PCBs in Painted Structures and Adhesives and a Novel Approach to Remediation

Kathleen B. Brooks

NASA Kennedy Space Center

Kathleen.b.brooks@nasa.gov

Contributors:

Jacqueline W. Quinn (NASA, Kennedy Space Center)

Christian A. Clausen, Cherie L. Geiger, Brian S. Aitken and Robert W. Devor (University of Central Florida)

What are PCBs? Why are they a problem?

- Polychlorinated biphenyls (PCBs) are a group of synthetic aromatic compounds $C_{12}H_{10-x}Cl_x$.
- Mixtures
- Very stable and long-lived
- Properties enhanced structural integrity, reduced flammability and boosted antifungal properties
- Known Carcinogen
- Found in at least 500 or the 1598 National Priorities List (Superfund) sites

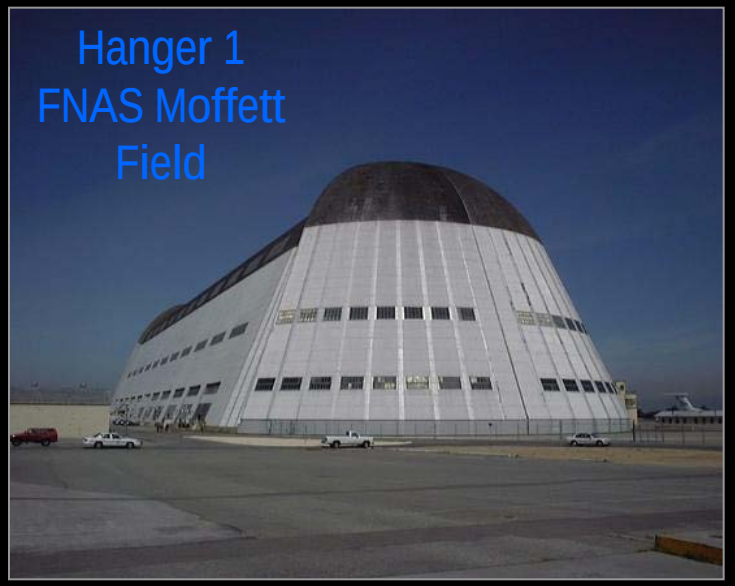
Where are PCBs found?

Lubricants, dated transformer oils

Paints (on structures painted earlier than the mid 1970's)

Caulking material

Binders or adhesive material



Example of PCBs Unexpectedly Found at KSC HQ Building

PCBs found in HQ Caulk at 21,000 ppm

EPA Regulatory limit 50 ppm

Bimetallic Treatment System (BTS)

