Joint sealants, an overlooked diffuse source of polychlorinated biphenyls (PCB) - results of a nationwide study in Switzerland

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Introduction

Polychlorinated biphenyls (PCB) are toxic, resist degradation, accumulate in terrestrial and aquatic ecosystems and are subject to atmospheric long range transport. PCB were used in heat transfer fluids, dielectric fluids, hydraulic fluids, paints, coatings, ceiling tiles, and sealants. Following the recommendation of the Organization for Economic Cooperation and Development (OECD) of February 20 1973 to its member states, the use of PCB in open systems was banned in many industrialized countries. Nevertheless, more than 30 years later, materials acting as diffuse sources of PCB are still present in surprisingly large quantities. While large efforts were made in the past 20 years to phase-out closed systems containing PCB such as transformers and large capacitors, open systems were often neglected. As a matter of fact, joint sealants are still not widely recognized as important diffuse sources of PCB. Elastic joint sealants produced between 1955 and 1975 may contain significant amounts of PCB added as plasticizers, and concrete buildings containing these materials do represent a significant inventory of PCB.
Initiated by reports on PCB-containing joint sealants in Germany and by a first investigation of joint sealants in 29 public buildings in East and Central Switzerland, a nationwide survey was initiated by the Swiss Agency for the Environment, Forests and Landscape (BUWAL). Sampling focused on concrete buildings erected between 1950 and 1980, and 1348 samples of joint sealants and 160 indoor air samples were analyzed.
A summary of the results of this campaign will be reported in this paper. The goals of this work were a nationwide assessment of the abundance of PCB-containing joint sealants present in buildings as well as an assessment of the impact of these materials on human health (indoor air quality) and environment (PCB inventory). The implementation of the results of this campaign

included a tentative guideline value for the maximum concentration of PCB in indoor air[1] as well as the publication of a guideline to assist building owners and contractors on how to identify and – if necessary – safely remove joint sealants containing PCB[2].

Methods and Materials

Sampling strategy: In cooperation with local authorities and building owners, 1348 samples of joint sealants and 160 indoor air samples from concrete buildings erected between 1950 and 1980 were collected and analyzed by selected laboratories. Sampling techniques, analytical methods and requirements for documentation were discussed and harmonized, and an interlaboratory study on the determination of PCB in joint sealants was started in cooperation with the participating laboratories at an early state of the project.

PCB analysis in joint sealants: Each participating laboratory which fulfilled the requirements of the interlaboratory study was qualified to use its own method based on extraction and quantitative determination of PCB by gas chromatography / mass spectrometry (GC/MS) or gas chromatography / electron capture detection (GC/ECD). Extraction methods included soxhlet, ultrasonic and accelerated solvent extraction with solvents such as acetone, *n*-hexane, cyclohexane, *n*-octane or toluene.

Screening of elemental composition of joint sealants using wavelength dispersive x-ray fluorescence spectrometry (WD-XRF): Eighty-five samples were analyzed without further preparation on a wavelength dispersive x-ray fluorescence spectrometer. Selected samples were analyzed for chlorine and lead with independent methods to verify the WD-XRF results.

PCB analysis of indoor air: Air samples were analyzed by selected laboratories participating in this project. All laboratories were instructed to air the rooms the evening before sampling took place, and to keep windows and doors closed over night and during air sampling. The total PCB content for an indoor air sample was estimated as the sum of the congeners PCB-28, -52, -101, -138, -153, and -180 multiplied by a factor of 5. Our analytical method, based on sampling of 180 L air at a flow rate of 1 L/min with four stacked Florisil sampling tubes and analysis by gas chromatography / high-resolution mass spectrometry (using ^{13}C-labelled PCB as internal standards) was validated by several parallel measurements of indoor air concentrations with two other participating laboratories[3]. The precision achieved was between 5 and 25 %. Based on a sampling volume of 180 L, blank levels for the individual PCB congeners were between 0.1 and 1 ng/m^3.

