 hormones or hormone transformation products, and 6 parabens. Analyte concentrations in the biosolids were consistent with those detected in other surveys. Eight of the 141 analytes were detected in one or two crop replicates at concentrations ranging from 0.33 to 6.25 ng/g dry weight, but no analytes were consistently detected above the detection limit in all triplicate treated plots. Overall, this study suggests that the potential for micropollutant uptake into crops under normal farming conditions is low."

EPA: Targeted National SS Survey

- 74 randomly selected publically operated treatment works (POTWs) in 35 states
- Sampled solids in 2006 and 2007
- 145 analytes
- wide spectrum of concentrations of polycyclic aromatic hydrocarbons (PAHs) and semi-volatiles at the part per billion (µg/kg) scale
- flame retardants in the part per trillion (ng/kg) to part per billion (mg/kg) range
- pharmaceuticals in the part per billion (µg/kg) to part per million (mg/kg) range
- steroids and hormones in the part per billion (µg/kg) to part per thousand (g/kg) range (many natural hormones and steroids)

– USEPA 2009

EPA currently conducting risk assessments on 9 elements & compounds.

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Large review on fate & impacts

Hydromantis, 2010
Available free at
www.weao.org.

Assessing the Fate and Significance of Microconstituents and Pathogens in Sewage Biosolids

Update of the 2001 WEAO Report on Fate and Significance

Water Environment Association of Ontario

Process Rankings for Microconstituent Removal (in order by removal of analyzed compounds, with best removal at top of list)

From Monteith, Nov 2010. See "Monteith" under "Session 4" at http://www.nebiosolids.org/index.php?page=annual-north-east-residuals-biosolids-conference

Location	Treatment Process Assessed	Score total	Number of MCs (counts)	Reduction efficiency (avg score)
Gatineau Val.	Biological – compost	49	27	1.81
Moncton	Biological – compost	57	31	1.84
Prince Albert	Biological – compost	72	29	2.48
Halifax N-Viro	Phys.-chem. (alkaline stabilis'n)	116	35	3.31
Red Deer	Biological – meso. an. dig.	115	34	3.38
Eganville (Septage)	Physical – geotextile bag dewatering	97	28	3.46
Salmon Arm	Biological – ATAD	111	32	3.47
Saskatoon	Biological – meso. an. dig	118	34	3.47
Smiths Falls	Physical – thermal drying	100	27	3.70
Gander	Physical – filter press dew.	102	27	3.78
Saguenay	Physical – filter press dew.	108	27	4.00

