DETERMINATION AND OCCURRENCE OF ORGANOPHOSPHOROUS COMPOUNDS (POC) IN HOUSE DUST AND INDOOR AIR

VORKOMMEN UND BESTIMMUNG VON PHOSPHORORGANISCHEN VERBINDUNGEN IN HAUSSTAUB UND RAUMLUFT

PRESENCE ET DÉTERMINATION DE COMPOSÉS ORGANOPHOSPHOREUX (POC) DANS LA POUSSIÈRE ET L'AIR D'INTÉRIEUR

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SUMMARY

With the available work the results of the determination are presented by Tris(2-chlorethyl)-phosphate [TCEP], Tris(2-butoxyethyl)-phosphate [TBEP], p-Triskresylphosphate (p-TKP) and Triphenylphosphate [TPP] in the indoor media like house dust and indoor air of public buildings. In these buildings, which indicate partial wide blocked TCEP containing building products, TCEP concentrations in the house dust to 2200 occurs mg/kg. In that parallel to it can the TCEP concentrations to approx. 4 µg/m³ entered interior air of these buildings be proven. In not contaminated interiors TCEP indoor air concentrations from < 0.01 to 0.03 µg/m³ are detectable. The compounds TBEP and TPP are not to be proven in the indoor air in relevant concentrations (> 0.05 µg/m³). In dust from buildings with TBEP or TPP containing building materials or consumer goods concentrations can be found between 100 and 1300 mg/kg in the dust. For the hygienic evaluation of a TCEP load in the interior both exposure paths – dust and indoor air must be in our opinion Other POC with according to higher boiling points can after clarifying the questions regarding the influence of the source (POC in floor preservative agents; Secondary contamination of the floor) on the concentration in the dust only over the exposure path house dust to be judged.

ZUSAMMENFASSUNG

Mit der vorliegenden Arbeit werden die Ergebnisse der Bestimmung von Tris(2-chlorethyl)-phosphat [TCEP], Tris(2-butoxyethyl)-phosphat [TBEP], p-Triskresylphosphat (p-TKP) und Triphenylphosphat [TPP] in den

Innenraummedien Hausstaub und Raumluft öffentlicher Gebäude vorgestellt. In diesen Gebäuden, die teilweise großflächige verbaute TCEP-haltige Bauprodukten aufweisen, treten TCEP Konzentrationen im Hausstaub bis 2200 mg/kg auf. In der parallel dazu erfassten Innenraumluft dieser Gebäude können die TCEP-Gehalte bis ca. 4 µg/m³ nachgewiesen werden. In nicht belasteten Innenräumen sind TCEP-Raumluftgehalt von < 0,01 bis 0,03 µg/m³ nachweisbar. Die Verbindungen TBEP und TPP sind in der Raumluft in relevanten Konzentrationen (>0,05 µg/m³) nicht nachzuweisen. In Stäuben aus Gebäuden mit TBEP- oder TPP-haltigen Baustoffen oder Gebrauchsgütern lassen sich im Staub Gehalte zwischen 100 und 1300 mg/kg finden. Für die hygienische Beurteilung einer TCEP-Belastung im Innenraum müssen nach unserer Ansicht beide Expositionspfade – Raumluft und Hausstaub – herangezogen werden. Andere POC mit entsprechend höheren Siedepunkten können nach Klärung der Fragen hinsichtlich des Einflusses der Quelle (POC in Fußbodenpflegemittel; Sekundärkontamination des Fußbodens) auf den Gehalt im Staub nur über den Expositionspfad Hausstaub beurteilt werden.

RESUME

Cet article présente les résultats de la détermination de la concentration en tris(2-chloréthyl)-phosphate [TCEP], tris(2-butoxyéthyl)-phosphate [TBEP], p-triscrésylphosphate (p-TKP) et phosphate de triphényle [TPP] dans la poussière et l'air à l'intérieur de bâtiments publics. Dans ces bâtiments, qui contiennent partiellement de grandes quantités de produits de construction contenant du TCEP, la concentration en TCEP dans la poussière atteint 2200 mg/kg. La teneur en TCEP de l'air intérieur, mesurée parallèlement, atteint 4 µg/m^3. Dans les pièces non contaminées, la concentration en TCEP varie entre 0,01 et 0,03 µg/m^3. Des concentrations significatives (>0,05 µg/m^3) en TBEP et TPP n'ont pas été mesurées. Dans les poussières des bâtiments avec des matériaux contenant du TBEP ou du TPP, la teneur mesurée varie entre 100 et 1300 mg/kg. A notre avis, les deux voies d'exposition, air et poussière, doivent être pris en considération dans l'évaluation hygiénique d'une contamination en TCEP en intérieur. La contamination avec d'autres POC ayant des points d'ébullition plus élevés ne peuvent être jugés que sur la voie d'exposition "poussière" et en connaissance de la source (POC dans les produits d'entretien de plancher; contamination secondaire du plancher).

