

Dioxins, Furans, Dioxin-Like PCBs (DL-PCBs) and Polybrominated Diphenyl Ethers (PBDEs) in Sewage Biosolids

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Purpose of the Presentation

- To present the results from the 2004 survey of 25 Sewage Treatment Plants (STPs) for dioxins, furans and DL-PCBs (PBDEs) in biosolids.

Outline of Presentation

- Background

Nutrient Management Act, 2002

Biosolids

Dioxin, Furans, DL-PCBS and PBDEs

- Experimental Plan
- Results of Survey
 - *other media and persistent organic pollutants*
- Current & Future Initiatives

Nutrient Management Act (NMA), 2002

- The NMA establishes comprehensive, province-wide standards for the land application of materials containing nutrients.
- The NMA Ontario Regulation 267/03 establishes quality standards for all land applied materials including sewage biosolids, pulp and paper mill biosolids and livestock manure.
- Regulation focuses on the nutrient content, metals and pathogens.
- The ministry is participating in a number of research initiatives to assess potential contamination of water resources by biosolids use in Ontario agriculture.

Biosolids

- Biosolids are the solid by-product of the wastewater treatment that have been stabilized by one of several different processes (aerobic / anaerobic digestion).
- Non-stabilized solids produced during the wastewater treatment process are known as sludge.
- Approximately 150,000 tonnes of sewage biosolids are applied to agricultural soils annually. An additional 150,000 tonnes are either incinerated or land filled.

Dioxins, Furans and DL-PCBs

- Polychlorinated dibenzo-p-dioxins (PCDDs) and the polychlorinated dibenzofurans (PCDFs) are chlorinated, planar tricyclic aromatic hydrocarbons.
- Dioxins and furans are ubiquitous in the environment and have no known use. Found as by-products of combustion of organic materials, emissions, waste incineration and petroleum refining.
- Polychlorinated biphenyls (PCBs) are chlorinated compounds that have been used as coolants and lubricant in transformers.
- The WHO identified 12 PCBs as being similar toxicity to PCDD/Fs. All 12 DL-PCBs, and 17 PCDD/F congeners, have an assigned toxicity equivalence factor (WHO-TEF).

PBDEs

- Flame-retardant additives used in high-impact plastics, foams, textiles and as coatings on fabrics and furniture to slow the ignition and rate of fire growth.
- Commercial products consist predominantly of penta-, octa, and decabromodiphenyl ether (Penta-BDE, Octa-BDE and Deca-BDE) mixtures.
- There are 209 possible BDE congeners.
- Similar structure and physical properties as PCBs.