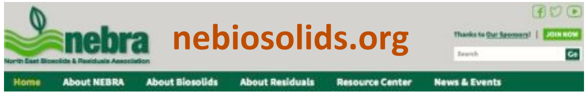
WERF: State of the Science

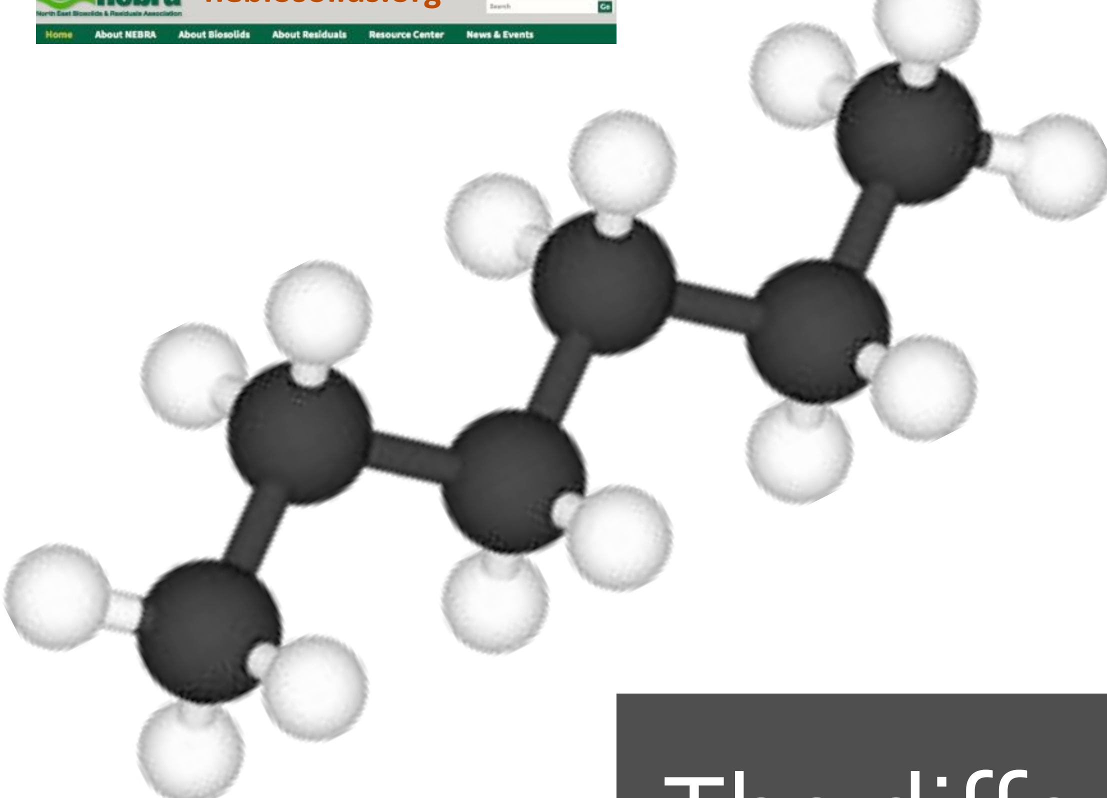
EXECUTIVE SUMMARY — WERF

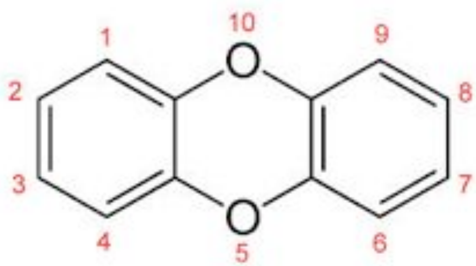
WATER ENVIRONMENT RESEARCH FOUNDATION — BIOSOLIDS

Trace Organic Chemicals in Biosolids-Amended Soils: State-of-the-Science Review

- Available from WERF website
- Foundation for future WERF research on the topic







Information on the following 14 slides mostly from Clark and Smith, 2010

The different microconstituents…

…antibiotics to pharmaceuticals to dibenzo-p-dioxins

Antibiotics / antimicrobials

- Main concern: spread of antibiotic resistance
- Found in solids: **norfloxacin**, **ofloxacin**, **ciprofloxacin**, trimethoprim, sulfamethoozole and **doxycycline**. (**Bold indicates most commonly found in low mg/kg range.)**
- More persistent in soils than in aquatic environment.
- Natural antibiotics are synthesized in soils, and natural resistance develops.
- Maintenance of resistance is not a benefit when stressor disappears / degrades.
- Ciprofloxacin more resistant and of potential concern.
- Antibiotic use in animals is much greater than human use.

Antibiotics / antimicrobials: solids treatment & time reduce resistance

Analysis of viable pathogenic bacteria or antibiotic-resistant coliform bacteria on plate counts did not reveal significant treatment effects of fertilization with Class B biosolids or untreated sewage sludge on the vegetables. Numerous targeted genes associated with antibiotic resistance and mobile genetic elements were detected by PCR in soil and on vegetables at harvest from plots that received no organic amendment. However, in the season of application, vegetables harvested from plots treated with either material carried gene targets not detected in the absence of amendment. Several gene targets evaluated using qPCR were considerably more abundant on vegetables harvested from sewage sludge-treated plots compared to controls in the season of application, whereas vegetables harvested the following year revealed no treatment effect. Overall, results of the present study suggest that producing vegetable crops in ground fertilized with human waste without appropriate delay or pre-treatment will result in an additional burden of antibiotic resistance genes on the harvested crops.

– Rahube et al., 2014

Same results found in study of manure applications (Marti et al., 2013)

Bisphenol A

- Widely used, high production (diminishing in consumer products)
- Degrades in wastewater treatment
- In solids in low *ug* / kg to mid mg / kg
- Half-life in soil ~ 3 days
- Greatest human exposure is in domestic environment

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Nanoparticles

- Increasing use in consumer products – especially silver
- Colman, 2010 (Duke Univ.) found negative impacts on soil microbial activity and plants when biosolids and spikes of silver nanoparticles were added to soil in a microcosm study. Significant publicity ensued, including in Scientific American. This research methodology is not representative of field conditions with nanoparticles aged in solids.
- Continued research suggested.

Organotins

- Highly toxic in aquatic environment
- Use being phased out in UK and elsewhere
- Rarely > 1 mg/kg in wastewater solids.
- 20% - 50% remained in soil after 2 months in laboratory study (Marcic et al, 2006)

Phthalate acid esters

- 20% - 40% of many plastics
- High K_{ow} - sorbs to solids
- Large variability in concentrations in different solids and same solids over time: 1 – 3500+ mg/kg
- Most common is DEHP di(2-ethylhexyl) phthalate
- Wastewater treatment and composting degrade them (AD less so, variably)
- Sorption to solids precludes significant plant uptake
- Greater phthalate on crops from plastics used in agriculture

PBDEs

polybrominated diphenyl ethers

- Most common are BDE47 and BDE99 (penta) and BDE209 (deca)
- Persistent (UNEP POP since 2008)
- Manufacture of penta ended in 2004 in No. America and it and octa are now restricted in EU.

Are replacements better environmentally?

- e.g. Tetrabromophthalate: .12 - 3.749 mg/kg in biosolids (Davis et al. 2012)

- No significant plant uptake.
- Greatest human exposure is in domestic environment (house dust)

Polychlorinated alkanes

- More than 10,000 possible congeners
- Found in solids from 1 – thousands mg/kg, but data are limited
- Greater controls on use are underway in EU
- Risk assessment using UK mean concentration of 1800 mg/kg showed direct ingestion by pica child could lead to exceeding tolerable daily intake of 100 *ug* / kg
- Further research recommended (Clark & Smith, 2010)

Polydimethylsiloxanes

- Industrial applications and in consumer products
- U. S. range of biosolids concentrations: 290 – 5155 mg/kg, but more research would be helpful
- Low toxicity
- Degrade in soils via abiotic processes; drier soil estimated half life of 4 – 28 days. Measured half life in moist soil: 876 – 1443 days.

