Treatment of PCB Contaminated Caulking Using AMTS

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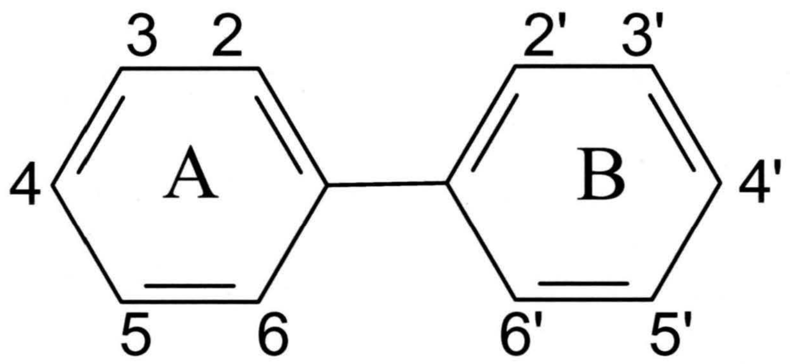
Outline

- Background Information
  - PCB Concerns
  - BTS/AMTS Technologies
- Treatment of PCBs
  - Paints
  - Concrete
  - Caulk
- Future Work

Polychlorinated Biphenyls (PCBs)



$C_{12}H_{10-n}Cl_n$

- 209 Congeners
- Synthetic
- Heavy Industrial Use
- Bioaccumulate and Concentrate in Fatty Tissue
- TSCA Regulated Since late 1970's
- Persistence due to Stability

Health Effects of PCBs

- Bioaccumulates in fatty tissue
- Shown to cause cancer in animals
  - Possible human carcinogen
- Immune system suppressant
- Affects reproductive system
  - Lowers birth rate
  - Can be passed through breast milk

Where are PCBs Found?

- Prior to 1979, PCBs were used extensively in:
  - Industrial paints
  - Caulking material
  - Coatings
  - Adhesives
- Due to the environmental stability of PCBs, they are a ubiquitous pollutant
  - PCBs are found in soils, sediments, water table, etc...

PCBs in Caulking

- Commonly used as a plasticizer in caulks
- Arochlor 1254 most often used
- Currently, testing of caulk for PCBs is not required
  - Caulk is a unrecognized source of PCB contamination
  - Regulatory limit of 50ppm
- PCB contamination can penetrate surrounding surfaces as well (concrete, wood, etc…)

PCBs in Caulking Material

- Found in masonry buildings and concrete structures built between the 1940's and late 1970's
- Used in concrete expansion joints
- Caulk can contain up to 15% PCBs (by mass)

Why is this a Concern?

- PCBs found in caulking materials can:
  - Cause impacts to soil and storm water
  - Possibly impact indoor air quality
  - Cause personnel exposure during renovations
  - Dramatically increase costs for disposal during demolition or renovation projects
  - PCBs from the caulk can leach into the surrounding materials, spreading the contamination problem (increasing the concerns listed above)

PCBs in Schools

- Recent studies have shown that building materials have begun to leach PCBs into the surrounding materials of school buildings
- Growing concern for school administrators and concerned parents
- Once PCBs have leached into the surrounding environment, can affect children and personnel

Westchester, New York

- French Hill Elementary School
- Prompted by parent who had scraps of caulking tested
  - PCBs found at ~38,000ppm (760x EPA allowable limit); sample collected/paid for by parent
  - Soils around the school were found to have levels above the NY State 1ppm clean-up requirement; sample collected/paid for by parent
  - Repeated testing showed soil levels as high as 40ppm

Westchester, New York

- Total decontamination costs - ~$300,000
- Statement by Kenneth Stoller, Chief of Pesticides and Toxic Substances. EPA Region 2

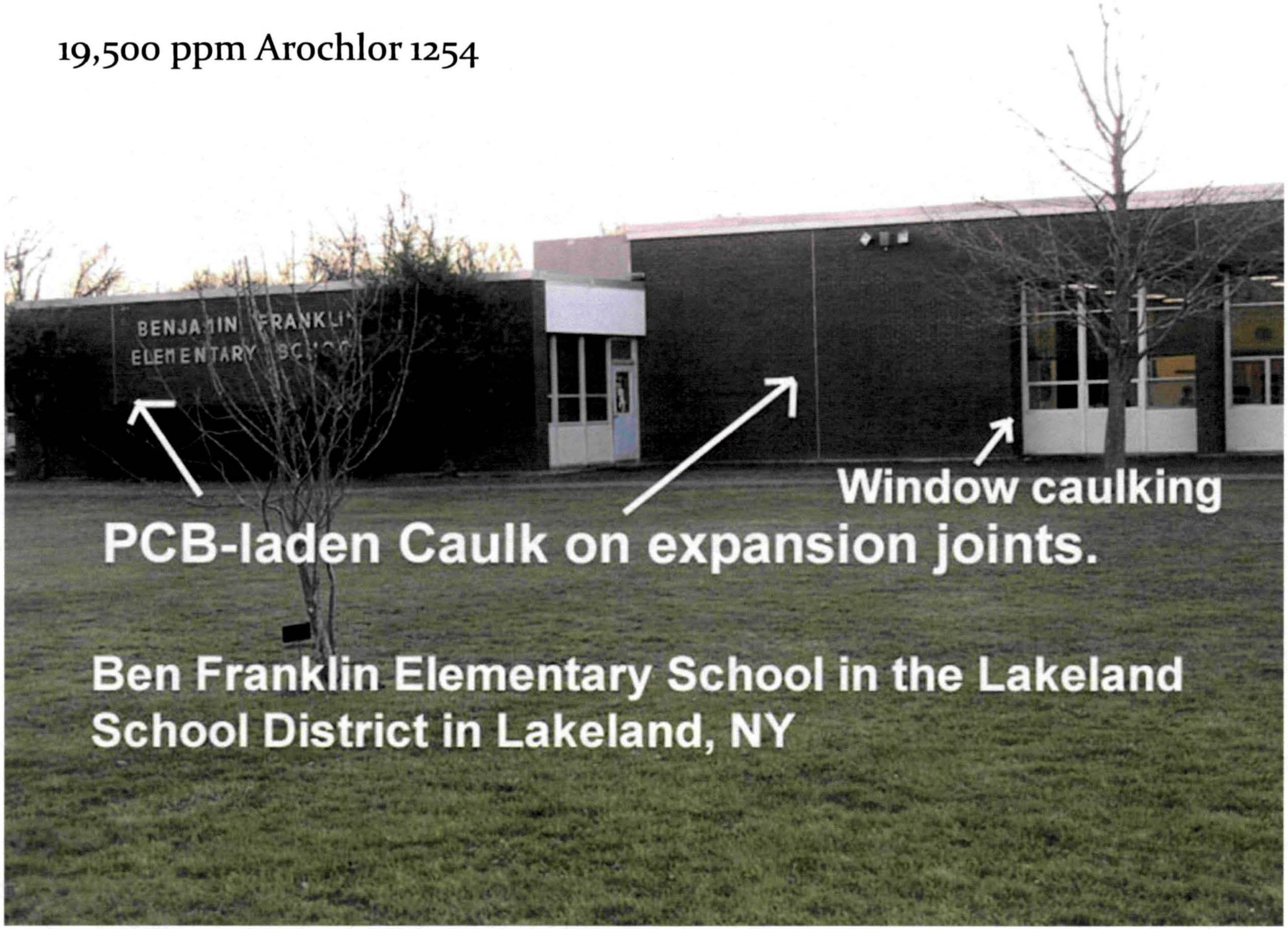
"The use of PCBs in caulking and sealant materials has never been authorized by the Environmental Protection Agency. In general, the placement of such materials pre-dates the enactment of the Toxic Substances Control Act and its use today is not authorized. Therefore, the prospect of authorizing the continued use of this material in residential settings, or where children could be exposed, is extremely unlikely. Because it is illegal, and the potential for exposure may be significant, PCB-containing caulk must be removed upon discovery"

U.S. Environmental Protection Agency, Letter to Michael Kaplowitz, November 3, 2005, http://www.pcbinschools.org/EPA%20LETTER.pdf accessed September 30, 2009.

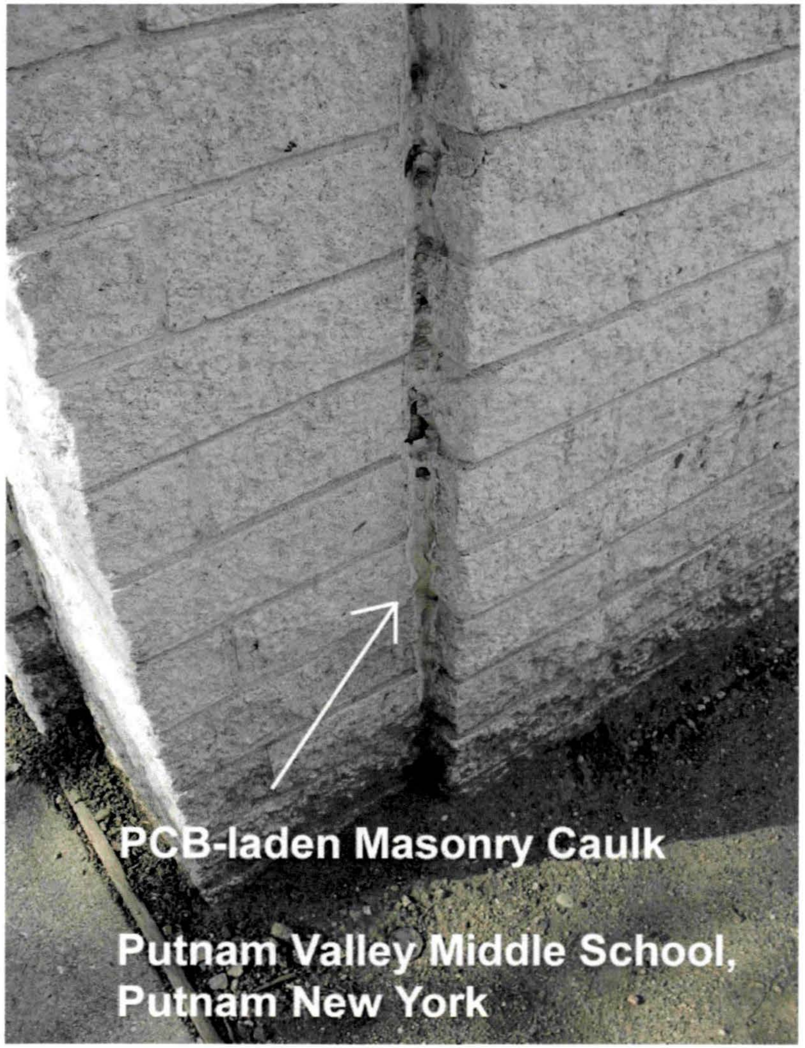
Greater Boston Area

- Harvard School of Public Heath
  - Tested 24 buildings
  - 33% of the buildings exceeded regulatory limits for PCBs
  - Found in schools, universities buildings, and other public buildings
  - Some buildings had almost as high as 50,000ppm PCBs
  - Identified caulk and other sealing materials as widespread and an unrecognized source of PCB contamination

