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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 (≤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),

indicating that the variability in caulk samples was not due to issues with instrumental quantitation.

2.3. XRF analysis

A portable XRF analyzer (Delta model, Innov-X Systems, Woburn, MA) was used as a screening tool to estimate the chlorine concentration in each caulk sample. Previous studies have shown that caulking compounds contain a predominance of Aroclor 1254 with some use of Aroclor 1260 (Herrick et al., 2004; Kohler et al., 2005; Robson et al., 2010). Aroclor 1254 contains approximately 52–54% of Cl by weight (Erickson and Kaley, 2011) and, given that caulk often contains in excess of 1% PCBs and detection limits of portable XRF may be in the ppm range, it was hypothesized that portable XRF may be able to detect chlorine within caulk containing PCBs down to about 0.1%. The analysis was performed on the sample remaining after GC–MS analysis using a test stand compatible with the instrument and provided by an Innov-X Systems representative. The analyzer was calibrated for chlorine using plastic pellet European reference materials (EC680 and EC681) upon first use, and standardized each time the instrument was turned on and prior to any caulk monitoring. The standardization procedure entailed a calibration analysis of the metal disk provided with the XRF analyzer. A 30 second measurement in 'three beam soil' mode was used (chlorine factor = 0.5). Analyses were conducted in triplicate on each sample and the mean was used for comparison to GC–MS results.

2.4. Caulk PCB mass inventory

In the absence of an inventory of building types for the San Francisco Bay study area, a geographic information system (GIS)-based approach was used to estimate the total PCB mass in caulk in the study area buildings. The study area consisted of the most populous and historically industrialized counties and cities in the San Francisco Bay Area: Alameda, Contra Costa, Santa Clara, and San Mateo counties, and the cities of Fairfield, Suisun, and Vallejo. Since one of the intents was to examine areas where urban stormwater flows to the Bay without treatment, San Francisco was excluded from the study area because it is serviced by a combined wastewater and stormwater sewer system. In 1980 (the approximate end of the main use period for PCBs), this area accounted for 73% of the population of the nine-county San Francisco Bay Area and thus represented a reasonable balance between coverage and effort. An extent of urban land uses likely containing caulk with PCBs was created based on available historical data representing the time period of high PCB use (approximately 1950s–1970s). This extent was compared with modern land use data to determine which of these urban areas have buildings from that period currently standing, and statistics about their number, area, and volume were calculated. Estimates of the mass of caulk, the PCB concentrations in caulk in various building types, and the frequency of anticipated PCB detection in buildings were calculated in GIS using the results from the present study in combination with estimates obtained from previous surveys of PCB in building caulk in Boston, Toronto, and Switzerland. Details of the methodologies used are provided in the Supporting information (SI).

3. Results and discussion

3.1. PCB Caulk concentrations

Of the 25 caulk samples analyzed in the present study, 22 (88%) contained detectable concentrations (>25 ppm) of PCBs and 10 of these (40% of all samples) exceeded 50 ppm, the USA EPA PCB regulatory threshold (Table 1). Detectable PCB concentrations in caulk samples from the San Francisco Bay Area buildings ranged over six orders of magnitude, from 1 to 220,000 ppm (see SI for a discussion on PCB caulk sample heterogeneity). It was not possible to determine the number of buildings with PCB-containing caulk because blind sampling procedures prevented the association of samples with a particular building and in some cases more than one sample per building may have been analyzed for PCBs (note, however, that as stated in the Methods section, only one sample representing a specific caulk type or function was collected from each building). When considering only the samples containing greater than 50 ppm PCBs, the median concentration in the San Francisco Bay samples (9580 ppm) was comparable to the medians in the Boston (Herrick et al., 2004) and Toronto surveys (Robson et al., 2010) (7990 and approximately 7500 ppm, respectively), and the concentration distribution was comparable to that observed in the Switzerland survey (Kohler et al., 2005) (>20–550,000 ppm; median not provided). Further, the portion of samples greater than 10,000 ppm in the present study (20%) was similar to those in Boston (9%), Toronto (10%), and Switzerland (20%). The maximum concentration detected in Bay Area caulk samples (220,000 ppm) was lower than the highest concentration detected in the Switzerland survey (550,000 ppm), but higher than the maximum concentrations detected in the Boston and Toronto surveys (36,200 and 82,000 ppm, respectively). Based on these results, it appears that use patterns of PCBs in caulk in the San Francisco Bay Area were similar to those in Boston, Toronto, and Switzerland.