Perfluorinated compounds

- Persistent and widely found in environment
- Bioaccumulative
- Normal concentrations in solids (without manufacturer input): low *ug* / kg
- PFOA and PFOS are being restricted by EU and phased out in No. America too, but their long use and persistence means they will be around a long time.
- Application of biosolids at Decatur, AL led to EPA remedial action; treatment plant received manufacturer discharges

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Pharmaceuticals

Table 2

Risk assessment evaluation concentrations (mg kg^{-1} dw) of selected pharmaceutical compounds in sludge-amended soil (Eriksen et al., 2009).

Therapeutical group	Drug substance	Predicted environmental concentration (PEC)		Predicted no-effect concentration (PNEC)
		Agricultural soil (60 t ha^{-1})	Park areas	
Alimentary tract and metabolism	Mesalazin	0.08	6.70	12
	Ranitidin	0.04	0.30	5277
Blood and blood forming organs	Dipyridamole	0.03	0.17	–
Cardiovascular system	Sotalol	0.02	0.15	4095
	Metoprolol	0.02	0.13	589
	Losartan	0.03	0.23	–
	Atorvastatin	0.05	0.34	11
Antibacterial drugs	Tetracycline	0.01	0.08	8.8
	Ciprofloxacin	0.04	0.29	26
Muscular–skeletal system	Carisoprodol	0.10	0.68	24368
Nervous system	Gabapentin	0.06	0.39	20480
	Levetiracetam	0.02	0.12	–
	Chlorprothixene	0.02	0.16	–
Respiratory organs	Fexofenadine	0.03	0.17	–

Norwegian study that evaluated ~1400 pharmaceuticals in use there. These 14 were identified as needing further research regarding their potential impacts via the biosolids pathway (Ericksen et al., 2009)

Quaternary ammonium compounds

- Cationic surfactants
- Sorb strongly to solids & sediments
- One study found 22 – 103 mg/kg in solids
- Degrade quickly in wastewater treatment and anaerobic digestion
- Short half-life in soil: 17 – 40 days

Steroids / hormones

- Negative impacts known in aquatic environments
- Also enters environment via livestock
- High rate of degradation in WRRFs
- Fast degradation in soils.

Synthetic musks

- persistent
- Concentrations in solids: 0.1 – 81 mg/kg
- Germany and other EU countries proposing limits in biosolids
- More research recommended

EPA Biosolids Dioxin Review

“The most highly exposed people, theoretically, are those people who apply sewage sludge as a fertilizer to their crops and animal feed and then consume their own crops and meat products over their entire lifetimes. EPA's analysis shows that even for this theoretical population, only 0.003 new cases of cancer could be expected each year or only 0.22 new cases of cancer over a span of 70 years. The risk to people in the general population of new cancer cases resulting from sewage sludge containing dioxin is even smaller…”

– EPA dioxin assessment, 2003: http://water.epa.gov/scitech/wastetech/biosolids/dioxinfs.cfm

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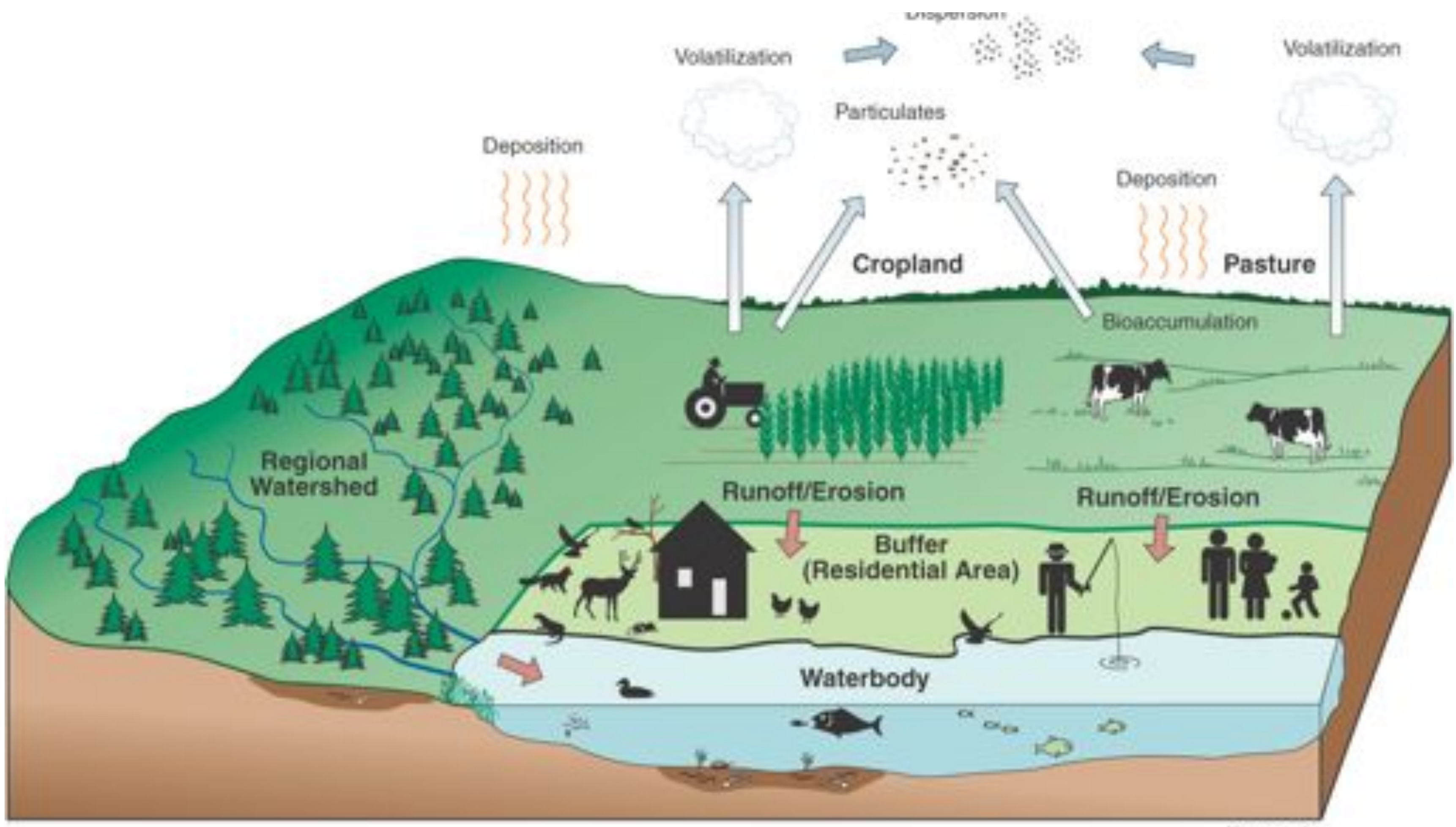
EPA Biosolids Dioxin Risk Assessment