Results and Discussion

PCB in joint sealants - analytical methods: Concentrations of PCB in 1348 samples of joint sealants from buildings erected between 1950 and 1980 were analyzed, according to the procedures derived from an interlaboratory study with 17 participants. Comparing the analytical methods of the individual laboratories and the results submitted, no significant differences between extraction methods, solvents, clean-up method (none versus filtration using Na_2SO_4) and detection methods (GC/MS versus GC/ECD) were found. Digesting of the polymer matrix with oleum prior to extraction, however, was not successful because recoveries were reduced significantly due to partial dechlorination of all quantified PCB-congeners, mostly PCB-28 and -52. As an alternative, rapid screening method for a large number of samples, wavelength dispersive x-ray fluorescence spectrometry (WD-XRF) was evaluated. Eighty-five samples of joint sealants were analyzed, and chlorine concentrations between < 0.1 % (detection limit) and 20 % were found. WD-XRF can be used for rapid screening of joint sealants suspected to contain PCB. Positive samples, however, need to be verified by the conventional GC/MS or GC/ECD methods. WD-XRF analysis revealed – next to sulfur from the polymer matrix (Thiokol rubber) – the presence of lead (up to 2 %) and smaller amounts of characteristic traces of barium, titan and manganese in several samples.

PCB in joint sealants – occurrence and inventory in Switzerland: Figure 1 represents the PCB contents determined in 647 of 1348 samples collected from public buildings in Switzerland. Sampling focused on concrete buildings erected between 1950 (estimated start of use of joint sealants containing PCB as a plasticizer) and 1980 (eight years after the use of PCB in open applications has been banned in Switzerland).

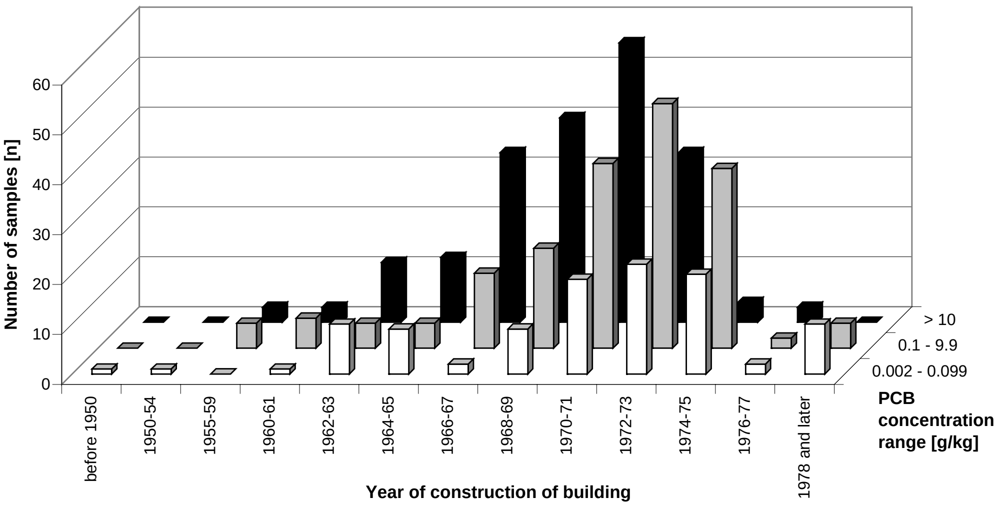

Figure 1: Number of joint sealants from buildings erected between 1955 and 1975, containing PCB in various concentration ranges (0.002 – 0.1 g/kg, 0.1 – 10 g/kg and >10 g/kg). Joint sealants containing more than 0.1 g/kg PCB are most likely to be encountered in buildings erected between 1966 and 1973.

