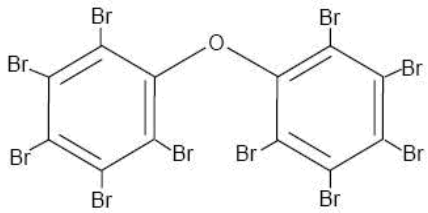
TETRA TECH

complex world | CLEAR SOLUTIONS™

Polybrominated Diphenyl Ethers as a Source of Contamination from Landfills



Monica Danon-Schaffer, PhD. P.Eng.

October 2010

Topics of Discussion

- The Problem
- Why do we Care?
- Brominated Flame Retardants (BFRs)
- Toxic Chemicals
- Polybrominated Diphenyl Ethers (PBDEs)
- Sources to Environment
- PBDEs in landfills and leachate
- Canadian Arctic
- Modelling
- Conclusions

What is the problem?

Brominated Flame Retardants (BFRs)

- Polybrominated diphenyl ethers (PBDEs) belong to BFR group
- Applied to ~2.5 million tonnes polymers/year
- Added to polymers to enhance flame retardancy
- Thermally stable, low cost, readily available
- Lipophylic, bioaccumulative, persistent, LRT
- Endocrine disrupters

Why do we care?

- Persistent, bioaccumulative, long-range transport (PBT), lipophilic
- Find their way into food chain and human population
- Endocrine disrupting chemicals
- Concentrations in environment have been increasing since 1970s
- Leach out of products; end up in sewage

Toxic chemicals – human health

- **Reproductive Hormone Effects**
  - Meeker et al., 2009 –

    Decrease in Androgens and LH; Increase in FSH and Inhibin
  - Meijer et al, 2008

    Decrease in Testosterone

- **Reproductive Effects**
  - Eskenazi et al., 2009

    Low Birth Weight; Altered Behaviours
  - Harley et al, 2010

    Increased time to pregnancy

- **Decreased Sperm Quality**

  - Akutse et al, 2008

- **Diabetes**

  - Lim et al, 2008
  - Turyk et al, 2009 (only in hypothyroid subjects)

- **Thyroid Homeostasis**

  - Herbstman et al, 2008 – decrease in TT4
  - Turyk et al, 2007 – elevated T4
  - Meeker et al, 2009 – elevated T4, TBG
  - Dallaire et al, 2009 -Elevated T3 ~BDE47
  - Eskenazi et al, 2009 – Low TSH

Toxic chemicals – animal health

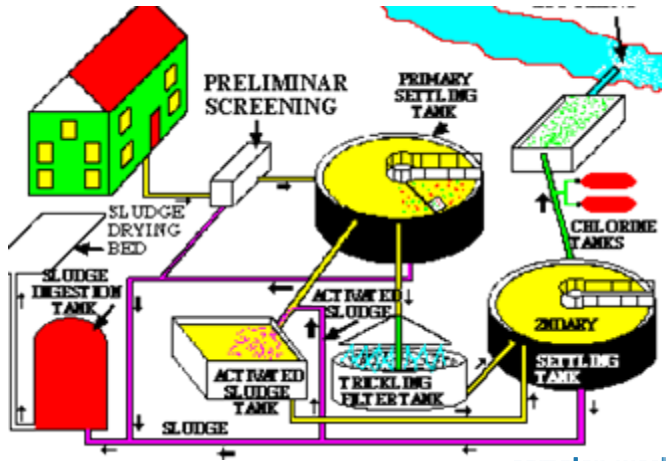
- Reproductive
  - Abnormal gonadal development, reduced ovarian follicles, reduced sperm count
- Neurological
  - Decreased memory, learning deficits, altered motor behavior, hyperactivity
- Thyroid hormone action
  - Interference
- Endocrine disorders
  - Obesity and diabetes
- Cancer