In previous surveys of caulk in buildings in Boston, Switzerland, and Toronto, the frequency of detection of samples containing greater than 50 ppm PCBs was comparable to our study, although the overall frequency of PCB detection in those studies was lower (Table 2). Compared to the previous surveys, a higher proportion of samples in the present study (48%) contained detectable concentrations of less than 50 ppm. In addition to the small sample size used in the present study, it is plausible that this difference may have been due to the inclusion of more than one caulk sample per building for some of the buildings, if the same caulk formulation was used for the different applications of caulk on the same building (e.g., if the formulation that was used between concrete blocks was the same as that used around window frames). Because of the blind sampling approach used, it was not possible to determine the extent to which this may have been a factor. A third possibility is that analysis of a larger number of congeners in the present study may have contributed to this difference. When all the samples in the present study were considered, the median PCB concentration was 32 ppm. It has been hypothesized that when used as plasticizers in caulk, PCBs were added in concentrations that were at least 10,000 ppm (1%) to maintain the elasticity of the material (Kohler et al., 2005). Kohler et al. (2005) suggested that samples containing less than 10,000 ppm may be due to the use of PCB contaminated equipment during the application of caulk in the building construction process (e.g., when alternative, non-PCB plasticizers such as chlorinated paraffins were used on the same equipment instead) or because of secondary contamination by migration of PCBs from adjacent construction materials (originating from caulk containing PCB replaced previously). Though the sample size was limited, the detectable PCB concentrations in caulk in the present study appear to generally support this hypothesis, since concentrations were either less than 90 ppm or greater than 3600 ppm. However, building owners/consultants/contractors that provided the caulk samples for the present study stated that it was not likely that the caulk had been replaced since building construction. Therefore, we suggest that the low PCB concentrations in our study may have more likely been the result of construction equipment contamination rather than secondary contamination by migration. It was not possible, based on physical appearance, to determine the age of the caulk samples, and thus the likelihood of having been relatively recently replaced.

3.2. Caulk PCB congener profile

The congener profiles for the San Francisco Bay Area caulk samples suggest that Aroclor 1254 was the primary PCB commercial

Table 1
Polychlorinated biphenyl (PCB) and chlorine (Cl) concentrations in caulk samples extracted from the exterior joints of San Francisco Bay Area buildings measured by laboratory analysis and a portable X-ray fluorescence (XRF) analyzer.

Construction year	Construction type[a]	Caulk location on building	PCB (ppm)	GC–MS Cl (ppm)	XRF Cl (ppm)
1950s	PC2	Between concrete	220,000	119,046	72,000
1950s	PC2	Between concrete	198,000	110,245	49,300
1950s	PC2	Between metal window frame and concrete	146,000	81,446	53,200
1960s	W2	Between glass and window frame	12,500	7,031	6,770
1950s	PC2	Between concrete	11,500	6,419	100,000
1950s	PC2	Around metal window frame	7,630	4,216	100,000
1950s	PC2	Between glass and metal window frame	3,600	1,989	46,400
1960s	C2	Between window glass and window frame of unknown material	89	48	171
1980s	RM	Unknown	87	49	<694
1970s	W2	Between wood and wood	60	34	1,103
1960s	C2	Between window glass and window frame of unknown material	48	26	143
1950s	W1	Between glass and metal window frame	15	8	461
Unknown	Unknown	Around window frame	15	8	<645
1970s	W2	Between glass and window frame	11	6	100,000
1970s	W2	Between window frame and wood	10	5	<3072
1970s	W2	Around doorframe	8	4	3,180
1950s	W1	Around doorframe	6	3	<787
1950s	W1	Around doorframe	5	3	<65
1950s	W1	Between glass and window frame of unknown material	3	2	<350
1950s	W1	Between metal window frame and concrete	2	1	17,800
1960s	PC1	Between concrete	2	1	<891
1950s	W1	Between wood window frame and wood	1	0.4	<231
1950s	W1	Between wood and concrete	<MDL	<MDL	<816
1950s	W1	Between wood and wood	<MDL	<MDL	1,777
1960s	RM	Between glass and window frame	<MDL	<MDL	NA