INTRODUCTION

The group of organophosphorous compounds (POC) is lately strengthened into the focus of the public. Particularly the classification of Tris(2 chlorethyl) - phosphate (TCEP) and tributyl phosphate (TBP) as substance with the suspicion on carcinogenic effect made the public sensitive for this group of compounds. The organophosphorous compounds (POC) are widely used in products, which appear in the interior of buildings (1,2). The technical characteristics of these compounds permit their use as plasticizer and/or flame retardants means in different plastic products. The application as flame retardants takes place in acoustic panels, plastics, glass fiber wallpapers and PU assembly foams or padding. Besides POC are also used in floor preservative agents and floor lacquers. When using POC as flame retardant means POC concentrations in the products are between approx. 10 – 20 %. Using POC as plasticizer, are POC concentrations in the product on the average under 5 %. This application and the toxicological evaluation of TCEP and TBP require a very careful review of the occurrence of these compounds in house dust and indoor air. These applications can lead to it that in certain buildings large surfaces with building materials are occupied, the POC to contain. The application width and the physicochemical characteristics of the POC, here in particular the polarity and the boiling points of this group of compounds (e.g. 330°C for TCEP), suggest the fact that these compounds in the indoor transfer media (dust and air) can occur in relevant concentrations. The available literature data is summarized in table 1.

Table 1. Occurrence of various organophosphorous compounds in the environment [5,6,7]

Medium	TCEP	TBEP	TBP	TPP
House dust	Mean 3,4 mg/kg	No data available	No data available	No data available
Indoor air	< 0,01 – 0,4 µg/m³	No data available	0,01 – 0,09 µg/m³	0,01 – 0,03 µg/m³
Air	0,002 – 0,005 µg/m³	No data available	No data available	No data available
Drinking water	0,0002 – 0,05 µg/l	No data available	No data available	0,12 µg/l
Surface water	0,2 – 1 µg/l	No data available	0,1 – 3 µg/l	No data available

With the available work results of the determination of Tris(2-chlorethyl)-phosphat [TCEP], Tris(2-butoxyethyl)-phosphate [TBEP], p-Triskresyl-phosphate (p-TKP) and Triphenylphosphat [TPP] in the indoor media house dust and indoor air of buildings are presented. For all examined buildings a first suspicion for the application of such building products was given.

INVESTIGATION SCOPE

After development of a determination procedure for the representatives for the POC [6], examined here, the POC concentrations was measured in the house dust in 8 public buildings (6 schools and 2 kindergartens), from which the suspicion existed that POC are available in building materials (in particular TCEP–containing acoustic panels) in the building. The sampling of dust takes place with the plan filter system (viz. VDI 4300 Bl.8) and indoor air was measured in accordance with the rules from the VDI 4300 Bl. 1.

POC IN HOUSE DUST

Besides the concentrations of TCEP the concentrations of Tris(2-butoxyethyl)-phosphat (TBEP), Triphenylphosphat (TPP), p-Trikresylphosphat (p-TKP) and in an exceptional case Triethylhexylphosphat (TEHP) in dust were determined (viz. table 2).

Table 2. Results of the determination of POC in house dust in public buildings

Object	Organophosphorous compound concentration in mg/kg				
	TCEP	**TBEP**	**TPP**	**p-TKP**	**TEHP ***
CBS – Room 1	**3**	**270**	**3**	**< 0,5**	**86**
CBS – Room 2	**2,5**	**1310**	**220**	**< 0,5**	**320**
MS – Room 1	**320**	**11**	**< 1**	**< 0,5**	**n.d.**
MS – Room 2	**530**	**2**	**< 1**	**< 0,5**	**n.d.**
MPG – Room 1	**772**	**723**	**1,8**	**< 0,1**	**n.d.**
MPG – Room 2	**2190**	**107**	**0,8**	**< 0,1**	**n.d.**
RS – Room 1	**1455**	**15**	**0,7**	**< 0,1**	**n.d.**
RS – Room 2	**412**	**0,7**	**0,7**	**< 0,1**	**n.d.**
EHS – Room 1	**665**	**655**	**1,6**	**< 0,1**	**n.d.**
EHS – Room 2	**532**	**n.d.**	**0,8**	**< 0,1**	**n.d.**
G – E	**24**	**11**	**1**	**n.d.**	**n.d.**
G – T	**310**	**330**	**< 1**	**<0,5**	**n.d.**