Sources of PBDEs to the Environment

- **Electronic waste (*e-waste*)**

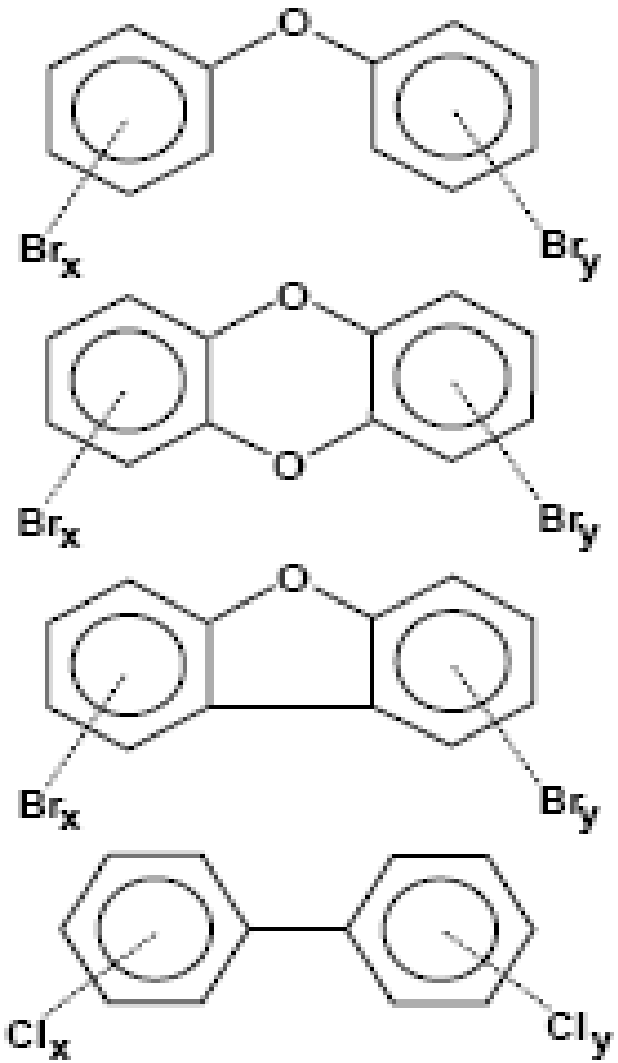
- **Consumer products (*Non electronic waste solids or NeWS*)**

- **Wastewater or sewage treatment plants (*STPs*)**



E-waste – Not in my backyard!

Compounds with similar structures



Polybrominated Diphenyl Ether (PBDEs)

Polybrominated Dibenzo-p-dioxin (Dioxin)

Polybrominated Dibenzo-furan (Furan)

Polychlorinated Biphenyl (PCBs)

Polybrominated Diphenyl Ethers (PBDEs)

- Used globally as flame retardants
- Highly toxic, persistent; endocrine-disrupting chemicals, with potential for long-range transport
- Persistent organic pollutants (POPs)
- Two of the three commercial products added to Stockholm Convention (2009)
- PBDEs added to products to reduce ignition; thought to save lives

Polybrominated Diphenyl Ethers (PBDEs)

- PBDEs spread globally
  - Polar regions surpassing “classical” POPs (e.g. dioxins, furans, PCBs)*
- Rising concentrations of PBDEs in environment
- Ecological and human health risks require early implementation of best-management practices to contain PBDEs

*(12-fold with a doubling period of 1.6 years)

