SEMI VOLATILE ORGANOCHEMICALS IN INDOOR ENVIRONMENT - CHLORINATED PHOSPHORUS AND ORGANOTIN COMPOUNDS IN MATERIAL UND HOUSE DUST SAMPLES

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ABSTRACT
Semi volatile organochemicals such as chlorinated organophosphorus and organotin compounds are detected in many indoor materials and residential house dust samples. Chlorinated phosphorus based flame retardants are found in 90 % of over 1,500 house dust samples ranging from 0.1 to 1,300 mg/kg. The results of material samples show that many polyurethane soft foams, sealants, and finishes contain significant concentrations of organophosphorus additives. High organotin concentrations are detected in dust samples derived from homes with polyvinyl chloride flooring with maximum values of 2,200 mg/kg. Our organotin pilot study presents the first available house dust sample results. The results show in many cases, that indoor dust ingestions of organotins from vinyl flooring dramatically exceed guideline values for Tolerable Daily Intake (TDI) or Reference Dose for Chronic Oral Exposure (RfD). For long term exposure, especially, there is a considerable concern given by indoor appearances of chlorinated organophosphorus and organotin chemicals.

INDEX TERMS
SVOCs, Organophosphorus Flame Retardants, Organotin in PVC, House Dust, Exposure Assessment

INTRODUCTION

Semi volatile organic compounds (SVOC) are frequently observed as indoor pollutants. Materials emit SVOCs, which condense on available surfaces and dust particles. Due to the fact, that only low concentrations of the free chemicals can be monitored in indoor air, the examination of settled dust represents a reliable tool to specify indoor exposures and identify sources for many of the toxicologically relevant SVOCs (Pöhner et al., 1997) and other chemical and microbial pollutants (Macher, 2001). Qualitative and quantitative analysis of house dust samples enables the possibility of evaluation of potential long term exposures and chronic adverse health effects related to direct oral and dermal dust ingestion. As the average volatile organic compound (VOC) contributions seem to drop down due to consumer product regulations, the increasing quantity of health related SVOC emitting products are considered as an important issue for the future of analysis. This concerns indoor air quality control, defining testing and analytical standards, guidelines, and toxicological assessment. In Germany, extraordinary discoveries were made from chemical indoor exposures to SVOCs. They were related to the wood preservative pentachlorophenol (PCP) and other pesticides as DDT, polychlorinated biphenyls (PCBs) from sealants in schools and commercial buildings, and polyaromatic hydrocarbons (PAHs) from tar based adhesives used for wooden flooring in homes. Those findings explained the demand for exposure control via material, air, and house dust testing which resulted in federal regulations and guidelines being established in

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Germany. Chlorinated organophosphorus chemicals are commonly used as flame retardant additives and/or plasticizers especially in polyurethane (PU) products. Contamination studies on semivolatile and nonvolatile pollutants in indoor environment demonstrated the presence of tris(2-chloroethyl) phosphate (TCEP) and tris(monochloroisopropyl) phosphate (TCPP) in most of the analyzed house dust samples (Pöhner et al., 1997 / Ingerowski et al. 2001). Emission chamber experiments demonstrated that TCEP and TCPP diffuse from their matrix to yield significant air concentrations (Pardemann, 2000). Organotin compounds are used as stabilizers and/or biocides in polyvinyl chloride (PVC) products in e.g. vinyl area carpets, flooring and vinyl wallcoverings. PVC area carpets and flooring materials represent indoor sources of the most concern. In the year 2000, occurrences in human clothing shocked and made uncertain the consumers in Germany. Only little toxicological information and exposure data are available for both groups of SVOCs, although significant adverse health effects are reported for TCEP and tributyltin (TBT). The presented data show results from our ongoing SVOC house dust exposure study and summarize our recent organotin study in Germany (Thumulla and Hagenau, 2001). Data for chlorinated organophosphates TCEP, TCPP, tris(dichloroisopropyl) phosphate (TdCPP), and organophosphonates bis(2-chloroethyl)-vinyl phosphonate (BCVP) and bis(2-chloroethyl)-2-chloroethyl phosphonate (BCCP) and the organotin compounds monobutyltin (MBT), dibutyltin (DBT) and TBT are derived from material and house dust samples.