Context for dioxin

Source	Concentration (ppt TEQ dry weight)
Maine Biosolids Average (31 samples 1995-1997)	6.3
Maine Biosolids Regulatory Limit	27
U.S. soils average (rural) EPA data	4
U.S. soils average (urban) EPA data	19
Leaf and yard waste composts (range of 29 samples)	5 - 91
Cow Manure (6 samples from 2003 European study)	3.6
Fish (EPA data)	0.59
Ben & Jerry's Vanilla Ice Cream (1 sample)	0.79
Times Beach, Missouri	Up to 340,000

Slide courtesy of Andrew Carpenter, Northern Tilth

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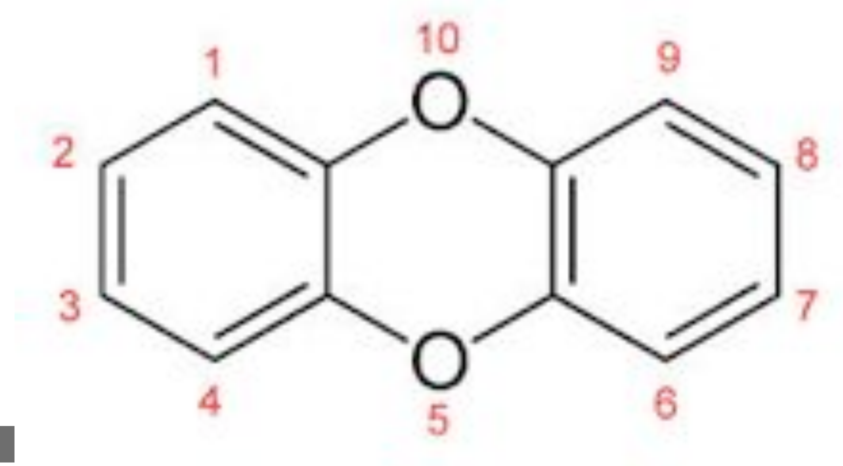
Context for dioxin…
…after 30 applications of biosolids

The levels of dioxins in soil were only 79.9, 115.5, and 247.5 ng toxic equivalents (TEQs) kg−1 in the 0, 504, and 2016 Mg biosolids ha−1 plots, respectively. Dioxins were not detected in the corn grain, and only trace levels (6.8–7.5 ng TEQs kg−1) were found in the corn stover; however, these values were not statistically different between control and biosolids amended soils.

– Hundahl et al., 2008



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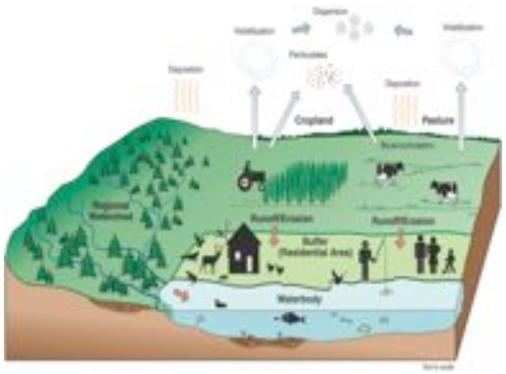
How to proceed?

