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# 1 Organophosphate esters in dust samples collected from 2 Danish homes and daycare centers 3

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25 **Keywords:** exposure, flame retardants, indoor environment, plasticizers, SVOC  
26

## 27 Highlights

- 28 • Organophosphates were determined in dust from 497 homes and 151 daycare centers
- 29 • Mass fractions in dust from daycare centers were larger than in dust from homes
- 30 • Estimated exposures to organophosphates via dust ingestion were relatively low
- 31 • The country-to-country distribution of organophosphates is more variable than that of  
32 phthalate esters

## 33 **Abstract**

34 Organophosphates are used in a wide range of materials and consumer products and  
35 are ubiquitous in indoor environments. Certain organophosphates have been associated with  
36 various adverse health effects. The present paper reports mass fractions of organophosphates  
37 in dust samples collected from 500 bedrooms and 151 daycare centers of children living in  
38 Odense, Denmark. The identified compounds include: tris(isobutyl) phosphate (TIBP), tri-n-  
39 butyl phosphate (TNBP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl)  
40 phosphate (TCIPP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), tris(2-butoxyethyl)  
41 phosphate (TBOEP), triphenylphosphate (TPHP), 2-ethylhexyl-diphenyl phosphate (EHDPP),  
42 tris(2-ethylhexyl) phosphate (TEHP) and tris(methylphenyl) phosphate (TMPP). Both the  
43 number of organophosphates with median values above the limit of detection and the median  
44 values were higher for samples from daycare centers than for samples from homes.

45 Organophosphates with median mass fractions above the limit of detection were: TCEP from  
46 homes ( $6.9 \mu\text{g g}^{-1}$ ), and TCEP ( $16 \mu\text{g g}^{-1}$ ), TCIPP ( $5.6 \mu\text{g g}^{-1}$ ), TDCIPP ( $7.1 \mu\text{g g}^{-1}$ ), TBOEP  
47 ( $26 \mu\text{g g}^{-1}$ ), TPHP ( $2.0 \mu\text{g g}^{-1}$ ) and EHDPP ( $2.1 \mu\text{g g}^{-1}$ ) from daycare centers. When present,  
48 TBOEP was typically the most abundant of the identified OPs. The sum of the  
49 organophosphate dust mass fractions measured in this study was roughly in the mid-range of  
50 summed mass fractions reported for dust samples collected in other countries. On a global  
51 scale, the geographical distribution of organophosphates in indoor dust is quite variable, with  
52 higher concentrations in industrialized countries. This trend differs from that for phthalate  
53 esters, whose geographic distribution is more homogeneous. Exposure to organophosphates  
54 via dust ingestion is relatively low, although there is considerable uncertainty in this  
55 assessment.

56

## 57 **1. Introduction**

58 Semivolatile organic compounds (SVOC) are ubiquitous in indoor environments,  
59 and, depending on their chemical properties, can persist for a very long time (Weschler and  
60 Nazaroff, 2008; Shin et al., 2013). Indoor SVOCs commonly include organophosphate  
61 triesters. The use of the organophosphates is increasing because of their favorable properties  
62 as both flame retardants and plasticizers (Marklund et al., 2003). The halogenated  
63 organophosphates are mostly used as flame retardants while the non-halogenated compounds  
64 are generally used as plasticizers (Andresen et al., 2004). Organophosphorus flame retardants  
65 are found in a wide range of commercial products including textiles, rubber, polyurethane  
66 foam (PUF), antistatic formulations, cellulose, cotton, cutting oils, electronic equipment,  
67 glues, engineering thermoplastics, epoxy resins and phenolic resins (Marklund et al., 2005).  
68 Polyvinyl chloride (PVC) is an example of a product where phosphorus flame retardants also  
69 function as plasticizers (Marklund et al., 2003).

70 Organophosphates have been implicated in various adverse health effects, including  
71 skin irritation and contact dermatitis in humans, and neurological and carcinogenic effects in  
72 rats (WHO 1991 a,b, 1998, 2000). Araki et al. (2014) have recently found associations  
73 between organophosphates flame retardants and atopic dermatitis, asthma and allergic rhinitis.  
74 Organophosphates have also been associated with altered hormone levels and decreased  
75 semen quality in men (Meeker and Stapleton, 2010).