METHODS

Dust samples (1-5 g) were collected by vacuuming following VDI guideline 4300-Bl. 8 (VDI, 2001). The dust collections were performed after a general cleaning of the surfaces had been carried out one week before sample collection. During this period, no surface cleaning was allowed. The samples were collected by industrial hygienists, environmental consultants, environmental physicians, and homeowners, because of health complaints. Only the fine dust fractions were analyzed. Material samples were cut in small pieces and ground after liquid nitrogen treatment. Internal quality control was implemented to check for systematic errors.

Organophosphorus Analysis: Samples for organophosphorus analysis were collected over representative areas of residential living space surfaces using conventional vacuum cleaners with two chamber filter dust bags. The organophosphorus data for TCEP, TCPP, TdCPP, BCVP, and BCCP were derived from over 1,500 house dust sample results for the years 1996 to 2001. Dust samples were collected from residential homes, schools, and commercial buildings. Many of the house dust samples have been tested also for pesticides, heavy metals, lead, and microbial contaminations. Materials were analyzed to identify primary sources of previous findings in the dust and related emissions. Further materials were analyzed in advance for material selection purposes integrated into environmental consulting programs (Haumann, 2001). Dust and material samples were extracted with acetone/cyclohexane (1+1) in an ultrasonic bath (2 x 10 min) and analyzed by GC/MS using SIM-mode and internal standards. The limits of determination were 0.3 - 0.5 mg/kg.

Organotin Analysis: The organotin chemicals MBT, DBT, and TBT were analyzed in an independent study to determine the possible organotin exposures resulting from PVC flooring in representative homes. Dust samples were collected using flat filter sampling devices attached to the vacuum cleaner nozzles. Material samples were collected for all 33 locations. Dust and material samples were treated and extracted with diethyl ether/hexane mixture, sulfuric acid, and then drying, following standard E DIN 38407 and analyzed by GC/MS following DFG standard (DFG, 1992). The limits of determination were 0.1 - 0.5 mg/kg.

RESULTS

The results show, that chlorinated organophosphorus chemicals are ubiquitously distributed in the indoor environment in Germany. They are present above the limit of determination in 90 % out of more than 1,500 house dust samples ranging from 0.1 to 1,300 mg/kg (see table 1). The phosphonates BCVP and BCCP were included just recently into the SVOC dust screening program. Few data show high contributions in indoor environment due to the higher emission rates compared to the less volatile phosphoric acid triesters. In cases of primary sources with large surface areas, high concentrations are found in dust samples. In addition, many of the non halogenated organophosphorus chemicals like tris(2-ethylhexyl) phosphate (TEHP), tris(2-butoxyethyl) phosphate (TBEP), tris(n-butyl) phosphate (TBP), tricresyl phosphate (TCP) and triphenyl phosphate (TPP) appear in many dust and material samples significantly above the limits of detections. The results of material samples demonstrate that PU soft foams, insulation foams, mattresses, paints, and finishes are the major indoor sources (see table 2). In some cases, material concentrations of 5 % - 10 % are declared by the manufacturers.

Table 1. Chlorinated Organophosphorus Compounds in Dust Samples

Percentiles	50.	90.	95.	Max
TCEP (n = 1569) in mg/kg	0.6	4.2	8.4	330
TCPP (n = 1337) in mg/kg	1.0	6.7	14	470
TdCPP (n = 503) in mg/kg	< 0.5	0.9	2.3	120
BCVP (n = 8) in mg/kg	--	--	--	940
BCCP (n = 8) in mg/kg	--	--	--	1,300

