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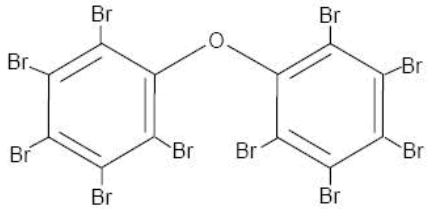
One More Geared Toward the PBDE Problem of E-Waste in Landfills



Monica Danon-Schaffer, PhD. P.Eng.

April 2011

Topics of Discussion

- The Problem – Why do We Care?
- Toxic Chemicals
- Brominated Flame Retardants (BFRs)
- Polybrominated Diphenyl Ethers (PBDEs)
- Sources to Environment
- Experiments and Modeling
- Future Work
- Conclusions

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
  - Eskenzai 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

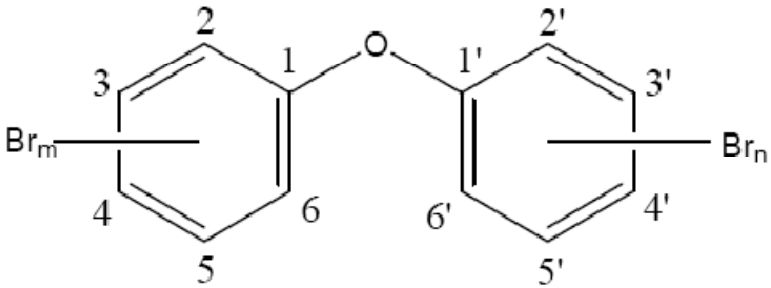
Brominated Flame Retardants (BFRs)

- 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

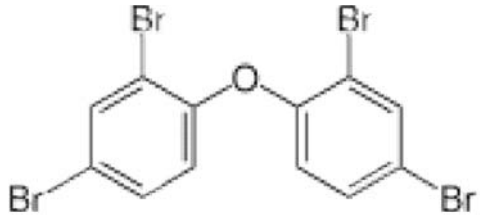
Polybrominated Diphenyl Ethers (PBDEs)

- PBDEs *added* to products to reduce ignition; thought to save lives
- Used globally as flame retardants
- Highly toxic, persistent; endocrine-disrupting chemicals, with potential for long-range transport
- PBDE *levels* in environment *increasing*; widespread in the world, including northern Canada
- Solid waste including e-waste *(~85%)* ends up in landfills
- Expensive and *challenging* to analyse
- Persistent organic pollutants (POPs), added to Stockholm Convention (2009)

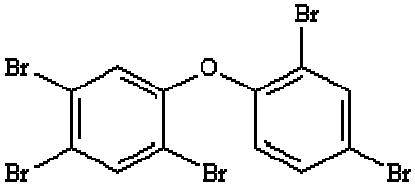
PBDE Structures



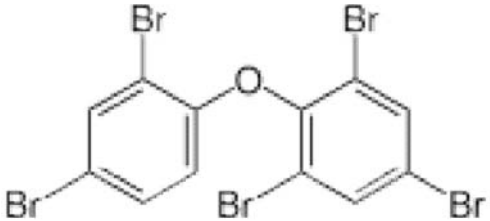
where m + n = 1–10



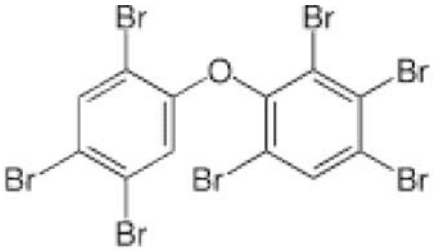
2,2'4,4'-tetra-BDE
(**BDE-47**)



2,2',4,4',5-penta-BDE
(**BDE-99**)



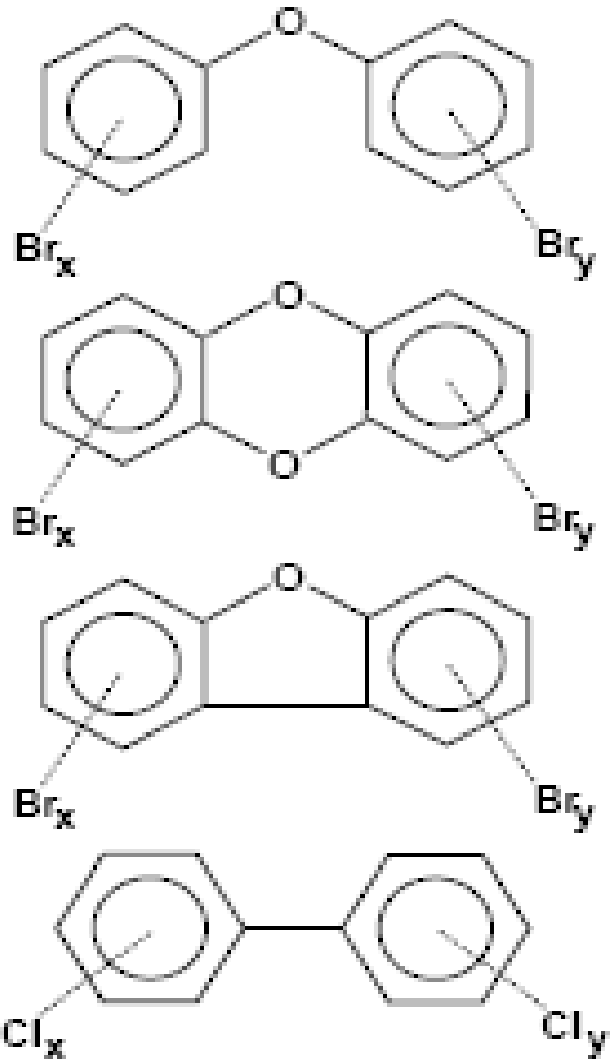
2,2',4,4',6-penta-BDE
(**BDE-100**)



hepta-BDE
(**BDE-183**)

deca-BDE
(**BDE-209**)

Compounds with Similar Structures



Polybrominated Diphenyl Ether
(PBDEs)

Polybrominated Dibenzo-p-dioxin
(Dioxin)

Polybrominated Dibenzo-furan
(Furan)

Polychlorinated Biphenyl
(PCBs)

Objectives

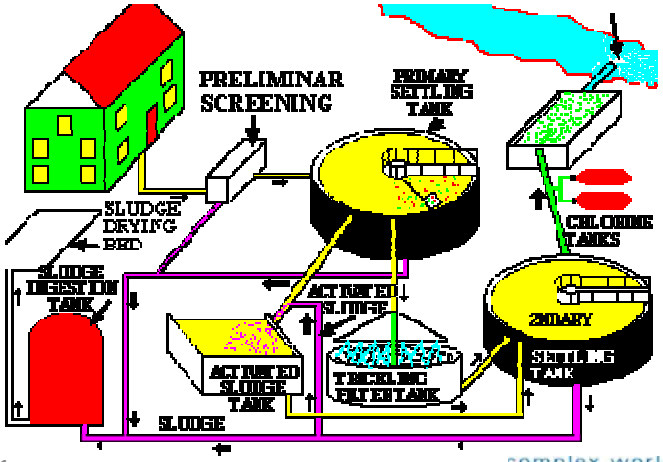
1. To measure *PBDE levels* in e-wastes, landfill leachates and soils *across Canada*
2. To *calculate mass transfer rates* and *mechanisms* of transfer of PBDEs from e-waste to landfill leachate;
3. To *model* the flow of PBDEs through a landfill;
4. To provide missing data required for *policy changes*

Sources of PBDEs to the Environment

- Electronic waste (e-waste)

- Consumer products (Non electronic waste solids or NeWS)

- Wastewater or sewage treatment plants (STPs)

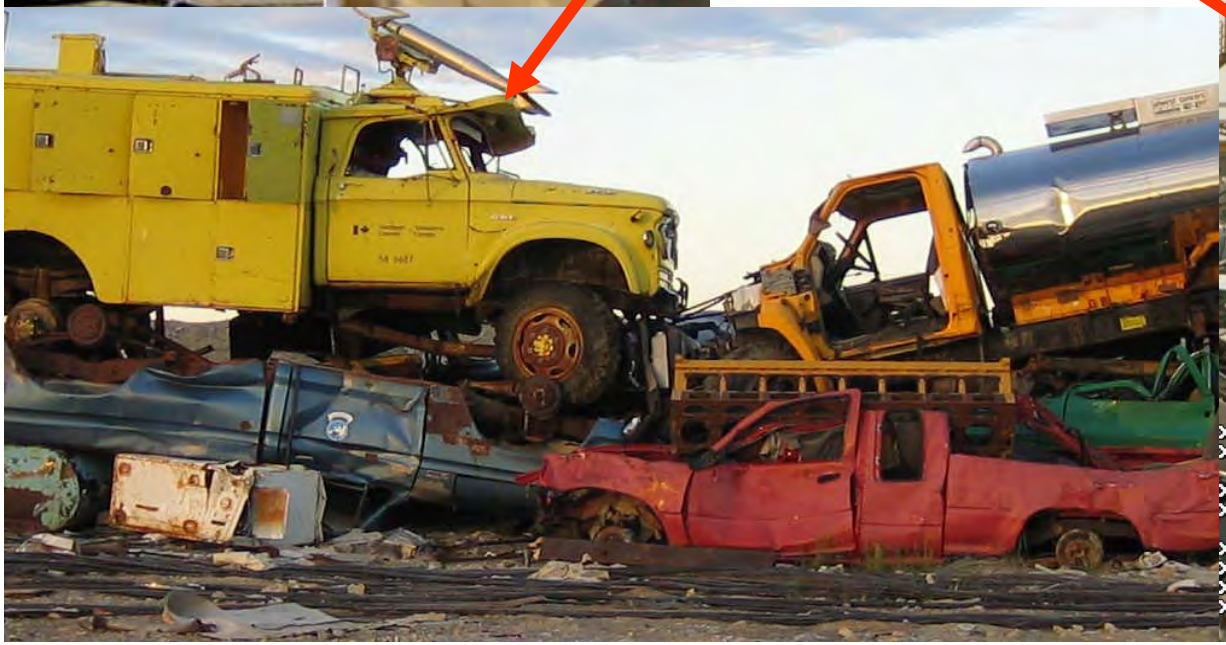


PBDEs in the Environment

- Major source of PBDEs
  - Plastics in electronic equipment
  - Polyurethane foam
  - Textiles
  - Vehicle interiors
- Concern with release of PBDEs into environment
  - Leaching from landfills
  - Incineration
  - Sewage treatment effluent
  - Applied as biosolids
- PBDEs still entering disposal or end-of-useful life phase from multiple consumer products
- Most e-waste still ending up in landfills/fastest growing waste stream