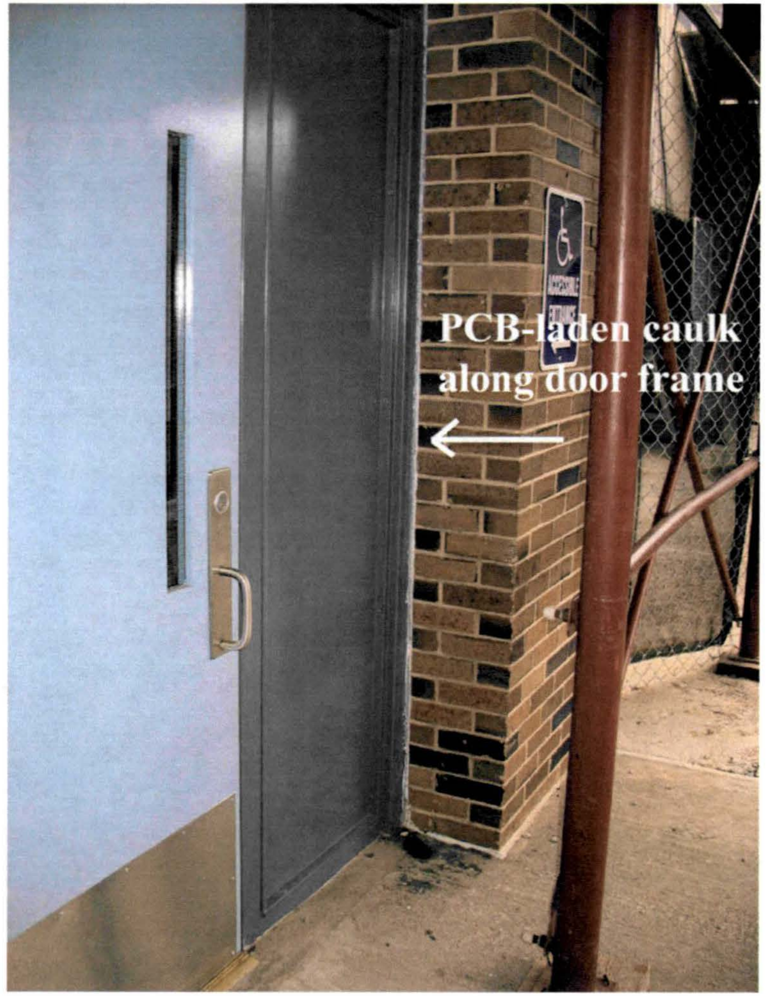
19,500 ppm Arochlor 1254



http://www.pcbinschools.org/Photos%20of%20caulk.htm



Putnam Valley Middle School,
Putnam NY, 2006
10,000 ppm Arochlor 1260



PS 181, Bronx NY, 2007
6180 ppm Arochlor 1254

http://www.pcbinschools.org/Photos%20of%20caulk.htm

Burlington High School, Burlington, Massachusetts, 2006
Masonry Caulk 106,611ppm Arochlor 1260

http://www.pcbinschools.org/Photos%20of%20caulk.htm

Current EPA Guidance

CURRENT BEST PRACTICES FOR PCBS IN CAULK FACT SHEET
Removal and Clean-Up of PCBs in Caulk and PCB-Contaminated Soil and Building Material
Last Updated: September 2009

Removal of PCB-contaminated Caulk during Renovations and Repairs

- Where schools or other buildings were constructed or renovated between 1950 and 1978, EPA recommends that PCB-containing caulk be removed during planned renovations and repairs (when replacing windows, doors, roofs, ventilation, etc.)
- It is critically important to ensure that PCBs are not released into the air during renovation or repair of caulk in affected buildings. EPA is recommending simple, common sense work practices to prevent the release of PCBs during these operations.

Caulking containing PCBs at levels > 50 ppm is not authorized for use under PCB regulations and must be removed

Previous Treatment Methods

- Physical removal of caulk, paint, brick/masonry
  - Still treated as hazardous material
  - Can release PCBs into the air
- Concrete Scarification
  - Treats only top layer (~1")
  - Concrete removed is still contaminated
  - PCBs may penetrate much deeper into concrete
- Sealants to isolate PCBs
  - Doesn't treat source of the problem
  - Sealants can degrade overtime
  - PCBs may migrate into sealant material

Zero-Valent Metals (ZVMs)

- ZVMs (including Fe and Mg) have proven to be capable of degrading chlorinated contaminants
  - PCBs, TCE, Chlorobenzenes, etc…
- Mg more effective for remediation purposes
  - High reduction potential (-2.2V vs. SHE) compared to iron (-0.44V vs. SHE)
  - Self-limiting oxide layer helps resist oxidation over time
  - Free Mg^{0} metal less environmentally toxic than free Fe^{0}

BTS and AMTS

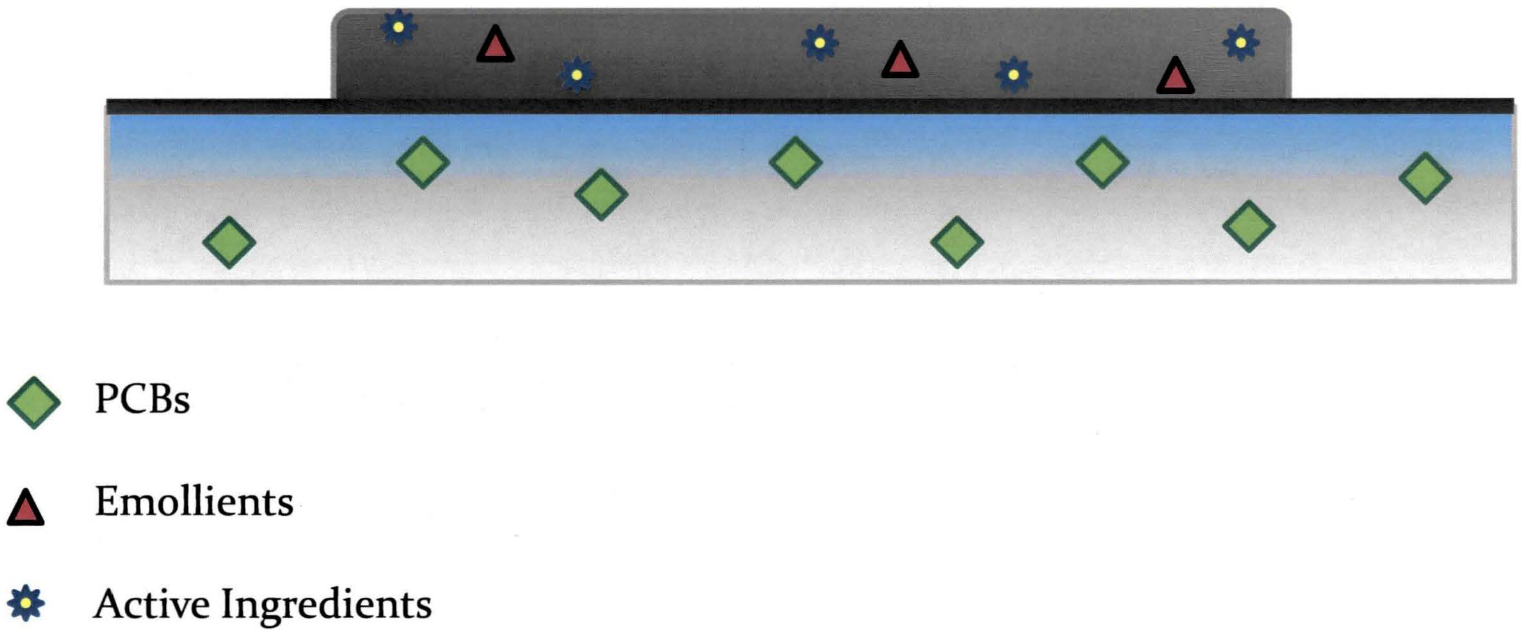
- NASA and UCF developed technology for the treatment of PCBs
  - Caulk, concrete, paints…
- BTS – Bimetallic Treatment System
  - Mg metal (ZVMg) with Pd
- AMTS – Activated Metal Treatment System
  - Mg metal (ZVMg) in acidified ethanol