[a] Construction codes: PC1 = Precast/tilt-up concrete shear-wall; PC2 = Pre-cast concrete frame; C2 = Concrete shear-wall; W1 = Light wood-frame residential and commercial smaller than or equal to 5000 square feet; W2 = Light wood-frame larger than 5000 square feet; RM = Reinforced masonry.

mixture used. This is supported by the predominance of PCBs 87, 95, 99, 101, 110, and 118 in the samples (Frame et al., 1996). This observation is consistent with the previous surveys in Boston, Toronto, and Switzerland, which primarily detected the presence of Aroclor 1254 with some use of Aroclor 1260, (Herrick et al., 2004; Kohler et al., 2005; Robson et al., 2010) and a recent review of applications of polychlorinated biphenyls (Erickson and Kaley, 2011). PCB 11, a congener not present in Aroclor mixtures (Frame et al., 1996) but commonly detected in wastewater effluent and environmental samples, was not detected in any caulk samples (MDLs ~1 ppm). The consistency of the congener profile with expected patterns (i.e., use of heavier Aroclors, lack of PCB 11) provides some assurance that the data are free of spurious PCB sources or other interferences.

3.3. Caulk PCB age profile

PCBs were detected in samples that were collected from buildings constructed in the target age range (1950–1980), supporting previous observations of the use of PCBs in caulk in buildings constructed during this time period (Table 3). PCBs were also detected in one sample collected from a building reportedly constructed in the 1980s, past the year in which the sale and production of PCBs was banned. This latter observation conflicts with the Toronto survey, which did not detect PCBs in caulk from buildings constructed after 1980 (Robson et al., 2010). This suggests that the addition of PCBs to caulk may have continued for a limited number of years after the ban of PCBs in the United States in 1979. The Bay Area caulk samples containing more than 10,000 ppm (1%) PCBs were all collected from buildings constructed in the 1950s and 1960s (Table 3), with the samples collected from structures constructed in the 1950s containing the highest PCB concentrations (Table 1). In the Toronto and Switzerland surveys, most caulk samples containing more than 10,000 ppm (1%) PCBs were collected from buildings constructed in the 1960s (Kohler et al., 2005; Robson et al., 2010). Due to the small sample size, it was not possible to evaluate significant differences in PCB concentrations in relation to building age in the present study.

3.4. Caulk PCB use profile

Samples of caulk located between concrete building components and around the window frames of concrete buildings contained the highest PCB concentrations in the present study (>3600 ppm) (Table 1). One exception was a sample obtained from between the concrete components of a building constructed in the 1960s which

Table 2
Summary of results from this study and previous surveys of polychlorinated biphenyls (PCBs) in caulk in buildings.

	San Francisco Bay Area[a]	Greater Boston Area[b]	Toronto[c]	Switzerland[d]
Sample size (n)	25	24	95	1,348
Building use types	Mixed	Institutional	Commercial, industrial, residential, infrastructure	Institutional
Construction types	Concrete, wood, masonry, unknown	Concrete, masonry	Concrete, brick, other	Concrete
PCB detection frequency	88%	54%	14% (27% not including residential)	48%
PCB detection frequency for samples >50 ppm	40%	33%	14% (27% not including residential)	42%
Range of PCB concentrations detected in caulk samples (ppm)	1–220,000	70–36,000	570–82,000	>20–550,000
Method detection limits (ppm)	≥25	0.5	50	20

[a] This study. Note the limitations of the sampling design in the Methods section.
[b] Herrick et al., 2004.
[c] Robson et al., 2010.
[d] Kohler et al., 2005.

Table 3
Temporal distribution of polychlorinated biphenyl (PCB) concentrations in caulk samples from San Francisco Bay Area buildings.