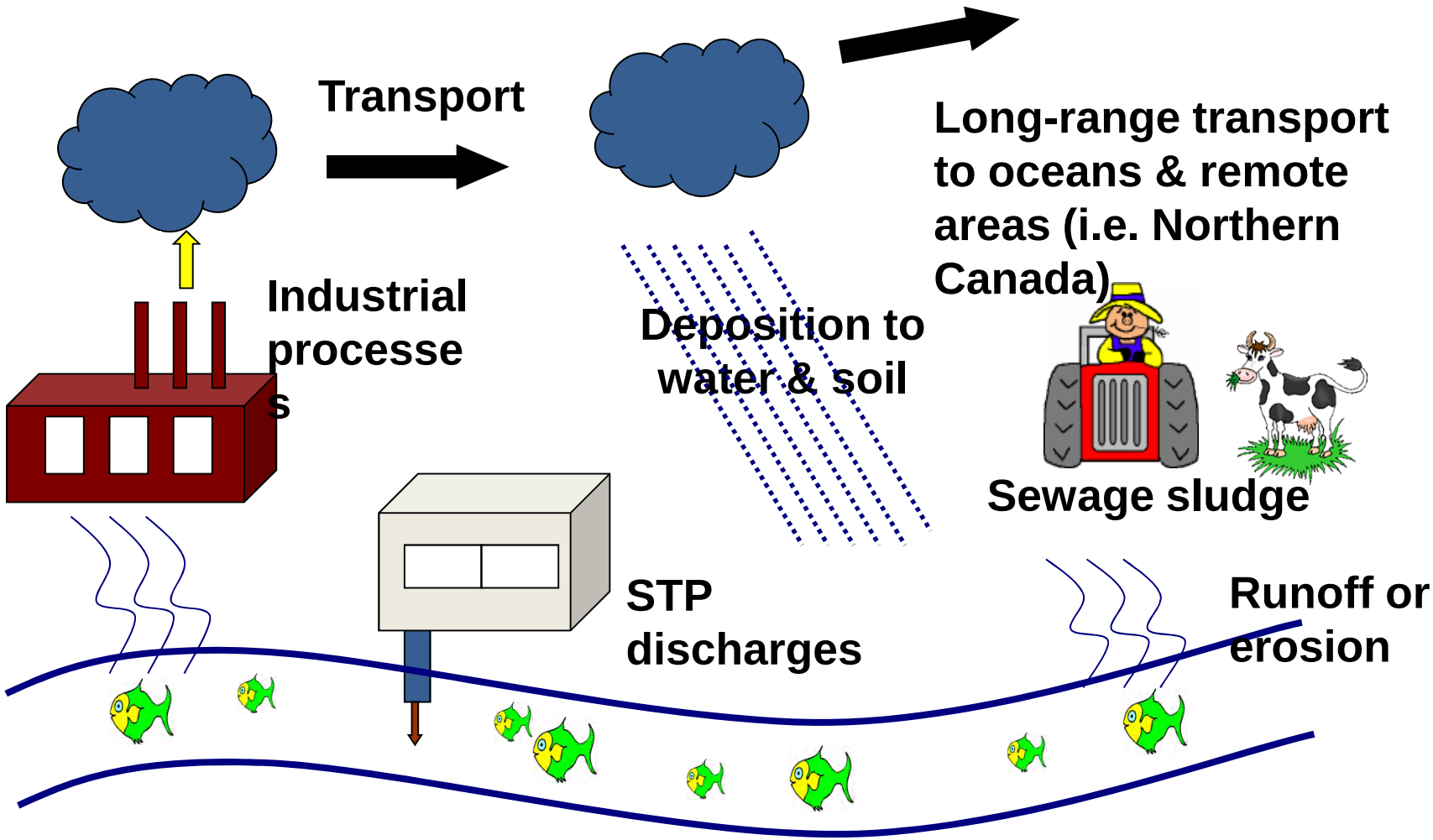
PBDEs in Landfills – Possible Sources

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



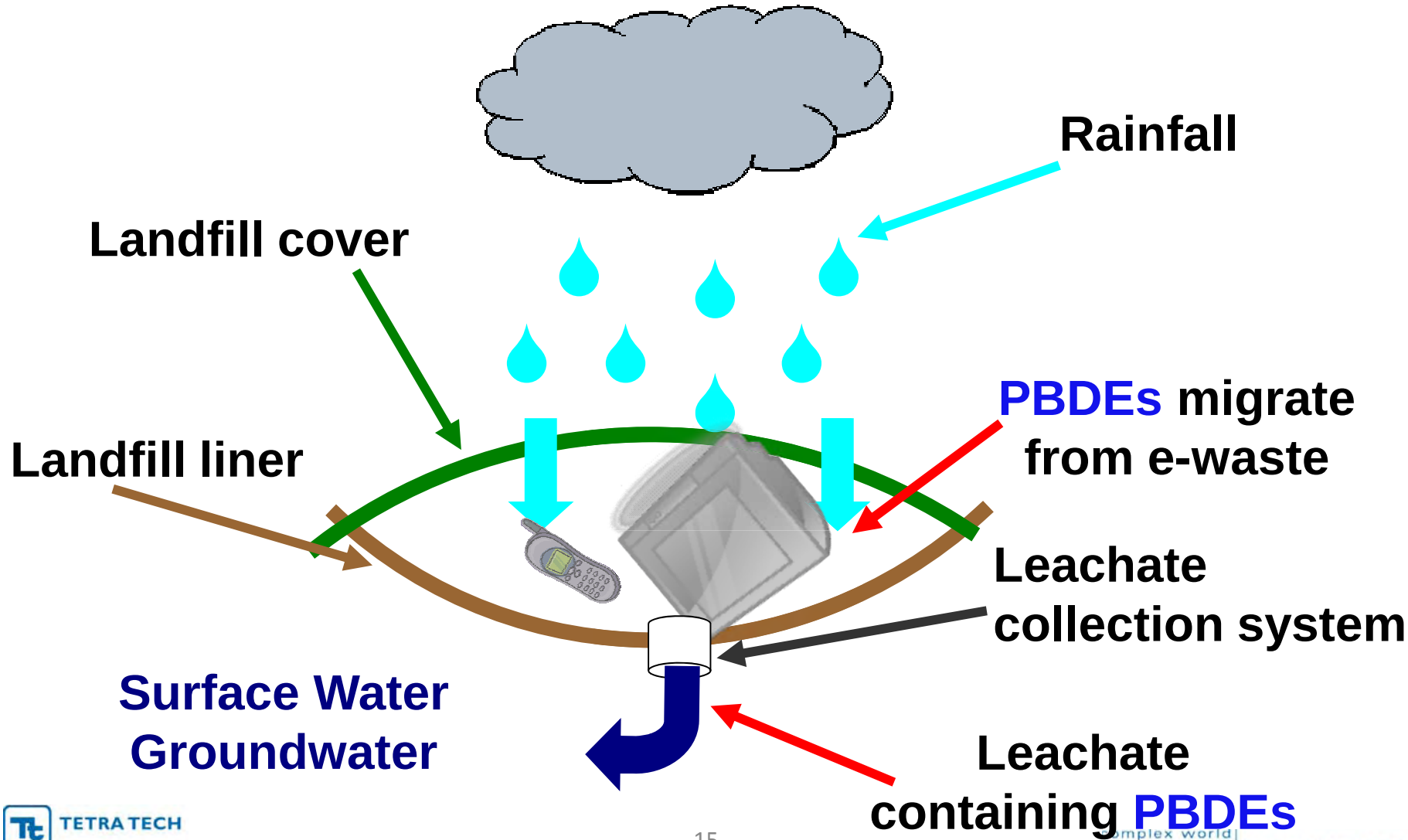
Source: Alex Stone, WA Dept of Ecology

Environmental Transport of PBDEs



Adapted from: McRandle (2005)

E-waste in Typical Landfills



Source: K. Bush & G. Webster, 2009

What ends up here?
7.29.04

Where should flame
retarded furniture go?