76 The widespread use of organophosphates in everyday products results in  
77 redistribution from their original source into other indoor compartments, including indoor air,  
78 airborne particles, settled dust and all exposed indoor surfaces (*e.g.* Marklund et al., 2005;  
79 Wensing et al., 2005). They were first reported in indoor airborne particles in 1980 (Weschler,  
80 1980). Their concentrations have been found to be much higher indoors than outdoors,  
81 reflecting the much greater presence of their sources indoors compared to outdoors (Weschler  
82 et al., 1984; Staaf and Östman, 2005; Wensing et al., 2005). The mass fractions of various

83 organophosphates in settled dust have been determined over the past 14 years in samples  
84 collected from homes, daycare centers and workplaces in various countries throughout the  
85 world (Brommer and Harrad, 2015; He et al., 2015; Hoffman et al., 2015; Luongo and  
86 Östman, 2015; Abdallah and Covaci, 2014; Araki et al., 2014; Cequier et al., 2014; Fan et al.,  
87 2014; Fromme et al., 2014; Shin et al., 2014; Tajima et al., 2014; Ali et al., 2013; Brommer et  
88 al., 2012; Kim et al., 2013; Dodson et al., 2012; Ali et al., 2012a; Ali et al., 2012b, Bergh et  
89 al., 2011, Van den Eede et al., 2011; Dirtu et al., 2010; Kazanawa et al., 2010; Meeker and  
90 Stapleton, 2010; Stapleton et al., 2009; García et al., 2007; Wensing et al., 2005; Marklund et  
91 al., 2003; Nagorka and Ullrich, 2003, Kersten and Reich, 2003; Becker et al., 2002;  
92 Ingerowski et al., 2001). Human exposure to organophosphates is apparent from  
93 biomonitoring studies, which have detected various organophosphate metabolites in urine  
94 samples (e.g., Reemtsma et al., 2011; Fromme et al., 2014; Hoffman et al., 2014). A recent  
95 study found that levels of such metabolites in urine correlated with levels of  
96 organophosphates in dust, and that children's exposure to organophosphates can be related to  
97 levels found in their indoor environments (Cequier et al., 2015).

98         The aim of the present paper is threefold: to report the mass fractions of selected  
99 organophosphate esters (OPEs) measured in the dust samples collected from children's  
100 bedrooms (n = 500) and daycare centers (n = 151) as part of the IECH investigation; to  
101 examine potential correlations between levels of the individual organophosphates, both in the  
102 children's bedrooms and daycare facilities; and to compare the results with those reported in  
103 other studies to derive a sense of variations over geographic location and time. The  
104 information presented in this paper can be used to improve understanding of Danish  
105 children's exposure to organophosphate esters.

106

## 107 **2. Material and Methods**

### 108 **2.1 Study design**

109           The Danish study “Indoor Environment and Children’s Health (IECH)” has  
110 investigated the relationship between children’s health and their indoor environments. The  
111 design of the IECH study and the methods used in the investigations have been described by  
112 Clausen et al. (2012). Questionnaires were sent to 17,486 families that had children between  
113 the ages of one and five. All children in the study lived on the Danish island of Fyn (482,310  
114 inhabitants). The final database contained questionnaires from 11,082 children, *i.e.* the  
115 response rate was 63%. Using the information from the survey, 500 children between the ages  
116 of three and five and living in Odense (166,000 inhabitants) were selected for the case-base  
117 study: 200 “cases” with asthma/allergies and 300 randomly selected “bases”, *i.e.* both healthy  
118 and sick children. All of the daycare facilities attended by these children were also included in  
119 the study (n = 151). Settled dust was collected from the children’s bedrooms from non-floor  
120 surfaces such as shelves, ledges, and window sills as well as from horizontal non-floor  
121 surfaces in the daycare centers. Dust from floors was avoided, since it may be contaminated  
122 by direct contact with organophosphorus flame retardants or plasticizers present at the  
123 surfaces of flooring materials that contain these additives. The dust samples were  
124 subsequently analyzed for five phthalate esters and three polycyclic aromatic hydrocarbons  
125 (Langer et al., 2010) as well as for squalene and cholesterol (Weschler et al., 2011).