Construction year	# samples	# < MDL	# > MDL-50 ppm	# 50–10,000 ppm	# > 10,000 ppm	% > 50 ppm
1950s	14	2	6	2	4	43
1960s	5	1	2	1	1	40
1970s	4	0	3	1	0	25
1980s	1	0	0	1	0	100[a]
Unknown	1	0	1	0	0	0
Total	25	3 (12%)	12 (48%)	5 (20%)	5 (20%)	

[a] Note this result is based on one sample.

contained only 2 ppm PCBs. Wood frame buildings generally contained low PCB concentrations in caulk (≤60 ppm), with the exception of one sample located around a window frame that contained 12,500 ppm PCBs. These data are in agreement with results from the previous caulk surveys conducted in Boston, Toronto, and Switzerland, which primarily focused on buildings with concrete and masonry construction and observed generally comparable concentrations (Table 2). Due to the small sample size, it was not possible to evaluate significant differences in PCB concentrations in relation to building category type in the present study. In addition, because of the blind sampling procedure used, information on building use (e.g., industrial, commercial, institutional) was not collected so no comparisons in this regard could be made with previous studies.

3.5. Caulk PCB screening using portable XRF

Our ability to assess false positives was limited to the three samples (Table 1) in which PCBs were not detected by GC–MS. In these three samples, the results were not consistent: one sample indicated a false positive, one sample did not, and the third sample could not be analyzed by XRF because there was not enough sample material left over from the GC–MS analysis. False negatives (i.e., when chlorine was not detected by XRF but the GC–MS analysis indicated the presence of PCBs) were also observed at low concentrations, which were likely due to the higher detection limits of the portable XRF analyzer. When PCBs were present at concentrations greater than 3600 ppm (0.36%), portable XRF always detected chlorine, but there was no consistent relationship between the XRF-estimated chlorine concentration and the GC–MS measured PCB (or chlorine) concentration (SI Fig. SI-3). When PCBs were present at concentrations less than 100 ppm (0.01%), portable XRF detected chlorine about half the time, also with no clear relationship between the XRF-estimated chlorine concentration and the GC–MS measured PCB (or chlorine) concentration. When XRF did not detect chlorine (detection limit average 459 ppm), PCBs were present at concentrations less than 100 ppm in the caulk. These results indicate that portable XRF analysis may only be useful for identifying caulk that does not contain high concentrations of PCBs (≥10,000 ppm). However, users are cautioned that estimates of chlorine by portable XRF should not be used to estimate the PCB chlorine content of these materials because of the lack of a predictable relationship between XRF measured chlorine and GC–MS measured PCB (or PCB chlorine), in addition to the potential for false positives.

3.6. Caulk PCB regional mass estimate in buildings

Because PCBs have been used in a wide variety of applications in urban areas, an understanding of the remaining reservoir in caulk in buildings is an important step in determining the potential of these materials as an environmental source. Based on our analysis methodology there are an estimated 6288 standing buildings in the San Francisco Bay study area that were built during the era of PCB use in caulk (See SI Table SI-2). Almost half (48%) of these buildings were located in Santa Clara county, followed by 26% in Alameda, 19% in Contra Costa, and 6% in San Mateo counties. The cities of Fairfield and Vallejo each contained <1% of the total number of buildings identified. The pattern of standing buildings does not follow the population demographics for each subregion (e.g. for 1980, Santa Clara: 34%, Alameda: 29%, Contra Costa: 17%, San Mateo: 15%, and Fairfield/Suisun/Vallejo: 4%). However, the density of buildings with potential PCBs in caulk in Alameda, Contra Costa, Santa Clara, and Fairfield was similar (range 0.62–0.9; mean 0.77 buildings/km^2), and these were higher than the density of such structures in San Mateo and Vallejo (0.31 and 0.059 buildings/km^2, respectively). Of these areas, population increased the most in Santa Clara County as a whole from 1950 to 1980 (446%), followed by San Mateo (249%), Contra Costa (220%), and Alameda (149%) (USA Census Bureau). In some city areas, population increased much more than this. For example, the City of San Jose (the largest city within Santa Clara County) increased 661% and Fairfield/Suisun City/Vallejo increased 497%. The majority of buildings identified as built during this time period were commercial (67%), followed by industrial (30%), infrastructure (2%), and mixed use (1%) (residential land use area was intentionally excluded from this estimate because PCBs were not commonly added to caulk in residential structures). Thus, the methods used in the present study appear to be sensitive to the unique land use patterns of each county or city area helping to provide confidence in the results and highlight the need for not making aggregate assumptions across broad urban landscapes.