Environmental Fate of PCDD/Fs and DL-PCBs

- PCDD/Fs and DL-PCBs are stable chemically, physically, biologically and are lipophilic.
 - Tend to concentrate in organic material in soil. Not expected to leach from soil into water reservoirs.
 - Little capability for transfer from soil to the roots of vegetables.
 - Half life in soil is about 10 years.
 - Half life in the human body is about 6 years.
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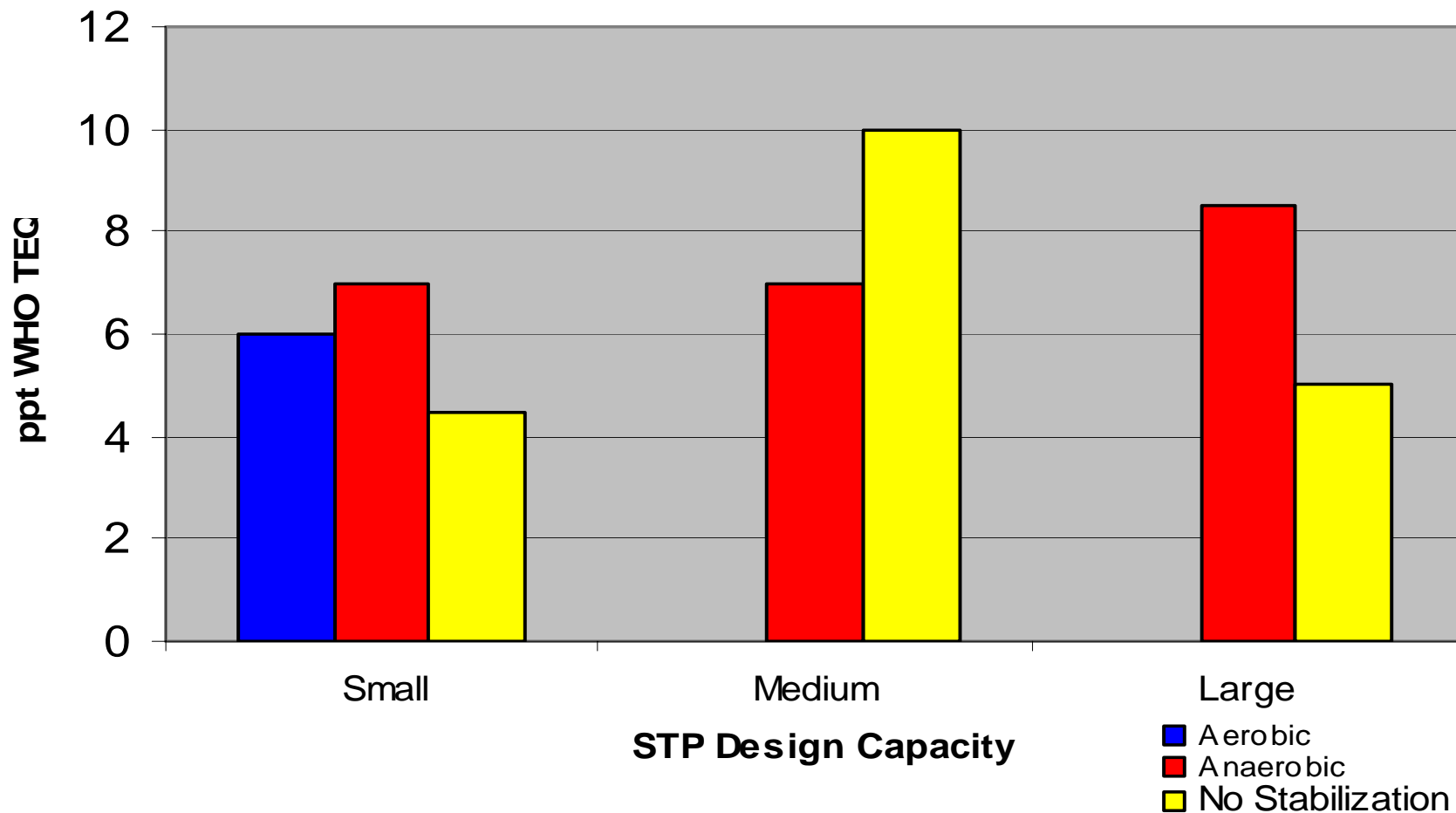
Environmental Fate of PBDEs

- Indoor air concentrations are 15 to 50 times higher than in outdoor air.
- Trace levels have been detected in surface waters of the Great lakes and connecting channels.
- Concentrations in sediments have rapidly increased since the early 1980s. The highest concentrations of PBDEs have been found in Lake Michigan and Lake Ontario.
- PBDEs have been found in human blood, serum, adipose tissue, breast milk, placental tissue and in the brain (doubling time of four to five years).

