

Case Study III: Industrial Chemicals

Brominated Flame Retardants

Carl Orazio

USGS Columbia Environmental Research Center
4200 New Haven Road, Columbia, Missouri 65201 USA

Renewable Natural Resources Foundation
*Congress on Assessing and Mitigating
Environmental Impacts of Emerging Contaminants*

Late 1960's: Polymer Proliferation

Fabrics

ABS resins

**Wire & cable
insulation**

Carpet

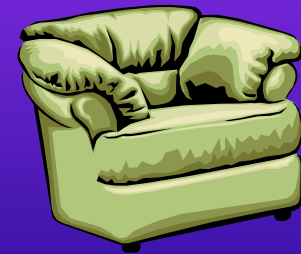
TVs

**Polyurethane
foams**

vinyl

Mattresses

Polystyrene

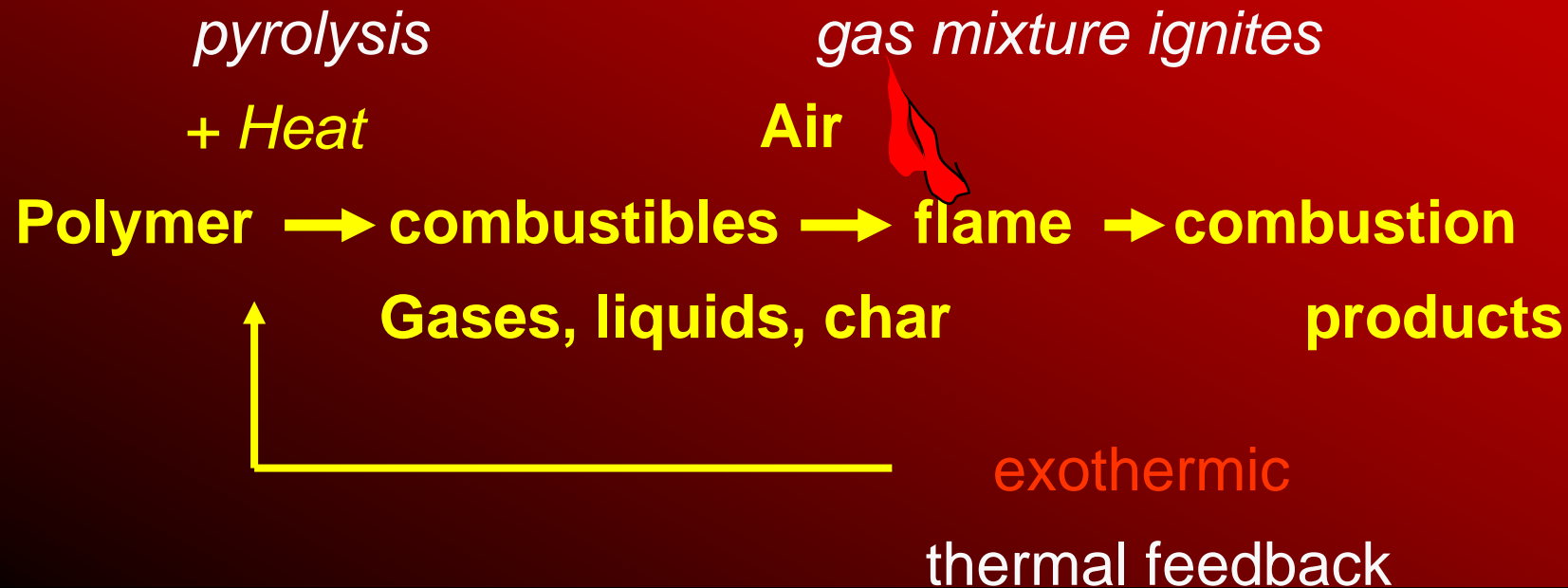


Polyamides

Textiles

cushions

Overview of Combustion



Flame retardants

physical and chemical actions

**Coating,
cooling,
Dilution**

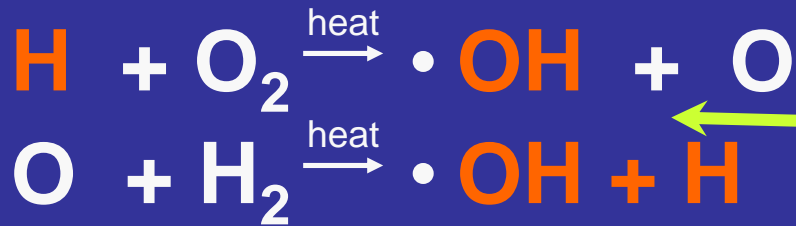
Phosphorous salts,
Antimony oxides,
Aluminum compounds