PCB were used as plasticizers in joint sealants for outdoor and indoor applications. In 330 samples (51 %) of outdoor joint sealants (n = 648) PCB could be detected, compared to 258 samples (43 %) of indoor sealants (n = 596). About half of all samples (48 %, n = 647) did contain more than 20 mg/kg PCB. PCB concentrations above 50 mg/kg, the lower limit for the PCB content for materials to be disposed as hazardous waste, were reached by 567 samples (42 %). A total of 279 (21 %) samples reached PCB concentrations between 1 and 55 %. Almost half of the samples (49 %) contained medium chlorinated PCB mixtures similar to Clophen A50, Aroclor 1248 or 1254. PCB mixtures with high chlorine content, referring to Clophen A60, Aroclor 1260 and -1262 could be

determined in 14 % of the PCB-containing joint sealants. Only 7 % of the samples could be attributed to low chlorinated PCB mixtures, such as Clophen A30 and A40 or Aroclor 1242. 30 % of the samples could not be attributed to a certain type of PCB mixture.
An analysis of the number of samples in the concentration ranges of 0.002 – 0.099 g/kg, 0.1 – 9.9 g/kg and > 10 g/kg revealed that joint sealants containing more than 0.1 g/kg PCB are most likely to be encountered in buildings erected between 1966 and 1975 (see Figure 1). The number of samples containing less than 0.1 g/kg PCB, however, does peak in the time period between 1970 and 1975. Most likely, these samples did not contain PCB originally, but reflect secondary contamination.
To our knowledge, there are no reports in the current literature on extensive surveys of the PCB content of joint sealants, as reported in this work. Data from individual objects reported by other researchers, however, do agree well with our findings. Benthe and coworkers found PCB concentrations between 1 and 40 % in joint sealants (Thiokol rubber) used in a German office building erected in 1969[4]. Sundahl and coworkers report PCB concentrations between 4.7 and 8.1 % in elastic sealants[5].
The widespread presence of PCB in joint sealants raises concerns about the environmental impact of this reservoir of persistent organic pollutants (POP). As a matter of fact, joint sealants represent a significant stockpile of PCB. Based on the data of our work, we estimate between 50 and 150 t of PCB still to be present in joint sealants in buildings in Switzerland. A Swedish study concludes that 150 to 600 t PCB are present in buildings in Sweden[6]. For Denmark, Wilkins and coworkers[7] cite the Organization of Sealant Branch's Manufacturers and Distributors, reporting an estimated inventory of 75 t PCB in caulking materials.
Removing of old joint sealants from construction materials and disposal after they reached the end of their service time is a critical issue in terms of preventing significant amounts of PCB to be released into the environment and finally into the food chain. Thus it's important to recognize that sealants are significant diffuse emitters of PCB. These materials need to be identified, carefully removed with suitable techniques and disposed of by high temperature combustion.

PCB in indoor air – results of investigations in Switzerland: Figure 2 represents a histogram showing the concentrations of PCB in indoor air determined in 160 cases where joint sealants containing PCB were present. In 42 cases (26 %), clearly elevated PCB indoor air concentrations > 1 $\mu g/m^3$ were encountered, and in 8 cases (5 %), levels were higher than 3 $\mu g/m^3$. In one case (0.6 %), the Swiss tentative guideline value of 6 $\mu g/m^3$ for PCB in indoor air was exceeded. PCB indoor air concentrations were shown to increase with increasing room temperature. The mean PCB indoor air concentration of all 160 sites was 0.79 $\mu g/m^3$ (median 0.41 $\mu g/m^3$).
This data clearly shows that the tolerance limit of 6 $\mu g/m^3$ is rarely reached, although joint sealants containing PCB were present in all cases. The range of PCB indoor concentrations reported herein corresponds well with the data from other studies. However, higher maximum values were reported by other authors[8, 9]. From our data and from what has been reported in the literature so far, we conclude that the range of PCB concentrations encountered in buildings where joint sealants containing PCB were present may easily span two orders of magnitude. Cleary, the impact of the presence of these materials on indoor air quality is strongly dependent on highly variable factors such as the air-exchange rate of the room or the ratio of the size of sealant's surface exposed and room volume. Typical air-exchange rates[10] in buildings may vary between 0.02 h^{-1} and 3.6 h^{-1}, translating into PCB indoor air concentrations varying by two orders of magnitude (assuming that the rate of emission of PCB from the joint sealants is constant).

Other parameters having an impact on the resulting indoor air PCB concentrations include the type of PCB used (high vs. low chlorinated) and the temperature.