Experimental Plan

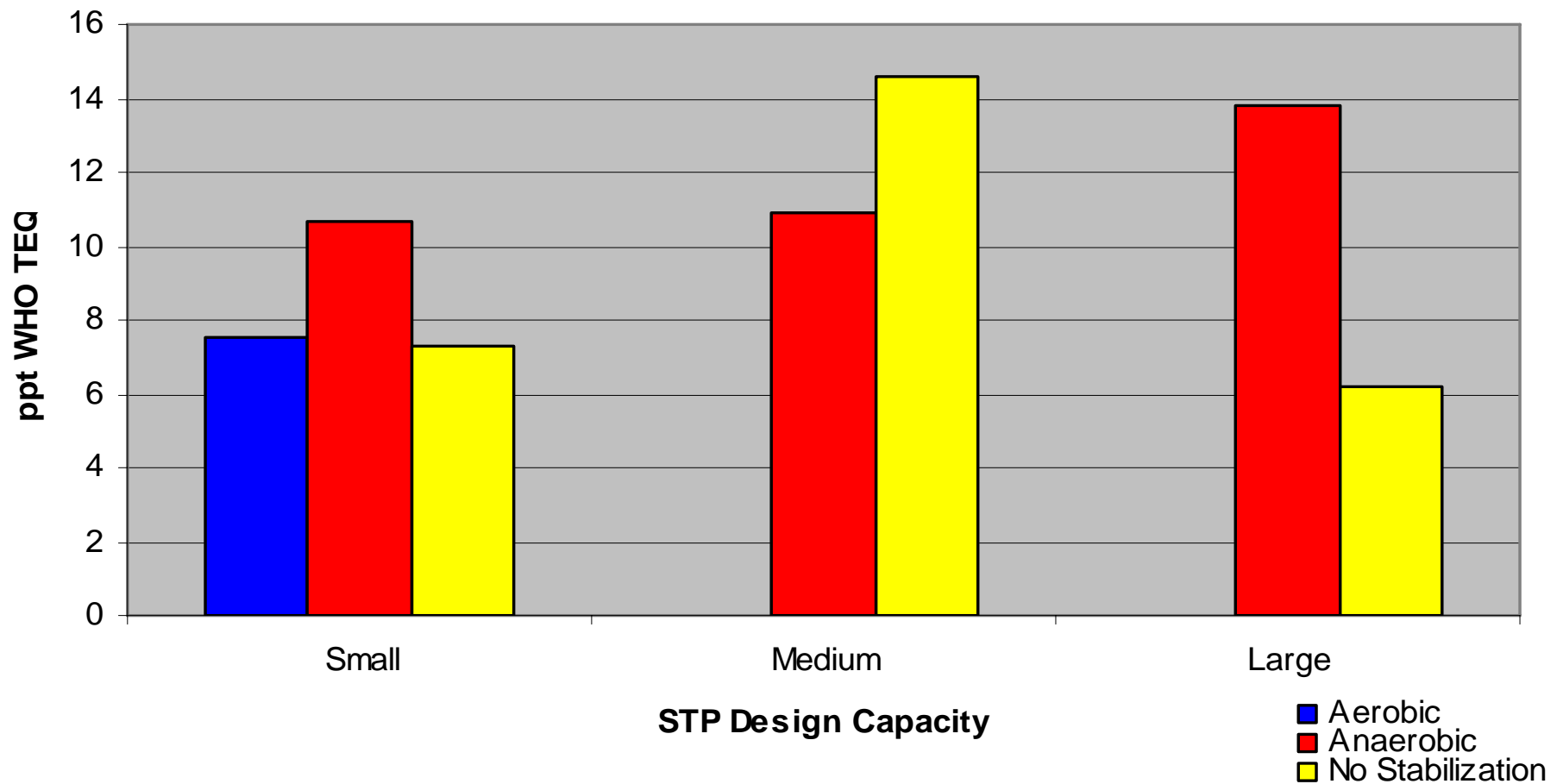
- 90 biosolid samples were collected from 25 STPs (Small, Medium, Large) in Ontario.
- Small STP – design capacity of 22,700 cubic meters per day or less (N=36).
- Medium STP - design capacity of greater than 22,700 cubic meters per day but less than 45,400 cubic meters per day (N=8).
- Large STP - design capacity of 45,400 or greater cubic meters per day or less (N=46).
- Samples were analyzed for dioxins, furans, dioxin-like PCBs, and PBDEs.

