



# Case study of a non-destructive treatment method for the remediation of military structures containing polychlorinated biphenyl contaminated paint



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## ABSTRACT

Restricted by federal regulations and limited remediation options, buildings contaminated with paint laden with polychlorinated biphenyls (PCBs) have high costs associated with the disposal of hazardous materials. As opposed to current remediation methods which are often destructive and a risk to the surrounding environment, this study suggests a non-metal treatment system (NMTS) and a bimetallic treatment system (BTS) as versatile remediation options for painted industrial structures including concrete buildings, and metal machine parts. In this field study, four areas of a discontinued Department of Defense site were treated and monitored over 3 weeks. PCB levels in paint and treatment system samples were analyzed through gas chromatography/electron capture detection (GC-ECD). PCB concentrations were reduced by 95 percent on painted concrete and by 60–97 percent on painted metal with the majority of the PCB removal occurring within the first week of application. Post treatment laboratory studies including the utilization of an activated metal treatment system (AMTS) further degraded PCBs in BTS and NMTS by up to 82 percent and 99 percent, respectively, indicating that a two-step remediation option is viable. These findings demonstrate that the NMTS and BTS can be an effective, nondestructive, remediation process for large painted structures, allowing for the reuse or sale of remediated materials that otherwise may have been disposed.

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## 1. Introduction

### 1.1. General introduction

Polychlorinated biphenyls (PCBs) are a family of 209 compounds regulated in the United States by the 1976 Toxic Substance Control Act and are considered an environmental contaminant (US Congress, 1976). Due to their chemical and physical properties, PCBs were often additives in industrial, maritime, and military materials including caulking, iron pipe coatings, and paint (Jartun et al., 2008). PCB congeners can be detected in water, air, and soil

despite their predominate use in synthetic materials (Hu et al., 2008; Jartun et al., 2009). The mobility of PCBs in the environment is evidenced by contamination detected in industrial and rural habitats, including the arctic despite its isolation (Cornelissen et al., 2008; Jartun et al., 2008; Kalinovich et al., 2008, 2012). PCBs in marine environments can originate from onshore sources including military sites which warrant specific concern given their frequent coastal location (Jartun et al., 2009; Kuzyk et al., 2005; Poland et al., 2001).

Building materials are of particular interest because they are a major point source for PCBs (Herrick et al., 2007, 2004; Jartun et al., 2009). Paint, for example, does not make up a large volume of contaminated material, but its large surface area and potential to spread to other areas through runoff pose a serious threat to the environment and human health (Hu and Hornbuckle, 2010; Jartun et al., 2008). Not only can paint contaminate the surrounding environment through paint chips resulting from the intentional

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restoration of a building and unintentional weathering of the surface, but PCBs can volatilize while the paint remains attached to the structure (Hu and Hornbuckle, 2010; Jartun et al., 2008). Therefore, it is advantageous to remove PCBs from paint before the contaminant enters the environment. Painted structures at military sites are of particular interest due to the volume of contamination remaining after they are no longer utilized (Poland et al., 2001).

In the United States, the action limit for PCBs is 50 mg/kg. Those responsible for the oversight of buildings containing PCB-contaminated materials, like paint, have limited options. Current techniques include disposal of the building material as hazardous waste, physical removal of paint, and incineration, each of which come with unique challenges. Disposing of large structures is expensive considering licensed landfill costs are often based on the amount of contaminated material. Mechanically removing paint from structures often result in the production of mobile hazardous waste. For example, sandblasting produces contaminated sand which can spread PCBs to surrounding areas (Franzblau et al., 2009). Incineration is costly and can produce harmful byproducts if combustion is incomplete (Kastanek and Kastanek, 2005). A valuable alternative to the aforementioned options is chemical remediation and its ability to break down PCBs. Chemical destruction of PCBs has been gaining popularity since the 1990's (Gomes et al., 2013). The stability of the aromatic structure leads PCBs to be more resistant to degradation than chlorinated aliphatics traditionally requiring high temperatures and pressures to break down. Reactions involving bimetal, however, have been shown to achieve reductive dechlorination, including hydrodehalogenation, in both aqueous and organic solvents at ambient conditions (Devor et al., 2008; Negroni et al., 2012). Advances in large scale ball milling have allowed for sufficient quantities of bimetal to be produced making large remediation projects a possibility (Coutts et al., 2011). Bimetals, including Magnesium/Palladium (Mg/Pd), have been utilized in soil and sediment remediation with limited success as field matrices prove to be more complex than solutions (Agarwal et al., 2009; Korte et al., 2002). Although PCBs in sediments and soils have been the subject of several studies, field research on reductive remediation of PCBs in paint adhered to a surface has been virtually unpublished. The following field evaluation utilizes a treatment system designed to remove and dechlorinate PCBs directly from painted walls and metal tanks of a decommissioned military site leaving the physical structures intact.