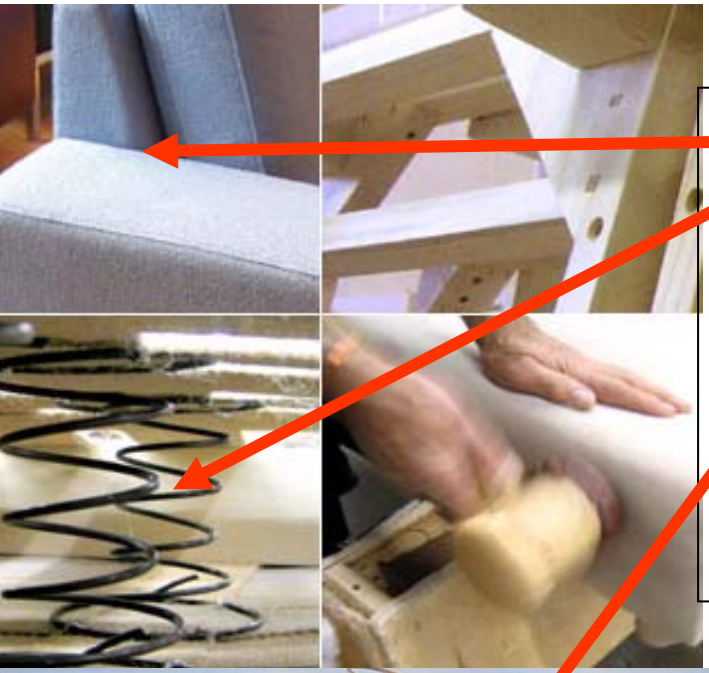
PBDEs in the Environment

- Major source of PBDEs
  - Plastics in electronic equipment
  - Polyurethane foam
  - Textiles
  - Vehicle interiors
- Most electronic equipment discarded, ending up in landfills as e-waste
- Use of computer equipment expanded by orders of magnitude since the 1980s, making e-waste fastest growing waste stream

PBDEs in the Environment

- PBDEs still entering disposal or end-of-useful life phase
- Concern with respect to release of PBDEs into environment
  - Leaching from landfills
  - Incineration
  - Sewage treatment effluent
  - Applied as biosolids