Results Dioxins & Furans



Results

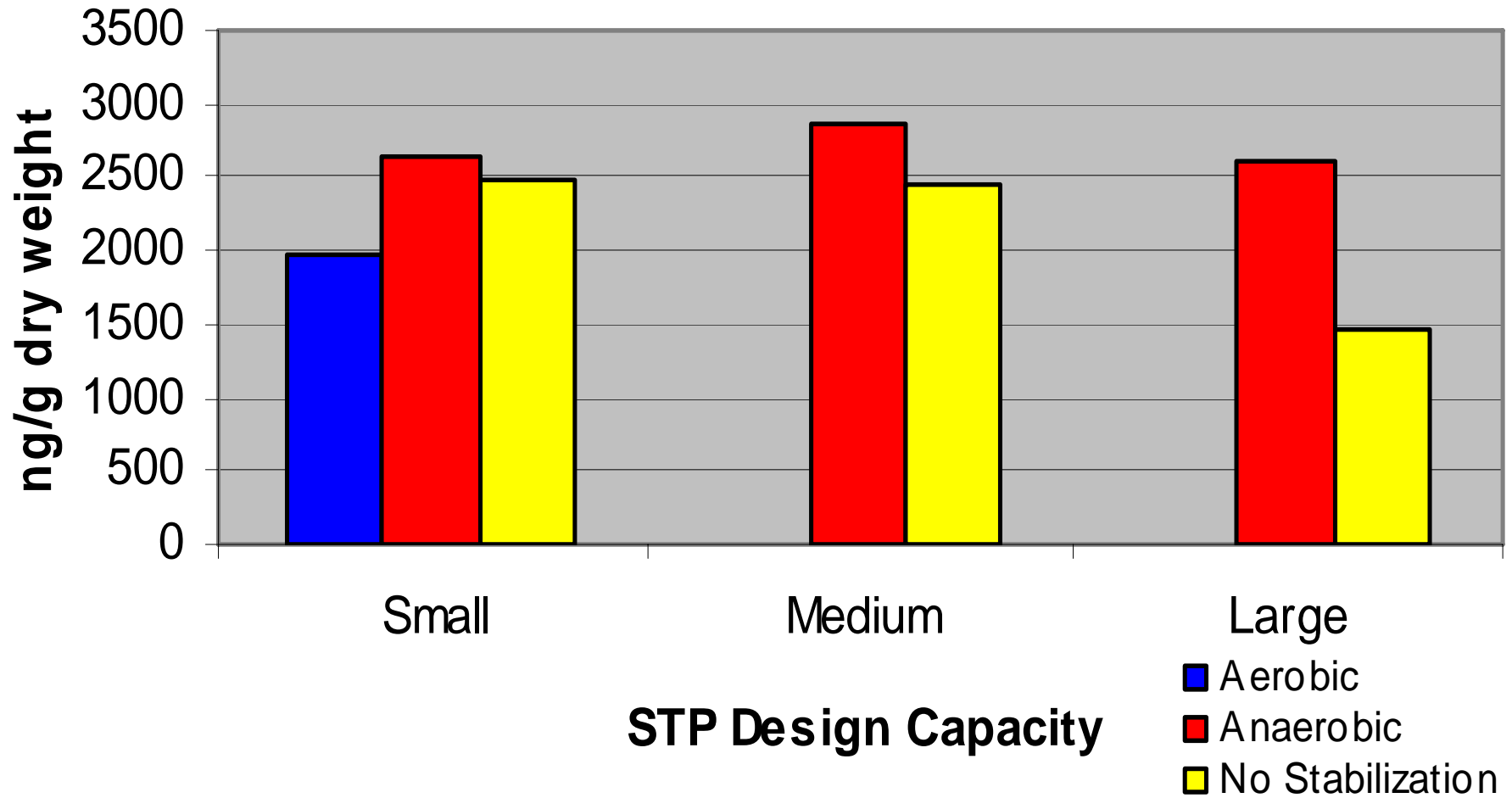
Dioxins, Furans and DL-PCBs



Results PCDD/Fs and DL-PCBs

- PCDD/Fs were detected in all biosolid samples (2 – 19 ppt WHO TEQ).
 - DL-PCBs were also detected in all samples (1.5 – 10 ppt WHO TEQ).
 - Neither the size of the STP nor the biosolids treatment processes used appeared to have an impact on the concentration of PCDD/Fs in biosolids
 - The contribution of DL-PCBs varied from 24%-34% of the total WHO TEQ for each sample.
 - The results from all 25 STPs ranged from 3 – 25 ppt WHO TEQ for PCDD/ F and DL-PCBs with a median value of 15 ppt WHO TEQ.
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Results PBDEs



Results - PBDEs