**Quenching
chain reactions
in the flame**

**Brominated Flame
Retardants (BFRs)**

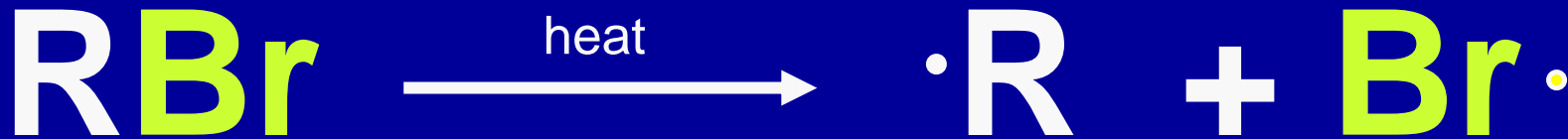
BFR Chemical Quenching Action

chain reaction perpetuates flame



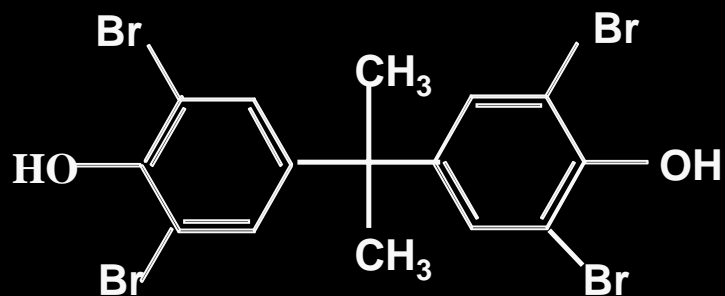
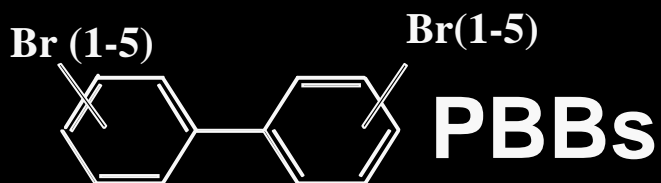
Interferes
with
chain
reaction

*Flame retardant designed to
release reactive Br*



Various Brominated Flame Retardants

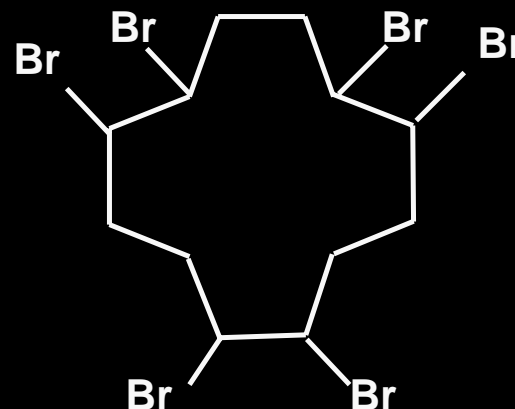
Polybrominated biphenyls



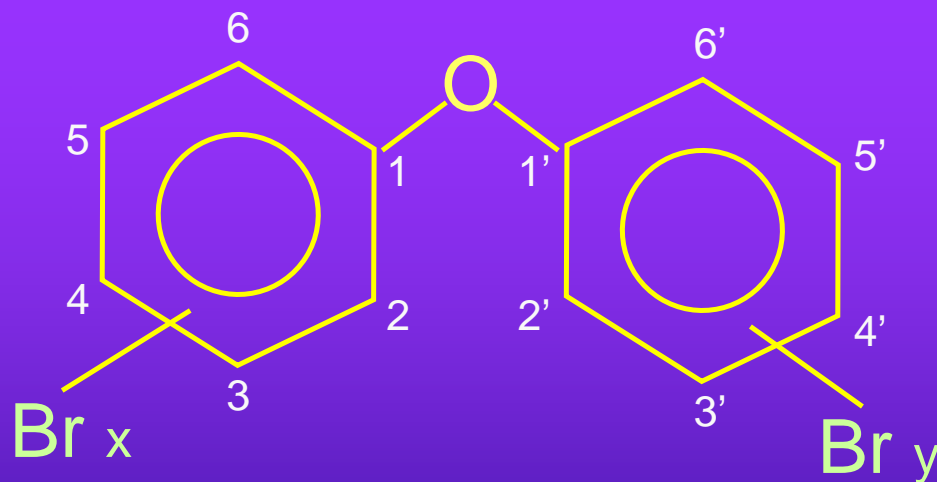
Tetrabromo-bisphenol A

Covalently bound or added to polymer

Hexabromocyclodecane additive



Polybrominated diphenylethers (PBDEs)



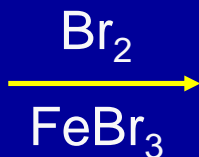
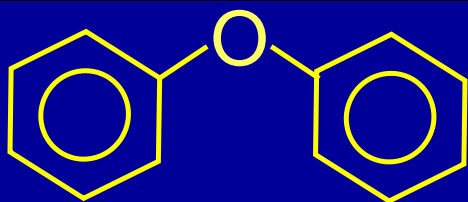
$$X + Y = 1 \text{ to } 10$$

1,1'-oxy(bis)polybromo-benzene

Polybrominated diphenyl oxides (PBDPO)

Manufacture of the PBDEs

Bromination of diphenyl ether



limited congeners

ortho and para

producing 3 major technical mixtures

deca, octa & penta BDEs

PBDE Commercial Formulations

Technical Product	Br 4	Br 5	Br 6	Br 7	Br 8	Br 9	Br 10	PBDE congeners
Deca powder Polymers, electronics, textiles						2%	98%	209 (98%) 208 (2%)
Octa powder Polymers, Office equipment			11%	44%	33%	11%	1%	183 (40%) 203 (33%) 208 (10%) 154 (5%) 153 (5%)
Penta visc liquid PUF, textiles	44%	55%	6%					99 (50%) 47 (25%) 100 < 10% 153 & 154 <5%

Lipophilic, low water solubility, low volatility

	Log K _{ow}	Vapor Pressure @25° C Pa
Br 8-10 BDE	~ 9	Extremely low
Hepta-BDE	6.9-7.9	Very low
Hexa-BDE 153	7.1	7.6 e-6
Penta-BDE 99	6.8	4.2 e-5
Tetra-BDE 47	6.4	2.7 e-4
Tri-BDE 28	5.8	2.0 e-3
Di-BDE 15	5.5	1.4 e-2

From Alcock et al (1999) and Wania et al (2003)

Similar to PCB Properties

PBDEs: additive flame retardants

blended into thermoplastics and elastomers
up to 30% of the weight of the plastic
not locked in place- not a co-polymer

Fabrics

Deca-BDE

ABS resins

Octa-BDE

Wire & cable
insulation

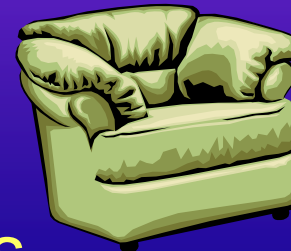
TVs Computer

Carpet

High Impact Polystyrene
HIPS (Deca)