### 126 **2.2 Dust collection**

127           Dust was collected from non-floor surfaces in the children’s bedrooms and daycares  
128 using ALK dust filters (ALK-Abelló A/S, Hørsholm, Denmark) mounted in a holder  
129 connected to a vacuum cleaner. Collection of dust from plastic surfaces and textiles was

130 avoided. In 5% of the homes (randomly chosen) a field blank was obtained (filter was  
131 mounted in the holder but no sampling was performed).

### 132 **2.3 Chemical analysis**

133 Prior to sampling, the virgin filters were pre-conditioned at a temperature of  $23 \pm 1$   
134  $^{\circ}\text{C}$  and relative humidity of  $50 \pm 5\%$ , weighed and assigned an ID number. The loaded filters  
135 or blanks were returned to the laboratory (shipped at ambient temperature) where they were  
136 conditioned, weighed, wrapped in aluminum foil and re-packed in their original bag. The net  
137 dust mass on the loaded filters ranged from 43 to 1396 mg (average 198 mg; median 160 mg).  
138 Of the total number of more than 700 filters that were analyzed, 33 (~ 5%) were field blanks,  
139 and 42 were laboratory blanks.

140 The organic compounds in the dust were extracted using the procedure described by  
141 Rudel et al. (2003). Logistics and details of the chemical analysis are presented in the  
142 Supplementary Material.

143 The organophosphate esters evaluated in this study, in order of retention times, were:  
144 tris(isobutyl) phosphate (TIBP), tri-n-butyl phosphate (TNBP), tris(2-chloroethyl) phosphate  
145 (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloroisopropyl) (TDCIPP),  
146 tris(2-butoxyethyl) phosphate (TBOEP), tri-phenylphosphate (TPHP), 2-ethylhexyl-diphenyl  
147 phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP) and tris(methylphenyl) phosphate  
148 (TMPP). The compounds were named and abbreviated according to the nomenclature  
149 proposed by Bergman et al. (2012).

150 The original target compounds in these dust samples were phthalate esters and  
151 polycyclic aromatic hydrocarbons (Langer et al., 2010). After the samples were extracted and  
152 analyzed, we recognized peaks in the Total Ion Chromatograms (TIC) that corresponded to  
153 organophosphate esters. As the organophosphates were not targeted from the beginning, their

154 recoveries could not be determined using appropriate isotopically labelled standards. Given  
155 that phthalate esters and organophosphate esters span similar ranges of physical and chemical  
156 properties (Wensing et al., 2005), we assume that the efficiency with which they are extracted  
157 from the dust, using 6% diethyl ether in hexane for 16 h, is similar (Toda et al., 2004). To  
158 support this, we have determined the recoveries of a phthalate ( $d_4$ -di-isononyl phthalate  
159 (DnOP- $d_4$ ); c.f. Langer et al., 2010) and a phosphate (triethylphosphate (TAP); c.f. Brommer  
160 et al., 2012) from dust samples collected onboard the Swedish icebreaker Oden. Seven dust  
161 samples were extracted and analyzed by the same procedure as the samples from this study.  
162 The recoveries were similar:  $0.96 \pm 0.09$  and  $0.99 \pm 0.09$  for TAP and DnOP- $d_4$ , respectively.  
163 Furthermore, using methods similar to those used in the present study, good procedural  
164 recoveries of 90-110 % for the organophosphates have been reported in the literature (e.g.,  
165 Van den Eede et al., 2011).