Description of AMTS

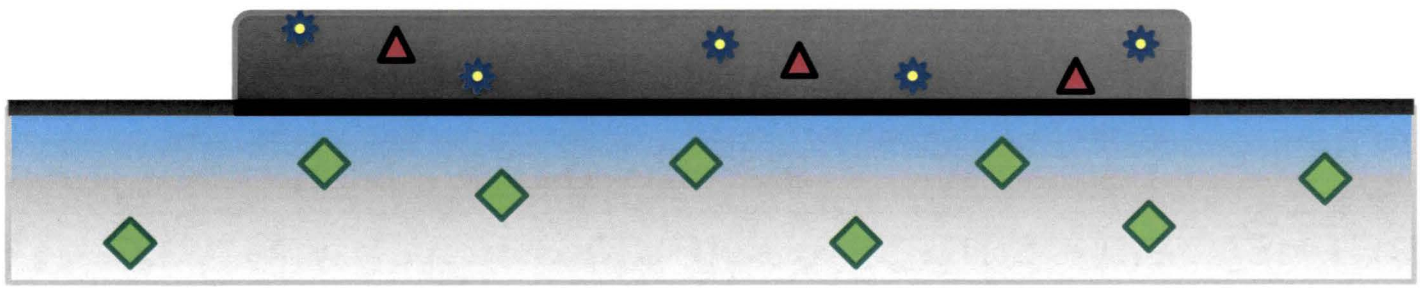
- Paste made up of components with different purposes
  - Magnesium, acetic acid, ethanol – active ingredients
  - *D*-limonene – emollient
  - Calcium stearate – bulking agent
  - Polyethylene glycol
  - Sodium polyacrylate or *Powdersorb*
  - Glycerol
- Ratio of reagents can be modified to suit specific applications

Description of AMTS

- AMTS paste containing emollients and active ingredients is applied to contaminated surface

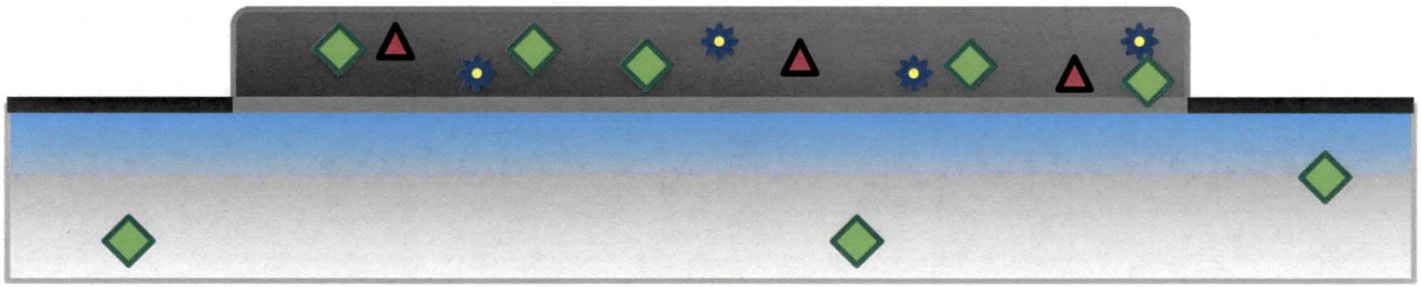


Description of AMTS



- ▲ Emollients soften the surface and promote absorption of PCBs into paste matrix

Description of AMTS



- Magnesium and acidified ethanol dechlorinate absorbed PCBs

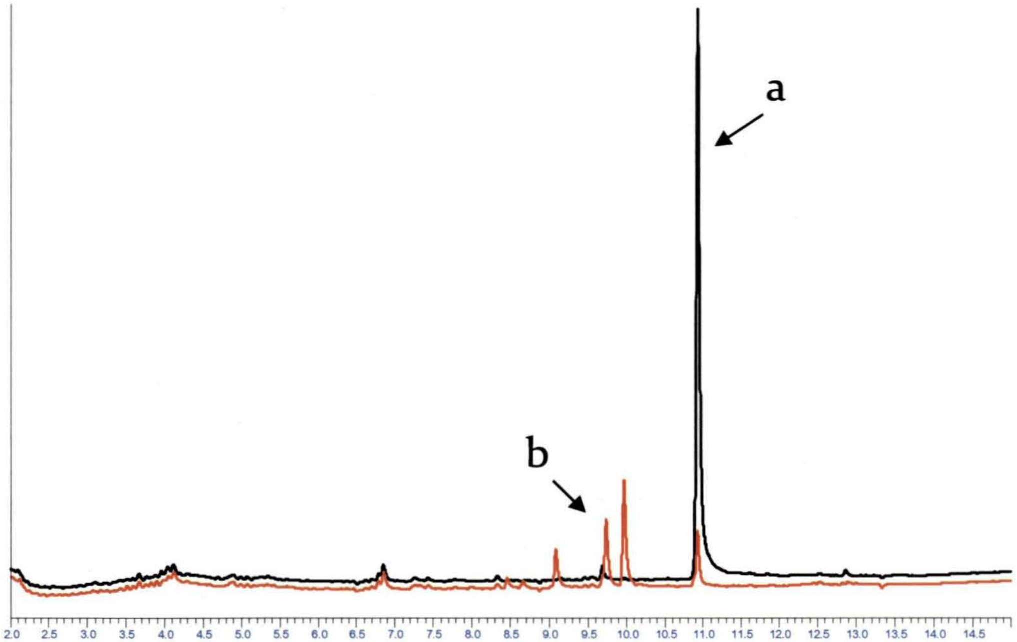
AMTS or NMTS?

- AMTS incorporates Mg into the treatment system
  - Faster, remediates during removal
  - *In-situ* degradation
- NMTS is a non-metal treatment system
  - 2-step process
  - PCBs are first removed, then remediated by activating the NMTS with Mg
  - Allows for removal and *ex-situ* remediation
  - More cost-efficient use of Mg

Proof of Concept Studies

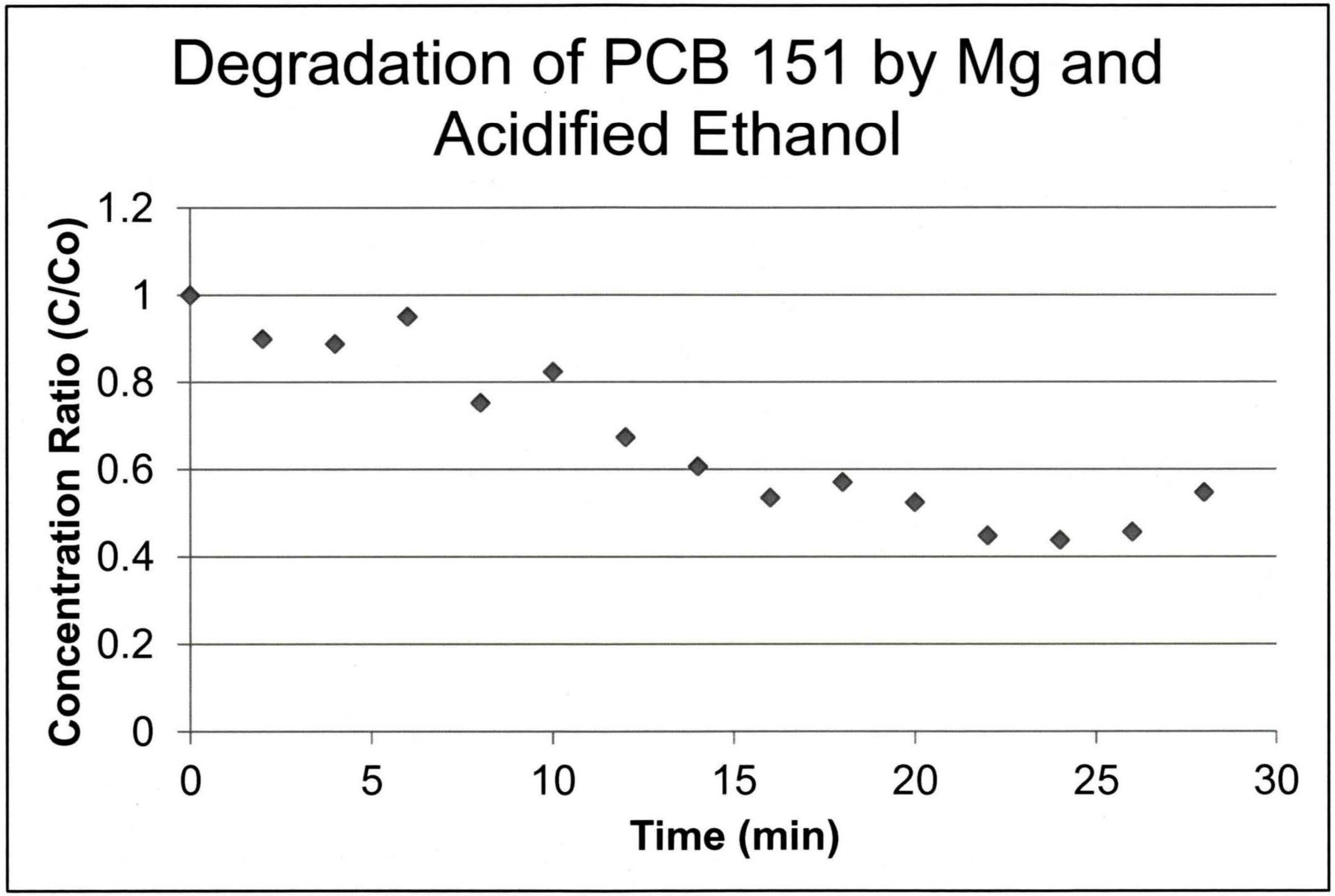
- Dechlorination of PCBs by active components of AMTS in controlled laboratory setting
- Individual vials prepared using ethanol, acetic acid, magnesium, and a PCB spike
- Single congener studies enhance product peak visibility, analyzed by GC-ECD