Table 2. Chlorinated Organophosphorus Compounds in Material Samples

Maximum Concentration	Soft Foams	Paints/Finishes	Mattresses	Foam Sealants
TCEP (n = 563) in mg/kg	6,400	840	890	89,000
TCPP (n = 563) in mg/kg	16	20	16	190,000
TdCPP (n = 563) in mg/kg	6,500	< 5	24	no analysis
BCVP (n = 165) in mg/kg	1,900	1,500	no analysis	no analysis
BCCP (n = 165) in mg/kg	3,000	16,000	no analysis	no analysis

Table 3. Organotin Chemicals in Dust and Material Samples from PVC-Flooring

Dust Samples, Percentiles (n = 33)	50.	90.	95.	Max
Monobutyltin (MBT)* in mg/kg	0.5	7.2	17	24
Dibutyltin (DBT)* in mg/kg	3.4	413	870	2,200
Tributyltin (TBT)* in mg/kg	0.5	2.6	2.8	15
Material Samples, Percentiles (n = 33)				
Monobutyltin (MBT)* in mg/kg	5.5	35	57	70
Dibutyltin (DBT)* in mg/kg	120	450	520	920
Tributyltin (TBT)* in mg/kg	< 0.1	7.0	32	34

* referring to the specified organotin cation

Organotin compounds monobutyl-, dibutyl- and tributyltin were detected in house dust samples of 33 homes with PVC-flooring ranging from 0.1 to 2,200 mg/kg (see table 3). In general, we found a good correlation between the dust and the material concentrations. Dibutyltin gives the major organotin contribution, due to the wide usage of dibutyltins as stabilizers in PVC products. TBT is found in relevant amounts, most likely added as a biocide, which is a common application for trisubstituted alkyltins. The age of the flooring does not correlate with the total material and dust concentrations. Samples originating from 1982 show about the same results as products from 1999.

DISCUSSION

On the basis of the analytical data an assessment of the distribution of chlorinated organphosphorus chemicals in domestic dust samples can be derived (tables 1 and 2). In case of ubiquitously distributed substances, the 50. and the 95. percentiles are generally used to describe the typical prevalence of a substance in the environment. Therefore, concentrations of less than 1 mg/kg in house dust may be regarded as background values. Quantities above 10 mg/kg significantly indicate indoor sources. The organotin results confirm the relatively high emission potential derived from PVC flooring. The data display a high level of concern due to the often realistic "worst case" scenario, especially when sensitive young children are exposed directly to PVC flooring. These conclusions are contrary to a study of the PVC industry (Piringer et al., 2000). Based on organotin emission chamber test results, the study concluded, that organotin chemicals are fixed in a satisfactory way in their PVC matrix and are not critically released into the environment.

Indoor Exposure Assessment and Toxicity

Organotin chemicals reveal high toxicological potential due to the significant immunotoxicity. TBT, used as a biocide, is extremely toxic for aquatic life. Potential human exposure to house dust may be estimated as follows: A typical daily oral ingestion of dust for a 1 year old child is 100 mg/d. TDI and RfD-values are available for organotin chemical TBT in the range of 0.25 - 0.3 µg/kg per day (WHO, 1993 / EPA, 1997). As long as no further toxicological data are available for the disubstituted organotin DBT, the existing TDI-value for TBT is transferable to DBT also (BgVV, 2000). For determining the total daily intake, additional dermal, oral and inhalation ingestion should be taken into account. Therefore, exposure to 10% of the TDI is an allowed result from oral dust reception, leading to 0.025 µg/kg/d and a tolerable dust concentration of 2.5 mg/kg organotin only (see table 4). Based on the DBT data only, this calculation clarifies the fact, that the present dust concentration of the median (50. percentile) of 3,4 mg/kg is already higher and the 95. percentile (870 mg/kg) is dramatically higher than the proposed tolerable organotin dust exposure. Although this complex derivation consists of many weak points and approximations it is a reliable tool to demonstrate the potential organotin health impairment due to PVC flooring based on available toxicological data and real exposure results.