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)
- ~ 20-50 million tonnes e-waste generated/yr worldwide (UNEP, 2005)

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

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

The Research

1. Field sampling (Northern and Southern Canada)
   - Measure PBDE levels in soil, leachate, effluent, drinking water

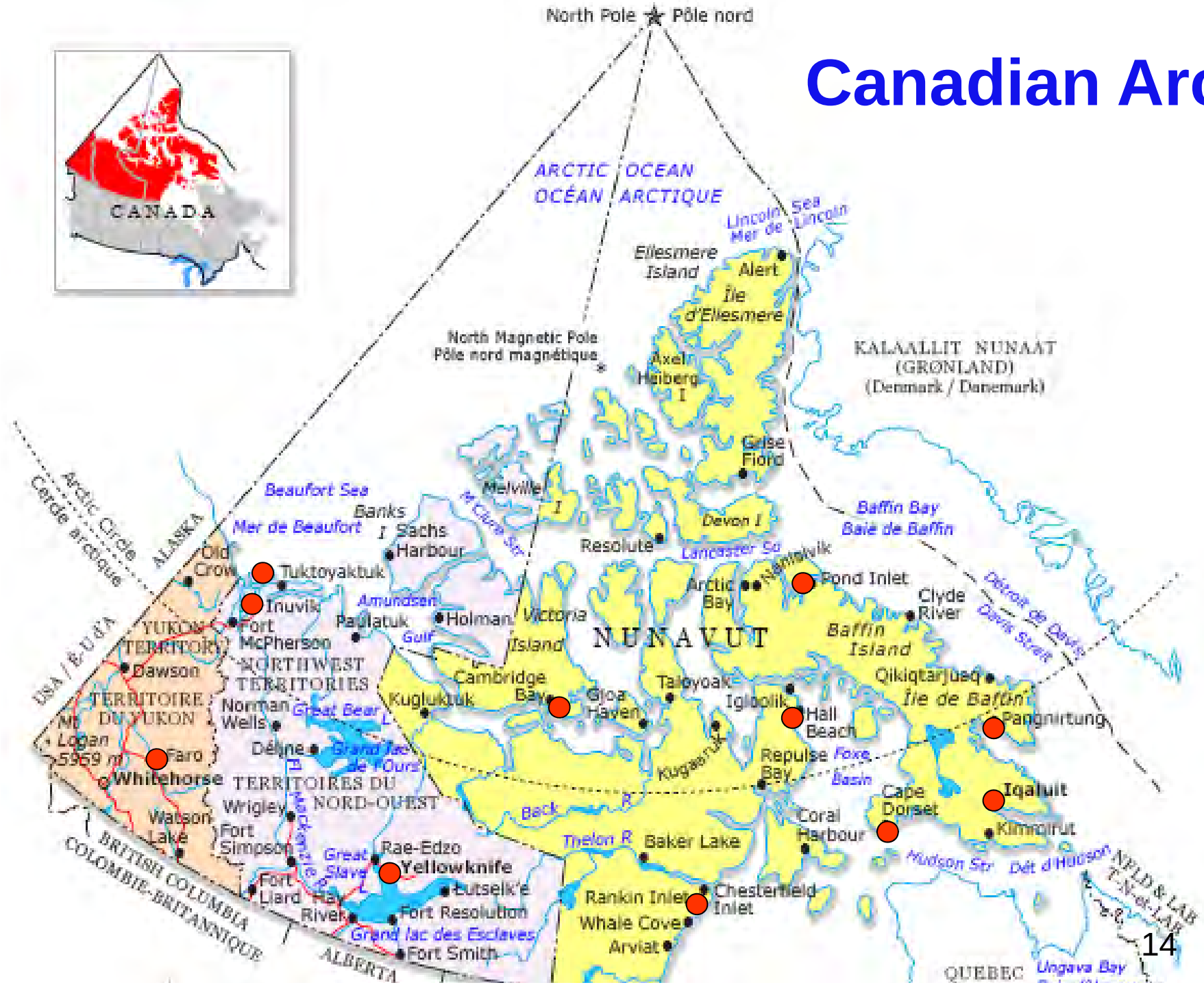
2. Lab experiments (UBC)
   - Determine rate of PBDE transfer from e-waste and other products (NeWS) into landfill leachate

3. Modeling (UBC)
   - Simulate PBDE flow from e-waste/NeWS in landfill
   - Test different policy scenarios

Canada-wide Results
Southern and Northern

- Total PBDE concentrations: BMDL-867,000 pg/L
- BDE-209: 60-90% of total principal BDEs
- TOC determined for 21 sites, correlated well when small subset used to compare
- PBDEs in leachate higher than other international jurisdictions

Canadian Arctic



Landfills/Dumpsites in Canadian Arctic

- 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

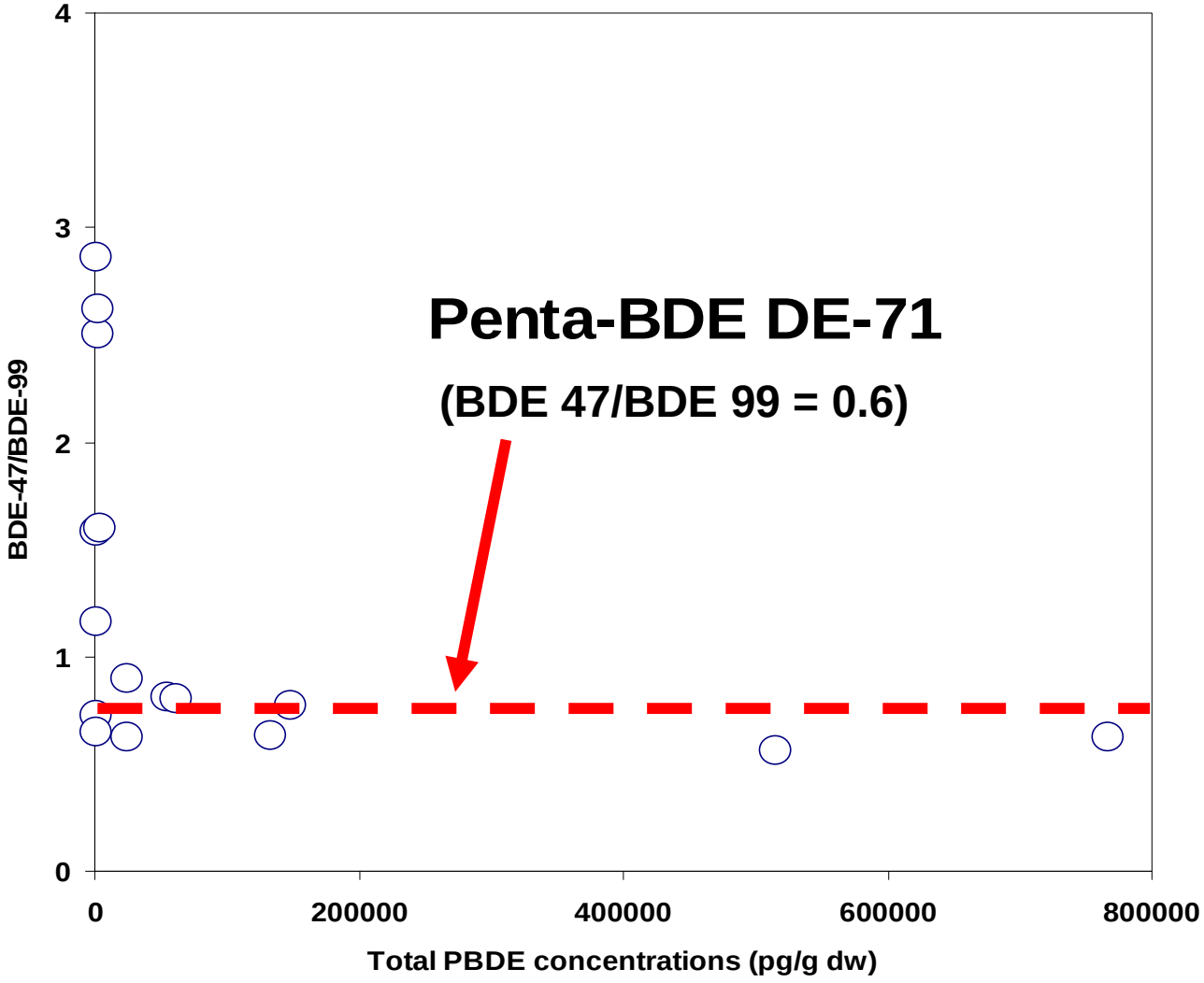
Canadian Arctic Results

- Increasing concentrations of PBDEs in northern environment
- Examined PBDEs in soils, leachate, sewage effluent and background water
- Distinct congener patterns found
- First time this type of work conducted in northern Canada

Landfill in Northern Canada

Canadian Tire of the North

Canadian Arctic Results
Typical Penta-BDE ratio



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Major BDE Congeners in Surface Soil Samples Canadian Arctic (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)		8,256	12,405	2,529	4,946	1,939	15,980	2,038	3,404	62,275	133,746	46.6		
Average background (3)		102	54	14	5	4	15	40	33	1,634	2,182	74.9		