166 The organophosphate esters were first identified by their mass spectra in the TICs  
167 and matched against their mass spectra in the NIST (National Institute of Standards and  
168 Technology) Mass Spectral Library. They were later also matched against the mass spectra of  
169 the authentic compounds used to prepare the calibration standards. The 10 target compounds  
170 were then quantified with the “Extraction Ion” procedure from the full scan chromatograms  
171 using the  $m/z$ -ratio (mass-to-charge) for the most abundant ion in each compound (Table 1);  
172  $m/z = 266$  was selected for 1,2,3,4-tetrachloronaphthalene. For the purpose of quantification,  
173 a five-point standard curve for each of the ten organophosphates was prepared, in the range of  
174  $0.1 - 5.0 \text{ ng } \mu\text{L}^{-1}$  with  $2.0 \text{ ng } \mu\text{L}^{-1}$  of 1,2,3,4-tetrachloronaphthalene as the injection standard,  
175 also using the  $m/z$  ratio for the most abundant ions (Table 1). The limits of detection (LOD)  
176 were calculated from the standard deviations of the repeated injections of the analytical  
177 standards plotted against their concentrations (Taylor, 1987). The value of the standard  
178 deviation as the concentration approaches zero ( $S_0$ ) was determined as the intercept of the



179 best-fit straight line of this plot. Limits of detection were then calculated as  $3 \times S_0$ . These  
180 limits of detection are on the high end of those reported in the literature (see studies  
181 summarized in Table 4). The magnitude of the detection limits using GC/MS is partially a  
182 consequence of the operating mode of the mass spectrometer. Selected Ion Monitoring (SIM)  
183 is more sensitive (lower amounts detected) than using extracted ions from the TICs.  
184 Nonetheless, some studies report comparable limits of detection (e.g. Tajima et al. (2014).

185           The organophosphates in the blanks were all below the limits of detection, with the  
186 exception of TIBP ( $0.06 \pm 0.05 \mu\text{g}/\text{filter}$ ). After correcting for the amount of TIBP found in  
187 the blank samples, the values of all the other organophosphates below the LOD were replaced  
188 with a value one-half the LOD. The amounts of the organophosphates in the dust samples  
189 were expressed as their mass fractions in units of  $\mu\text{g}$  of the compound per gram of dust ( $\mu\text{g g}^{-1}$ ).  
190 <sup>1</sup>).

191

### 192 **3. Results and Discussion**

193           Reliable measurements were obtained for dust samples from 497 homes (1 sample  
194 lost, 2 with analytical issues) and from all 151 daycare centers. Not all the targeted  
195 compounds were found in all samples. Only TCEP, TCIPP and TDCIPP were identified in  
196 more than a third of the home samples, while only TCEP, TCIPP, TDCIPP, TBOEP, TPHP  
197 and EHDPP were identified in more than a third of the daycare samples. Descriptive statistics  
198 of the results are presented in Table 2 for both the homes and daycare centers. For each  
199 organophosphate the table lists detection frequency (DF; i.e., the percentage of samples with  
200 values above the LOD), LOD, and the median, 90<sup>th</sup> percentile, and maximum mass fractions.

#### 201 **3.1 The organophosphates in dust from homes and daycare centers**

202 Figure 1 (a - c) presents plots of the natural logarithm of selected organophosphate  
203 mass fractions in homes and daycare centers against the cumulative distribution function, with  
204 the x-axis scaled according to the normal error function. The figures show only the  
205 organophosphates evaluated in this study that had median values above  $\frac{1}{2}$  the LOD. For each  
206 compound, in both homes and daycare centers, the plots are roughly linear, indicating that the  
207 distribution of the concentrations is better described as “log-normal” than “normal”. This is  
208 consistent with expectations (Ott, 1995) and earlier studies of indoor volatile organic  
209 compounds (*e.g.* Shields et al., 1996).

210 Table 3 presents Spearman correlation coefficients for the individual  
211 organophosphates. While there are many statistically significant correlations, there are only a  
212 few compounds that are strongly correlated. These are TCEP/TIBP in homes and  
213 TDCIPP/TCIPP and EHDPP/TPHP in daycare centers. The mass fractions of all  
214 organophosphates except TIBP, TEHP and TMPP were significantly different between homes  
215 and daycare centers ( $p < 0.05$ ; non-parametric two-sample Wilcoxon rank-sum (Mann  
216 Whitney) test, as the data were not normally distributed; STATA software, release 11.2 for  
217 Windows, StataCorp LP, College Station, Texas, USA).