n.d. = not detected

It shows up that with exception of p-TKP all other organophosphates can be detected in varying concentrations in the dust of these buildings. In the building “CBS” occur TBEP, TPP and TEHP next to each other in the dust, whereby it becomes clear that the concentrations vary from room to room within this building strongly. Remarkable it is however that TCEP and/or TBEP are

found in concentrations higher than 1000 mg/kg. The TCEP concentrations in the building "CBS" are situated in the area of the TCEP average for normal house dust.

POC IN INDOOR AIR

Non contaminated buildings

In the context of the investigations the concentrations of POC in the indoor air of an obvious not contaminated building and parallel to it in outside air were determined. The results of this investigation are shown in the following table 3. With exception of TCEP no other POC is detectable in the indoor air.

Tab. 3. Concentration of POC in indoor air of not contaminated buildings

Object	**Concentration in µg/m³**			
	POC			
	TCEP	**TBEP**	**TPP**	**p-TKP**
Air outside	<< 0,01 (< 0,001)	<< 0,01	<< 0,01	<< 0,01
L 205	0,02	< 0,01	< 0,01	< 0,01
L 135	0,02	< 0,01	< 0,01	< 0,01
R 207	0,02	< 0,01	< 0,01	< 0,01

Contaminated buildings

The concentrations for different POC, found under the given conditions, are summarized in table 4. The available results prove that from the POC examined here only TCEP occurs in the indoor air in measurable concentrations. The concentrations in the indoor air vary between 0,3 and 3,9 µg/m³. Under the given conditions, the detection limits for TCEP, TPP, TBEP and p-TKP of 0,01 µg/m³ is secured. In the building "CBS" the indoor air concentration of TBEP of 30 ng/m³ was measured. This means that only TCEP, whose boiling point is comparable with by γ-HCH [Lindan] in indoor air is important. Regards one the available results is noticeable that the concentrations of TCEP can be arranged in the indoor air in three concentration levels. First an indoor air concentrations between 0,2 and 0,5 µg/m³ (objects ms; HvZ and EHS)second a level around approximately 1 µg/m³ (objects EHS and KG-t) and third an indoor air concentrations between 2 and 4 µg/m³ (objects MPG and RS).

Table 4. Results of the determination of POC in indoor air of public buildings (buildings with suspicion for the use of POC in building materials or consumer goods)

Objects	Organophosphorous Compound Concentration in µg/m³			
	TCEP	**TBEP**	**TPP**	**p-TKP**
CBS – Room 1	**0,03**	**0,03**	**<0,01**	**<0,01**
CBS – Room 2	**0,02**	**<0,01**	**<0,01**	**<0,01**
MS – Room 1	**0,38** **0,43**	**<0,01**	**<0,01**	**n.d.**
MS – Room 2	**0,36** **0,36**	**<0,01**	**<0,01**	**n.d.**
MPG – Room 1	**1,18**	**<0,01**	**<0,01**	**<0,01**
MPG – Room 2	**3,02**	**<0,01**	**<0,01**	**<0,01**
MPG – Room 3	**3,90**	**<0,01**	**<0,01**	**<0,01**
RS – Room 1	**2,04**	**<0,01**	**<0,01**	**<0,01**
EHS – Room 1	**0,32**	**<0,01**	**<0,01**	**<0,01**
HvZ – Room 1	**0,21**	**<0,01**	**<0,01**	**n.d.**
HvZ – Room 2	**0,51**	**<0,01**	**<0,01**	**n.d.**
HvZ – Room 3	**0,40**	**<0,01**	**<0,01**	**n.d.**
G-E	**< 0,01**	**< 0,01**	**<0,01**	**n.d.**
G-T	**1,2**	**n.d.**	**n.d.**	**n.d.**

n.d. = not detected

An interpretation of this result is not at present possible, since exact knowledge of the sources and their emission characteristics is missing and the question by secondary contamination in the examined buildings could not be clarified. The executed parallel measurements in one room and the measurements in different rooms of one building show in each case that the TCEP concentrations in the indoor air can be determined with sufficient reproducibility. The found deviations correspond to the well-known standard deviations for the determination of Lindan or Pentachlorphenole in indoor air. Under unfavourable structural conditions an indoor air concentration of 3-4 µg TCEP/m³ in the interiors of contaminated buildings could be detected. Other organophosphorous compounds with according to higher boiling points are not important in indoor air. This result covers with results shown in the literature [4]. The indoor air concentrations proven in this work exceed the concentrations described in the literature [4, 5] (max. 0.4 µg/m³). Under unfavourable

circumstances therefore TCEP concentrations in indoor air up to 5 µg/m³ are to be expected. The available data, from buildings with large areas of TCEP loaded acoustic panels show, that no concentrations are to be expected higher than 10 µg/m³ (regarded as annual average values) can occur.