- Research and risk assessment… chemical by chemical – long and costly process!
- Must prioritize (as has been done mostly so far):
  - high production chemicals
  - most toxic
  - most persistent
- Better = bioassays:
  - Screens for total impacts
  - Addresses concern of impacts of mixtures
  - Addresses concern of persistent exposure (of even short-lived compounds)



Bioassays…

…a logical & efficient approach to assessing potential impacts

Bioassay work…

- 1980s & '90s: Sopper (Penn State Univ.): testing of plant and rabbit health on sites reclaimed with biosolids (with focus on heavy metals)
- 2000s: Brown (Univ. of WA), USDA, and others: testing of plant and rabbit health on sites reclaimed with biosolids
- 2010: University of Guelph – fate of endocrine disruption during biosolids treatment processes
- 2010: College of William and Mary: bioavailability of PDBEs using earthworms and crickets in laboratory
- 2013: Park, et al. (Tom Young team, UC Davis): Triclosan has "little relative impact on overall community composition…" and "TCS slightly increased biomarkers of microbial stress, but stress biomarkers were lower in all biosolid treated soils, presumably due to increased availability of nutrients mitigating potential TCS toxicity."
- 2013: Puddephat thesis (Lynda McCarthy team, Ryerson Univ.): lab bioassays in Ontario using earthworms, springtails, *brassica rapa*, beans, corn, and various aquatic organisms

Puddephat / McCarthy research

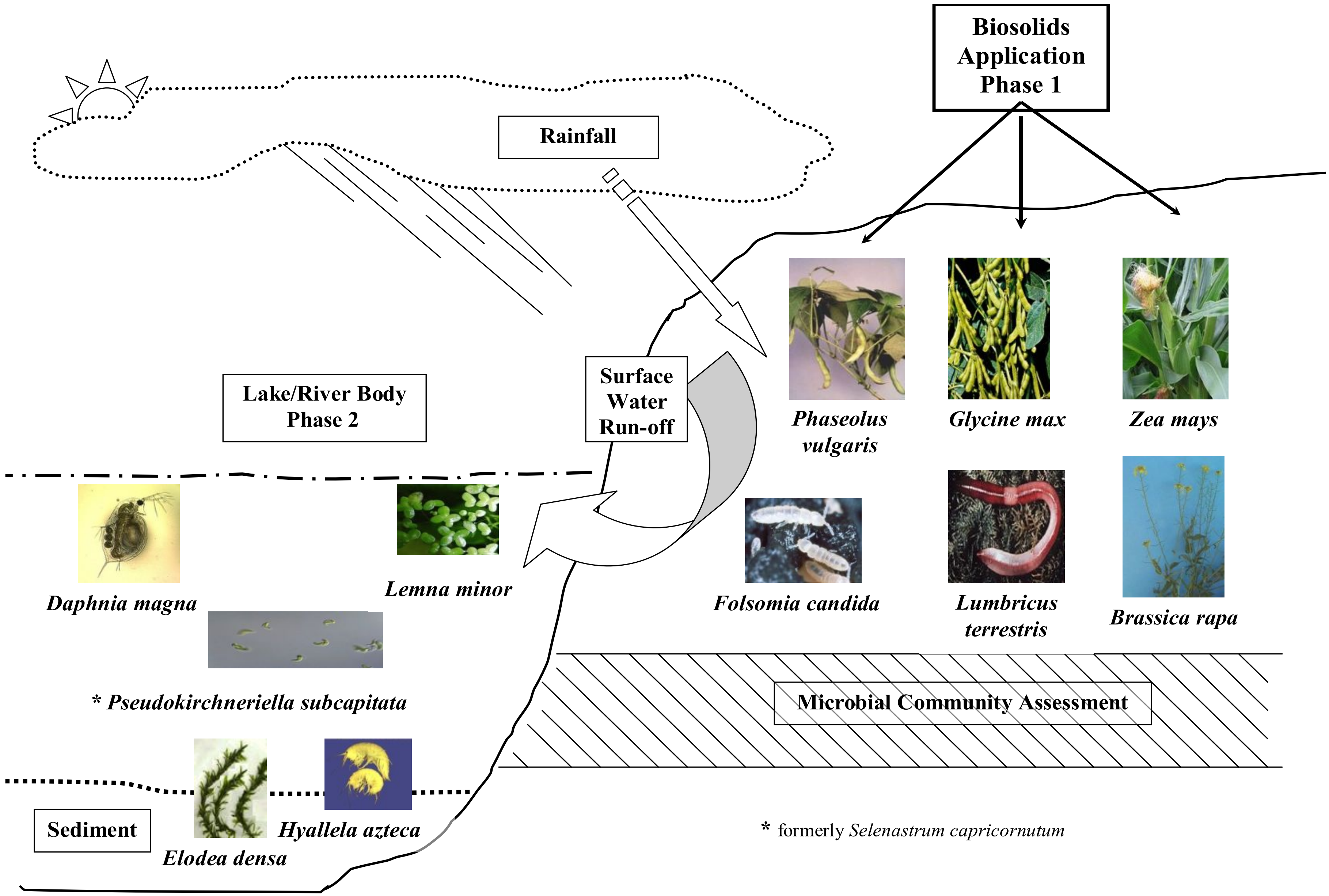
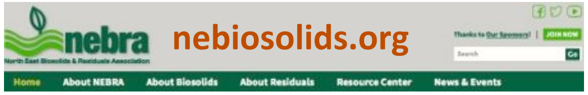
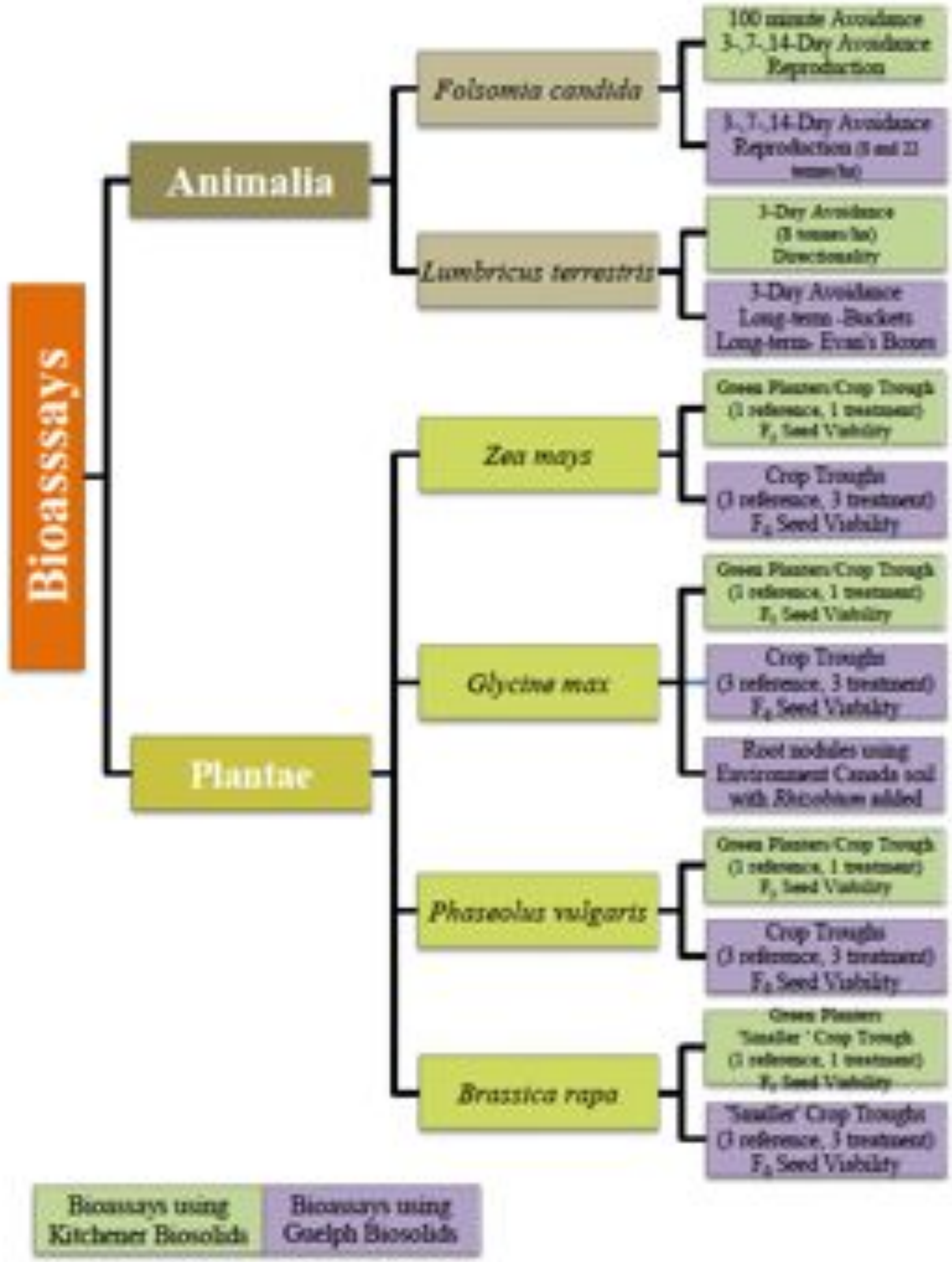