PBDEs in Landfills – possible sources

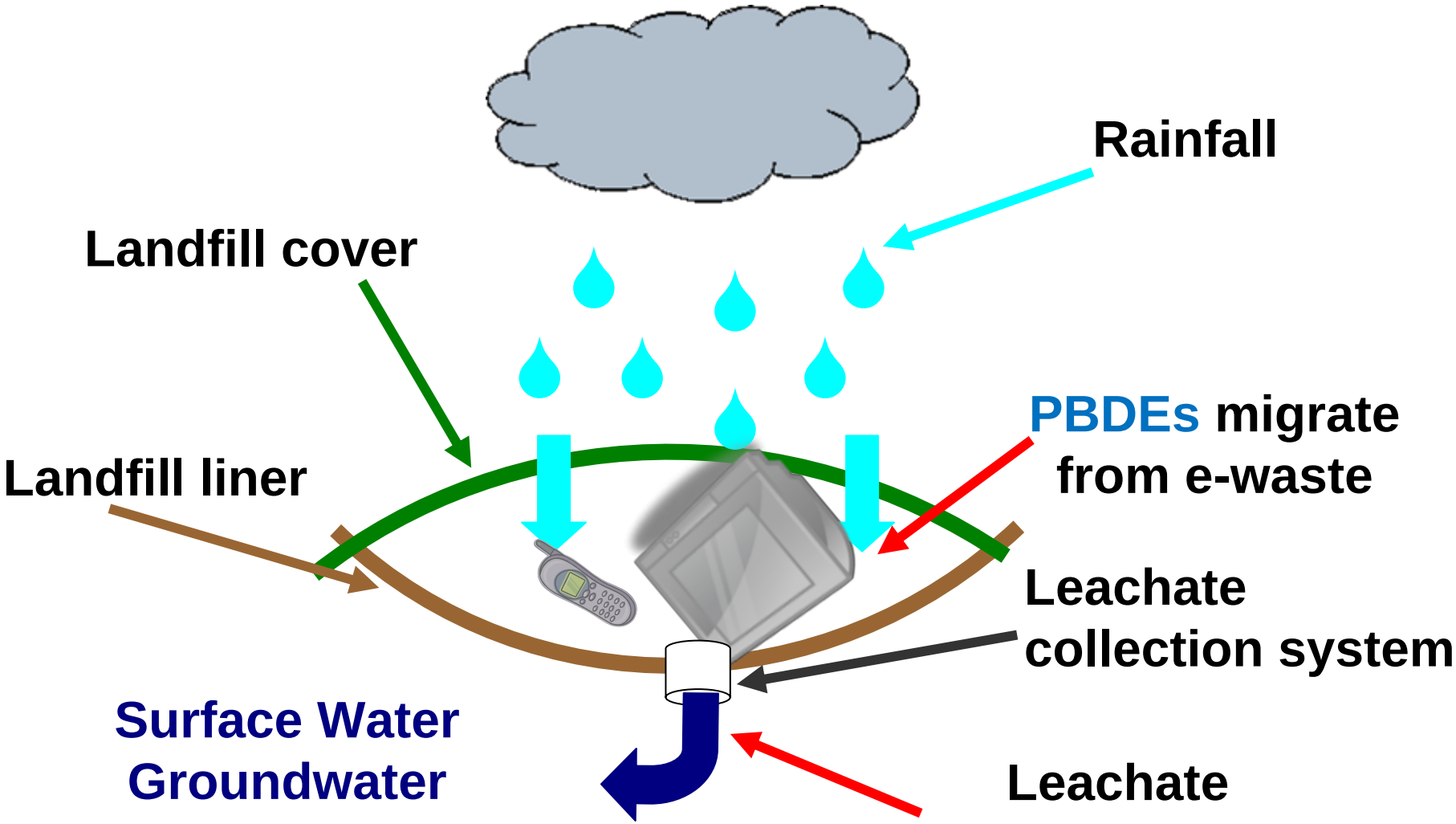


- upholstery
- mattresses
- electronics
- carpet padding
- vehicle parts
- auto shredder residue

Source: Alex Stone, WA Dept of Ecology


Where should the flame retarded furniture go?

E-waste in Typical Landfills



Source: K. Bush & G. Webster, 2009

What ends up here?

Well....

- Canadian federal government discards ~ 2,250 tonnes/yr e-waste (2008)
- >350,000 mobile phones discarded daily in US (2009)
- >130,000 computers discarded daily in US (2009)
- 2.6 million tonnes e-waste in US to landfills (2007)
- ~400,000 units e-waste enter Nigeria/mo; ~ 75% scrap (Origin: ~45% US, ~45% EU, ~10% other)
- ~ 20-50 million tonnes e-waste generated/yr worldwide (UNEP, 2005)
- ~50-80% of e-waste collected for recycling exported from US

and more ....

- Long-term diffuse emissions and leaching from landfills are possibilities
- Electric and electronic equipment (EEE) waste stream of concern because historically had high percentage of PBDEs
- Recent reduction in BFRs incorporated into new computers not been completely eliminated
- Legacy of historical waste remains

lots of them....

- PBDEs migrate from landfills into ground and surface water
- Landfills considered main entry for municipal wastes containing PBDEs
- Few studies evaluate fate of PBDE-containing products in landfills
- Once PBDEs enter a landfill, they may volatilise, leach and /or diffuse into different environmental compartments

and....

- Limited info on fate in waste disposal streams (landfills, sewage treatment plants, incinerators)
- Discarded plastics subject to ultra-violet radiation, thermal stress, grinding and other degradation processes at end of their useful lives
- Leach from plastic when added to polymer at moulding stage

An AHA moment....

PBDEs are so persistent and widespread that if we stopped manufacturing them today, it would take ~100 years to virtually eliminate them from waste in landfills

More ending up in landfills

- 6.6 million tonnes e-waste discarded from EU (2009)
- 70% of world's e-waste processed in China (2009)
- ~100 million electronic goods discarded/yr in UK; weight = 2,400 jumbo jets
- 130 million cell phones thrown out worldwide/yr (UNEP, 2007)

Canadian Tire of the North

Canadian Arctic


Landfill in Northern Canada

Landfills/dumpsites in Canada's North

- Assessed to identify local sources of PBDEs distinct from long-range atmospheric deposition
- First study in Canadian North to investigate PBDE congener patterns in aqueous media (leachate, effluent and background water), and in soil
- Investigated how PBDEs enter and transfer among landfill leachates and soils
- Provided better understanding of PBDE leachability from e-wastes, other PBDE-containing products, and mobility in soils