- **A commodity that removes and degrades PCBs from coatings or substrates.**

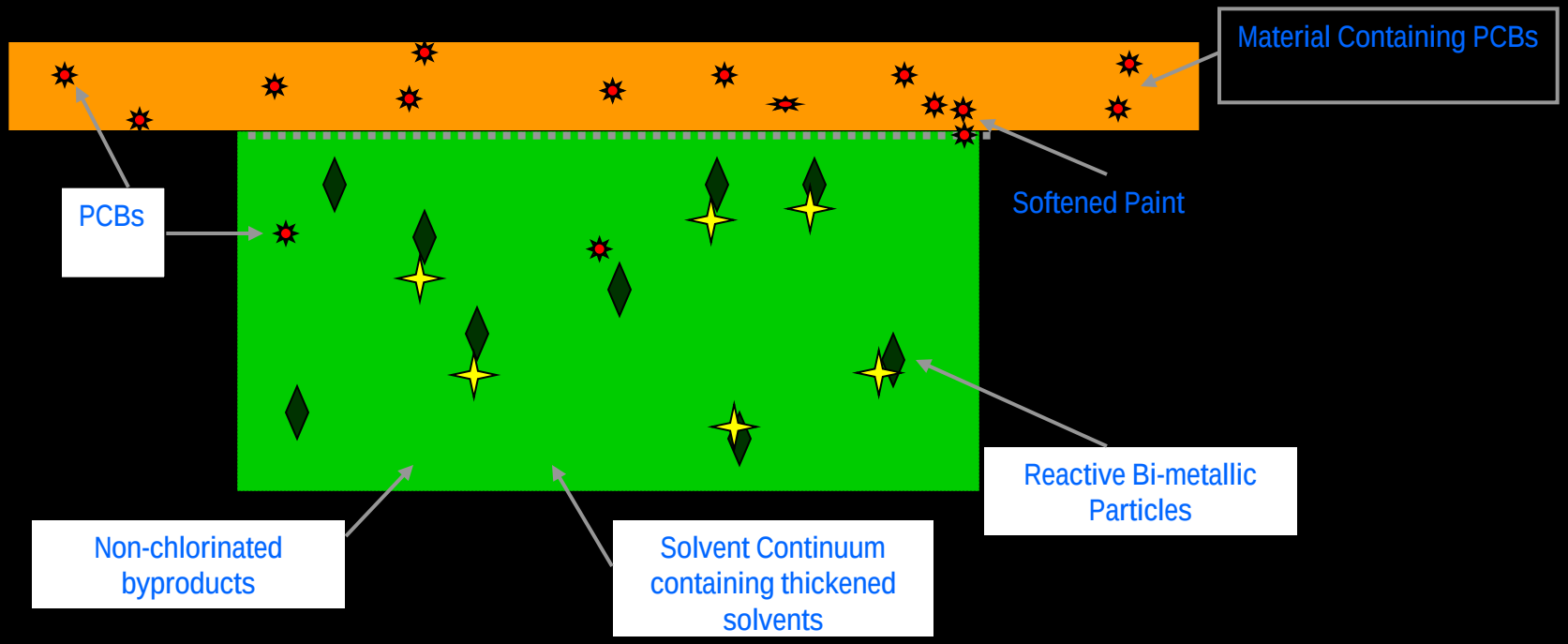
How BTS Works- A Two Independent Step Process

1. The solvent in the BTS softens the paint allowing the PCBs to migrate into the BTS continuum.

2. Once inside the BTS, the metal/catalysts system reductively dehalogenates the PCBs.

Description of the BTS

- BTS is a reagent comprised of elemental magnesium coated with a small amount of palladium incorporated into a solvent treatment system for the treatment of PCBs.



BTS Formulations Are Custom

- Each specific coating will require a solvent that's applicable

Painted Beam

Caulk from KSC HQ Building

Galbestos from Hanger 1

Percent PCB Removal from Paint

- **Launch umbilical tower (LUT) paint treated with BTS paste consisting of Mg/Pd, glycerin and methanol. Exposure time 24 hrs.**

Sample Identification	Initial Concentration Aroclor 1260 (mg/Kg)	After BTS Aroclor 1260 (mg/Kg)	% PCB Removal
LUT A Green 05/11/05	110	0.8	**>99 %**
LUT A Green 05/18/05	260	9.7	**96 %**
LUT Red 05/18/05	7.7	0.2	**97 %**