Polyurethane foams

Penta-BDE



cushions

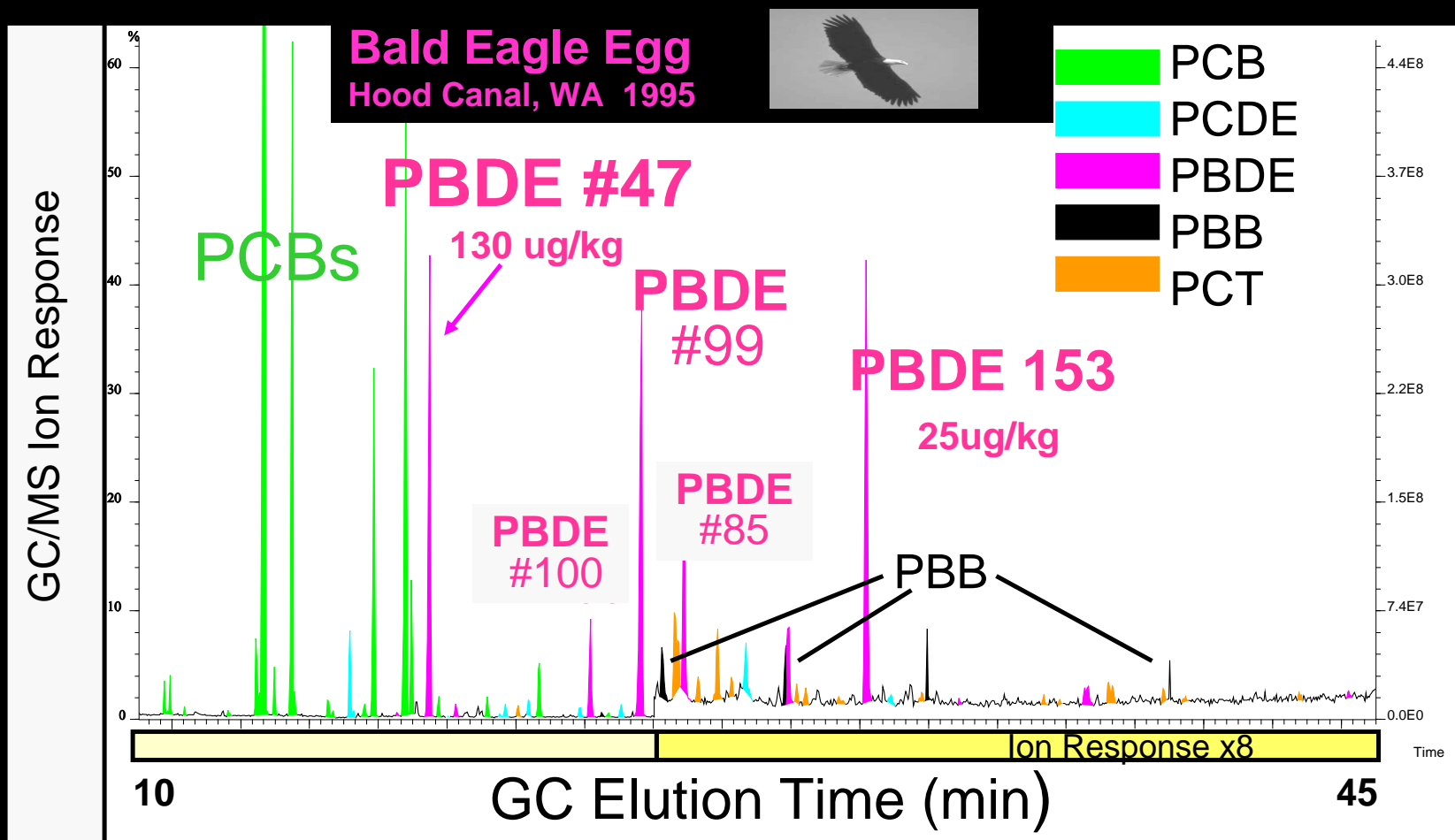
Textile coatings

deca

Mattresses

Nylon- Polyamides

1996: PBDEs Found in Fish and Wildlife

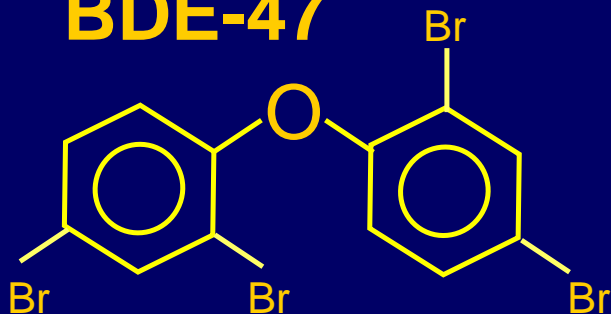


Peterman et. al, "Brominated Diphenyl Ethers Found in Aquatic Samples",

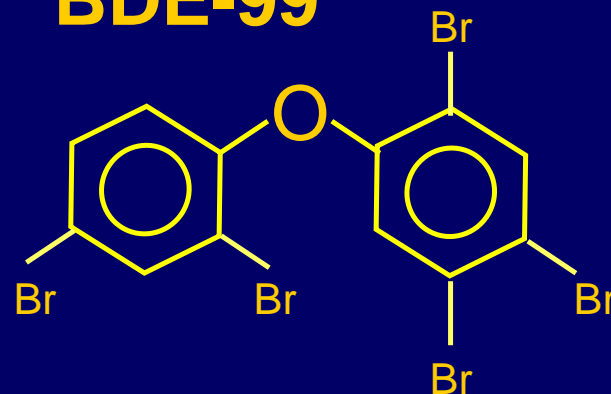
SETAC Annual Meeting, Nov 1996.