- PBDEs were detected in all biosolid samples. The median value for PBDE was 3000 ng/g (3 ppm).
- Congener dominance BDE 47, 99, 153 and 209.
- Neither the size or the biosolids treatment significantly impacted the concentration of PBDEs in biosolids.
- PBDEs concentrations in Ontario sewage biosolids are consistent with those in the United States (approximately 3 ppm), and exceed those in European biosolids by 10-100 fold.
- Based on annual sewage biosolids generation and land application, it is estimated that sewage biosolids potentially contribute about 0.5 tonnes of PBDEs to agricultural land and one tonne per year to the environment.

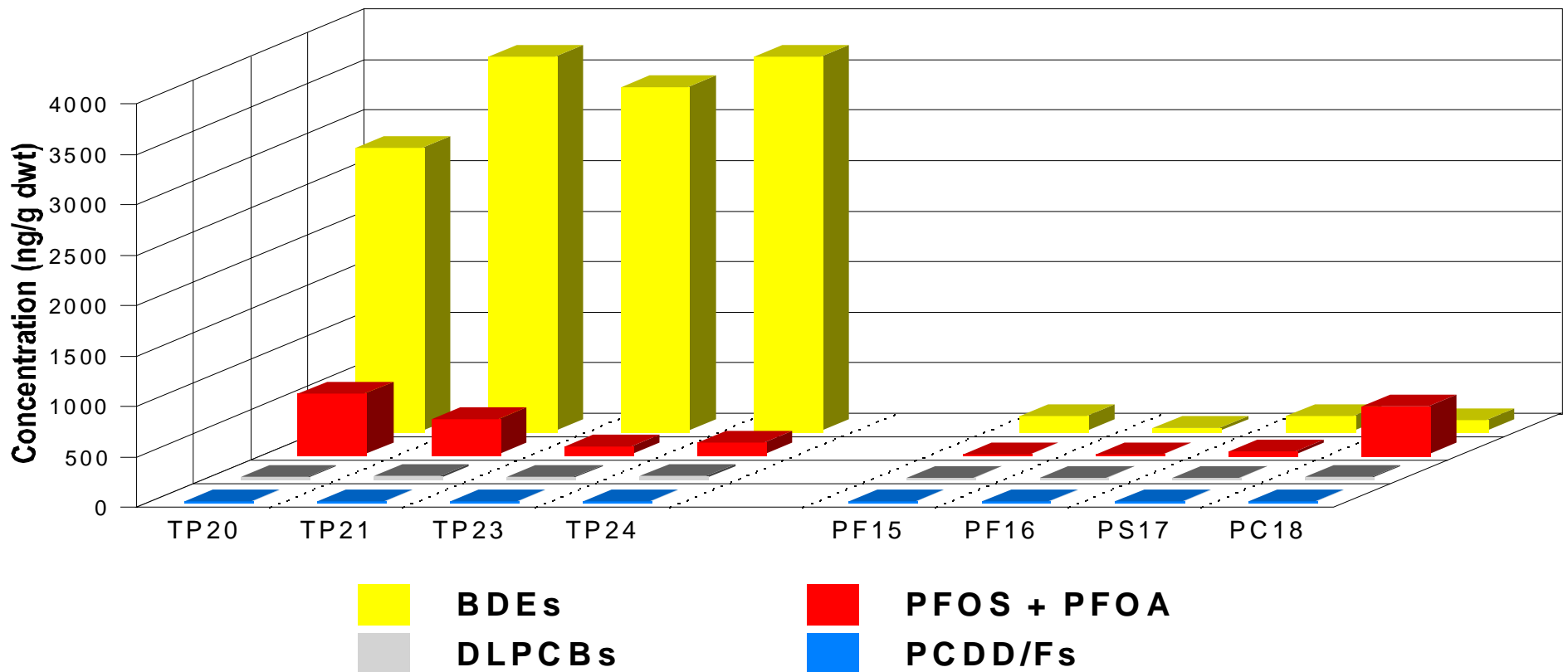
Dominant BDE congener in Different Land Applied Materials