218 TCEP was found in  $\geq 50\%$  of the dust samples from both the children’s homes and  
219 daycare centers. The median mass fraction of TCEP from the daycare centers ( $16 \mu\text{g g}^{-1}$ ) was  
220 more than twice as high as the concentration from homes ( $6.9 \mu\text{g g}^{-1}$ ). The median mass  
221 fractions of TCIPP and TDCIPP were noticeably different for the daycare center dust ( $5.6 \mu\text{g}$   
222  $\text{g}^{-1}$  and  $7.1 \mu\text{g g}^{-1}$ , respectively) and the home dust ( $0.5 \mu\text{g g}^{-1}$  and  $0.6 \mu\text{g g}^{-1}$ , respectively; both  
223  $= \frac{1}{2}$  LOD).

224 These findings indicate the presence of more flame retarded products at the daycare  
225 centers than in the homes. TCEP and TCIPP, which are chlorinated organophosphorus flame

226 retardants, are mostly used in flexible foams such as polyurethane foam (PUF) that can be  
227 found in products such as cushions, upholstered furniture, pillows and mattresses (WHO,  
228 1998). Bergh et al. (2011) also found TCEP and TCIPP to have higher concentrations in  
229 daycare centers compared to homes, with TCEP being the second most common  
230 organophosphate in the daycare centers. In the study by Marklund et al. (2003), TCEP and  
231 TCIPP had relatively low concentrations in the homes as well as the one daycare center they  
232 sampled, but the concentration was still higher in the daycare center compared with the  
233 homes. Concentrations of chlorinated OPEs in dust from homes in general seem to be lower  
234 compared to other public places such as work environments (Bergh et al., 2011). Marklund et  
235 al. (2003) found higher levels of TDCIPP ( $1.8 \mu\text{g g}^{-1}$ ) in a daycare center compared to the  
236 average value for two homes ( $0.75 \mu\text{g g}^{-1}$ ); the number of samples in that study is, however,  
237 very limited. The findings of Bergh et al. (2011) differ from the results of this study: they  
238 detected similar levels in the homes and daycare centers ( $10 \mu\text{g g}^{-1}$  vs.  $9.1 \mu\text{g g}^{-1}$ ). Fromme et  
239 al. (2014) report TCEP and TCIPP from German daycare centers with TCIPP being the  
240 second most abundant organophosphate in their study. In the present study it should be noted  
241 that even though TDCIPP was detected in a smaller percentage of samples from homes (DF =  
242 41%) than in samples from daycare centers (DF = 67%), when it was detected in homes the  
243 mass fractions tended to be high (P90 =  $54 \mu\text{g g}^{-1}$ , max =  $860 \mu\text{g g}^{-1}$ ).

244 It is apparent from Figure 1c that the range of mass fractions is largest for TBOEP in  
245 dust samples from daycare centers, with several extreme values exceeding  $1\ 000 \mu\text{g g}^{-1}$ .  
246 Although the detection frequency was much smaller in homes (28% in homes vs. 68% in  
247 daycares), when it was detected, its mass fraction was often high (P90 =  $44 \mu\text{g g}^{-1}$ , max =  $1$   
248  $300 \mu\text{g g}^{-1}$ ). TBOEP is often used in floor polishes, acting as a leveling agent as well as a  
249 plasticizer. In homes or daycare centers where the mass fraction is high, TBOEP may be a

250 constituent of the floor care product (Weschler, 1980; Marklund et al., 2003; Araki et al.,  
251 2014; Cequier et al., 2014).