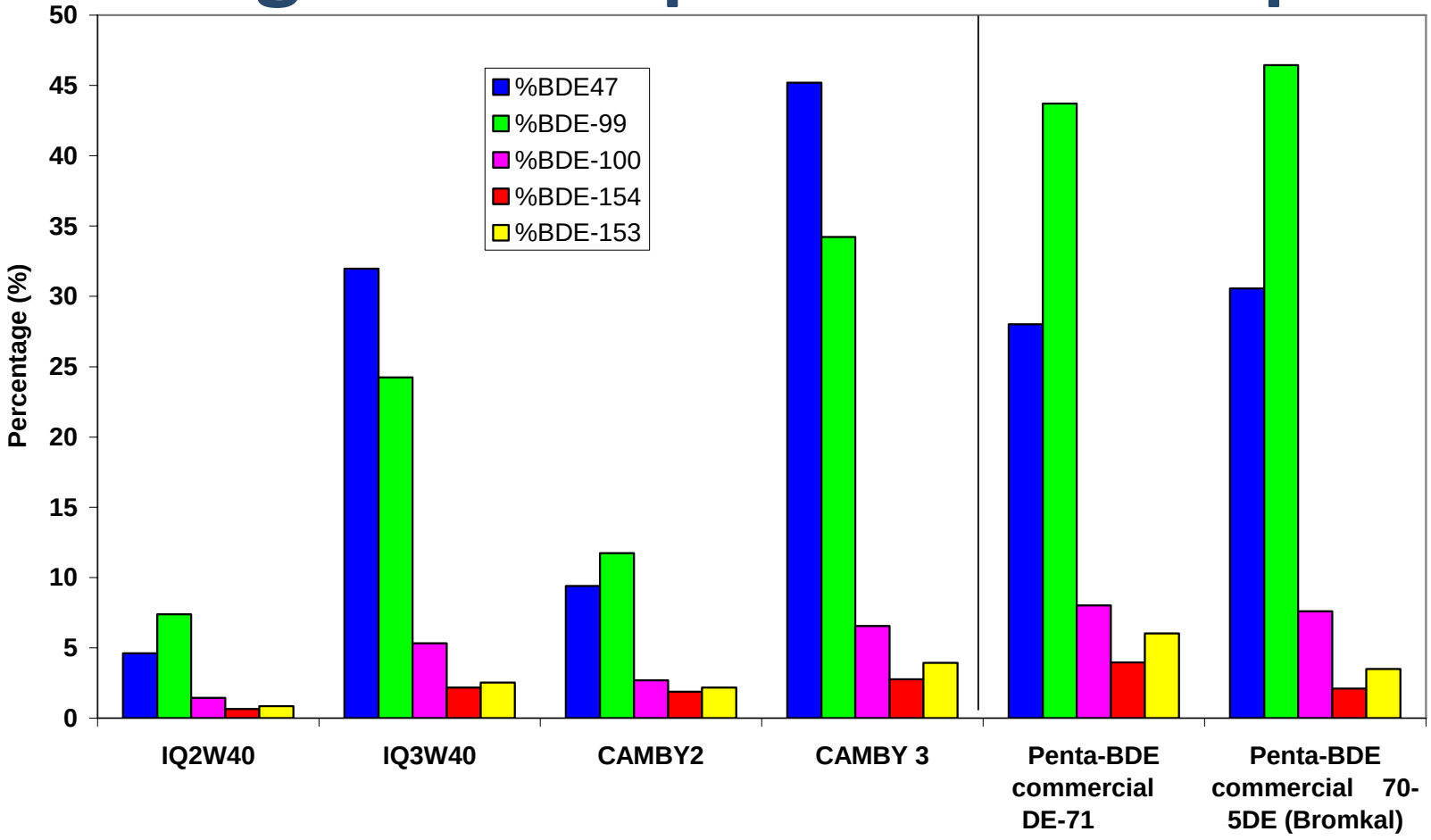
Major BDE congeners found in surface soil samples from the Canadian North (pg/g, dw)