Increase in reports of finding PBDEs in fish/wildlife/sediments...

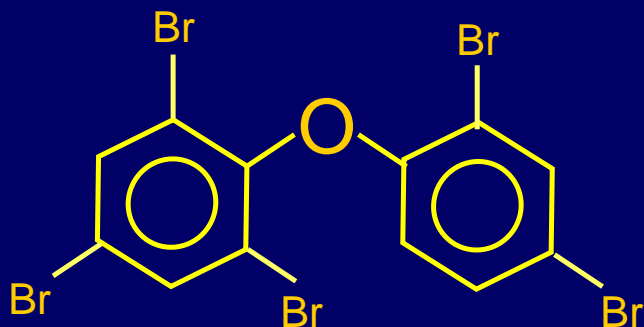
BDE-47



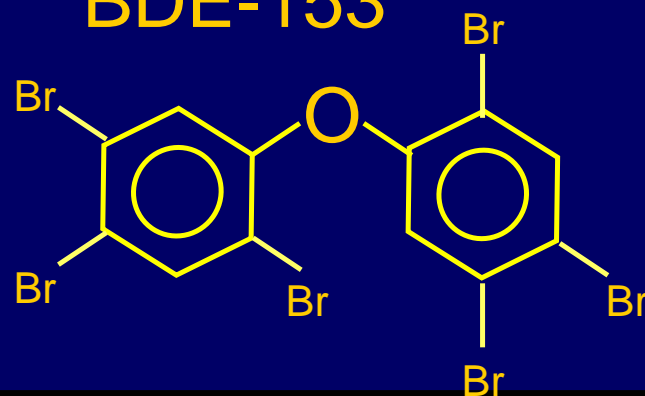
BDE-99



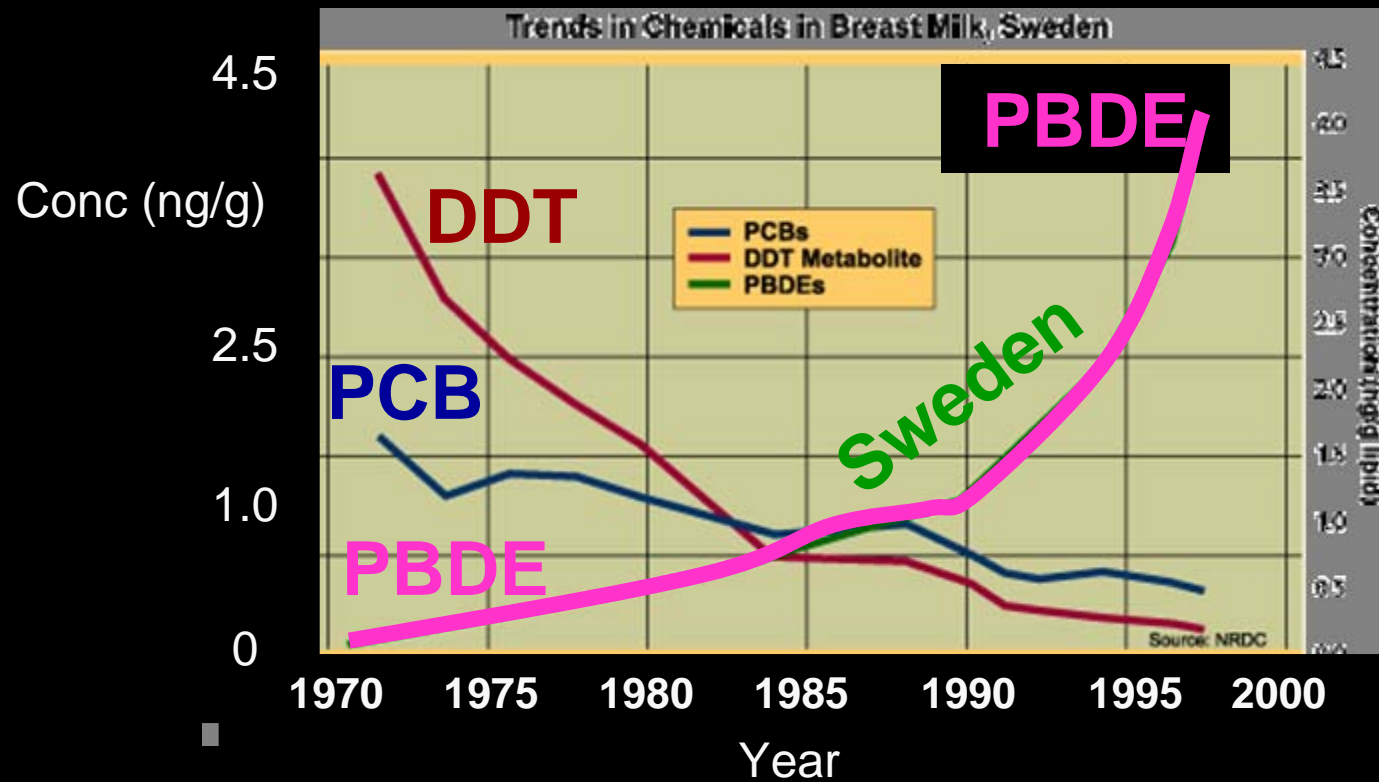
BDE-100



BDE-153



1998: PBDEs in Breast Milk in Sweden



From [Meironyté et al. 1998](#), NRDC

NFL
 Week 3

Broncos in a rout

QB Jake Plummer and Denver destroy rival Raiders ■ 1, 7C



By Ed Andrieski, AP

Plummer: 3 TDs in 1st quarter of 31-10 win.

USA TODAY

NO. 1 IN THE USA



Music

Listen up!