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

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

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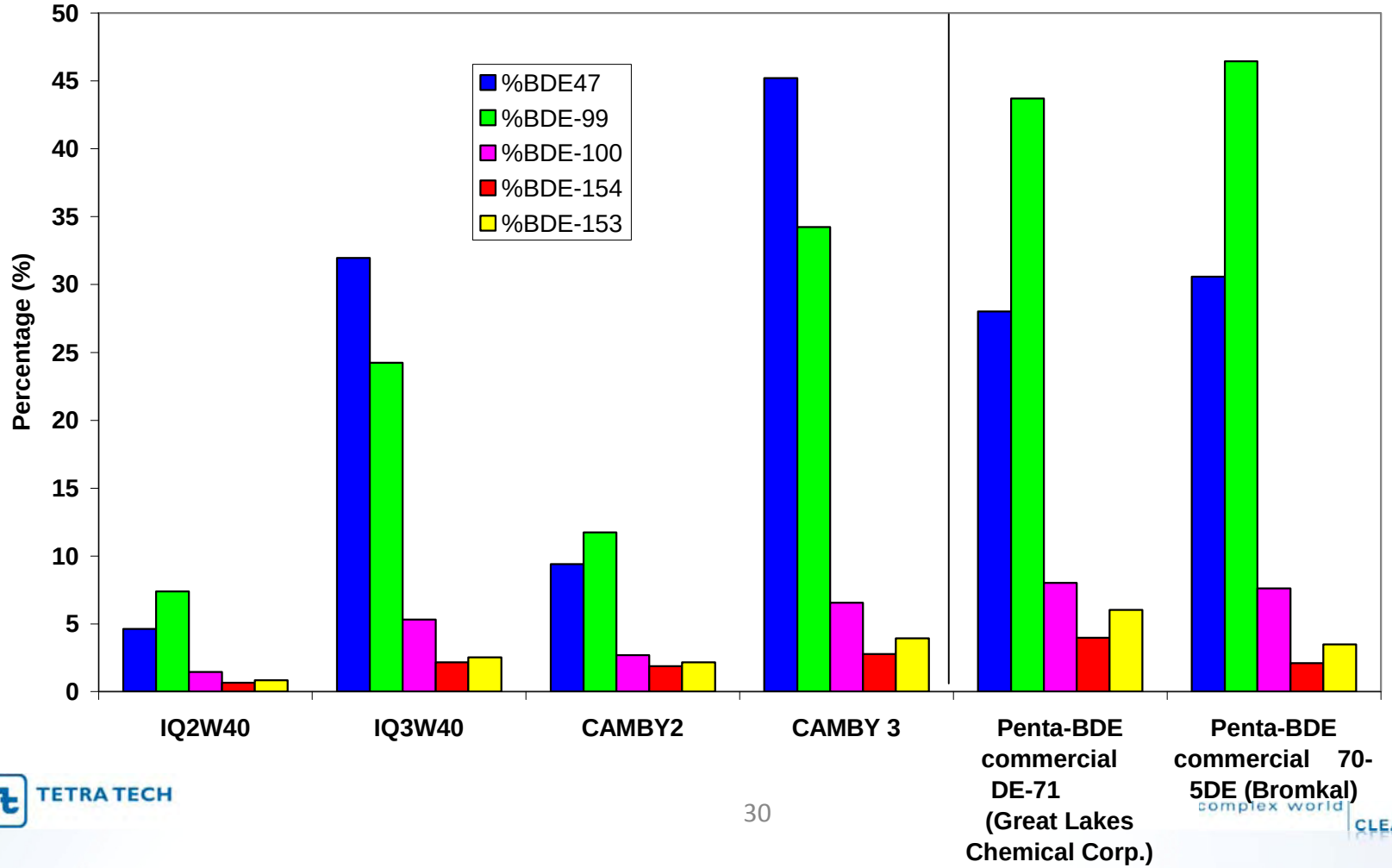
Penta-BDE product relative fractions of principal congeners vs. soil samples



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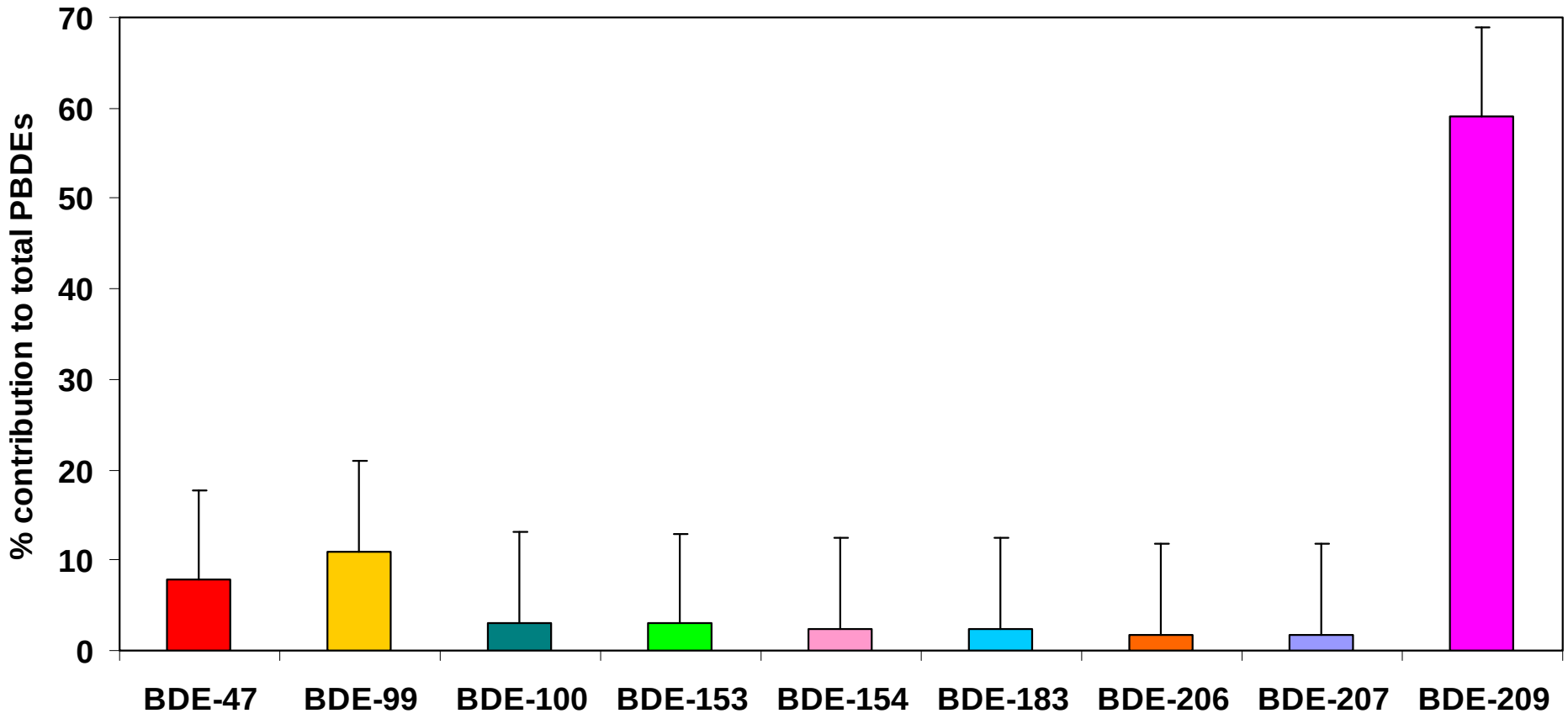
Results
BDE-209 - Predominant Congener



Southern Canada

- Relationship between total organic carbon (TOC) and total PBDE levels evaluated
- BDE ratios compared with Penta-BDE and Octa-BDE commercial products
- Population and Latitude vs. PBDEs in leachate
- PBDEs in aquatic environment

Lab Experiments

- Treatment of analytical data

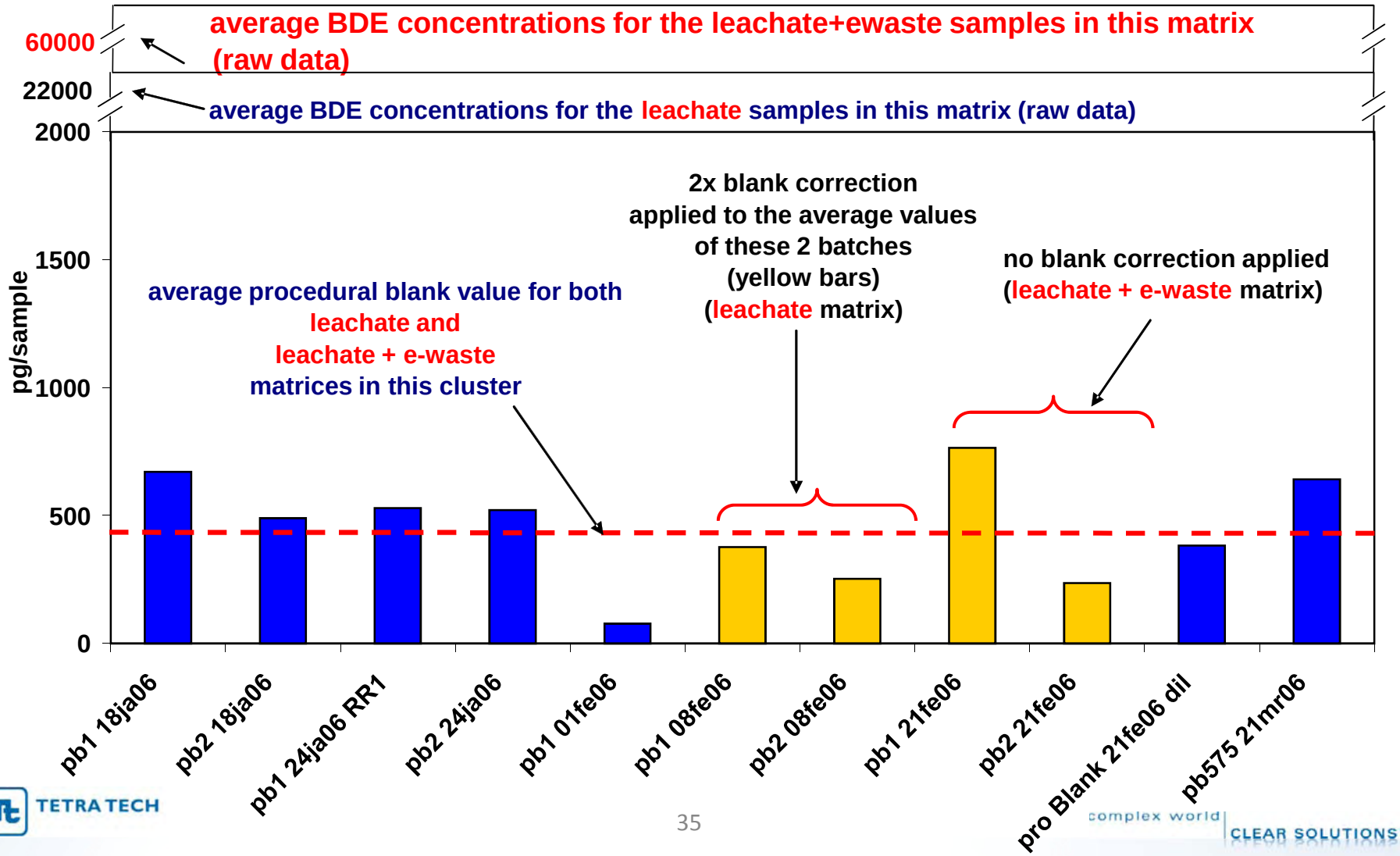
- E-waste (lab): end-over-end contactor
  - E-waste contacted either with distilled water or leachate