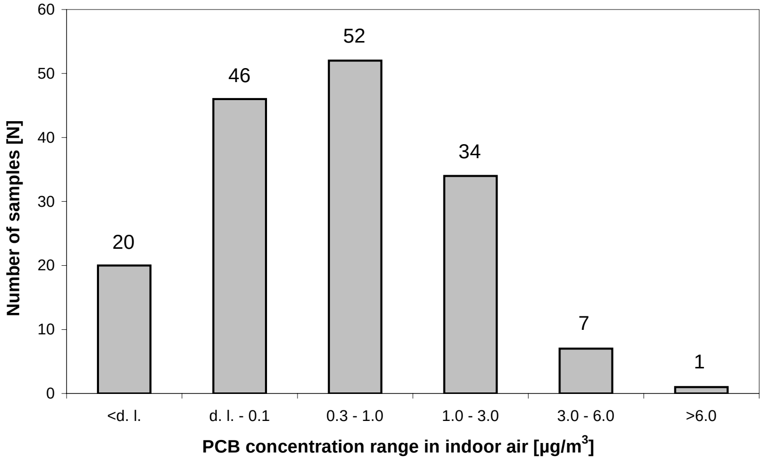

Figure 2: PCB indoor air concentrations determined in 160 cases where joint sealants containing PCB were present. In one case (0.6 %), the Swiss tentative guideline value of 6 µg/m^3 for PCB in indoor air was exceeded.

Joint sealants represent long-term diffuse sources for PCB. Sundahl and coworkers[5] calculated (based on building size and air-exchange rate) for an eight storey building that annual emissions of 60 g PCB are sufficient to sustain a permanent indoor air concentration of 0.6 µg/m^3. The total PCB inventory of 90 kg present in this building is – theoretically – sufficient to maintain elevated indoor air concentrations for many hundred years.

Environmental and remediation aspects. Although the use of PCB in open applications was banned almost 30 years ago, these persistent organic pollutants are still widely present in joint sealants, today. Almost half of all concrete buildings erected between 1955 and 1975 in Switzerland do contain joint sealants exhibiting PCB concentrations between 0.02 and 550 g/kg. Significant progress has been made with the phase-out of PCB in closed applications, e.g. by replacing transformers and capacitors containing PCB. In Switzerland, the inventory representing PCB in transformers could be lowered from 1800 – 2700 t in the years between 1975 and 1985 to less than 10 t, today. Based on this work, we estimate that there are still 50 – 150 t of PCB present in joint sealants, distributed over many hundreds of buildings all over the country. Joint sealants represent a major open PCB inventory and act as diffuse PCB sources.
The Stockholm Convention – ratified by Switzerland in 2003 – requires governments to take steps to reduce the release of dioxins, furans, hexachlorobenzene, and PCB as byproducts of combustion or industrial production, with the goal of their continuing minimization and, where feasible, ultimate elimination. Thus, from an environmental as well as from a legal point of view, joint sealants – representing a major PCB stockpile today – need to be localized, removed carefully by using suitable techniques and disposed of as hazardous waste in high-temperature incineration plants, whenever buildings are renovated or torn down. A guideline[2] tackling these issues –

including practical aspects on how to remove these materials safely – has been published by the Swiss Agency for the Environment, Forests and Landscape recently as a result of this work. It is recommended that joint sealants present in buildings erected between 1955 and 1975 should be analyzed before these structures are going to be renovated or torn down. If significant amounts of joint sealants are present indoors and their PCB concentration are in the percent-range, rooms where people are present for extended periods should be checked for indoor air PCB levels. If the tentative guideline value[1] of 6 $\mu g/m^3$ of PCB in indoor air (based on 8 h exposure) is exceeded, PCB sources need to be identified, removed and disposed of as hazardous waste, if their PCB content exceeds 50 ppm (this is the case for 42 % of all joint sealants in concrete buildings build between 1955 and 1975 in Switzerland). In all other cases, the presence of joint sealants containing PCB should be documented in order to ensure safe removal and disposal when the building is renovated or torn down. In this context, technical guidelines on improving emission control when maintaining PCB-containing sealants will be issued this year by the Federal Coordination Conference of the Construction and Immovables Administration (KBOB) and the canton of Basel-Landschaft.

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