Proof of Concept Studies



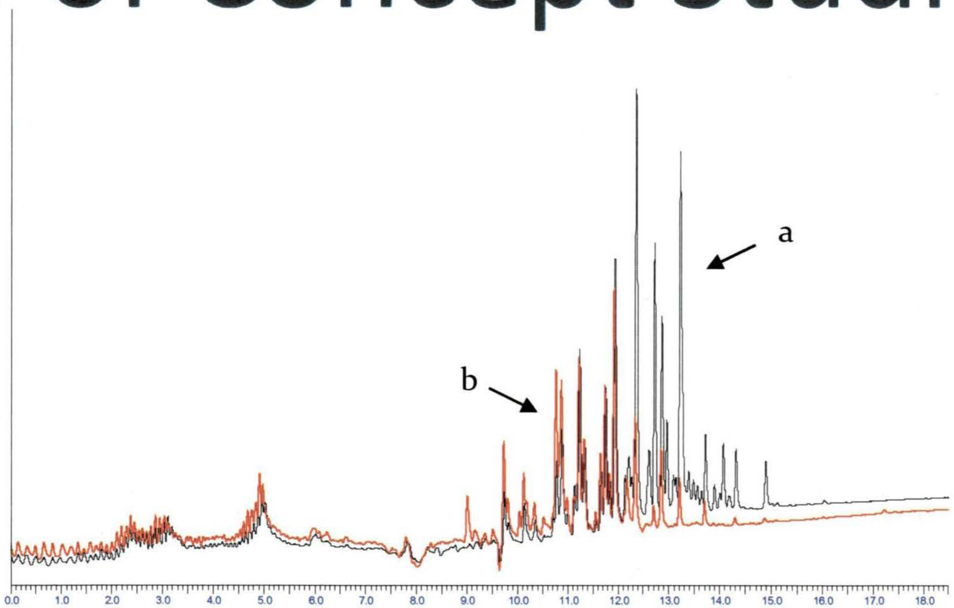
Overlaid chromatograms of PCB 151 in ethanol before treatment (a) and after 20 minutes treatment with Mg and acidified ethanol (b)

- Presence of product peaks as the main peak decreases indicates formation of lower chlorinated products, rules out strict sorption processes



- About 50% of degradation takes place within 30 minutes
- Total PCB level is reduced from ~5 mg/L of a single congener to below limit of detection within 1 hour

Proof of Concept Studies: AMTS



Overlaid chromatograms of AMTS paste spiked with Aroclor 1254 before activation (a) and one week after activation with Mg and acidified ethanol (b)

- Envelope shift from higher to lower chlorinated congeners again rules out a sorption-only process within the AMTS paste when activated

Field Readiness Studies

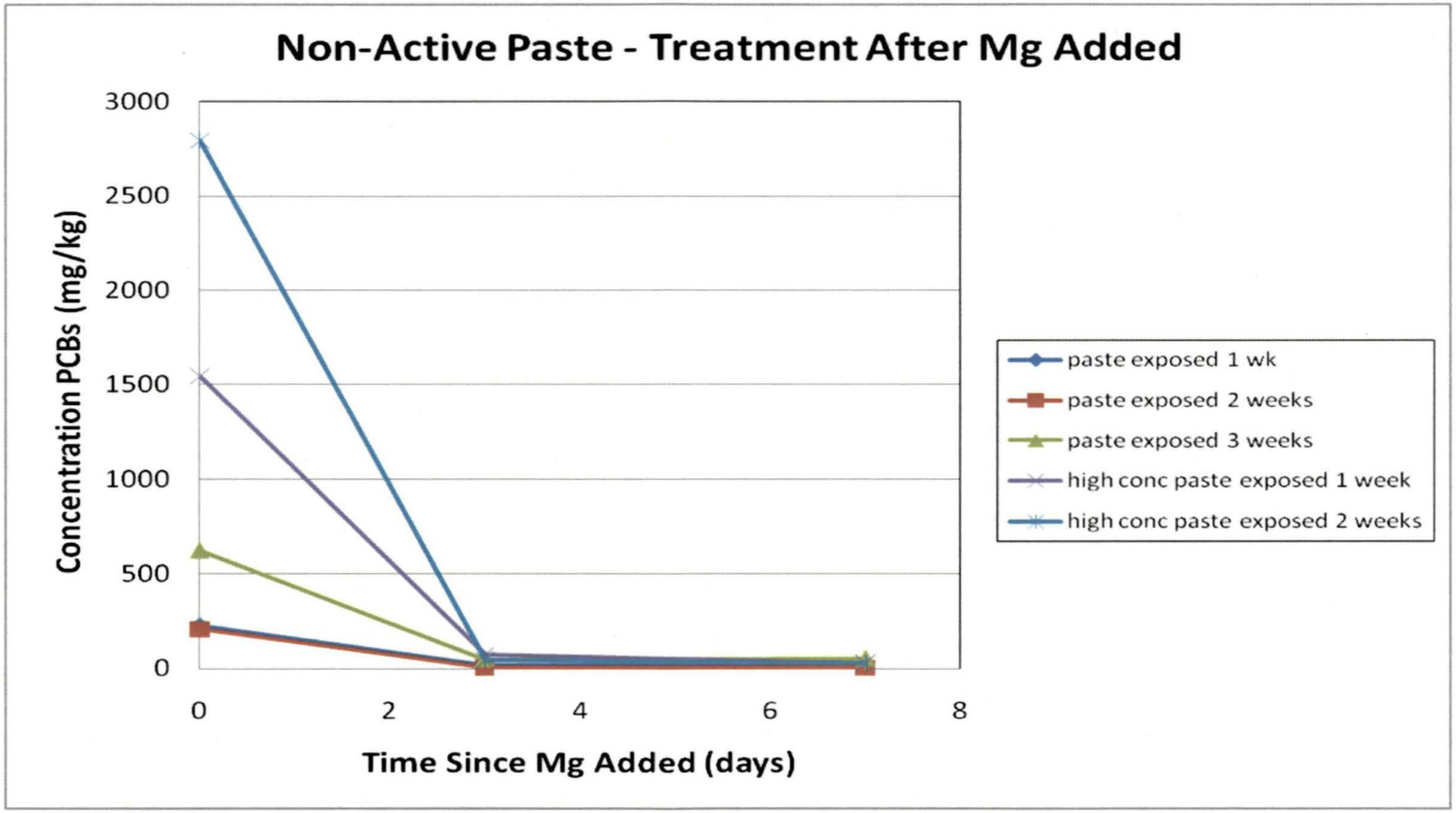
- In-laboratory treatment of materials from contaminated sites
  - Paint
  - Caulk
  - Concrete

Paint Treatment

Sample ID	Initial Conc (mg/kg)	7 days (mg/kg)	3 weeks (mg/kg)
C15 Truss	1377.8		42
C7 Truss	999.8		21.6
Blanchard	2778		55.7
G21	1385.5	392	42.6
E23	830.7	433.2	51.2
D21	2196.9	491.3	104
Lathe	2397	1049	52.3

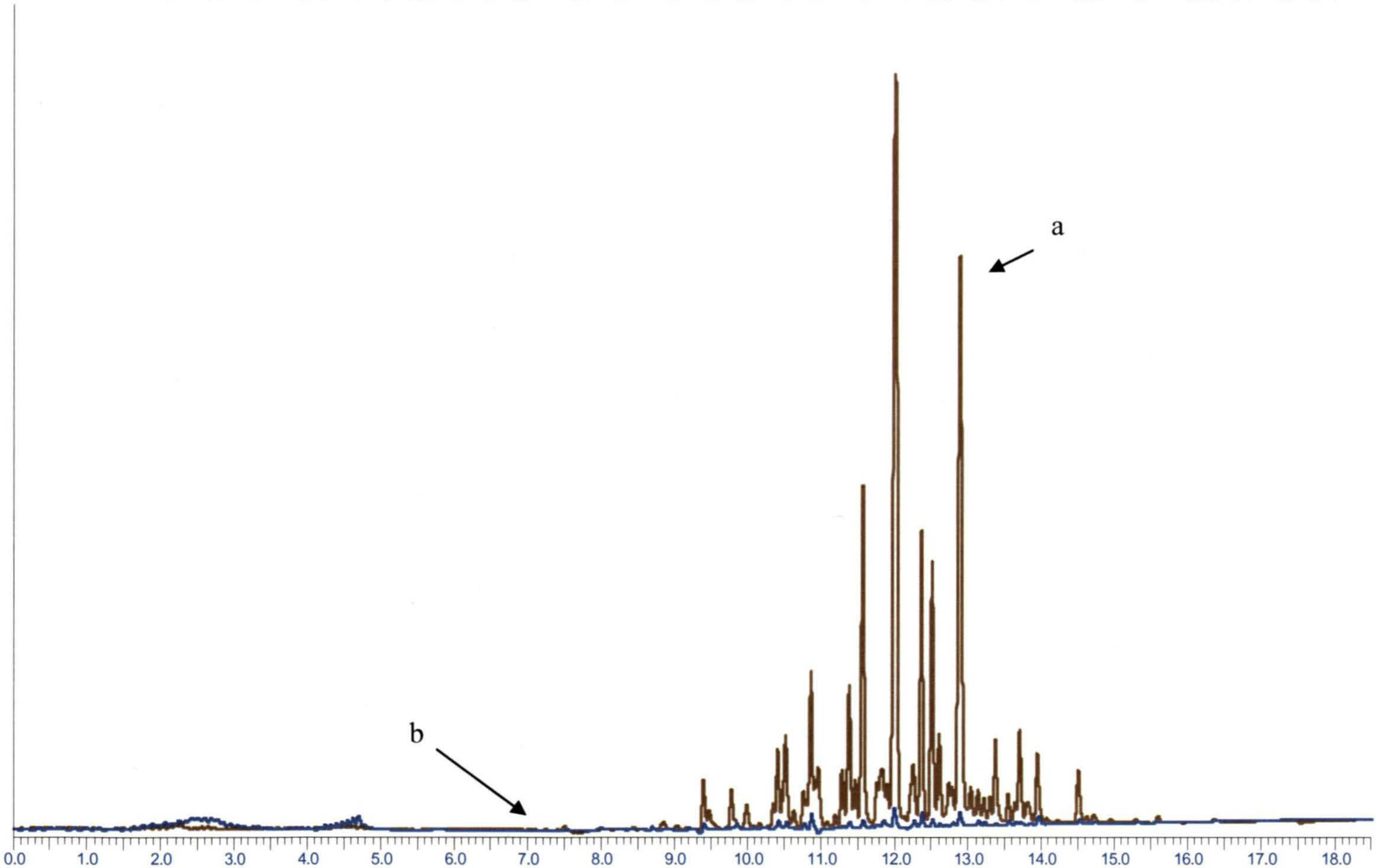
- AMTS paste applied to samples of contaminated paint and allowed to react in vials for specified time