- Specific to get numbers for the model
  - to determine rate of mass transfer of PBDEs from e-waste/NeWS to leachate and water

Treatment of Analytical Data

- Procedural blanks used to correct data for background levels of PBDEs
- Procedural blanks treated in two ways
- Inter-lab comparison to look at data quality

Treatment of Analytical Data: Method A



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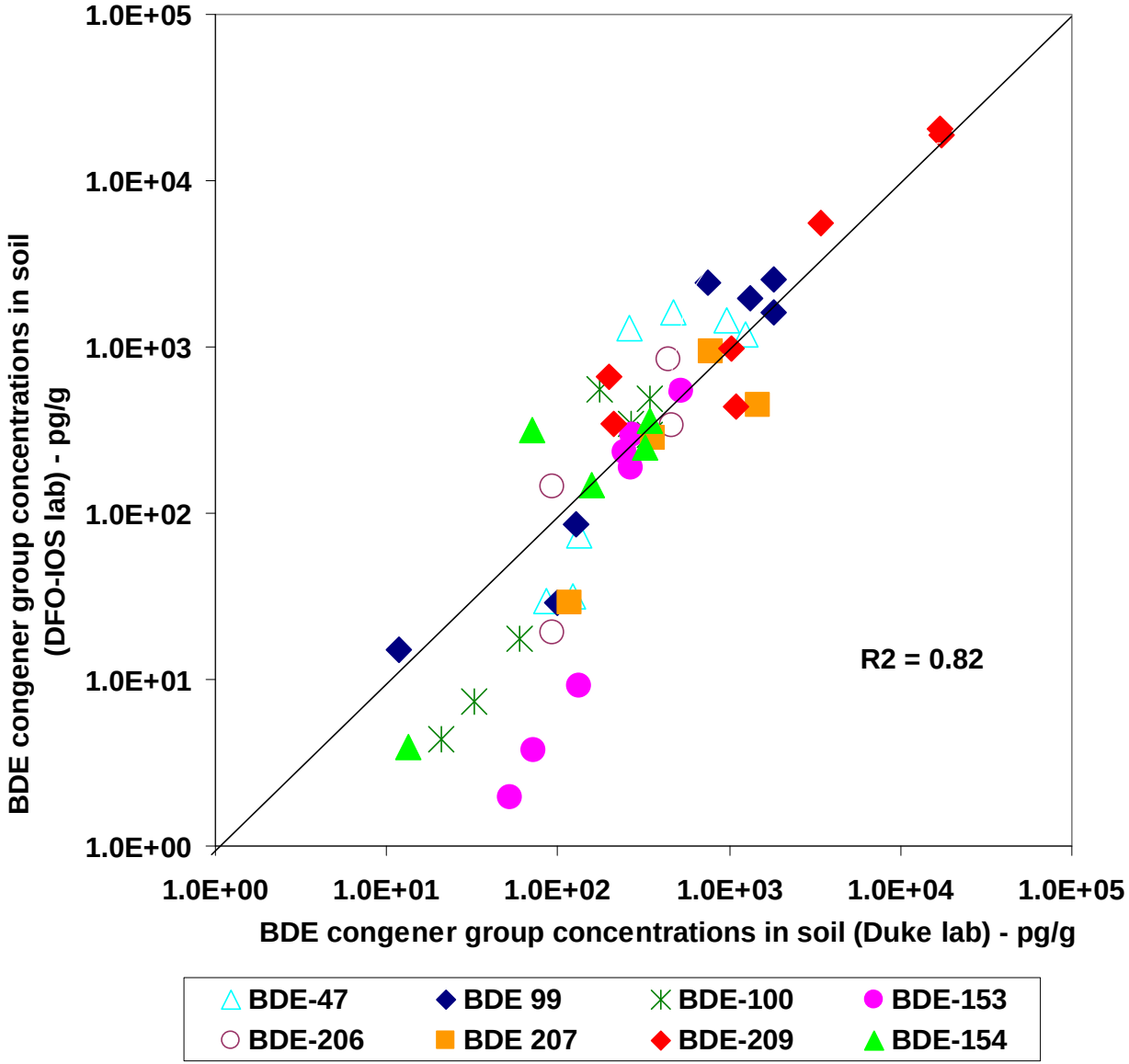
Treatment of Analytical Data: Inter-lab



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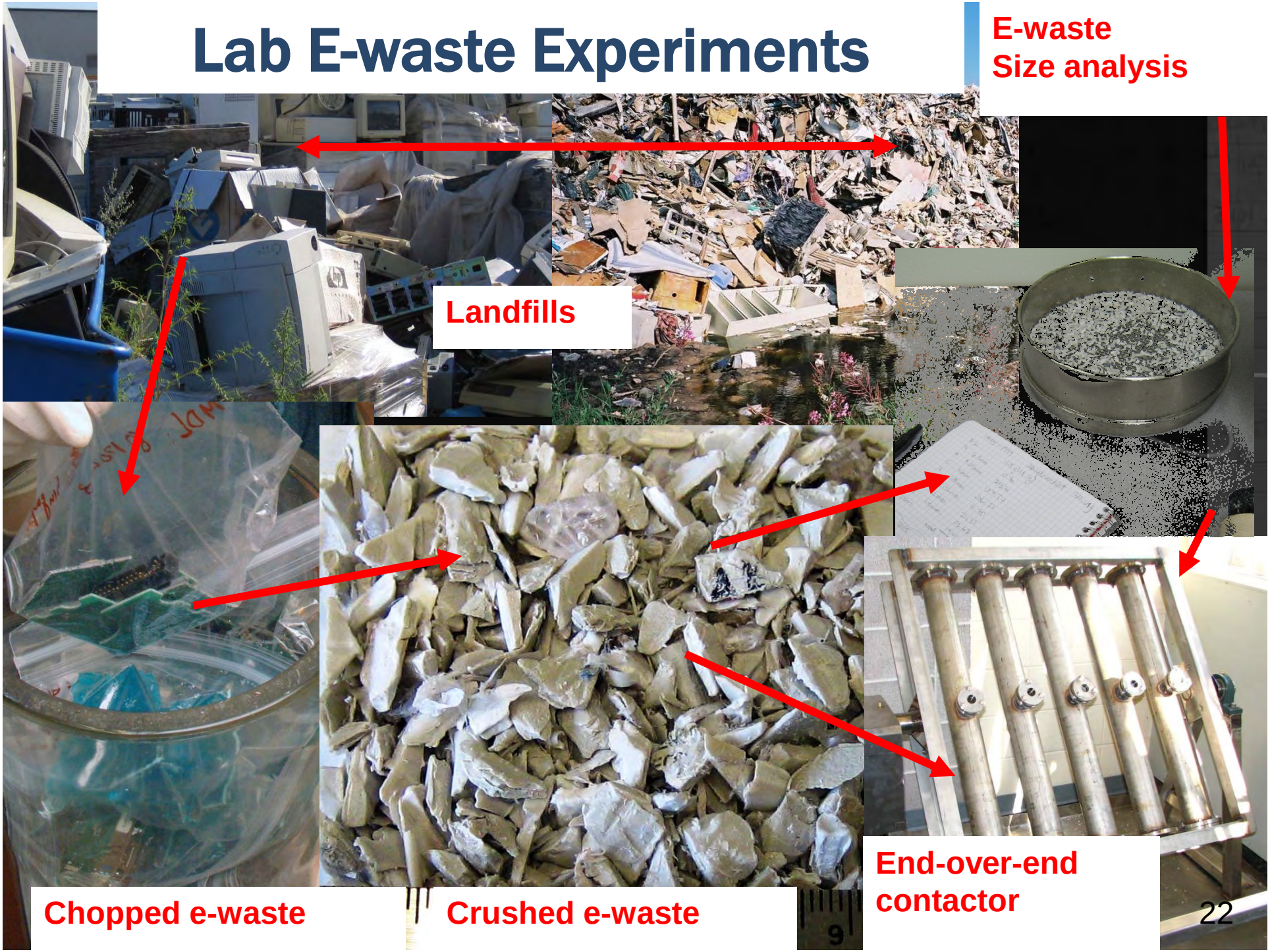
Lab E-waste Experiments