252 For small children, dust ingestion is common and, for certain SVOCs, can be a  
253 substantial fraction of a child's total intake. Assuming a 15 kg child ingesting 60 mg of dust a  
254 day (US EPA, 2009) in either indoor environment (home or daycare), daily intakes of the  
255 median mass fractions of organophosphates would be several orders of magnitude below the  
256 reference doses (RfD) presented in Van den Eede et al. (2011, and references therein). The  
257 mass fractions in dust required to exceed the RfD under such a hypothetical exposure are  
258 presented for each organophosphate in Table S1 of the Supplementary Material. The fractions  
259 of dust samples from homes with organophosphate mass fractions exceeding these limits were  
260 0.6% for TDCIPP and 0.8% for TBOEP; in the case of daycare centers they were 4.0% for  
261 TCEP and 13% for TBOEP.

262 The organophosphates identified in the dust from bedrooms and daycare facilities are  
263 also anticipated to be present in the gas phase (Weschler and Nazaroff, 2010), associated with  
264 airborne particles (Weschler et al., 2008), and present on indoor surfaces. Enriched surface  
265 concentrations are specifically anticipated in the case of materials that contain  
266 organophosphates as flame retardants or plasticizers or are treated with polishes that contain  
267 such compounds. Hence, in addition to dust ingestion, intakes also occur via inhalation and  
268 dermal absorption. The latter can occur following contact with organophosphates on surfaces  
269 or, for certain compounds, directly from the gas phase (Weschler and Nazaroff, 2012; 2014).  
270 Based on estimated transdermal permeability coefficients (final column of Table 1), dermal  
271 absorption from the gas phase may only be meaningful ( $k_{p-g} > 0.2 \text{ m h}^{-1}$ ) for TBOEP,  
272 TDCIPP, TPHP and TMPP. However, the gas phase concentrations of these low-vapor  
273 pressure compounds tend to be small, limiting the magnitude of their direct uptake from air.  
274 The overarching point is that, when inhalation intake and dermal absorption are also

275 considered, the percentage of daily intakes exceeding the RfD is anticipated to be larger than  
276 those presented in the previous paragraph.

277

### 278 **3.2 Comparison with other studies**

279 To our knowledge, in terms of the number of samples (497 homes and 151 daycare  
280 centers) in combination with the number of the analyzed organophosphates (10 compounds),  
281 this is the largest study of its kind to date. A larger number of samples were collected in a few  
282 studies, but they targeted fewer organophosphates (Becker et al., 2002; Ingerowski et al.,  
283 2001).

284 A comparison of median mass fractions of organophosphates from this study with  
285 mass fractions previously reported in the literature is presented in Table 4. Compound by  
286 compound comparisons of our results with those reported in the literature are not appropriate,  
287 since different studies target different compounds. Hence, the following discussion is based  
288 on “when available” values from the referenced literature. Additionally, when comparing the  
289 present results with a number of earlier studies from around the world, it should be borne in  
290 mind that those studies may have relied on different sampling and analytical methods. For the  
291 purpose of direct comparison, values reported in the literature as below the limit of detection  
292 or quantification were replaced with LOD/LOQ values.

293 In the case of the tributyl phosphate isomers, TNBP was identified in most studies,  
294 while TIBP was identified in a few studies. Median TNBP or TIBP values exceeded  $1 \mu\text{g g}^{-1}$   
295 in samples from Germany (Nagorka and Ulrich, 2003), Belgium (van den Eede et al., 2011),  
296 Sweden (Bergh et al., 2011; Luongo and Östman, 2015) and Japan (Kanazawa et al., 2010;  
297 Araki et al., 2014), while the median values for the homes and daycare centers in the present  
298 study were low (for both homes and daycares  $0.01$  and  $0.05 \mu\text{g g}^{-1}$  for TIBP and TNBP,

299 respectively). TPHP was also found in most studies. Values for both the Danish homes and  
300 daycare centers were comparable with the Swedish (Bergh et al., 2011) and Norwegian  
301 (Cequier et al., 2014) homes and daycare centers. TPHP values  $> 4 \mu\text{g g}^{-1}$  were found in dust  
302 samples from German, U.S., Japanese, English and Swedish homes (Nagorka and Ulrich,  
303 2003; Stapleton et al., 2009; Araki et al., 2014; Kanazawa et al., 2010; Brommer and Harrad,  
304 2015; Luongo and Östman, 2015) and Swedish workplaces (Bergh et al., 2011). EHDPP,  
305 TEHP and TMPP were reported in approximately half of all the studies. The median values  
306 were low, and some of the median values that are seemingly elevated reflect high LODs.