Figure 1. Possible contamination pathways and specific bioassays for the assessment of biosolids application impact.



Puddephat / McCarthy research

(Puddephat, 2013)



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Puddephat / McCarthy research (Puddephat, 2013)

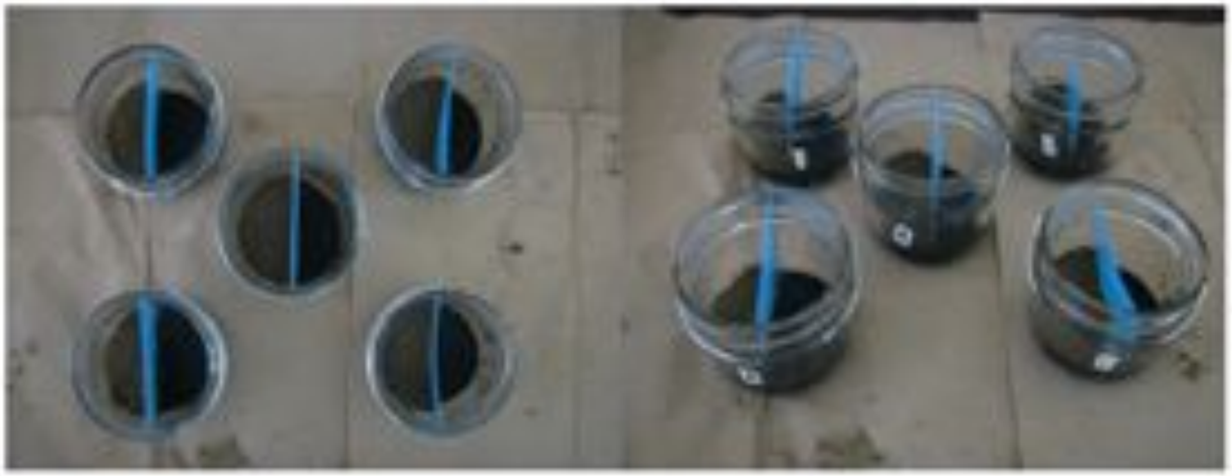


Figure 17: Avoidance chamber setup for *Folsomia candida*

Brassica rapa

Zea mays

Figure 30: Feeding of Earthworms in Ryerson Long-Term Bioassay Chambers. Image shows the mating chambers atop the Evan's Boxes