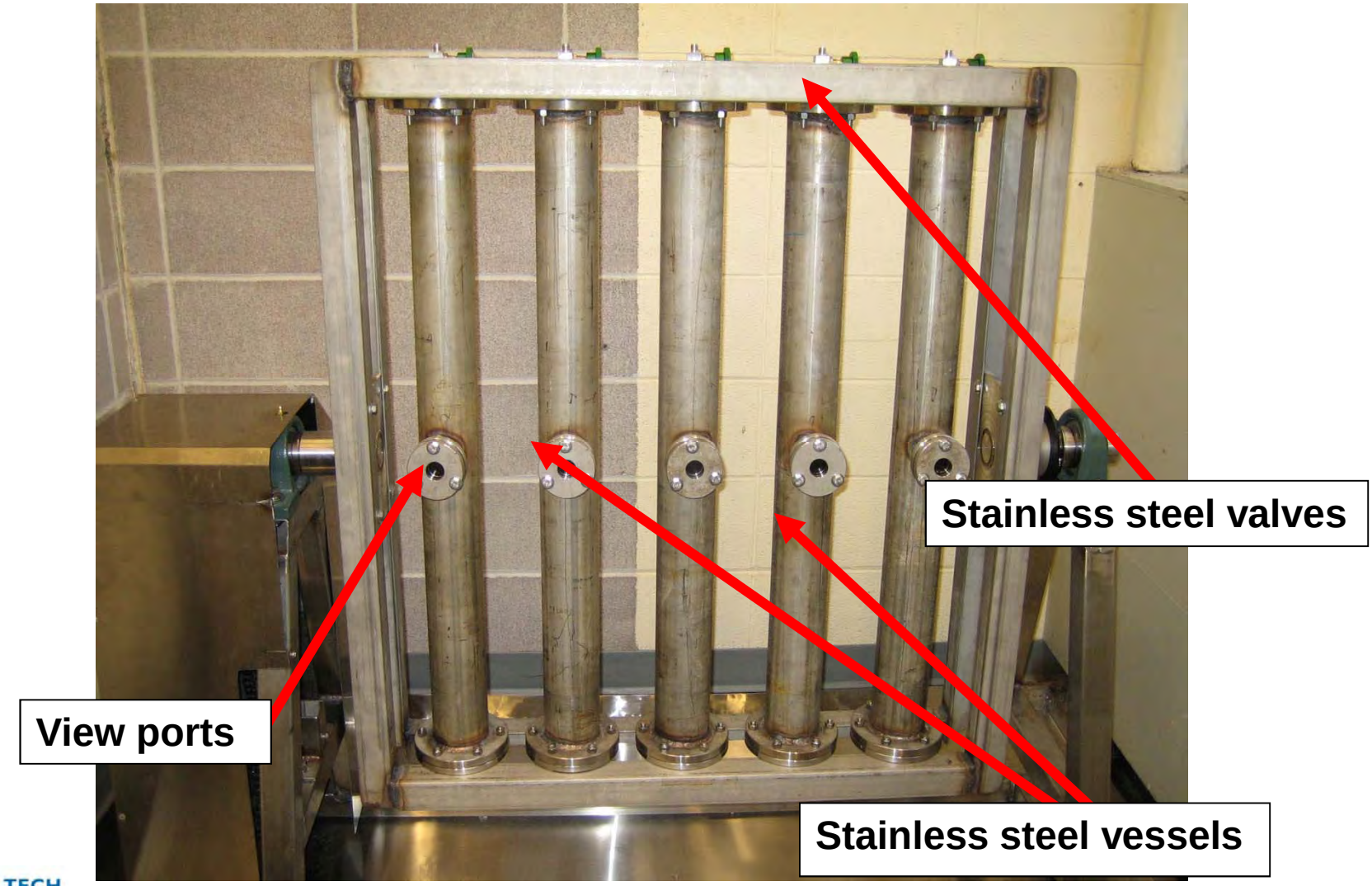
- PBDE concentration: 24-168 h contacting time
- Composite e-waste + distilled water: max PBDE concentration reached at 24 h
- E-waste + raw leachate: PBDE levels increased from 1 to 24 h, max at 168 h
- Lower pH resulted in higher PBDE transfer
- Uneven trends in Temperature

Lab E-waste Experiments

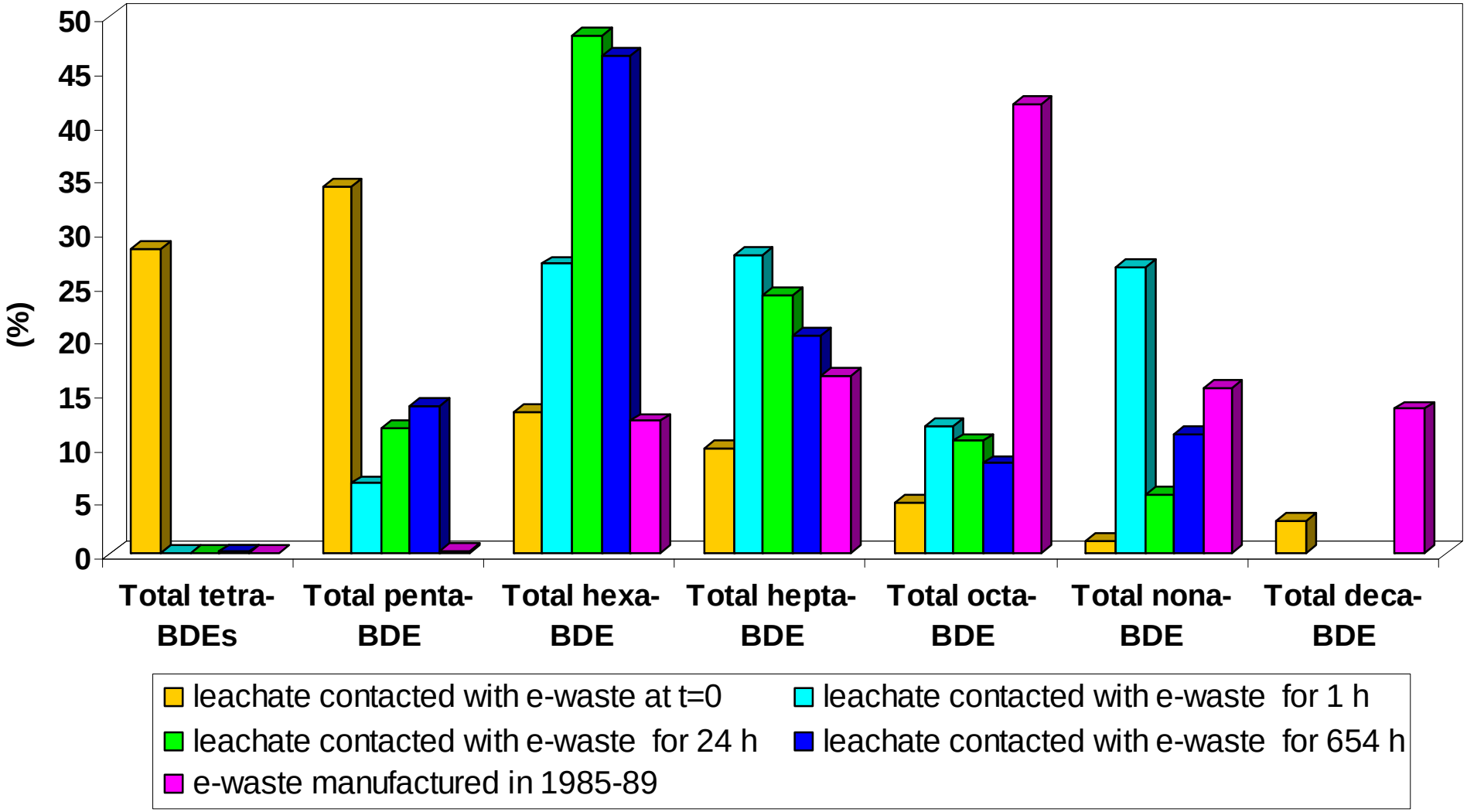
E-waste
Size analysis



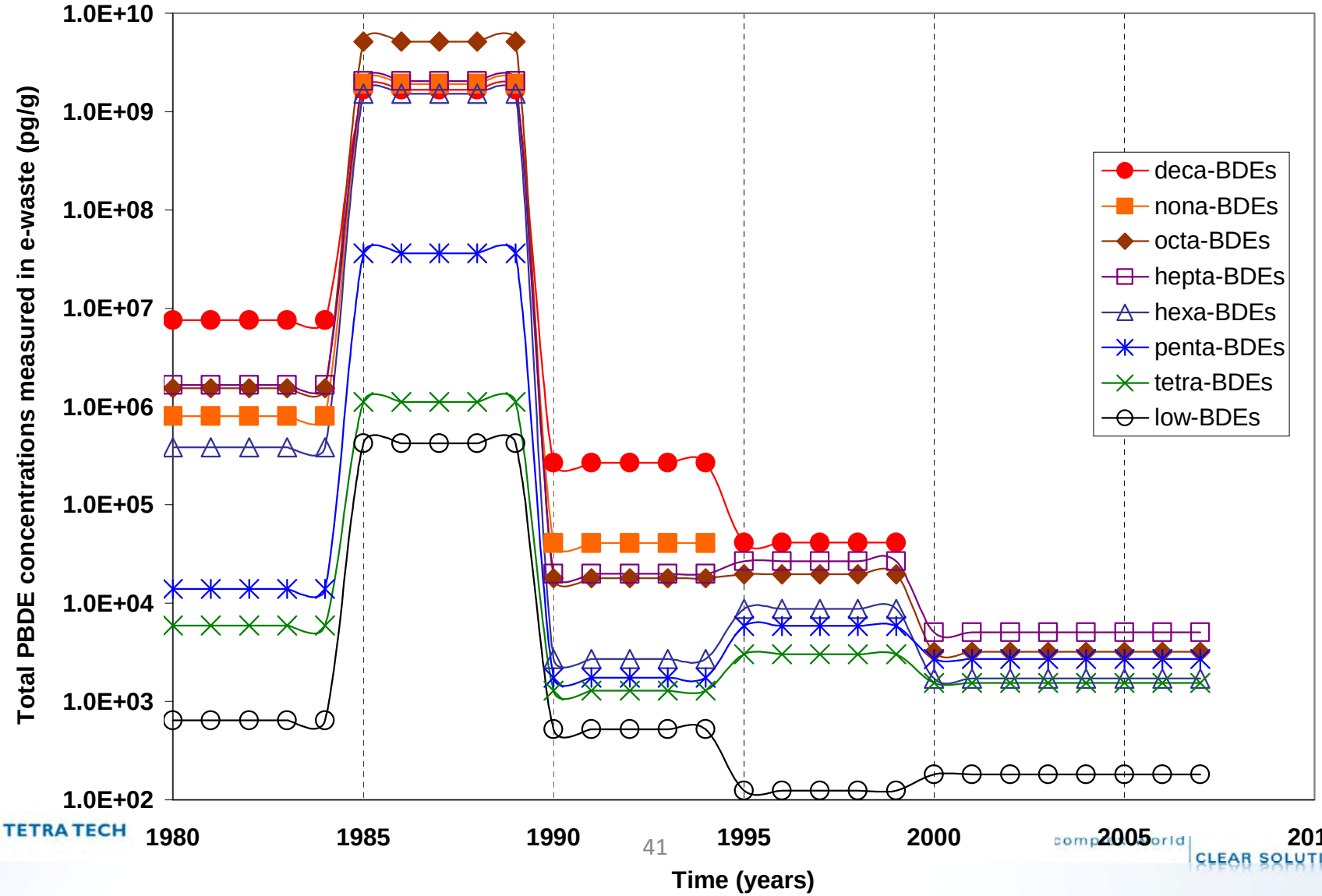
Lab E-waste Experiments
End-over-End Contactor