307 The chlorinated organophosphates were found in more than 2/3 of the studies  
308 summarized in Table 4. In the case of TCEP, the highest mass fractions were found in the  
309 Swedish (Bergh et al., 2011) and Danish (this work) daycare centers. Comparable median  
310 concentrations were measured in homes in Japan (Araki et al., 2014; Kanazawa et al., 2010),  
311 USA (Dodson et al., 2012) and Denmark (this work), as well as in the Swedish workplaces  
312 (Berg et al., 2011). The chlorinated organophosphates are mainly used as flame retardants and  
313 commonly added to polyurethane foam (WHO, 1998). The levels of the chlorinated  
314 organophosphates in the dust samples are expected to mirror the level of fire protection  
315 mandated by law for the furniture and furnishings in the respective countries.

316 In Table 4 the organophosphate whose levels in indoor dust stand out is TBOEP  
317 (tris-butoxyethyl phosphate). It was found in the majority of the tabulated studies. This  
318 compound was already detected in size-selected indoor aerosols in the very early 1980s  
319 (Weschler, 1980), and is common in floor polishes (see above). Median values as high as ~  
320  $1600 \mu\text{g g}^{-1}$  were found in samples from Swedish daycare centers (Bergh et al., 2011) and in  
321 Japanese homes (Kanazawa et al., 2010). Araki et al. (2014) report median mass fractions of  
322 TBOEP of  $\sim 500 \mu\text{g g}^{-1}$  in floor dust; houses with wooden floors had significantly higher  
323 levels of TBOEP in indoor dust, probably due to more frequent floor care.

324 Figure 2 shows the sum of organophosphate mass fractions in dust from various  
325 countries based on data from Table 4. Only entries with three or more individual  
326 organophosphates are included. The highest totals are for Swedish and Japanese homes and  
327 are due to high mass fractions of TBOEP. The sum of organophosphate levels from the  
328 Danish daycare centers was almost five times higher than the corresponding value from the  
329 Danish homes, which was comparable to most sums for other countries. The sums for daycare  
330 centers were also higher in Germany, Sweden, Norway and the UK compared to their  
331 counterparts for the homes. Subtracting TBOEP from the sums leads to a more even  
332 geographic distribution. Very low levels were found in samples from Egypt, Kuwait, New  
333 Zealand, Pakistan, the Philippines and Romania. The median mass fractions of the individual  
334 organophosphates from these countries were generally an order of magnitude lower than from  
335 the other countries. In general, the mass fraction of organophosphate esters in dust displayed  
336 greater country-to-country variation than observed for the mass fraction of phthalate esters in  
337 dust (Langer et al., 2010), reflecting less extensive global use of the organophosphates.

338

#### 339 **4. Summary**

340 The mass fractions of organophosphates in dust were higher in samples from daycare  
341 centres than in samples from homes. The targeted compounds were present at levels below  
342 the limit of detection in the majority of the dust samples. Median mass fractions above the  $\frac{1}{2}$   
343 the limit of detection were measured for TCEP from the home samples and TCEP, TCIPP,  
344 TDCIPP, TBOEP, TPHP and EHDPP from the daycare center samples. Although TBOEP  
345 was not the most frequently detected of the ten targeted organophosphates, its median mass  
346 fraction was the highest of all the organophosphates. The values measured in this study were  
347 in line with values reported for other industrialized countries.

348           The organophosphates show larger geographic variation than phthalates, which are  
349 more or less evenly distributed over the globe (Langer et al., 2010). For the children targeted  
350 in this study, based on mass fractions found in dust from their homes and daycare centers,  
351 intake of organophosphates through dust ingestion was in most instances below current  
352 guidelines. However, inhalation and dermal absorption are also anticipated to be substantial  
353 exposure pathways for organophosphates in indoor environments.