Location sampled	Description	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-206	BDE-207	BDE-209	Total PBDEs§	BDE-209 as % of Total PBDE	BDE-47 / BDE-99	BDE-47 / BDE-100
YELL01	Old dumping area of landfill; 2 samples averaged**	528	847	175	110	72	101	568	612	20,816	24,418	85.2	0.6	3.0
YELL02	White goods area of landfill; 2 samples averaged**	132	183	37	27	16	33	43	71	1,322	2,010	65.8	0.7	3.6
YELL03	Current landfill working area**	160	138	33	10	9	7	13	12	449	888	50.5	1.2	4.8
YELL04	2 km downstream from landfill boundary; **background***	99	62	14	5	3	8	11	24	666	903	73.8	1.6	7.1
IQ2W40	West 40 landfill (current)**	35,448	56,663	11,056	6,608	5,070	4,740	19,764	7,550	597,263	766,494	77.9	0.6	3.2
IQ3W40	West 40 landfill (current)**	27,743	36,003	7,910	3,755	3,238	999	ND	ND	42,499	148,617	28.6	0.8	3.5
IQ4W40	West 40 landfill (current)**	55	22	8	2	1	2	ND	ND	2,143	2,313	92.7	2.5	7.1
IQ6	Former military dump end of old runway**	71	27	8	2	1	6	47	32	2,295	2,502	91.7	2.6	8.6
IQ7	Former military scrap from 1940s**	191	295	73	34	29	33	34	50	960	1,810	53.0	0.6	2.6
IQ2	Apex flats, in tidal zone ~400m from shore; **background***	109	38	11	2	2	4	21	10	890	1,102	80.8	2.9	9.6
CAMBY2	Sewage effluent drainage area**	5,139	6,359	1,462	1,169	1,023	813	947	1,267	25,901	54,478	47.5	0.8	3.5
CAMBY3	Municipal dump**	26,648	42,364	8,124	4,858	3,429	1,361	825	1,040	29,063	133,659	21.7	0.6	3.3
CAMBY5	Downstream of CAMBY2, prior to ocean discharge**	2,231	2,495	531	313	297	241	664	571	14,315	24,849	57.6	0.9	4.2
CAMBY6	Metal dump, auto and other vehicle scrap, etc.**	8,569	15,344	3,332	47,350	11,970	199,344	2,531	32,457	14,275	514,874	2.8	0.6	2.6
CAMBY7	Mid town**	420	521	121	58	57	61	1,062	588	58,275	61,784	94.3	0.8	3.5
CAMBY8	Enroute to Mt Pelly 5km NE of town; **background***	100	62	16	7	5	33	99	89	4,011	4,540	88.3	1.6	6.3
Average: sites - tested (13) Average background (3)		8,256 102	12,405 54	2,529 14	4,946 5	1,939 4	15,980 15	2,038 40	3,404 33	62,275 1,634	133,746 2,182	46.6 74.9		

ND - non detect; * - background; ** - test sites

§ - Total of all detectable congeners, not just the 9 principal ones listed here.

Penta-BDE (DE-71, 70-5DE) commercial product relative fractions of principal congeners compared to soil samples



Mass balance modeling

Mass balance modeling of a landfill

- Mathematical rep of PBDEs transferring out from e-waste and other products in a landfill
- 3 subsystems:
  - e-waste
  - aqueous phase
  - non-e-waste solids or NeWS
- 24 ordinary differential equations (ODEs)
- To predict environmental fate of PBDEs in landfills

