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Polychlorinated biphenyls in the exterior caulk of San Francisco Bay Area buildings, California, USA

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ABSTRACT

Extensive evidence of the adverse impacts of polychlorinated biphenyls (PCBs) to wildlife, domestic animals, and humans has now been documented for over 40 years. Despite the ban on production and new use of PCBs in the United States in 1979, a number of fish consumption advisories remain in effect, and there remains considerable uncertainty regarding ongoing environmental sources and management alternatives. Using a blind sampling approach, 25 caulk samples were collected from the exterior of ten buildings in the San Francisco Bay Area and analyzed for PCBs using congener-specific gas chromatography–mass spectrometry (GC–MS) and chlorine using portable X-ray fluorescence (XRF). PCBs were detected in 88% of the caulk samples collected from the study area buildings, with 40% exceeding 50 ppm. Detectable PCB concentrations ranged from 1 to 220,000 ppm. These data are consistent with previous studies in other cities that have identified relatively high concentrations of PCBs in concrete and masonry buildings built between 1950 and 1980. Portable XRF was not a good predictor of the PCB content in caulk and the results indicate that portable XRF analysis may only be useful for identifying caulk that contains low concentrations of Cl ($\leq$10,000 ppm) and by extension low or no PCBs. A geographic information system-based approach was used to estimate that 10,500 kg of PCBs remain in interior and exterior caulk in buildings located in the study area, which equates to an average of 4.7 kg PCBs per building. The presence of high concentrations in the exterior caulk of currently standing buildings suggests that building caulk may be an ongoing source of PCBs to the San Francisco Bay Area environment. Further studies to expand the currently small international dataset on PCBs in caulking materials in buildings of countries that produced or imported PCBs appear justified in the context of both human health and possible ongoing environmental release.

1. Introduction

Beginning with a mass poisoning of Japanese residents through consumption of contaminated rice oil in 1968, extensive evidence of the toxic impacts of polychlorinated biphenyls (PCBs) in wildlife, domestic animals, and humans has now been documented for over 40 years (Colborn et al., 1993; Jensen, 1972; USEPA, 2012). Because of their chemical stability and low flammability, PCBs were used in a wide variety of applications beginning in the 1940s, including completely closed systems (dielectric fluids in transformers and capacitors), nominally closed systems (hydraulic and heat transfer systems, vacuum pumps), and open ended applications (plasticizer in chlorinated plastics, rubber, sealants and caulk) (Erickson and Kaley, 2011). The production and most uses of PCBs were banned in most countries in the 1970s and in May 1979 in the USA. Unlike the closed and nominally closed applications, which can be readily inventoried and removed, remaining open-ended uses are elusive and difficult to manage and remain an important ongoing exposure route (Herrick et al., 2004; Kohler et al., 2005).

PCBs were added to joint caulk (the largest volume open-ended application) to improve the flexibility of the material, increase the resistance to mechanical erosion, and improve adherence to other building materials (Andersson et al., 2004; Erickson and Kaley, 2011). Locations on structures where PCB-containing caulk has been found include outdoor seams in concrete and masonry structures (Astebro et al., 2000; Priha et al., 2005; Sundahl et al., 1999) and around windows and doorframes (Astebro et al., 2000; Persson et al., 2005). The application of caulk in this manner appears to have been common across Europe and North America (Astebro et al., 2000; Erickson and Kaley, 2011; Herrick et al., 2004; Kohler et al., 2005; Persson et al., 2005; Priha et al., 2005; Robson et al., 2010; Sundahl et al., 1999). Most studies have focused on PCB-containing caulk on building exteriors, but PCB-containing caulk has also been found indoors in Europe (Balfanz et al., 1993) and the USA (Coghlan et al., 2002; Lexington, Massachusetts Public Schools, 2011).

PCBs in building caulk may serve as an ongoing source of PCBs to the environment, as well as an ongoing source of exposure to persons inside and around buildings and demolition workers. Studies have indicated that PCBs can volatilize from the caulk into surrounding air (Kohler

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et al., 2002; Robson et al., 2010) and spread to indoor dust and soil surrounding the buildings' perimeters via natural weathering and deterioration (Herrick et al., 2007; Sundahl et al., 1999). Studies have also indicated that significant quantities of PCBs can be released into soil and water runoff during activities associated with the renovation of building caulk, such as concrete grinding and power washing (Astebro et al., 2000; Sundahl et al., 1999). It is also suspected that, without appropriate containment, PCBs may also be released to the environment during the demolition of buildings.

Despite these concerns, few surveys have documented the presence of PCBs in caulk. In the largest survey conducted to date, caulk samples were collected from 1348 buildings in Switzerland constructed between 1950 and 1980 (Kohler et al., 2005). They reported that almost half of the buildings contained PCBs in caulk (detection limits 20 ppm for total PCBs), with most samples containing concentrations greater than 100 ppm and 20% of samples containing 10,000 ppm (1%) or more PCB by weight. Less rigorous surveys have been conducted in Boston and other locations in Europe with comparable findings (Astebro et al., 2000; Herrick et al., 2004; Sundahl et al., 1999). In a more recent survey of 95 buildings in Toronto, 14% of the buildings sampled had detectable concentrations of PCBs in caulk, with concentrations ranging from 570 ppm to 82,000 ppm (mean 4600 ppm or ~0.5%) (Robson et al., 2010). PCBs have also been detected in caulk at a number of schools in New York and Massachusetts in a similar range of concentrations (http://www.pcbinschools.org). PCBs in caulk in California buildings have not been reported, with the exception of an article documenting the discovery of PCBs in the polysulfide caulking material used to seal joints at a drinking water reservoir in Northern California in the 1990s (Sykes and Coate, 1995). The caulk contained PCBs at concentrations of 15–20%, but has since been replaced.