Dave Matthews, left, goes solo; Gloria Estefan returns; and Nickelback is no slug
 ■ CD reviews, 1, 6D

By Mark Mainz, Getty Images

Tuesday, September 23, 2003

Newsline

■ News ■ Money ■ Sports ■ Life

■ Dollar slides— and stocks follow, 1, 5B

Index	Close	Change
Dow Jones industrial average	9535.41	↓ 109.41
Nasdaq composite	1874.62	↓ 31.08
T-bond, 30-year yield	5.14%	▲ 0.07
USA TODAY Internet 50	100.04	↓ 1.85

Sources: USA TODAY research, MarketWatch.com



Flame retardant found in breast milk

U.S. levels highest in the world, study says

By Elizabeth Weise
 USA TODAY

A toxic chemical used to make furniture, foam and electronics fire resistant is turning up in high amounts in the breast milk of women in the USA.

Two studies, one out today, found that all of the women tested were contaminated with polybrominated diphenyl ethers. Their PBDE levels were the highest in the world: 10 to 20 times higher than those in Europe, where the chem-

icals are being phased out.

The Environmental Working Group, a non-profit environmental research organization, tested the milk of 20 women. It found levels ranging from 9.5 to 1,078 parts per billion. The women were recruited via EWG's Web site.

It is not yet known how this chemical affects people; no studies have been done on what a safe level would be. But "this is another wake-up call," says Linda Birnbaum, director of the Environmental Protection Agency's experimental toxicology lab. Levels of PBDEs in humans are doubling every two to five years, she says.

A University of Texas-Houston

What are PBDEs?

Polybrominated diphenyl ethers are among the most common flame retardants in the USA. Starting next year, they will be banned in Europe. In 2008, they will be banned in California.

■ Experts say it's still safe to breast-feed.
 Story, 10A

study by Arnold Schecter, professor of environmental sciences, and Birnbaum found levels in breast milk from 5 to 418 parts per billion in 47 American women. It was published last month in *Environmental Health Perspectives*. Breast milk is tested because it's the least invasive way to test fat, where PBDEs are stored.

In mice and rats, studies show PBDEs may cause cognitive and behavior changes during development; it also may lead to higher cancer rates. Peter O'Toole, of the Bromine Science and Environmental Forum, says human effects can't be extrapolated from rodents.

Though the USA has the world's

toughest flame retardancy standards, 3,000 people die in fires each year. The Chemical Manufacturers Association estimates the number would be up to 960 higher without such flame retardants.

PBDEs may enter the environment during manufacturing or when products break down, though no one yet knows for sure. Some experts say the major source is animal fat in food. One study found them in house dust.

Schecter advocates using less toxic alternatives: "These are our babies. Do we want them to be dumber than we are because their brains are being attacked by these toxic chemicals?"

Studies tie disease to Gulf War vets

North American PBDE Levels

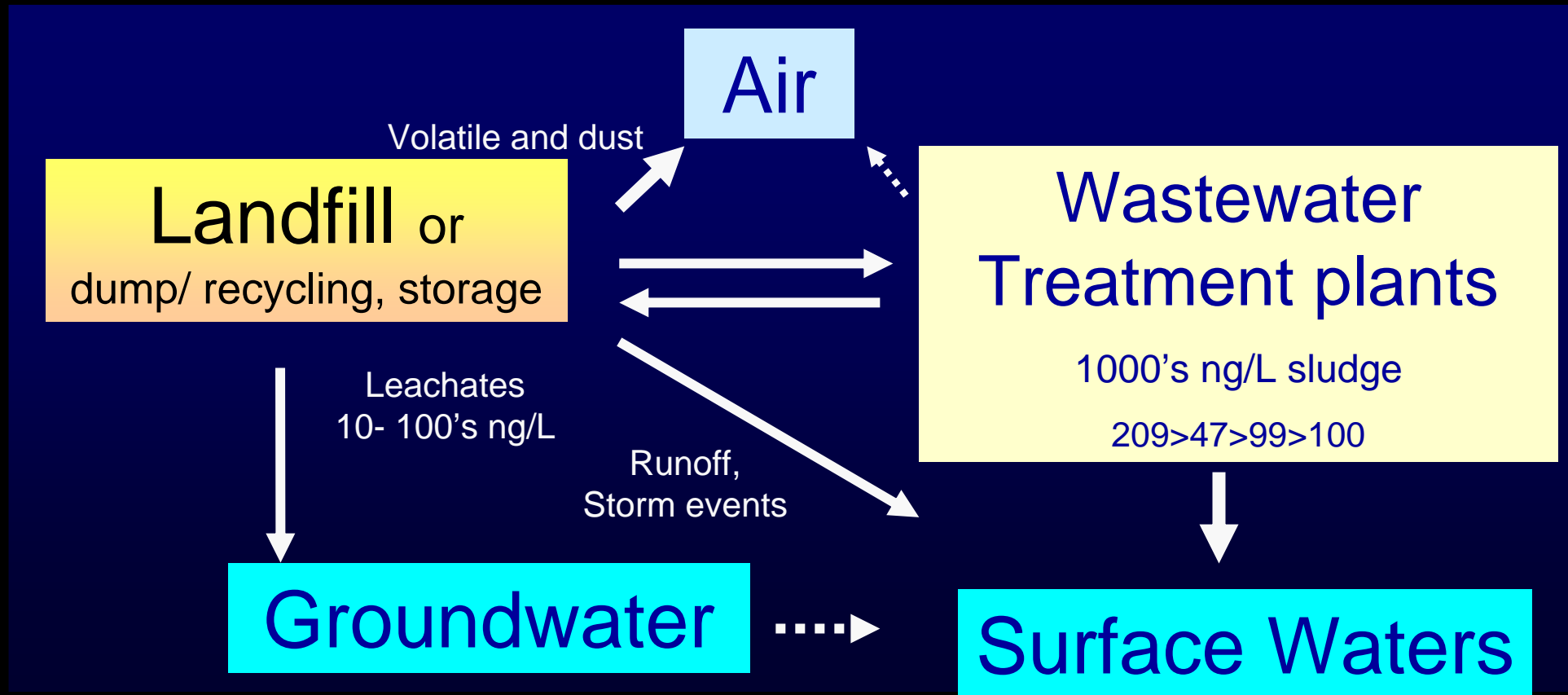
10-20x European levels; Doubling every 2-5 years

Potential sources of PBDEs-

Where are the PBDEs coming from?