The medium (i.e., mid-range) estimate of the PCB mass in caulk in buildings in the San Francisco Bay study area (counties of Alameda, Contra Costa, Santa Clara, San Mateo, and the cities of Fairfield, Suisun City, and Vallejo) was 10,500 kg (Table 4). This mass equated to an average of 4.7 kg PCB per building (calculated by dividing the total PCB mass in caulk in the study area buildings by the estimated total number of buildings with PCB-containing caulk in the study area). This total PCB mass in buildings is very similar to the estimate of 13,000 kg made recently for PCBs in building caulk in the city of Toronto (Robson et al., 2010), which had a population comparable to the study area in 1980. Although the results presented above suggested that population does not appear to be a perfect correlate at the sub-regional scale, it may be a reasonable proxy at the scale of a large multi-city urban area since city infrastructure allows commuting from place of residence to place of business. The 1980 population of the counties of Alameda, Contra Costa, Santa Clara, San Mateo, and the cities of Fairfield, Suisun City, and Vallejo was 3.8 million, and the population of the Toronto Census Metropolitan Area in 1980 was 3.0 million. These estimates of PCB mass in caulk for the San Francisco Bay study area and Toronto are lower than the estimate made recently for the Puget Sound Area (59,000 kg,

Table 4
Estimates of polychlorinated biphenyl (PCB) mass in caulk in the San Francisco Bay study area buildings.

	PCB mass in caulk in study area buildings (kg)	Average PCB mass in caulk per building (kg)
Low estimate	767	0.6
Medium estimate	10,500	4.7
High estimate	46,000	16

range 39,000–79,000 kg, 2010 population 4.475 million), which included the entire Puget Sound watershed (Roberts et al., 2011). These estimates are both lower than the estimate of the PCB stock in caulk in Switzerland, which ranged from 50,000–150,000 kg (Kohler et al., 2005).

4. Summary and implications

Based on our study, the use patterns of PCBs in caulk in the San Francisco Bay Area appear to be similar to those in Boston, Toronto, and Switzerland. This is substantiated by similarities between all studies in the frequency of detection of samples containing greater than 50 ppm PCBs, similarities in the congener profiles indicating a predominance of Aroclor 1254, similarities in the use profile (greater concentrations in concrete construction buildings), and similarities in the estimate of standing mass in relation to population despite the use of independent methodologies. The Bay Area age profile indicates that although likely less common, buildings constructed during the 1980s may still contain some caulk contaminated with PCBs. Results also indicate that some wood framed buildings may contain measurable amounts of PCBs around some of the fixtures. These two results appear to differ from other findings. As a management tool, portable XRF analysis may only be useful for identifying caulk that contains low concentrations of Cl (≤10,000 ppm) and by extension low or no PCBs. Portable XRF should not be used to estimate the chlorine content associated with PCB mass because of the lack of a predictable relationship.

The results from the San Francisco Bay Area study provide further support for continuing efforts to manage PCBs in building caulk and suggest that future guidance for management could incorporate instructions on the use of portable XRF during preliminary investigations to help select appropriate management techniques. Switzerland and Sweden have active programs for managing PCB-containing building materials, including caulk (references in Jansson et al., 2000; Kohler et al., 2005). In the USA, the EPA has released guidance on precautionary measures and BMPs to follow when repairing or renovating older buildings where PCB-containing caulk may be present (USEPA, 2010a). This guidance is communicated via a website containing 'Suggested Tools and Methods for Caulk Removal' (USEPA, 2010b).

Further studies to expand the currently small international dataset on PCBs in caulking materials (including the age and use profiles), to further explore the utility of a portable XRF analyzer as a reliable screening tool for management, and to quantify the remaining mass of caulk in concrete masonry buildings of countries that produced or imported PCBs appear justified. Such data will further illuminate the potential of these materials as an ongoing source of PCBs in relation to human and environmental health.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.envint.2014.01.008.

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