Dehalogenation Reactions

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

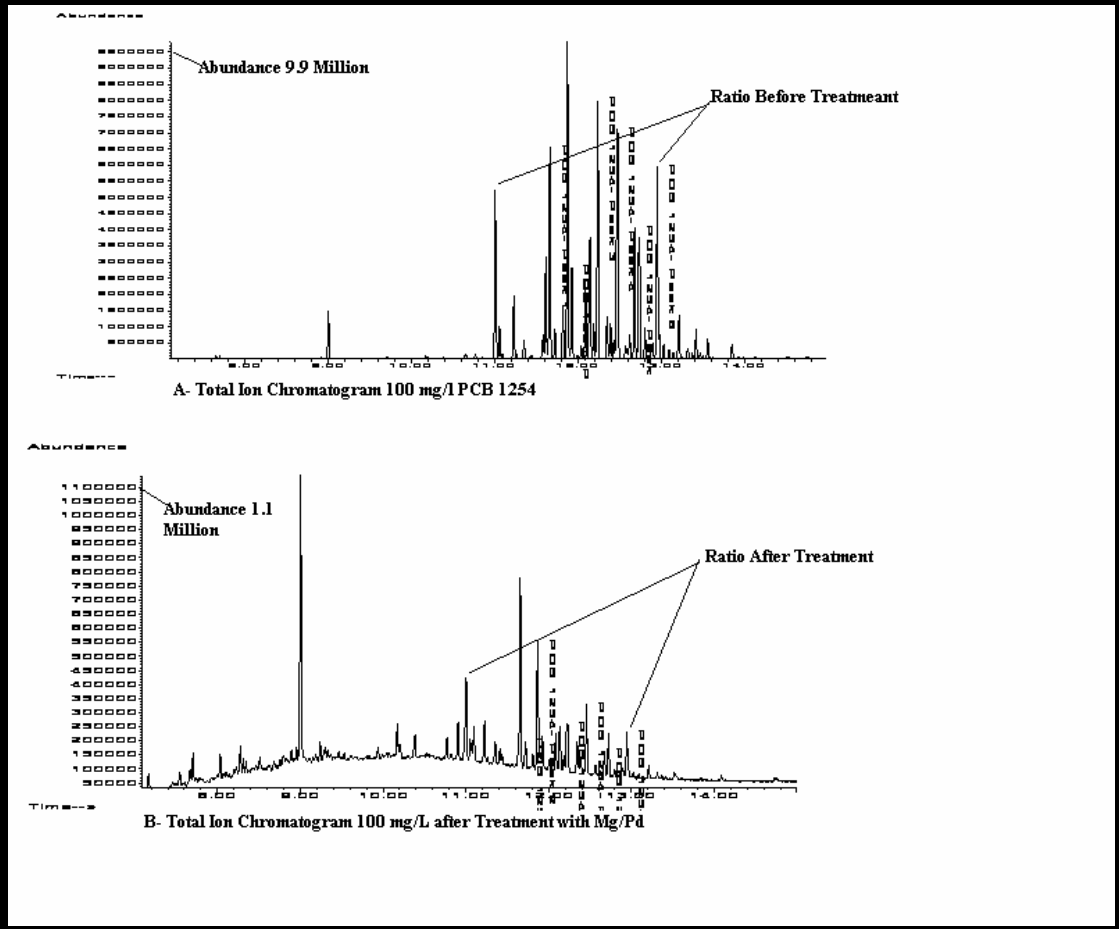
$$H_2 \text{ (Pd catalyst)} + RCl \rightarrow RH + HCl$$

- Zero-valent dehalogenation reactions have used historically in environmental remediation

Magnesium Palladium Bimetal

- Mechanical Alloying system- Typically 0.1% Pd on Mg
- Other catalytic systems under investigation
- Must be Earth-Friendly, prefer low cost!

Total ion chromatograms showing differing peak ratios of a 100mg/l Solution before and after treatment with Mg/Pd.



Lab Dehalogenation Results

- **Exposure of standard aroclor 1260 in 10% methanol in water solution to 1.0 g Mg/Pd**

Sample Identification	Aroclor 1260 (mg/l)	% PCB Degradation
Extracted Standard (no Mg/Pd) 5.9 mg/L Initial Concentration	5.9	0
Standard exposed to Mg/Pd 1.0 hr	0.4	**92 %**
Standard exposed to Mg/Pd 4.0 hr	<0.1	**>98 %**
Standard exposed to Mg/Pd 4.0 hr (dup)	<0.1	**>98 %**

Other Considerations

- Thickeners
- Stabilizing agents

Separating the Two Step Process

Advantages to dip/ treat method

- ✓Less engineering issues
- ✓Benefit of time
- ✓More Applicable to treating contaminated materials that are not structures

Marshall Space Flight Center

MSFC 4696 Test Stand

BTS test panels covered with aluminum foil or copper sheets

MSFC Data:

Initial laboratory testing of Marshall Space Flight Center paint chips treated with BTS paste consisting of Mg/Pd, glycerin and ethanol. Exposure time of 24 hrs.