- PBDE production site -
- Polymer manufacture -
- Release from product during use -
- End of use: disposal, recycling -

Release and transport of PBDEs



Example of a potential source

Auto Fluff

Penta release ?



Computer recycling: Potential source of PBDEs ?



PBDEs in the environment

Which congeners released ?

Which congeners found ?

Fish? Sediment? Air?
Particulate? Breast Milk? ...

Environmental Fate

- Sorption
- Water solubility
- **Photolysis**
- Vaporization

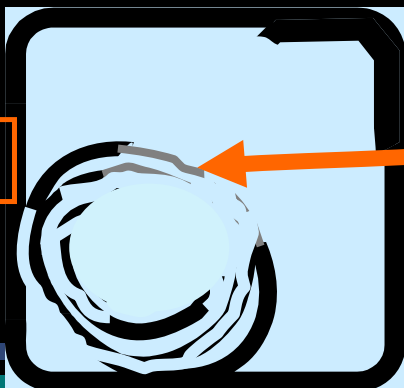
Toxicokinetics

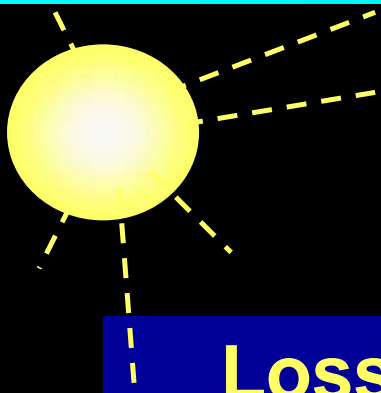
- Uptake
- Distribution
- **Metabolism**
- Elimination

PBDEs source



PBDEs found





Photolysis of PBDEs

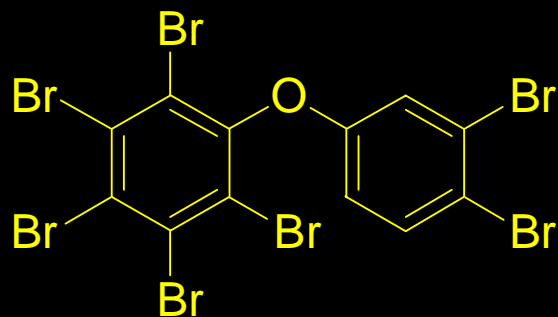
**Loss of bromines from certain PBDEs forms
lower brominated, more stable PBDEs**

Stable: 1- 3 Br BDEs

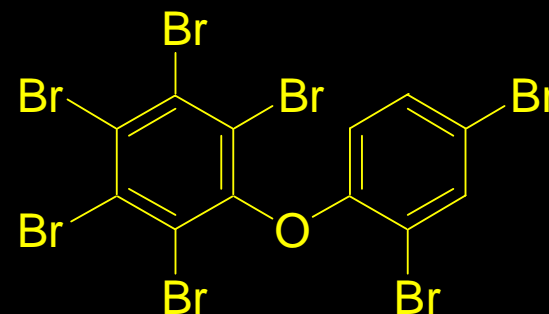
**Created Tetra- and Penta-PBDEs
(47, 66, 77, 99, & 100)**

**The most sensitive are fully-brominated on one ring,
as are deca and nona BDEs**

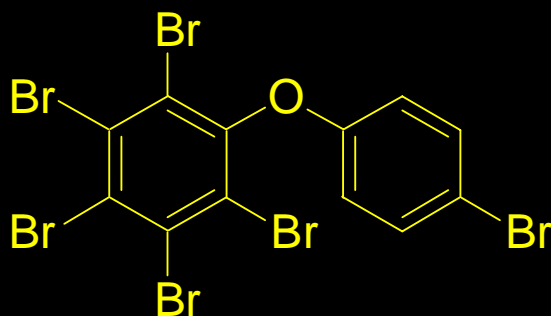
PBDEs Most Susceptible to Photolysis



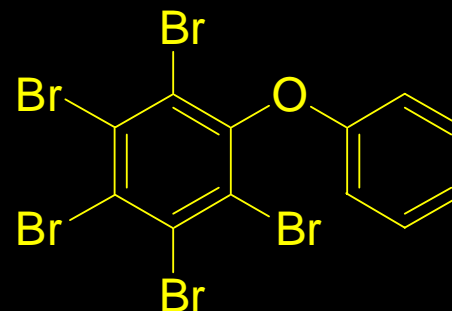
2,3,4,5,6- 3',4'-Hepta- (PBDE 190)



2,3,4,5,6- 2',4'-Hepta- (PBDE 181)



2,3,4,5,6- 4'-Hexa- (PBDE 166)



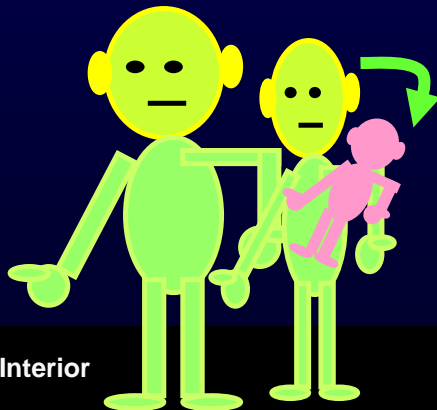
2,3,4,5,6- Penta- (PBDE 116)