Table 4. Reference Concentrations for Oral Exposure from House Dust

	Reference	Dust Concentration [mg/kg]	Daily Oral Intake from House Dust* [µg/kg/d]
Organotin (DBT)	50. Percentile	3.4	0.034
	95. Percentile	870	8.700
	TDI / WHO	2.5	0.025

*calculated for child exposure: 100 mg/d dust intake, total resorption, 10 kg body weight

For TCEP no TDI value is available. TCEP dust concentrations of e.g. 8.4 mg/kg (95. percentile) lead to an oral exposure of 8.4 µg/day, assuming complete resorption. In the past, organic phosphate triesters gained attention in literature because of their neurotoxic potential (Matthews, 1993 / Ingerowski, 1997). Brominated organic phosphoric triester tris(dibromopropyl) phosphate (TRIS), which had been used as a flame retardant in textiles until 1975, was prohibited in the late seventies. Meanwhile, TCEP is classified in Germany as carcinogenic and embryotoxic for animals (TRGS 905, 2000).

For the majority of the ubiquitous organophoshorus and organotin compounds used as flame retardants, additives, plasticizers, stabilizers and biocides no sufficient toxicological data are available to propose guideline values.

METHODS
No laboratory or test chamber study can replace environmental house dust chemical testing results derived directly from indoor environments. Chemical house dust analysis is an important method for evaluation and differentiation of background and significant exposure level assessment for a wide quantity of relevant SVOCs in indoor environment. Standards for collection and analysis are already available and help to enable quality control and comparability (VDI 4300, 2001 / ASTM, 2001). Previous results of house dust sample studies for biocides and other SVOCs could display strong similarities and lead to the same information for e.g. median and 95. percentile values (see table 5). A study of TCEP and TCPP displayed reasonable accuracy even for different dust extraction methods (Ingerowski, 2001).

Table 5. Results of SVOC Chemical Dust Analysis Studies

Percentiles		50.	95.	Max	References *
TCEP	in mg/kg	0.6 / 0.6	8.4 / 7.5	330 / 121	[1] / [2]
TCPP	in mg/kg	1.0 / 0.6	14 / 8.8	470 / 375	[1] / [2]
Biocides					
DDT	in mg/kg	< 0.3 / < 0.3	4.2 / 5.1	40 / 44	[3] / [4]
PCP	in mg/kg	1.0 / 0.3	8.0 / 13	40 / 43	[3] / [4]
Permethrin	in mg/kg	0.7 / < 0.5	37 / 25	150 / 100	[3] / [4]
Sum PCBs	in mg/kg	< 0.5	5.5	39.5	[4]
Sum PAHs	in mg/kg	2.4	8.4	158	[4]
Sum Phthalates	in mg/kg	680	2,651	8,690	[4]

* [1] this study, [2] Ingerowski et al. (2001), [3] Walker et al. (1999), [4] Pöhner et al. (1997)

CONCLUSION
The results of material and dust analysis show that especially for long term exposure there is a considerable concern caused by concentrations of chlorinated organophosphorus and organotin chemicals in indoor environment. Besides pesticides, other semi volatile chemicals like chlorinated organophoshorus chemicals can be considered as ubiquitous. For organotin chemicals, the data display the strong demand for further study and investigation. We recommend the avoidance of PVC flooring in homes with small children and e.g. in preschools. We consider the indoor usage of PU products as critical especially for large surface area applications in the form of any soft foams, acoustic ceilings, paints, and also mattresses due to the exposure to chlorinated organophosphorus flame retardant additives. Alternatives for e.g. foams, paints and floorings are available with the same flame resistance. This could be demonstrated in a large environmental material screening and testing study for a business jet. For the completion of a BBJ (737-700) acoustic and thermal insulations and interior design materials were selected in respect to minimal potential indoor exposures to VOCs, phthalates, biocides, and in the first line flame retardants and optimized for cabin air quality. In view of the ubiquitous distribution of SVOCs in the indoor environment and the possible adverse health effects, there is an urgent need for more toxicological data in order to establish reliable guideline values for indoor air, material, and house dust concentrations. So far, avoidance and prevention concepts enable minimization of potential long term indoor exposures and chronic adverse health effects.

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