COHERENCE OF TCEP IN INDOOR AIR AND HOUSE DUST

In the examined buildings regarded as suspicion objects in respect to a use of POC as flame retardants house dust and indoor air samples were taken. The coherence of TCEP in indoor air and house dust in the examined objects, resulting from the emission of construction materials contaminated by organophosphorous flame retardants are obviously.

It can be said in first approximation that high indoor air concentrations of TCEP (> 1 µg/m³) correlate with high TCEP concentrations in house dust (> 500 mg/kg) (viz. table 5).

Table 5. Coherence of POC in dust and indoor air (selected results from tables 3 and 4)

	TCEP in house dust in mg/kg	**TCEP in indoor air in µg/m³**
1	**2,5**	**0,02**
2	**3**	**0,03**
3	**310**	**1,2**
4	**320**	**0,4**
5	**530**	**0,4**
6	**532**	**0,3**
7	**772**	**1,2**
8	**1455**	**2,0**
9	**2190**	**3,0**

The interactions of polar compounds like the TCEP with depressions in the room will prevent a simple linear connection between dust concentration and indoor air concentration. For the POC TBEP and TPP it has to be assumed that according to their physicochemical characteristics as practically not volatile that they are not detectable in the indoor air except in traces.

DISCUSSION

Organophosphates are widely used in building products and consumer goods. This application is reflected in house dust and interior air of public buildings again. Due to the regulations for public buildings it is to be assumed that compounds which are used as flame retardants in these buildings are frequently detectable. The available data show the POC like TCEP or TBEP can be found in high concentrations in house dust and indoor air for public buildings. Depending upon contamination situation TCEP concentrations between 300 and 2200 is to be found mg/kg in house dust. Beside TCEP above all TBEP and TPP in house dust according to contaminated buildings are to be found. The dust data from the buildings "R-S" and "EHS", are not to be interpreted plausible without knowledge of the source. The questions, whether a relevant secondary contamination of the floor had been present, could not be answered in the present work. As already discussed the sampling of dust from contaminated surfaces represents a special situation. For such surfaces it has to be assumed that contaminated floor particles or material particles influence of the results for house dust. Despite the few examined objects it shows up, as already shown for usual house dust [6] that the organophosphates are in the house dust either in concentrations clearly under 10 mg/kg or very clearly over 10 mg/kg detectable. Tributylphosphate were examined not with, Trikresylphosphate could be proven in none of the samples. The results show that the boiling points of individual POC can be consulted as basis for the estimation of their source strength. An example of semivolatile organophosphorous compounds (SVOC) is the TCEP. The vapour pressure of TCEP, which is comparable with Lindan leads to TCEP concentrations in the indoor air between 0,2 and 4 $\mu g/m^3$. High TCEP concentrations in the indoor air correlate with high TCEP concentrations in house dust. Higher boiling POC e.g. TBEP (Trisbutoxyethylphosphat) and TPP (Trisphenylphosphat) are in agreement with literature specification [5] almost not detectable in indoor air. In the examined building maximum values were measured by 30 ng/m^3 TBEP. The POC TBEP and TPP exclusively appear in house dust. The max. concentrations of TBEP (1300 mg/kg) and TPP (220 mg/kg) in house dust show that house dust in such public buildings is to be considered. The wide use of POC containing building materials leads with security to a increased concentration of the appropriate POC in house dust or with use of TCEP in indoor air. Because of the physicochemical characteristics e.g. the polarity of the POC is to assume house

dust can only be regarded as indicator for an POC application in the building. The complex coherence between absorption and evaporation of TCEP lead in our opinion to the fact that no simple coherence between house dust and indoor air is possible. In buildings with high concentrations of POC in dust (> 500 mg/kg TCEP) an increased indoor air concentration (> 0.5 µg/m³) can be proven. The question of the coherence of indoor air concentrations and concentrations in house dust is influenced with high probability additionally by secondary contamination of the surfaces available in the room.

LITERATURE

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