Human Exposure to PBDEs

**Indoors: dust
and vapors**

US dust: [PBDEs]
10's to 10,000's ppb (ng/g)
PBDEs 47, 99, 100, 209

Drinking water



U.S. Department of the Interior
U.S. Geological Survey

Market Basket Survey (pg/g ww)


Adapted from Schechter, et al 2003

Chicken liver 2835

 **616**

 **190**

 **180 – 680**

 **~ 10**

Breast milk
6 – 418 ng/g lipid

**630,000 pg/day
USA intake**

*Ubiquitous, bioavailable, **persistent**
environmental contaminants with rapidly
rising concentrations*

***Are PBDE levels of concern
now or in the future ?***

**Are levels and kinds of PBDEs
being found in people,
environment, fish and wildlife at
*toxic levels?***

Summary of PBDEs' toxicities

*According to EPA and other researchers,
certain of the PBDEs are:*

- likely carcinogens -
- induce liver enzymes -
- may impact neurological, developmental,
and reproductive systems
- likely endocrine disrupters –

Some Mammalian toxicity studies -PBDEs

Penta DE71 Endocrine disruption screening program.
60mg/kg decreased the thyroid hormones T4 and T3.

BDE 99: delay in onset of puberty in female offspring
following an 8-day exposure.

BDE 99: Developmental neurotoxicity in mice: impair spontaneous motor behavior. Deficits in learning and memory.

DecaBDE 50,000 ppm in the diet resulted in neoplastic nodules in the liver of rats. Rat and mice 2 year feeding study

Some PBDE minimal risk levels (MRL) from Agency for Toxic Substances and Disease Registry (ATSDR) ^{9/04}

Oral

0.03 mg/kg/day PENTA acute-duration oral exposure

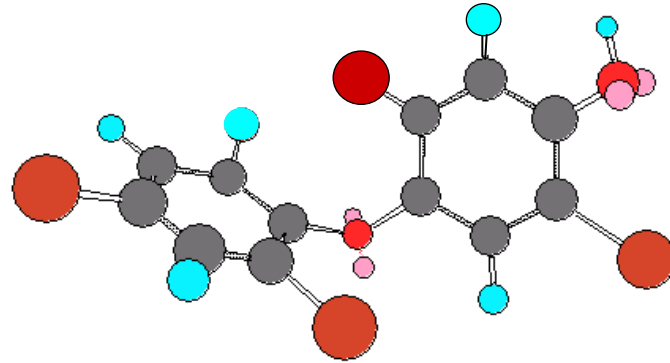
Zhou, 2002 rat study, reduced serum levels of thyroid T4 hormone NOAEL of 1 mg/kg/day.

***10 mg/kg/day DECA intermediate-duration oral exposure
(based on Hardy et al. 2002, developmental toxicity in rats)***

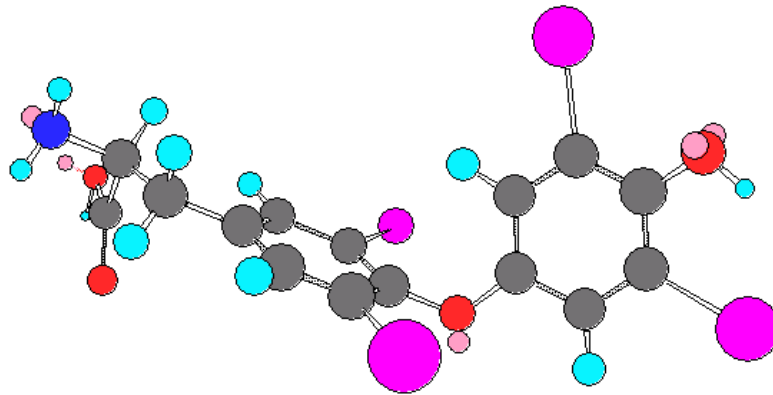
Inhalation

***0.006 mg /m³ OCTA based on NOAEL of 1.1 mg/ m³ for
thyroid effects in rats inhalation exposure*** *Great Lakes Chemical
Corp 2001*

PBDE metabolites likely mimic Thyroid Hormone



**Example of
Tetra-bromo-BDE
hydroxyl
metabolite**



Thyroxine (T4)

Ecological toxicity studies-

Limited to date

***Lower brominated mixtures generally
found to be more toxic.***

***Developmental and reproductive toxicities
– limited information***

Toxic Substances Control Act (TSCA) enacted in 1976

**is main federal vehicle for controlling chemicals that
are potentially dangerous to living things.**

**Authorizes EPA to regulate manufacture, importation,
processing, distribution, use, and disposal**

Existing Industrial Chemicals

TSCA Section 4 authorizes EPA to require companies to conduct testing on health and environmental effects

EPA must show

- the chemical poses unreasonable risk
- and is produced in major quantities and a substantial # of people are exposed

**Section 6 authorizes EPA to ban it if...
it presents or will present and unreasonable risk of
injury to health or the environment
...only a handful of banned, i.e. lead in paint**

Worldwide Regulatory Activities

**The European Union has banned Penta and Octa,
effective Aug 15, 2004.**

Japan instituted voluntary phase out penta & octa.

California passed a statewide ban for 2008.