Congener	Sewage Biosolids N=12	Sewage Biosolids N=3	Paper Biosolids N=4	Manure N=6
47	330-730	490-540	5.4-12	<1-2.6
49	12-89	13-15	0.13-0.39	<0.03-0.53
85	11-39	26-35	0.15-.04	<0.06
99	370-910	630-690	4.2-11	<2
100	68-150	70-90	0.79-2.1	<0.03
138	3.0-9.6	6.5-8.5	<0.04-0.14	<0.1
153	41-100	65-69	0.41-1.2	<0.08
154	31-81	48-52	0.25-0.69	<0.07
183	5.0-25	19-25	0.52-1.4	<0.1
209	460-2300	1500-2300	51-130	<4-12
Totals	1300-4500		70-160	0.1-12

Results in ng/g

Persistent Organic Pollutants (POPs) Comparison

Biosolids – 2004 POPs Results



Conclusions

- PCDD/Fs, DL-PCBs and PBDEs were detected in all sewage biosolid samples.
- The results for PCDD/Fs and DL-PCBs ranged from 3-25 ppt WHOTEQ with a median value of 15 ppt WHOTEQ.
- Neither the size biosolids treatment process appeared to have an impact on the concentrations.
- PBDEs > 1000-3000 times PCDD/Fs - total congener concentrations.
- Based on annual sewage biosolids generation and land application, it is estimated that sewage biosolids contribute about 0.5 tonnes of PBDEs to agricultural land.

International Regulatory Initiatives

- EC /HC released a draft scientific screening assessment of PBDEs in the Canada Gazette (2004).
 - highly persistent, bioaccumulative and subject to long-range transport
 - US EPA has reached a voluntary agreement with Great Lakes Chemical Company to cease production of penta-BDE & octa-BDE.
 - California, Washington, Maine, Massachusetts, Michigan, Hawaii and New York, have enacted or considered legislation to regulate PBDEs.
 - EU recently banned the production of octa-BDE and penta-BDE (2003), and is considering banning a third formulation, deca-BDE.
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MOE Future Initiatives

- Development of a model to predict loadings of PBDEs to soil from atmospheric deposition and application of biosolids on agricultural land.
- Determination of BMPs for the land application of sewage biosolids. Samples to be analyzed for PBDEs, Pharmaceuticals and Personal Care Products, Musks and Fluorinated Surfactants.
- Identification and quantification of PBDEs, Fluorinated Surfactants and Poly chlorinated Naphthalenes in different types of Pulp and Paper Mill Biosolids.
- Development of BMP to fulfill science gaps identified for the development of regulations developed under the *NMA* and the *Source Water Protection Act* (Bill 43).

Questions?

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