Sample Identification	Initial Concentration Aroclor 1260 (mg/Kg)	After BTS Aroclor 1260 (mg/Kg)	% PCB Removal
4696 F1 Stand	4.6	0.8	**83 %**
4553 F1 Stand	6.3	<0.3	**95 %**

MSFC Data:

Field results using a limonene-based BTS paste at MSFC building 4696 F1 stand.

Time of Exposure (hr)	Initial Concentration Aroclor 1254 (mg/Kg)	Concentration Post-BTS Application Aroclor 1254 (mg/Kg)	% PCB Removal
8 Panel F	3.46	2.65	23%
8 dup Panel F	3.21	2.87	11%
24 Panel D	3.28	2.39	27%
24 dup Panel D	3.11	2.23	28%
30 Panel H	4.16	22.82	-66%**
72 Panel B	4.18	1.79	57%
72 dup Panel B	12.35	6.54	47%
72 Panel I	4.36	2.55	41%
72 Panel K	3.69	3.03	18%
72 dup Panel K	4.17	3.52	16%
72 Panel L*	3.53	1.80	49%
72 Panel M*	2.50	1.82	27%
72 Panel N*	3.05	1.65	46%
72 Panel O	3.55	2.12	40%

Current Projects

- Environmental Security Technology Certification Program (ESTCP), a DOD sponsored demonstration and Validation Program
  - Badger Army Ammunitions Depot in Madison, WI
  - Vertical Integration Building, Cape Canaveral, FL
  - USS Adams in Philadelphia, PA – Ghost Ships

Future Considerations

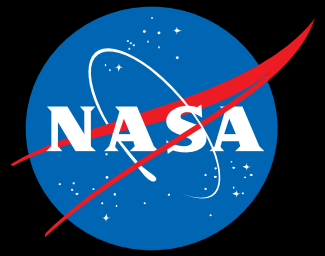
- Scaling up- engineering procedures
- Soil and Sediment Remediation

References

- Avedesian, M. and H. Baker, (Eds.). 1999. *Magnesium and Magnesium Alloys*. ASM International.
- Brown, LeMay, and Bursten. 2005. *Chemistry, The Central Science*, 10th ed., Prentice Hall,
- Doyle, J.D., T. Miles, E. Parker and F. Cheng, 1998. “Quantification of Total Polychlorinated Biphenyl by Dechlorination to Biphenyl by Pd/Fe and Pd/Mg Bimetallic Particles,” *Microchemical Journal,* Vol. 60,:290-295.
- Doyle, J (speaker). 1998, “Quantitation of Total PCB by Dechlorination to Biphenyl.” Abstract No. 27 53rd ACS-NORM, Pasco, Washington, , June 1998
- Engelmann, M.E. et al. 200.3. “Simultaneous Determination of Total PCB and DDT by Dechlorination with Pd/Fe and Pd/Mg Bimetallic Particles and GC-FID” *Microchemical Journal*, 74, 19-25.
- McMurray, John, Brooks/Cole, ed, 2000. *Organic Chemistry*, 5th ed., Thomsan Learning.
- Tsuji, J., 2004. *2000 Palladium Reagents and Catalysts, New Perspectives of the 21st Century*. John Wiley and Sons, LTD.

Special Thanks

- Dr. Jacqueline Quinn (NASA)
- University of Central Florida (Drs. Chris Clausen and Cherie Geiger)
- NASA, Office of Space Flight
- ESTCP


NASA