Treatment of Non-Active Paste



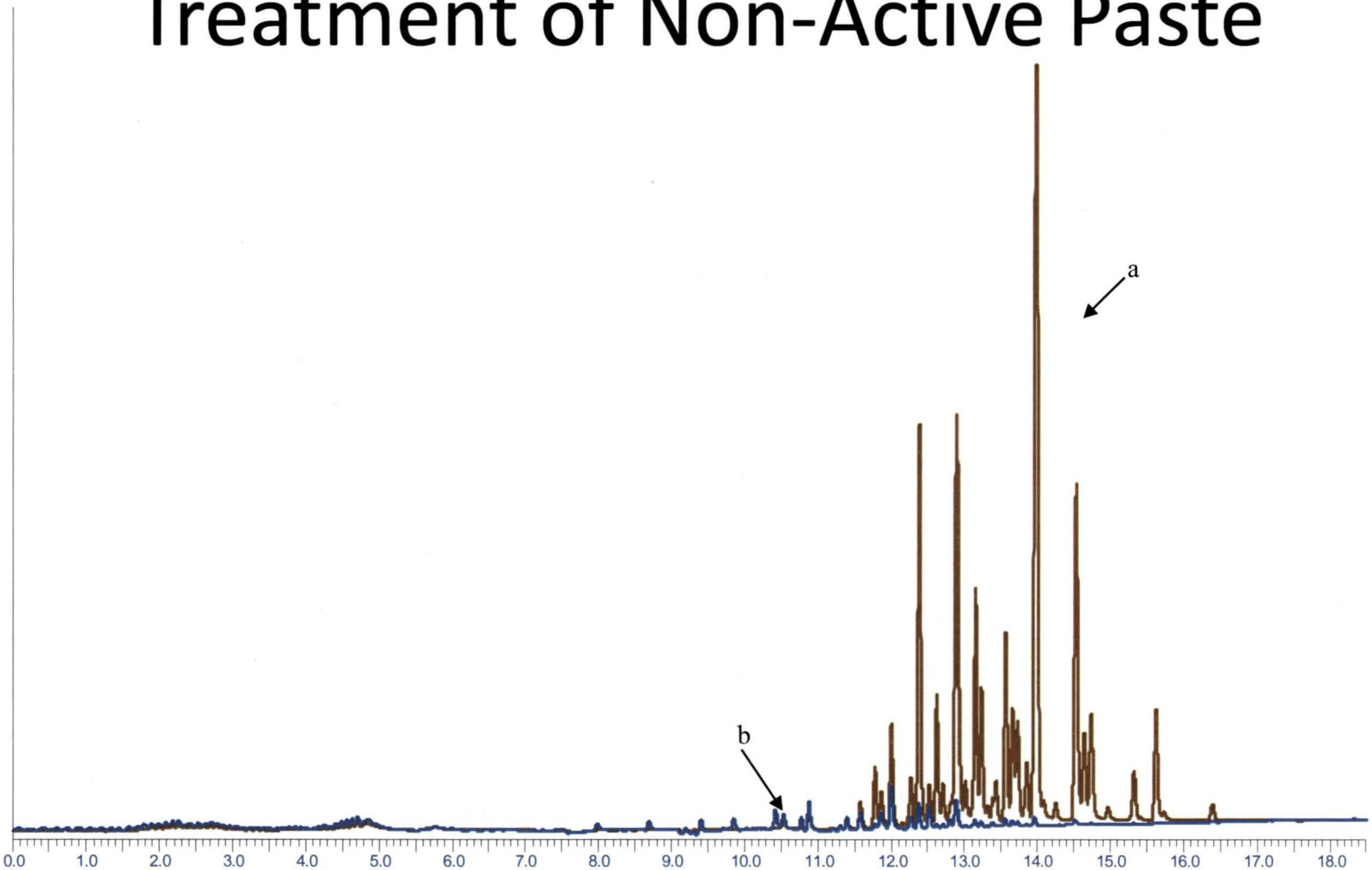
10% of activated Mg added to paste after removed from painted structures and successful treatment to below 50 mg/kg even with high starting concentrations

Treatment of Non-Active Paste



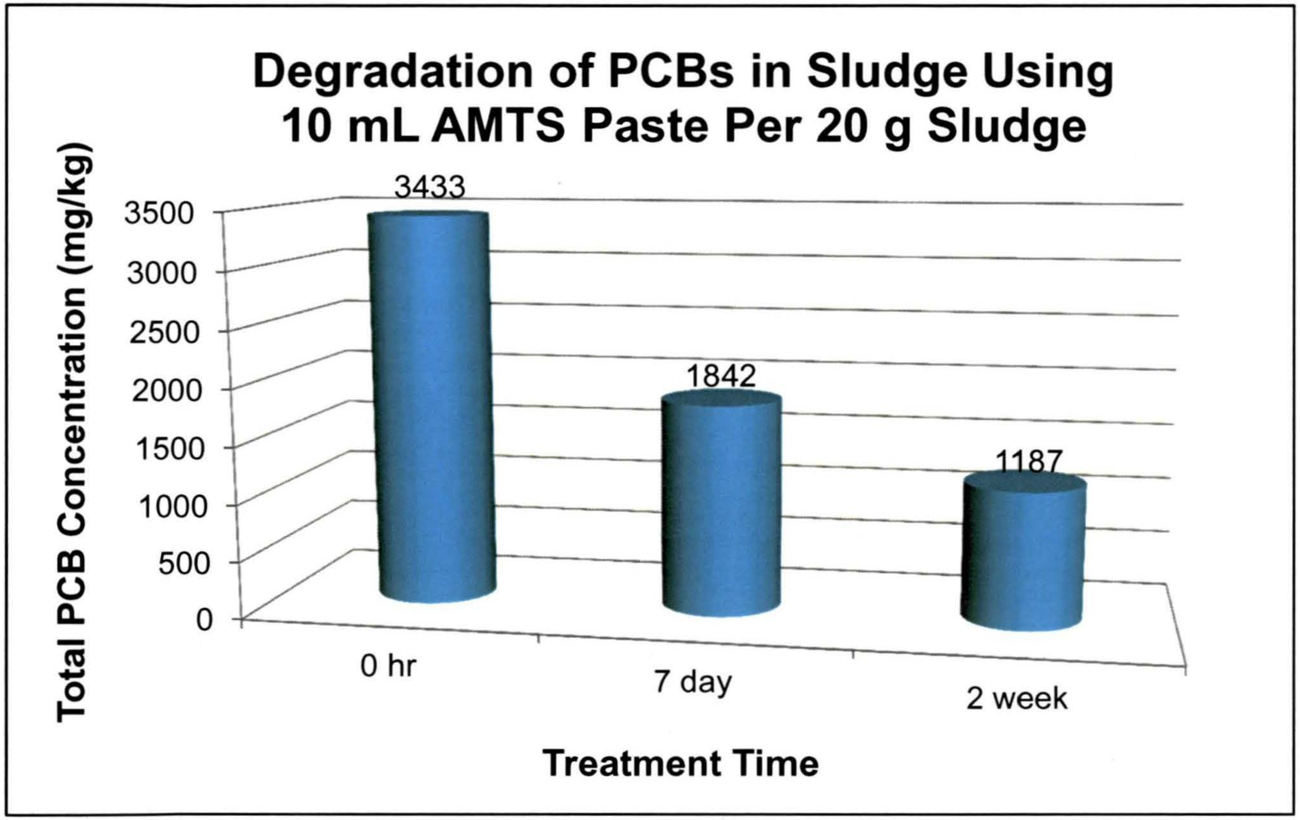
Overlap in chromatograms of paste sample a) NM 6657-02 (before treatment) 1,544 mg/kg= **brown**, and (b) after 3 days reacting with Mg metal 123 mg/kg= **blue.**

Treatment of Non-Active Paste



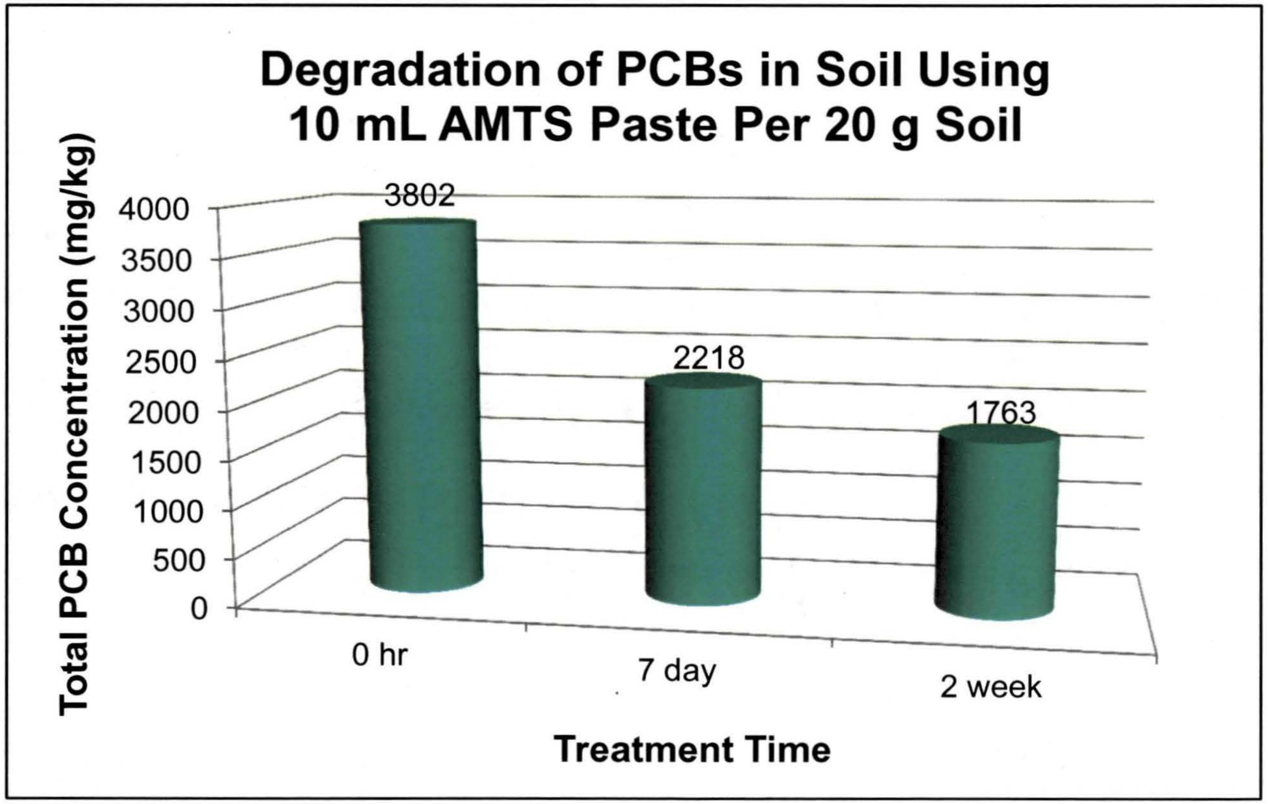
Chromatograms of the original paste and after 7 days of treatment. Data showing (a) NM 6810-36 1wk (original) 226 mg/kg = **brown** and (b) after 7 days reacting with Mg metal 11 mg/kg = **blue.**