## 1.2. Introduction to treatment technology

The treatment technology in this study was implemented through three different formulations each consisting of a thick paste which could be applied to a contaminated surface and sealed for the duration of the treatment. The treatment system was then removed and discarded, minimizing environmental exposure. The first formulation, and the foundation for the subsequent formulations, was the Non-Metal Treatment System (NMTS) comprised of solvent, a paint softener, and bulking agents (Saitta et al., 2014). The NMTS was formulated to extract PCBs from a painted surface and to act as a delivery system for metal reaction components. Therefore, NMTS was either used alone to simply remove PCBs or it was combined with metal to initiate the hydrodehalogenation reaction to degrade PCBs once they entered the system.

To remediate concrete walls and metal tanks on-site, NMTS was combined with Mg/Pd to create the second formulation termed the Bimetallic Treatment System (BTS). The BTS leverages information reported in laboratory studies regarding the degradation of PCBs at ambient conditions and incorporates it into an easy to apply reaction matrix suitable for the on-site remediation of large vertical structures.

While preparing for the field study, an emerging technique using magnesium metal in acidified alcohols to degrade PCBs was discovered by our team (Maloney et al., 2011). Although the discovery occurred too late to be incorporated into our on-site analysis, it was integrated into the post-implementation analysis by adding zero valent Mg to samples of NMTS creating an Activated Metal Treatment System (AMTS), the third formulation utilized in this study.

Two types of sealant, vinyl and silicon, were chosen for the field evaluation due to their success in laboratory pilot studies. Both sealants acted as a physical support for the treatment system as well as a barrier to solvent evaporation.

## 2. Experimental

### 2.1. Methods

#### 2.1.1. Production of bimetal

The Mg/Pd bimetal was produced in accordance with a previously optimized process and included mechanically alloying 78 g of Mg metal with 7 g of 1% Pd/C to make a final mixture that was 91.8% Mg, 0.08% Pd, and 8.12% C by mass (Aitken et al., 2006). The bimetal was prepared in stainless steel canisters (17.80 cm length and 5.03 cm in internal diameter) which contained 16 steel ball bearings (1.5 cm diameter). The components were milled in a nitrogen atmosphere for 30 min using a Series 5400 Red Devil Paint Shaker (Aitken et al., 2006).

#### 2.1.2. Production of treatment system

NMTS, the foundation for all of the treatment system formulations, was prepared in four gallon batches. To start, 1.280 kg of sodium polyacrylate was coated with 640 g of glycerol in a 5 gallon plastic bucket. In an effort to keep particulates from the bulking agents from dispersing during mixing, 4.0 L of ethanol was added to the mixture. To this, 1.280 kg of calcium stearate and 640 g of Polyethylene glycol (PEG) 8000 was added. The components were stirred with a drill affixed with a stir attachment to mix. In a separate container, 4.617 L of ethanol, 196 ml of acetic acid, and 979 ml of limonene were combined. Once the solvents were mixed, they were added to the bulking agents in the 5 gallon plastic bucket. The total mixture was stirred until a uniform consistency was reached. After one hour, the five gallon container was sealed and the contents were either used as is or combined with Mg/Pd to make the BTS.

To create the BTS, 640 g of Mg/Pd powder was coated with 640 g of glycerol and the combined mixture was added to the four gallon batch of NMTS. The container was sealed after one hour and was vented every few hours during the first 24 h.

### 2.2. Field study preparation

#### 2.2.1. Evaluation of site & pre-treatment sampling

The field study took place at a previously used United States Department of Defense (DOD) facility. Operations occurred from the 1940's to 1975 when the site became dormant and was eventually decommissioned in 1997. Military contractors identified multiple locations where paint was contaminated with PCB mixtures including Aroclor 1254 or 1260, the highest of which ranged from 1068 to 55,219 mg/kg. From the initial site evaluation, four locations were chosen for the PCB remediation field study as seen in Table 1. Press House A and Press House B consisted of interior painted concrete walls that, although covered overhead, were exposed to weathering from openings on the sides of the structures. The Nitrating House contained painted metal tanks housed indoors while the Staging Area was an outside area made up of

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