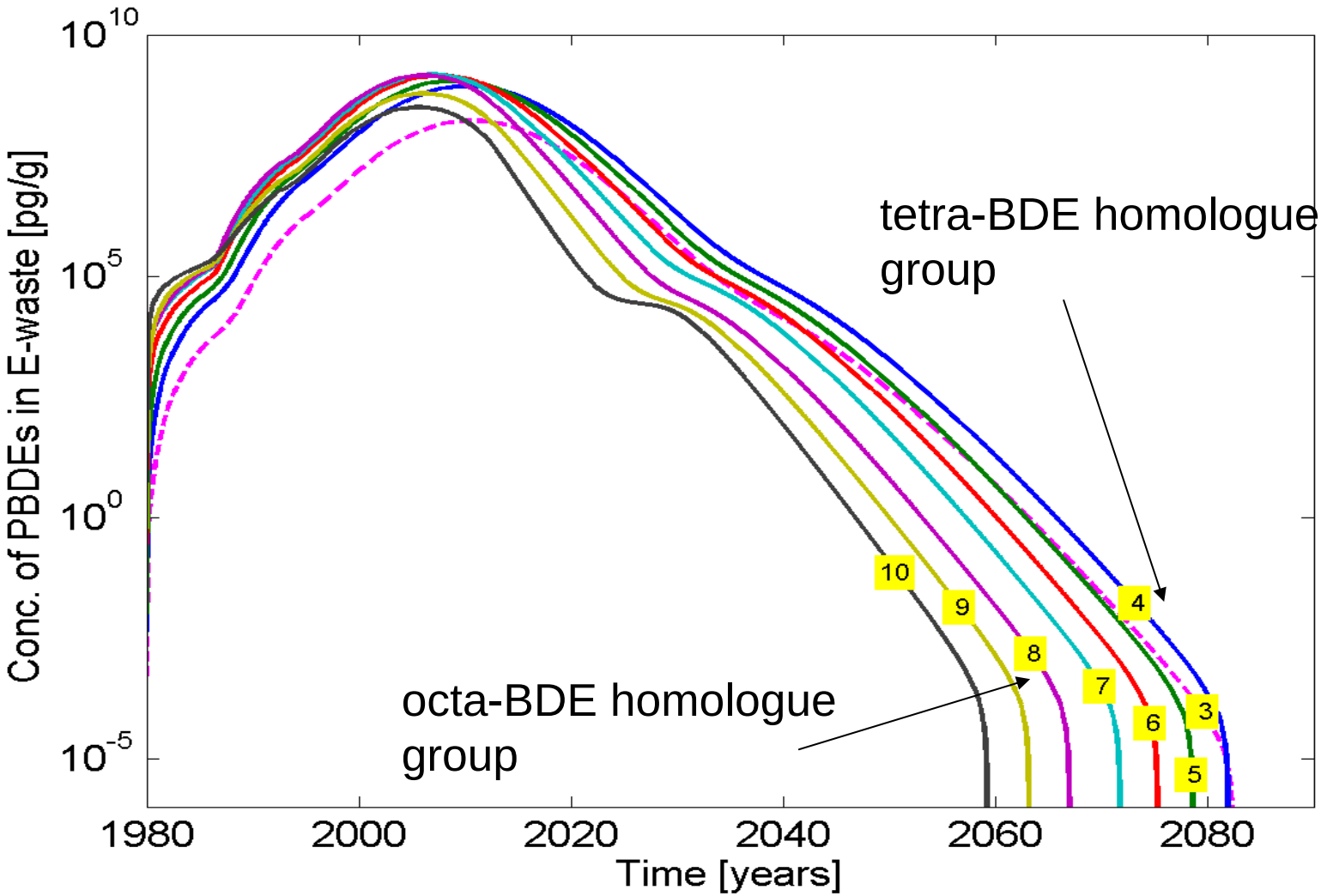
Mass balance modeling of a landfill

- **Assumptions:**
  - Well mixed
  - BDE congeners combined as homologue groups
  - Stepwise degradation of PBDEs
  - First order degradation kinetics
  - Reaction rate constants from half lives in literature
  - Mass transfer coefficients same as experimental data
  - NeWS subsystem assumed constant flow of soil, sand, bottom ash as landfill cover
  - Isothermal

Mass balance model: simulation scenarios

- Scenario 1
  - Past three decades
- Scenario 2
  - Future with PBDE ban and 16 sensitivity analysis
- Scenario 3
  - Future with all PBDE input terminated

Mass Balance Model Simulation: Scenario 2 – Future with PBDE bans



TETRA TECH

complex world | CLEAR SOLUTIONS™

Outcome

How PBDEs reach the environment, transfer from waste streams to air, water and soil, and transport to distant locations, such as Canada's far north

Conclusions

- Landfill leachate is source of PBDEs in environment
- Landfills in Northern Canada have lower PBDE concentrations than in Southern Canada
- Leachate sampled across Canada higher PBDE concentrations than reported from U.S., Japan, Sweden, and South Africa
- Determine process for leaching, degradation and spread of PBDEs from landfills

Conclusions

- Banning PBDEs today will take 70-100 years for virtual elimination in landfills
- PBDEs persist in environment for decades even if no longer manufactured
- Policy implications for end-of-life consumer products

TETRA TECH

complex world | CLEAR SOLUTIONS™

Questions?