Conclusions of Puddephat / McCarthy research:

McCarthy, 2011:

- sub-acute, acute, chronic, and reproductive bioassays indicated no deleterious impact of selected biosolids on selected biota under controlled, laboratory conditions
- use of multi-organism, environmentally-relevant bioassays adds scientific veracity to assessing the sustainability of the land-application process

Puddephat, 2013:

"The findings showed that biosolids had little negative impact on the terrestrial biota examined and as a general rule, there was no impact observed. Where effects were observed, the majority of instances were positive. In the few instances where there was negative impact observed, for example in the initial growth stages of the plant bioassays, with further development of the organism, there was no longer a significant difference between the reference and treatment plants."

What does it mean for biosolids management?

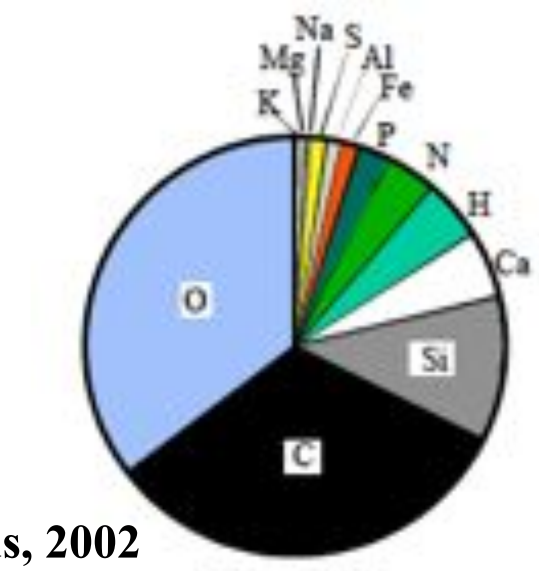
What does it mean?

Remember:

Biosolids are mostly water, organic matter, and inerts.
Microconstituents of potential concern = < 2%, maybe.

U. S. EPA measured elements in biosolids, 2007 TSSS:

Carbon ---- 31.4% or 314,000 mg/Kg
Oxygen --- 20.4% or 204,000 mg/Kg
Silicon --- 5.1% or 51,000 mg/Kg
Hydrogen -- 4.1% or 41,000 mg/Kg
Nitrogen --- 4.0% or 40,000 mg/Kg
Sulfur --- 1.2% or 12,000 mg/Kg



Univ. of WA estimate of elements in biosolids, 2002

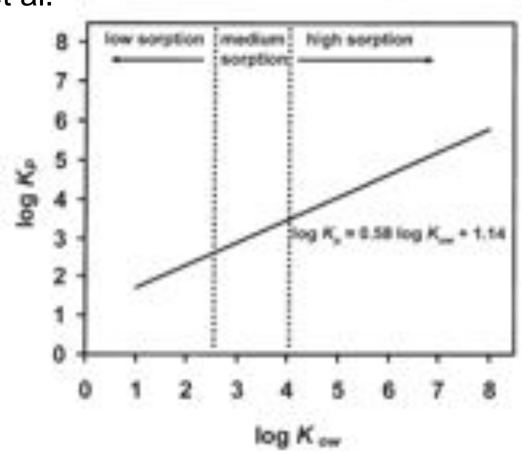
What does it mean?

All chemicals added to soils are subject to the same reactions/processes, including solid phase retention/release, degradation, bioaccumulation, volatilization, runoff, and leaching. The reactions/processes of organics have been studied for decades and the corresponding risk to human and environmental health assessed/estimated. Examples of organic chemicals so studied include pesticides, priority pollutants, and others with chemical and physical properties similar to many of today's "emerging chemicals of concern", also know as "microconstituents."

– George O'Connor, PhD, Univ. of Florida, 2009, WEF Residuals and Biosolids Conference

What does it mean?

Xia et al.
2005



Chemicals of greatest concern in biosc

- High log K_{ow} - octanol-water partition coefficient
- High toxicity (to some species)
- Long half-lives (persistent)
- Bioaccumulative
- Dioxins/furans are excellent example: thoroughly studied and not found to require regulation (EPA, 2003)

Far greater concerns and impacts are in the WRRF effluent and receiving aquatic environment.

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What does it mean?

Perspective:

4 times as much antimicrobials used in agriculture than humans

U. S. manure: ~ 1.1 billion wet tons / year

U. S. biosolids: ~ 36 million wet tons / year

Microconstituents in wastewater are removed/broken down during treatment or remain in effluent or solids. A few increase in concentrations due to biochemical processes.

Microconstituents in biosolids are generally strongly adsorbed to organic matter and in mineral form (hydrophilic compounds are in effluent). Their generally high log K_{OW} values mean that solid phase retention is great and that release is small, that leaching through soils and subsequent groundwater contamination is likely small, that water solubility is likely low, and that availability to organisms dependent on water solubility (plant uptake) is likely small.

Decades of research on organic compounds in soils provide understanding for microconstituents/PPCPs: most degrade (half-lives vary, but most are less than six months).