**US EPA is working with PBDE manufacturers on a
voluntary phase out plan**

US EPA Key Activities

Assess Substitutes for Penta BDE and Octa BDE

Assess and Evaluate Deca BDE

Assess Risks of Penta and Octa BDEs

Track Developments Concerning Other BFRs

PBDE State legislation introduced in last 2 years-

Regulating release

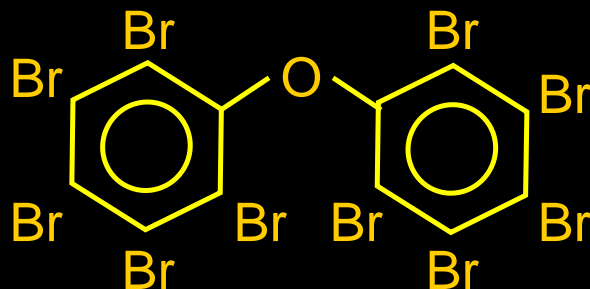
Phase out

Sentencing for environmental release of PBDEs

Incentives to recycle PBDE polymer wastes

ME, NY, HI, CA, MI, WA, WI, MA

Deca BDE Debate



Environmental Fate ?

Toxicity ?

Replacements ?

**EPA Deca Assessment Under the
Voluntary Children's Chemical Action Program**

Continuing Research on PBDEs

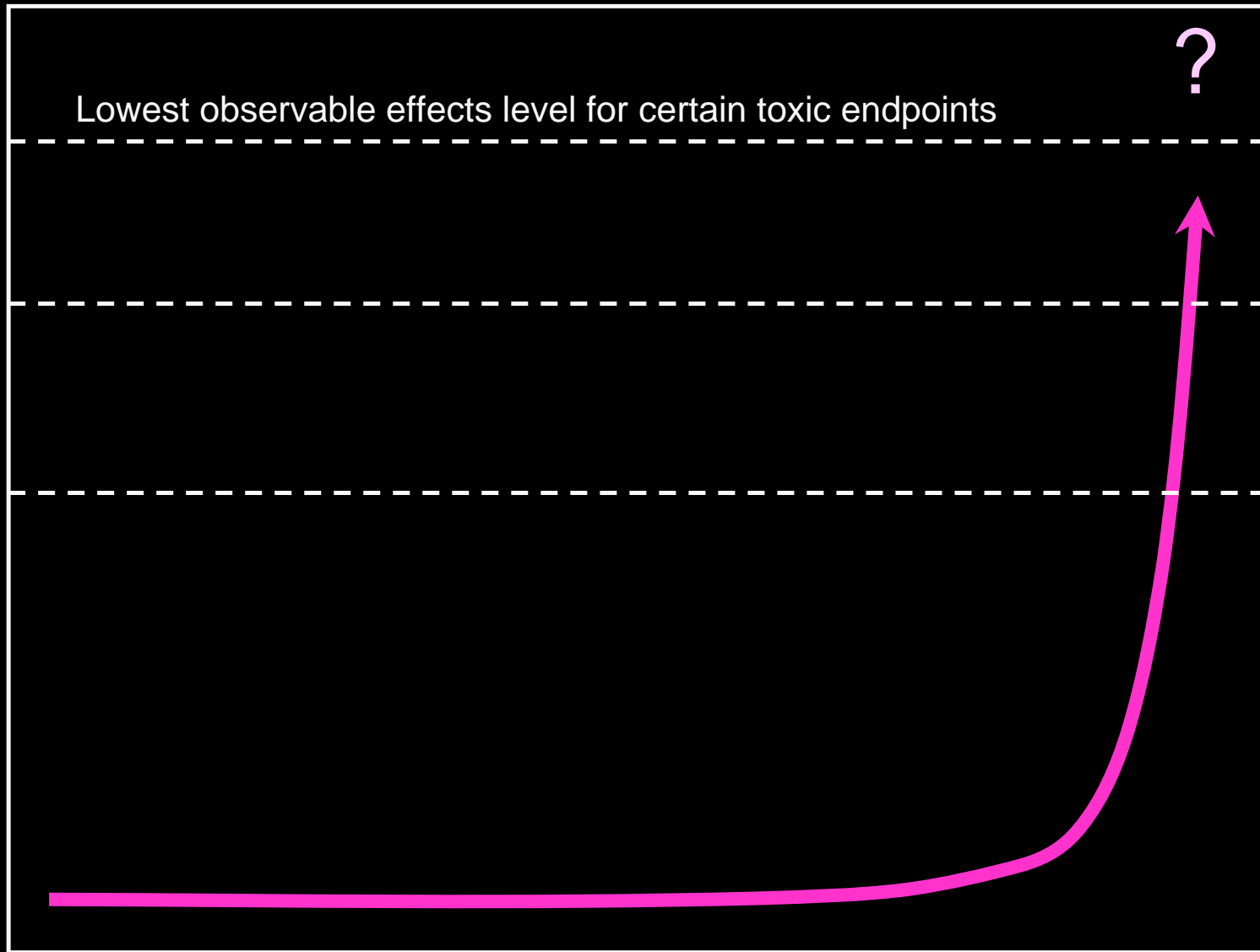
- **Toxicities of PBDE congeners and mixtures**
- **Environmental degradation rates of various PBDEs**
- **Mobility of PBDEs in soils, leaching from landfills**
- **Occurrence and distribution in the environment**
- **Detrimental effects in fish and wildlife**
- **Incineration- produces halogenated dioxins/furans**

PBDE congener concentration

Lowest observable effects level for certain toxic endpoints

?

1970 1980 1990 2000 2010 2020



File:BR0CPBDE1 #1-1100 Acq:27-SEP-2002 03:40:07 GC EI+ Voltage: SIR 70S

m/z 247.9837 327.8921 485.7111 F:2 563.6216 F:3 649.5302 F:3 643.5301 F:4 721.4406 F:5

Sample Text:PEDE CS6 CAL Std (50 uL) File Text:50m UI-2 130(1)-155@12-215@2-350@3 (5)

Acknowledgements

USGS Environmental Chemists

Paul Peterman
Robert Gale, Kathy Echols



Thank you