Lab E-waste Experiments



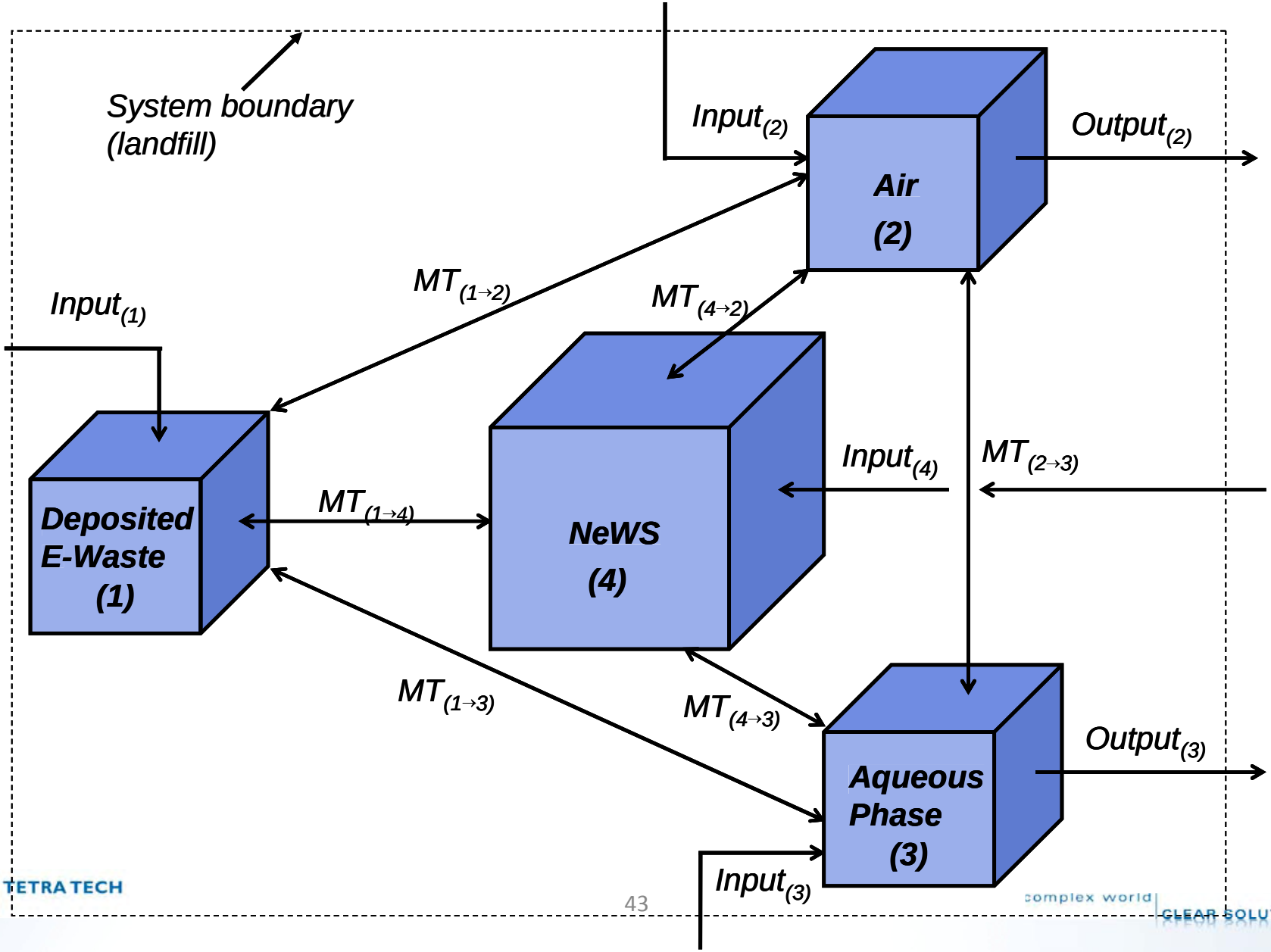
Lab E-waste Experiments
PBDEs in E-waste Over Time



Mass Balance Model

- Mathematical representation of PBDEs transferring out of e-waste and other products (non e-waste solids or NeWS) 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 Model: Schematic



Model 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

Model
Simplified Degradation Pathway

$$\text{deca} \xrightarrow[r_1]{k_1} \text{nona} \xrightarrow[r_2]{k_2} \text{octa} \xrightarrow[r_3]{k_3} \text{hepta} \xrightarrow[r_4]{k_4}$$

$$\longrightarrow \text{hexa} \xrightarrow[r_5]{k_5} \text{penta} \xrightarrow[r_6]{k_6} \text{tetra} \xrightarrow[r_7]{k_7}$$