Sludge Treatment



- Sludge used as received, mixed with AMTS and allowed to react in jars (single treatment)

Soil Treatment



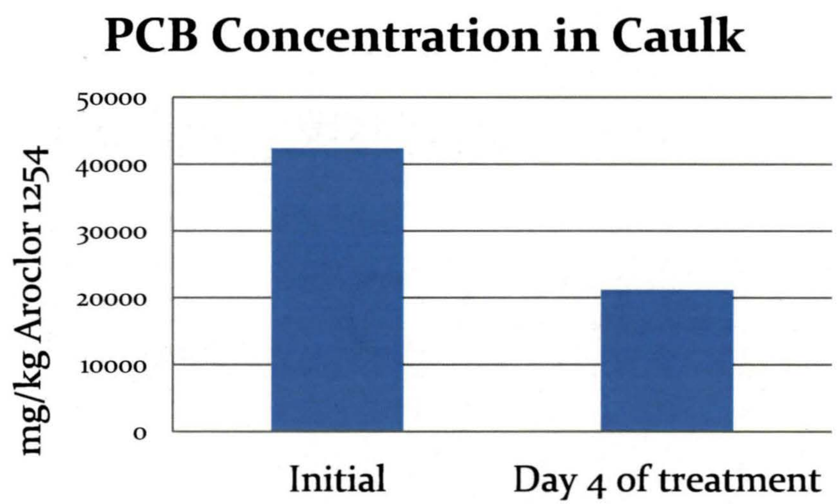
- Soil sieved and air-dried prior to experiments
- Mixed with AMTS and allowed to react in jars (single treatment)

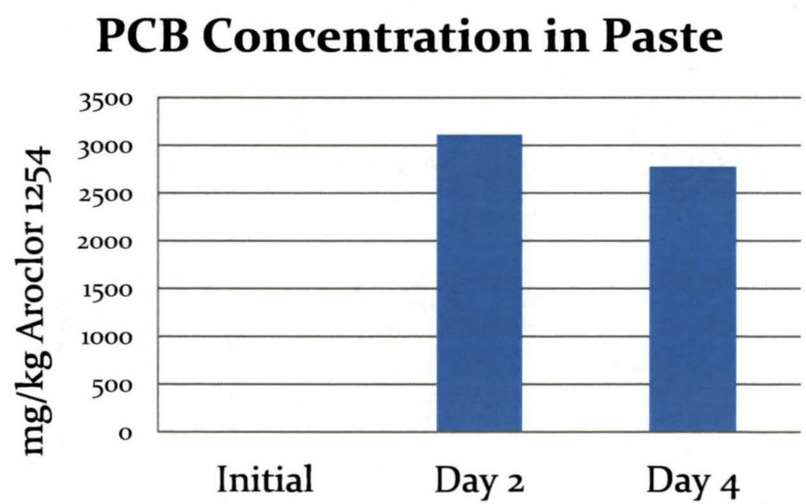
Remediation of Caulk

- Samples obtained for outside of the Operations and Checkout Building (KSC)
  - Caulk being replaced due to leaks in building
- Baseline concentration: 42,344mg/kg Arochlor 1254
- Caulk treated using NMTS
  - Dip-method used
  - Paste sampled at day 2 and 4
  - Caulk sampled at day 4

Remediation of Caulk Results

- NMTS dip-method used to treat caulk
- 50% removal of PCBs in 4 days
- Paste is becoming “saturated” 2nd day of the study

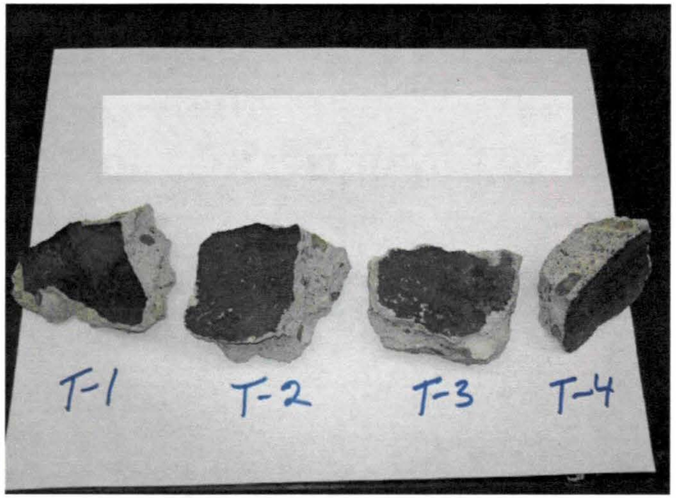


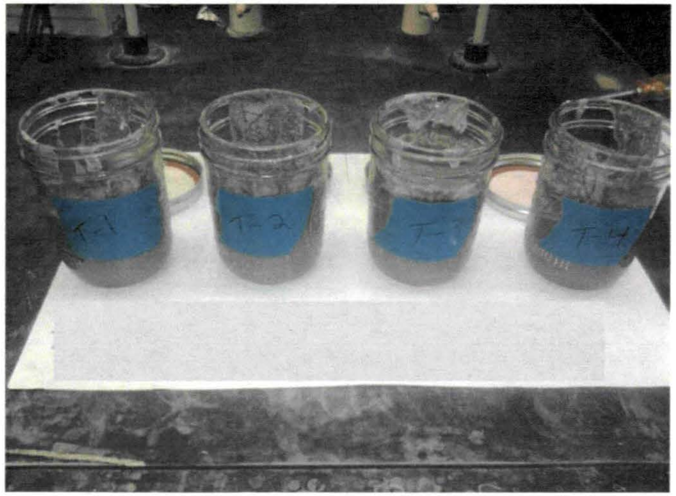


Concrete Treatment

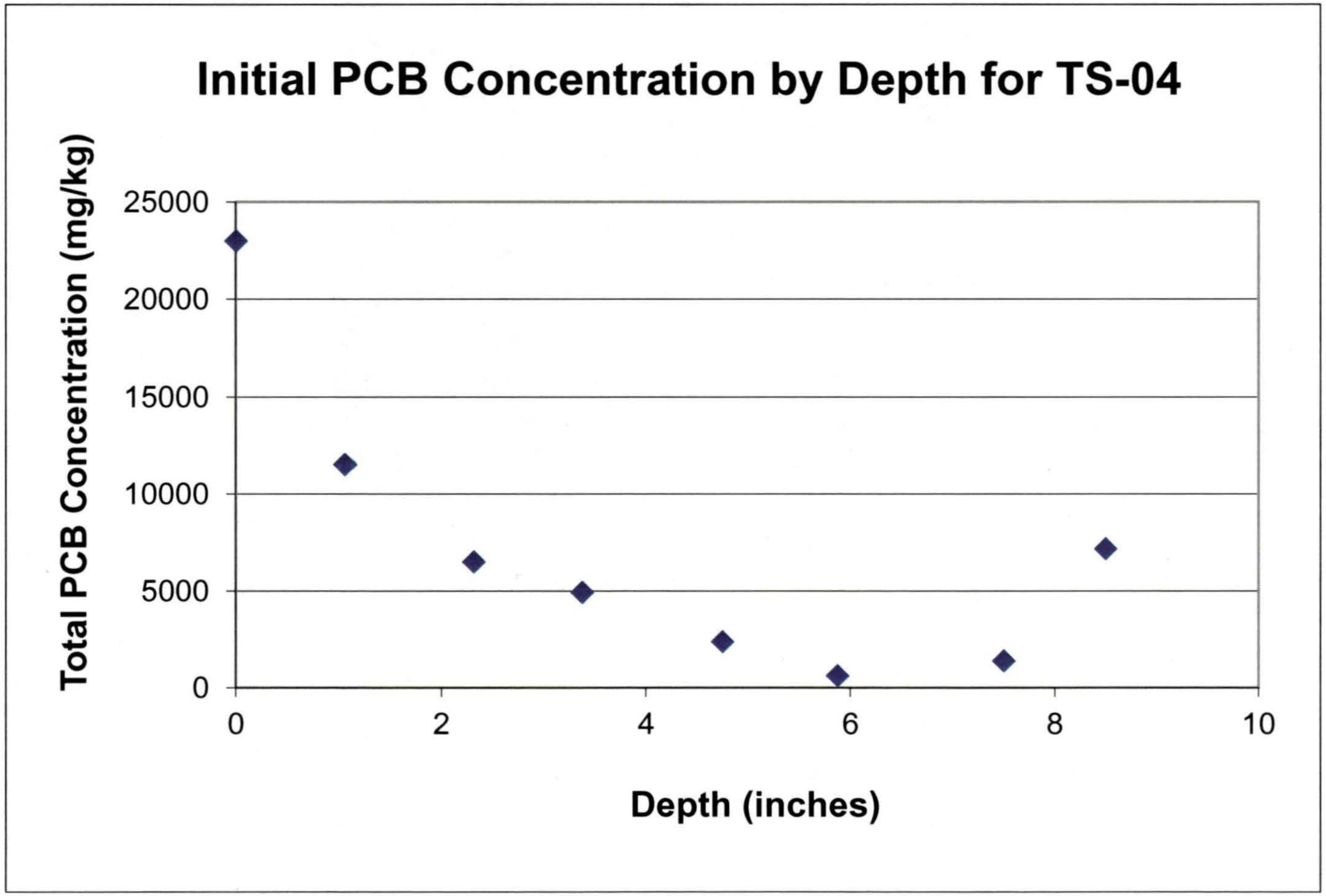
- AMTS applied, then allowed to react in a jar (pieces) or under sealant (corings) for alloted time