We conducted a field assessment to expand the currently small international dataset of PCBs in building caulk and provide additional data and information necessary to help management agencies identify the relative magnitude of PCB sources in the context of fish consumption advisories and wildlife impairments in San Francisco Bay (California, USA). The assessment specifically aimed to determine PCB concentrations in a small sample of currently standing buildings in relation to the construction type and building age (target decades: 1950s, 1960s, 1970s, and 1980s). We also investigated the utility of a portable X-ray fluorescence (XRF) analyzer, which estimates the elemental composition of a substance (e.g., chlorine, not PCBs specifically), as a reliable screening tool to estimate PCB concentrations in caulk. Lastly, the remaining reservoir in caulk in San Francisco Bay Area buildings was estimated as an important first step for determining the potential of these materials as an ongoing source of PCBs to the Bay Area environment.

2. Materials and methods

2.1. Field sample collection

In 2010 and 2011, 29 caulk samples were collected from the exterior of ten buildings in the San Francisco Bay Area. The counties and cities that defined the 'San Francisco Bay Area' in the present study are listed in Section 2.4. Since the objective was not to identify specific buildings that contained PCBs, a blind sampling approach was used and information that could have been used to identify sample street addresses with the study area was not retained. Project partners identified buildings for possible inclusion in the project and secured permission from the building owner, a consultant, or contractor prior to any collection or analysis of caulk samples. Samples received included archived samples provided by a consultant. The buildings were constructed during the 1950s, 1960s, 1970s, or 1980s with the exception of one building with an unknown year of construction. A variety of construction types were represented and included concrete, reinforced masonry and wood frame buildings. Buildings were selected by project partners primarily based on construction year and not construction type. Wood frame buildings were thus not intentionally targeted for sampling, particularly since previous caulk surveys for PCBs have primarily focused on buildings with concrete and masonry construction. One to seven caulk samples were taken from the exterior of each building, with each sample representing a specific caulk type or function (e.g., caulk around window, between concrete building components). A maximum of one sample per caulk type/function was collected from each building. The number of samples collected per building was determined by the availability of the different types of caulk/function on each building and what samples the project partners were willing to provide (i.e., not a specific design component of the study). Caulk samples were collected from buildings known or suspected to contain original caulk.

For most caulk samples, collection entailed removing at least a one-inch strip (or minimum of 3 g) of caulk from the structure using a utility knife with a solvent-rinsed, stainless-steel blade and placing it in a labeled, chemically-cleaned glass jar. However, a portion of samples were collected by the building owner, a consultant, or a contractor and transferred to an employee of the San Francisco Estuary Institute (SFEI). When this occurred, the samples were not collected with pre-cleaned instruments or containers. Once collected or received by SFEI, samples were refrigerated until analysis.

2.2. GC–MS analysis

As part of the blind sampling scheme, and as a result of the budget available for PCB analysis, 25 of the 29 samples collected were randomly selected and analyzed for PCBs using a modified Environmental Protection Agency (EPA) 8270 method protocol (semi-volatile organic compounds by gas chromatography–mass spectrometry (GC–MS)). A total of 40 PCB congeners were analyzed in the caulk samples: the congeners frequently detected in the highest concentrations in San Francisco Bay sport fish (IUPAC PCBs 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 87, 95, 97, 99, 101, l05, 110, 118, 128, 132, 138, 141, 149, l51, 153, 156, 158, 170, 174, 177, 180, 183, 187, 194, 195, 201, and 203: Davis et al., 2007); PCB 11, a non-Aroclor congener commonly detected in wastewater effluent and environmental samples (Rodenburg et al., 2010); and the coplanar PCBs 77, 126, and 169, 'dioxin-like' congeners which contribute substantially to the dioxin toxic equivalents observed in San Francisco Bay sport fish (Davis et al., 2007) were also analyzed.

Quality assurance procedures included the analysis of laboratory method blank samples, duplicate samples, and a laboratory-fortified matrix spike. Congener-specific method detection limits (MDLs) of 0.0006 to 0.007 ppm were initially estimated for a nominal sample of 10 g. However, only 0.1 g per sample was extracted due to high concentrations and the matrix being highly soluble in the extraction solvents, making it impossible to concentrate more than 1 g of sample in the extract. Some samples were further diluted to achieve concentrations within the instrument calibration range and avoid severe equipment contamination. As a result, actual MDLs in the study ranged from 0.06 to 284 ppm. Despite much higher MDLs, concentrations as low as 0.7 ppm were reported, and only three of the 25 samples analyzed had PCB concentrations below detection limits of 25 ppm or less (presented in the results as <MDL). PCB congeners were not detected in blank samples. Average recoveries (±one standard deviation) of surrogate standards were 68% (±15), 76% (±8), and 98% (±9) for individual congeners in matrix spike samples, mid-level blank spikes, and low-level blank spikes, respectively. Precision on replicate analyses of field samples was variable with relative percent differences over 100% for some congeners, perhaps in part due to difficulties in homogeneously subsampling the caulk (due to very high concentrations in some samples, extracted subsamples were made extremely small to avoid overloading and contaminating the analytical instrument). Precision on repeated analyses ($n = 3$) of low-level blank spike samples was much better, with relative standard deviations averaging 8% (±5),