$$\longrightarrow \text{lowBDEs} \xrightarrow[r_8]{k_8} \text{HBr + DE}$$

45

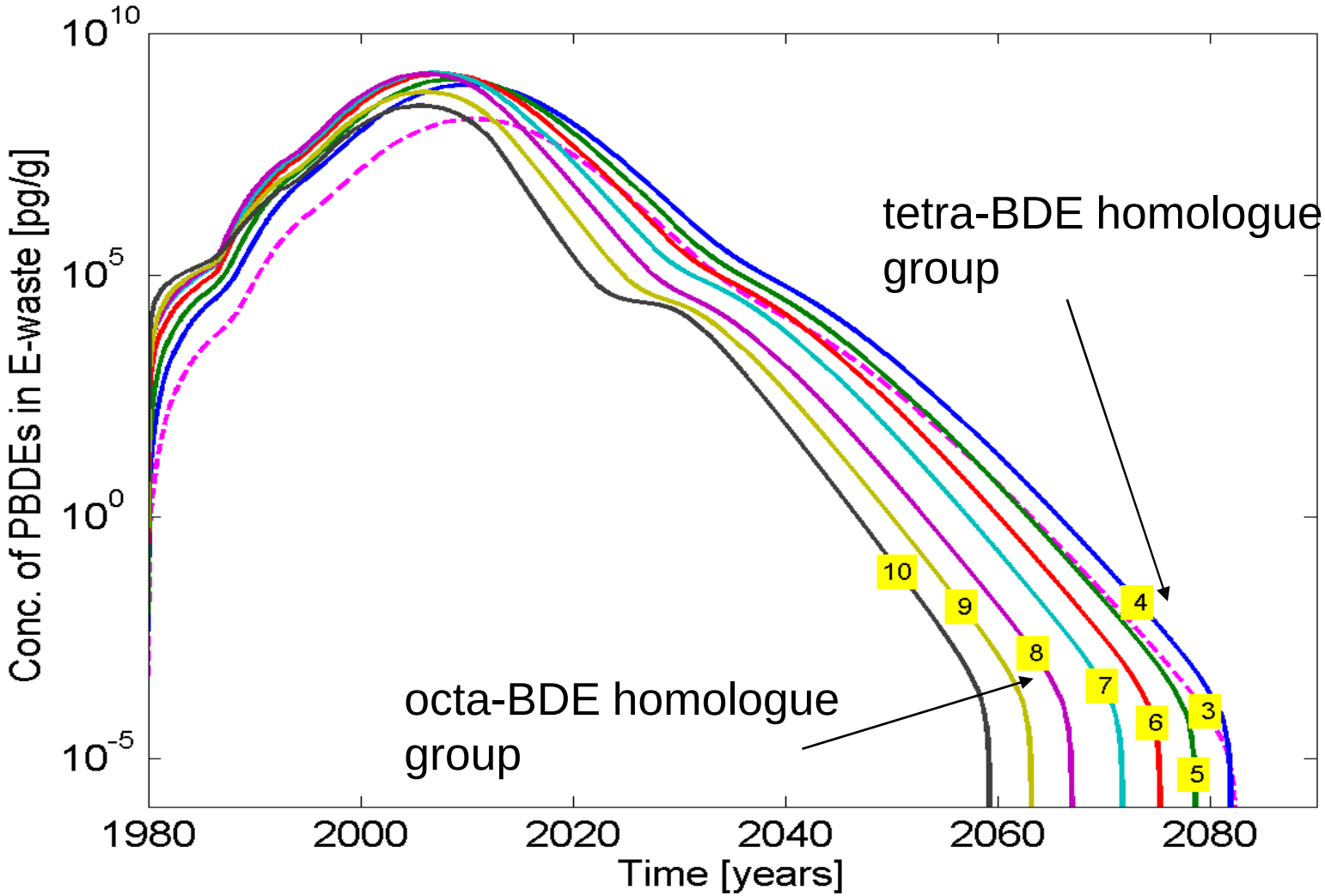
Model: Simulation Scenarios

- Scenario 1: Past three decades
  - time to virtual debromination: *~100 years*

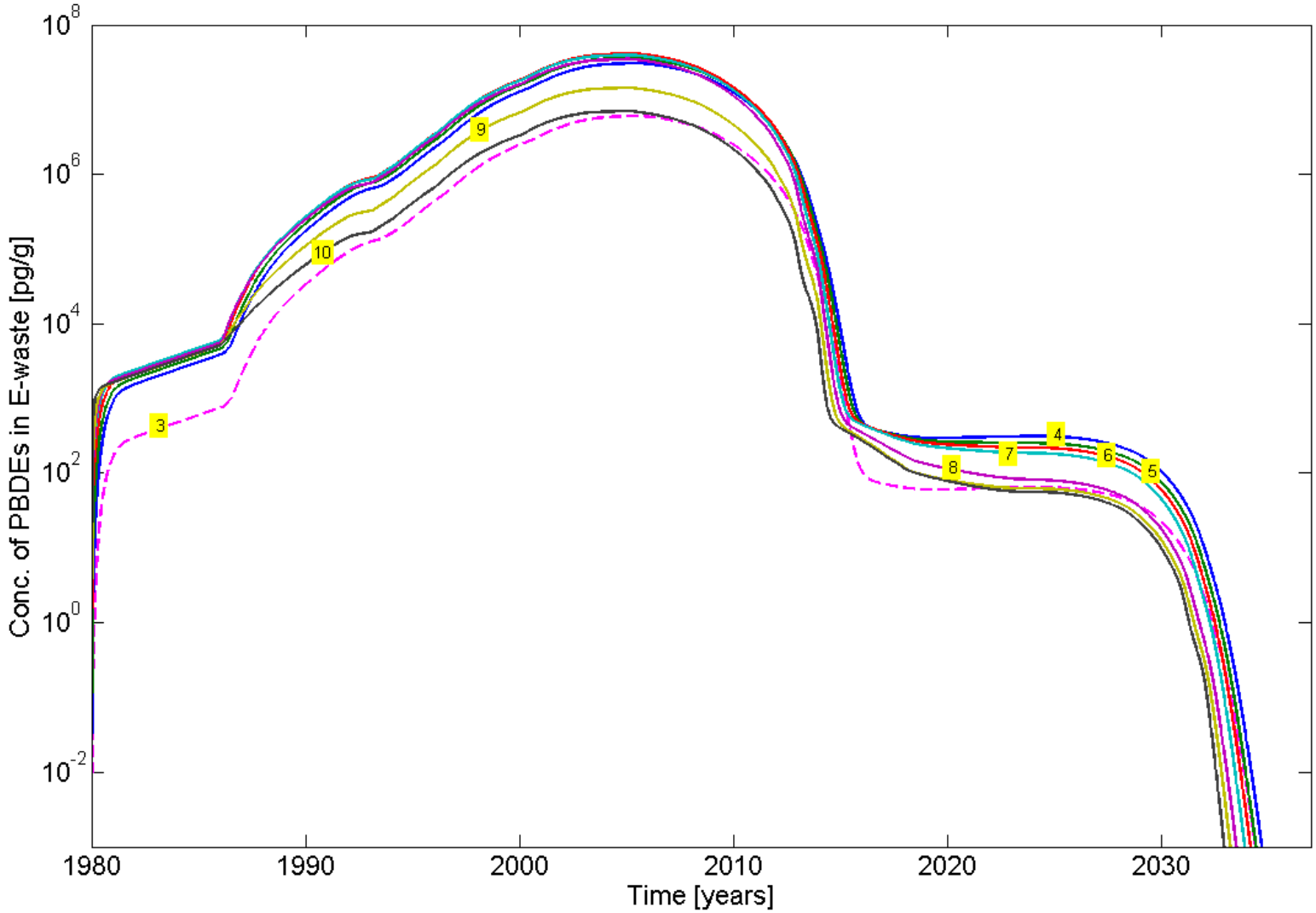
- Scenario 2: Future with PBDE ban and 16 sensitivity analysis
  - If one order of magnitude increase in value of reaction kinetic parameters, time to virtual debromination: *~45 yrs*
  - If one order of magnitude decrease in value of reaction kinetic parameters, time to virtual debromination: *>>100 yrs*

- Scenario 3: Future with all PBDE input terminated

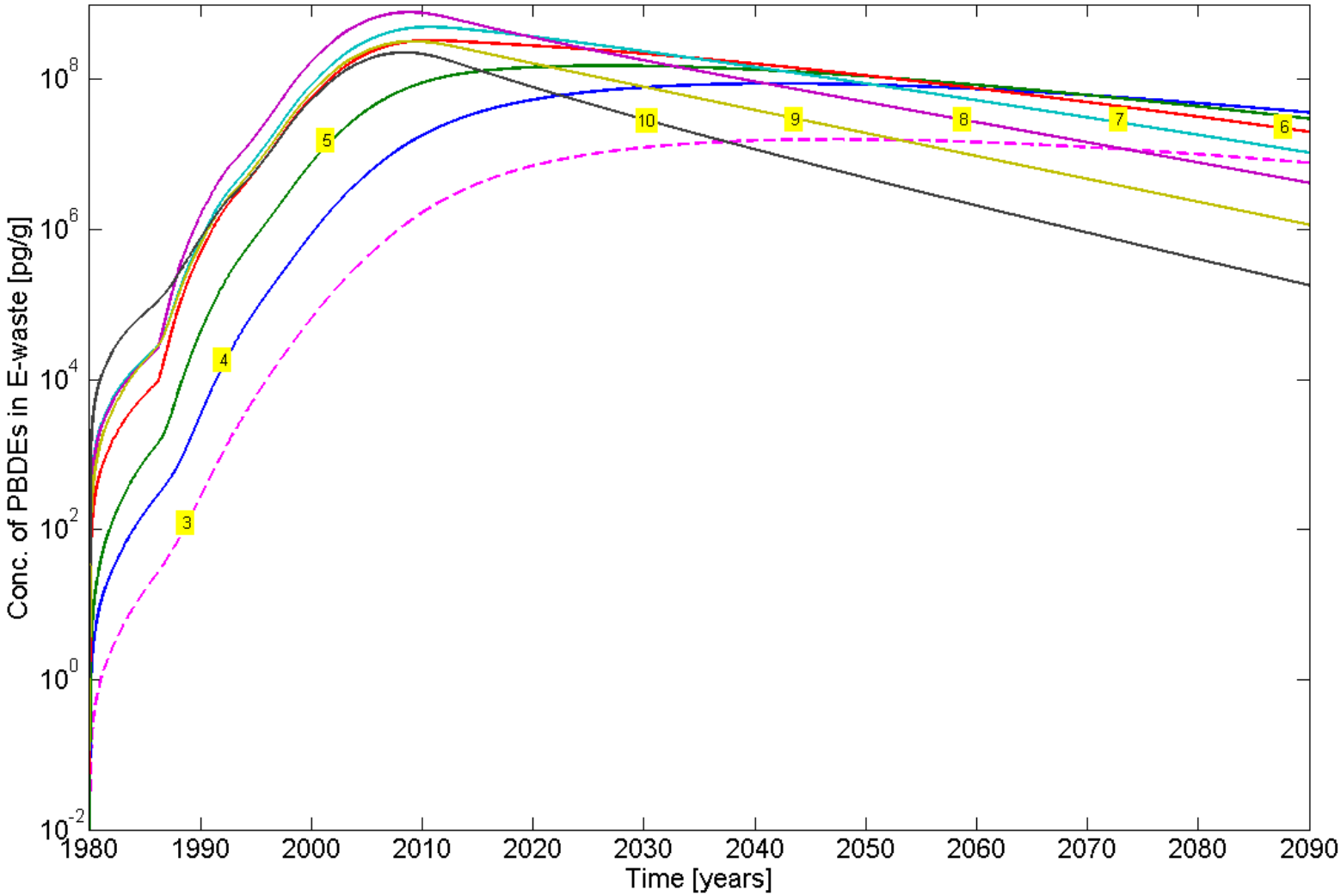
Mass Balance Model Simulation: Scenario 2 – Future with PBDE bans



Predicted PBDE concentrations in e-waste subsystem: Kinetic parameters *increase ten fold*



Predicted PBDE concentrations in e-waste subsystem: Kinetic parameters *decrease ten fold*



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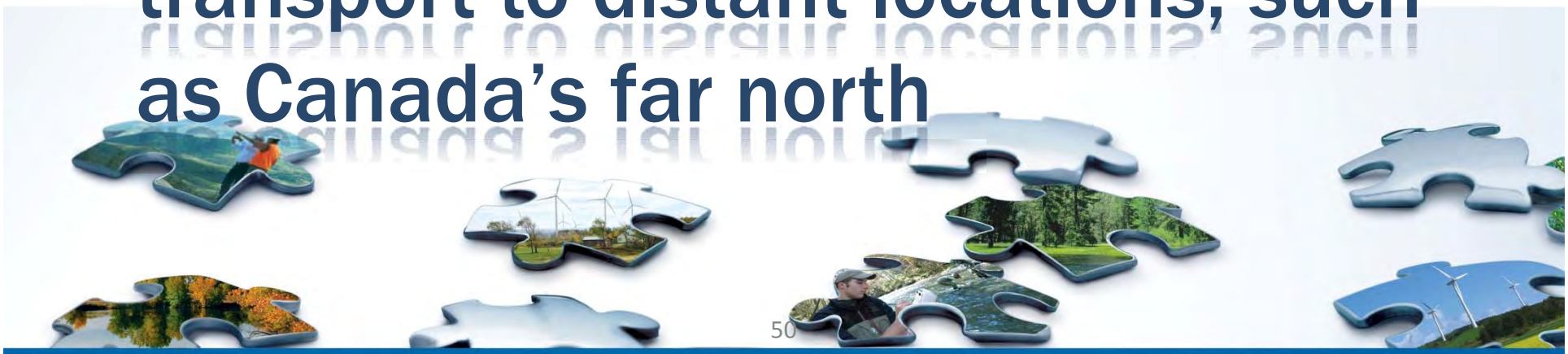
Outcome

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 (cont'd)

- 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

Future Work

- Determine accurate chemical kinetics of debromination reactions
- Determine process for leaching, degradation and spread of PBDEs from landfills
- Confirm fine particulates carry PBDEs thru atmospheric long range transport
- Experiments exposing e-waste to dH_2O for 168 h w/o agitation – ultra fines/abrasion hypothesis

Contributions

- *State of Washington*
- *Environment Canada*
- *Circumpolar countries*
- *Stockholm Convention Secretariat*
- *CACAR III Report*

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Questions?
Thank you for coming!