- Analysis challenging because PCB concentration varies with depth in concrete

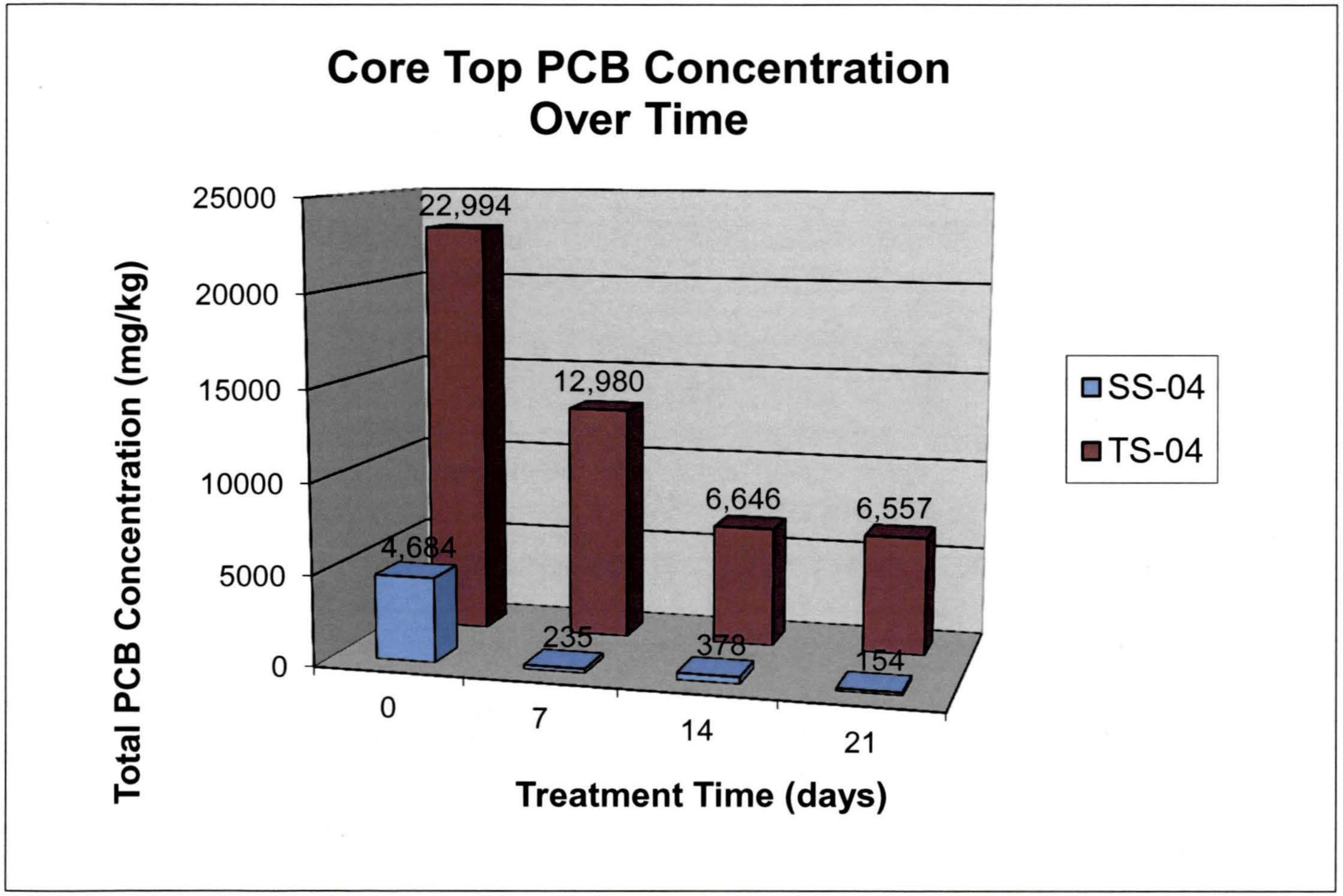




Concrete Treatment

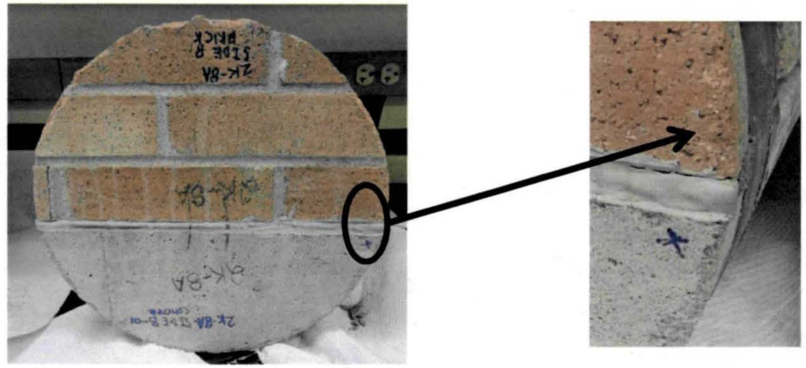


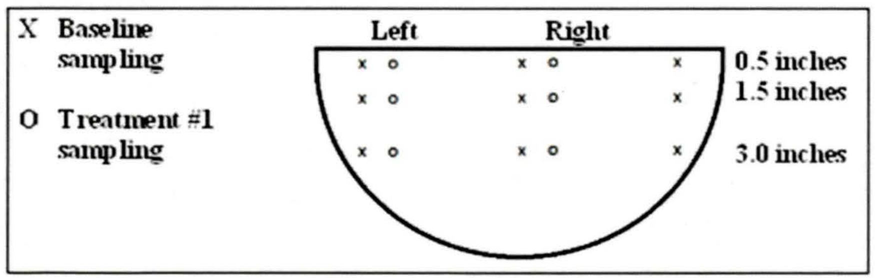
Concrete Treatment



TEA "Sock" Treatment

- Concrete in contact with PCB-laden caulk treated using AMTS "Pantyhose"
- Efficacy of "sock" treatment tested at various depths
- Baseline sampling showe penetration of PCBs at 3"away from caulk