Pot studies spiked with fresh chemicals (PPCPs, etc.) are not representative of field conditions.

What does it mean?

Remember:

1 ppm = 1 second in 11.6 days

1 ppb = 1 second in 31.7 years

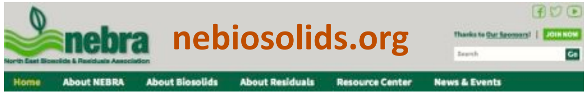
1 ppt = 1 second in 31,700 years

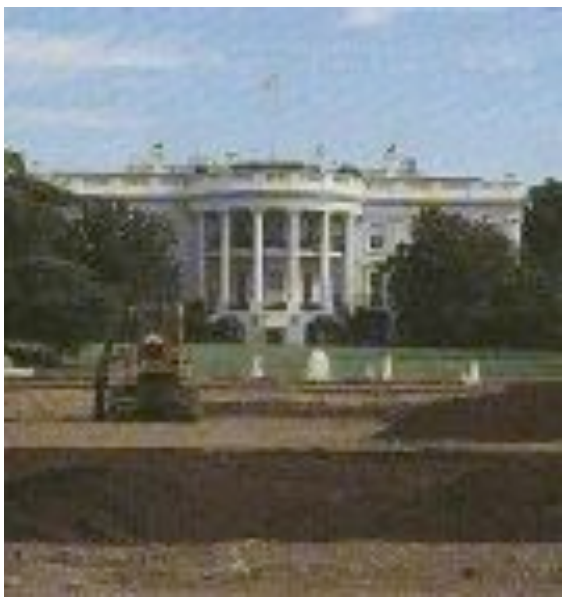
Healthy, microbially-active soils are the best medium for treatment of traces of organic chemicals.

Significant impacts to biota have been measured in aquatic environments, but not in biosolids-amended soils.

Risk to human health through biosolids-application-to-soil pathways appear to be negligible. Far greater human exposure to most are through daily use of products.

Source reduction should focus on persistent compounds with known or potential toxicity.





Biosolids & soils: Remarkable media for managing MCs!

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Q: Where do we want to put microconstituents?

(We can't remove every bit from wastewater.)

A. When possible, avoid disposal in wastewater. Once in wastewater, get them into the solids.

Biosolids management options include:

1. Solids incineration = destruction of MCs
2. Solids landfilling = sequestration & decomposition of MCs
3. Use on soils = sequestration & decomposition, with some potential for migration in environment.

Rationale:

- Complex management choices require maximizing benefits and minimizing risks. There is no pure & perfect solution.
- Benefits of recycling biosolids to soils are greater than risks.
- Use of biosolids on soils is the most sustainable biosolids management option, by many metrics (GHG emissions, nutrient cycling, soil improvement, fertilizer displacement, conservation of resources (recycling P, a critical, limited resource), etc.

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Q: Where do we want to put microconstituents?

(We can't remove every bit from wastewater.)

A: Get them into the solids…and into soils…

…because healthy soils (e.g. enriched with biosolids and/or other organic amendments) are the best media for degrading most microconstituents.

"These terrestrial systems have orders of magnitude greater microbial capability and residence time to achieve decomposition and assimilation compared with aquatic systems."

– Overcash, Sims, Sims, and Neiman, 2005

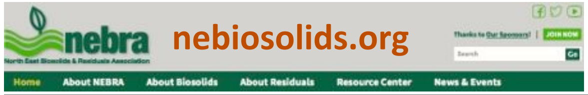
What biosolids managers can do…

Focus on biosolids quality.

Source reduction works. Enforce industrial pretreatment. Support phase-outs of persistent MCs.

Year	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
1973	33	712	700	1,261	148	2,031
1983	12.5	360	361	421	79	1,701
1993	7.3	209	764	225	51	1,444
2000	4.2	115	566	178	53	1,619

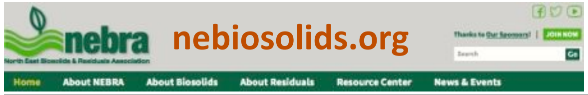
Philadelphia Water District biosolids quality over time, courtesy of Bill Toffey.



What biosolids managers can do…

Focus on biosolids quality.

- Support education about drug disposal: http://www.nodrugsdownthedrain.org/NoDrugs/
- Support drug take-back programs. http://www.deadiversion.usdoj.gov/drug_disposal/takeback/
- Test biosolids product(s) for most common or concerning microconstituents, just so you know. Compare your results to published results.



What biosolids managers can do…

Focus on biosolids quality.

- When possible, use treatment processes that degrade MCs: biological processes are most effective.
- Use multiple processes, e.g. anaerobic digestion followed by composting & application.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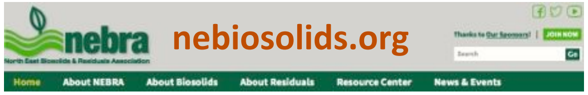
What biosolids managers can do…

Use Best Management Practices.

- Apply at agronomic rate*, which limits total mass of MCs while providing optimum level of benefits.
- Maintain setbacks from surface & groundwater*, which keeps MCs out of the more sensitive aquatic environment.
- Apply to aerated soils and incorporate when possible, which aids decomposition of MCs and avoids direct ingestion.
- Use the same BMPs for manures/other residuals.
- Follow research & update BMPs.



Thanks for… your invitation, your attention, & your questions and comments.

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