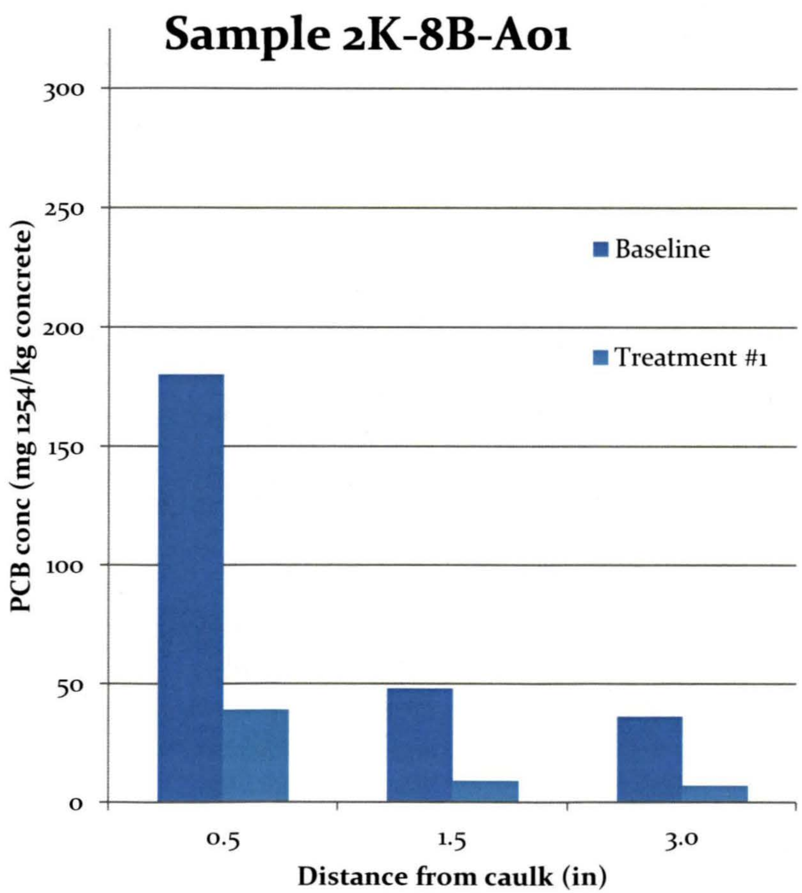
TEA "Sock" Treatment

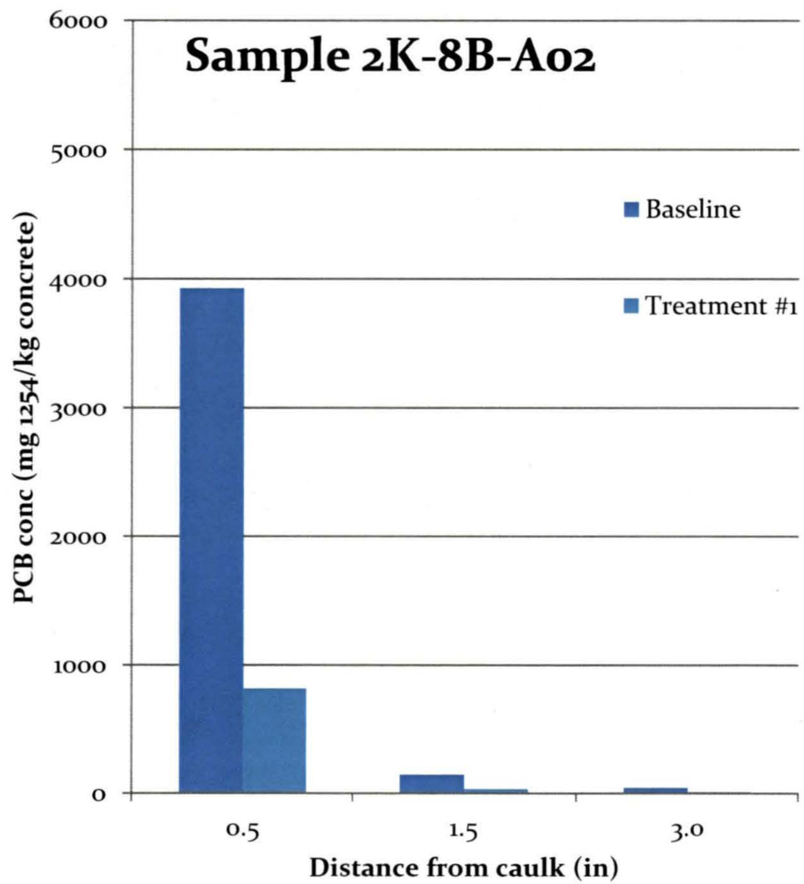
- Sampling was performed on the Left, Right and Center of the sample at distance of 0.5", 1.5", and 3.0" at a depth of 0.5"
  - Concrete powder was homogenized
  - Duplicate samples analyzed
  - Extracted using ethanol/sonicaton
  - Cleanup performed using EPA Method 3665A

TEA "Sock" Treatment

- "Sock" - nylon delivery system filled with NMTS applied to the area of the removed caulk
  - Sealed airtight with aluminum tape
  - Left in contact with contaminated concrete for 2 weeks

TEA "Sock" Treatment Results





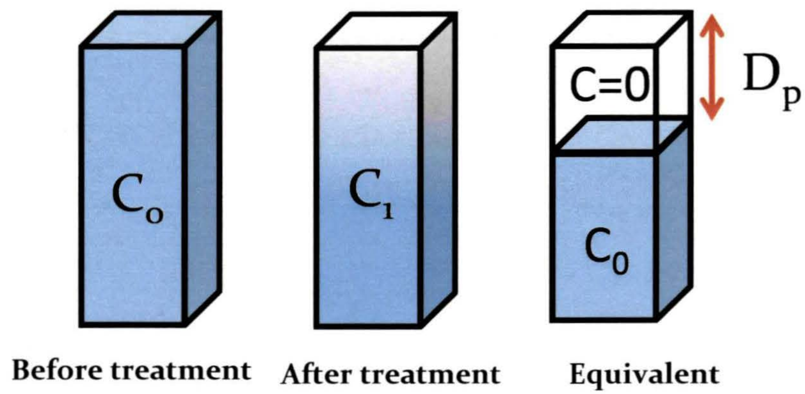
EPA Analysis of AMTS

- Mathematical modeling of AMTS treatment
  - PCBs are removed from top layer
  - “Clean” layer acts as barrier to migration
  - Reduces PCBs at surface and in room air
- Penetration depth of AMTS is greater than most encapsulants
  - “Clean” layer will perform better and be longer lasting
  - “Bleed-back” of PCBs into “clean” layer is a possible concern

Penetration Depth

- Penetration depth used to determine effectiveness of AMTS treatment for coating materials (affected by thickness)

$$D_p = L\left(1 - \frac{C_1}{C_0}\right),$$



D_p = penetration depth (mm)

L = thickness of the source (mm)

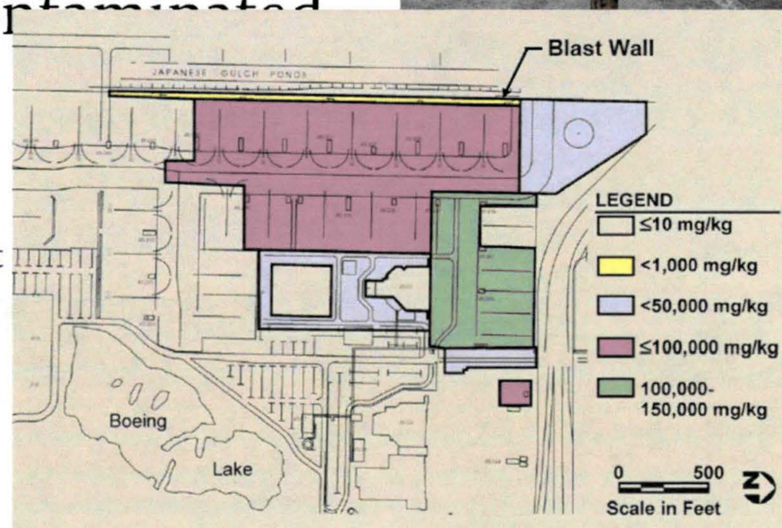
C_0 = uniform concentration of PCBs in the source before treatment (µg/g)

C_1 = average concentration of PCBs in the source after treatment (µg/g)

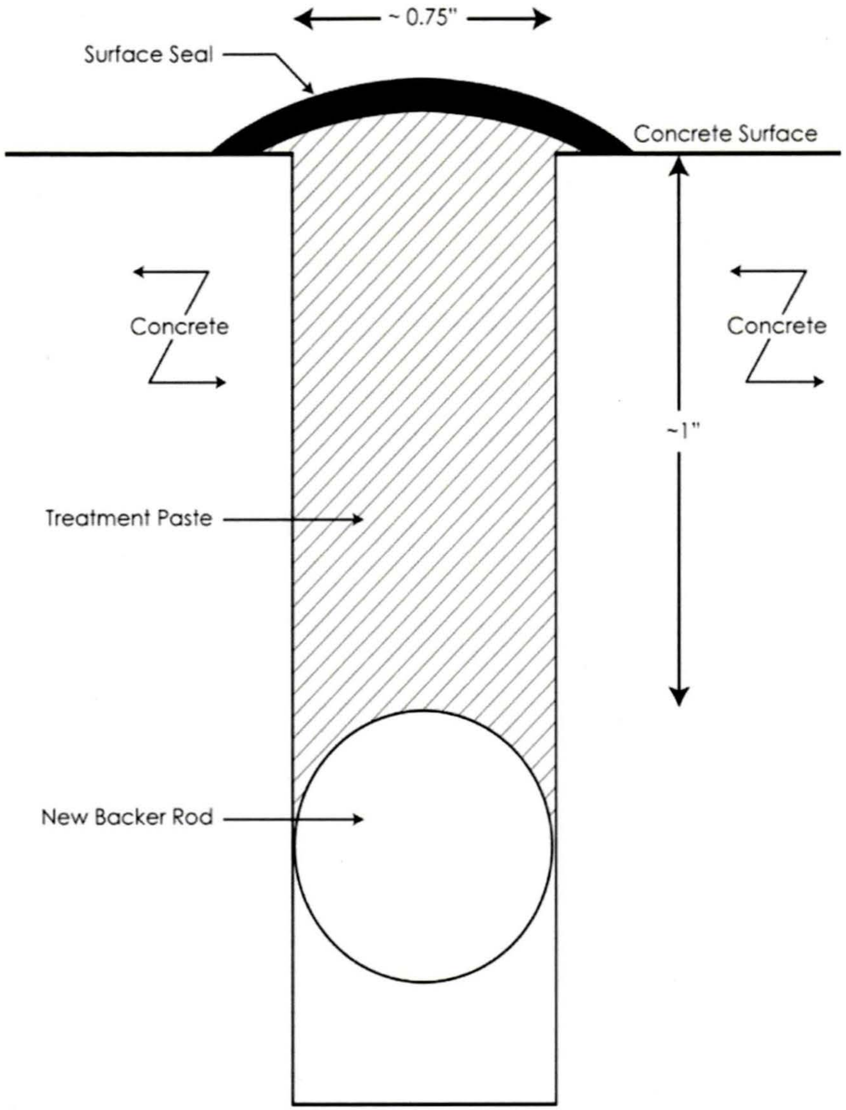
Proposed Treatment for Expansion Joints

- Expansion Joints used to relieve heat-induced stress
  - Found in building faces, roads, etc…
  - Filler material can be con
    with PCBs

50 miles of joints with PCBs



Garson, McCormack, Sugino and Molinari, 2004. Airport Flightline Expansion Joints – Unexpected Source of PCB Contamination. *Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterrey CA., May 2004.



Side View of Expansion Joint During Treatment with AMTS

Contaminated Caulk in Schools – Proposed Plan

- Remove caulk, treat using 2-step process
  - Dip-method using NMTS to remove PCBs from contaminated caulk (*ex-situ)*
  - Add Mg and acidified ethanol to NMTS to remediate contaminated paste (*ex-situ)*
- Treat window sills and concrete using “Sock” method
  - Remove PCBs using NMTS (*in-situ)*
  - Add Mg and acidified ethanol to NMTS to remediate contaminated paste (*ex-situ)*

Conclusions

- PCBs can be found in significant quantities in caulk
- Technology capable of removing the environmental health risk is necessary
- AMTS is an effective treatment for both the caulk and the underlying concrete areas
- Possible to treat contaminated caulk *in-situ* (depends on situation)using AMTS