354

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359

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**Table 1.** Names, abbreviations, CAS numbers, molecular weight (MW), the m/z of the most abundant ion and transdermal permeability coefficients  $k_{p-g}$  ( $m h^{-1}$ ) of the organophosphates investigated in this work.

Chemical name	Abbreviation*	CAS #	MW	m/z	$k_{p-g}^{**}$ ( $m h^{-1}$ )
Tris(isobutyl) phosphate	TIBP	126-71-6	266	99	0.0002
Tri-n-butyl phosphate	TNBP	126-73-8	266	99	0.002
Tris(2-chloroethyl) phosphate	TCEP	115-96-8	285	63	0.039
Tris(2-chloroisopropyl) phosphate	TCIPP	13674-84-5	327	125	0.011
Tris(1,3-dichloroisopropyl) phosphate	TDCIPP	13674-87-8	431	75	1.3
Tris(2-butoxyethyl) phosphate	TBOEP	78-51-3	398	57	5.3
Tri-phenyl phosphate	TPHP	115-86-6	326	326	0.68
2-Ethylhexyl-diphenyl phosphate	EHDPP	1241-94-7	362	251	0.046
Tris(2-ethylhexyl) phosphate	TEHP	78-42-2	434	99	0.002
Tris(methylphenyl) phosphate	TMPP	78-32-0	368	368	0.69

\*The compounds are abbreviated according to the nomenclature presented by Bergman et al. (2012).

\*\*Calculated using the procedure outlined in Weschler and Nazaroff (2012).

**Table 2.** Mass fractions ( $\mu g g^{-1}$ ) of the organophosphates found in settled dust from homes (n = 497) and daycare centers (n = 151). Values in each cell are listed as “homes/daycare centers”. Detection frequency (DF) is percentage of samples found in concentrations above the detection limit (LOD). LOD values are the same for both homes and daycare centers. Median mass fractions and P90, respectively, above the LOD are reported in the table.

Compound	DF (%)	LOD	Median	P90	Max.
TIBP	31/30	0.027	*/*	0.95/0.37	37/2.5
TNBP	22/14	0.11	*/*	0.26/0.13	4.0/4.3
TCEP	69/78	0.60	6.9/16	42/230	230/1 800
TCIPP	37/72	1.1	*/5.6	6.1/41	100/350
TDCIPP	41/67	1.2	*/7.1	54/69	860/320
TBOEP	28/68	0.40	*/26	44/420	1 300/11 000
TPHP	21/65	0.94	*/2.0	1.8/16	91/210
EHDPP	29/77	0.14	*/2.1	1.2/28	11/540
TEHP	0.80/1.3	2.5	*/*	*/*	11/3.8
TMPP	1.6/1.6	0.89	*/*	*/*	18/36

\*below LOD

**Table 3.** Spearman correlation coefficients for the individual organophosphates.

Homes	TIBP	TNBP	TCEP	TCIPP	TDCIPP	TBOEP	TPHP	EHDPP	TEHP	TMPP
TIBP	1									
TNBP	0.400*	1								
TCEP	<b>0.572*</b>	0.408*	1							
TCIPP	0.333*	0.375*	0.395*	1						
TDCIPP	0.192*	0.175*	0.376*	0.119*	1					
TBOEP	0.283*	0.145*	0.316*	0.248*	0.154*	1				
TPHP	0.314*	0.214*	0.366*	0.251*	0.098*	0.217*	1			
EHDPP	0.260*	0.242*	0.315*	0.351*	0.084	0.312*	0.422*	1		
TEHP	-0.002	0.105*	0.089*	0.020	0.049	0.046	0.018	0.073	1	
TMPP	0.048	-0.010	0.026	0.032	0.014	0.094*	0.104*	0.106*	-0.018	1

Daycare centers	TIBP	TNBP	TCEP	TCIPP	TDCIPP	TBOEP	TPHP	EHDPP	TEHP	TMPP
TIBP	1									
TNBP	0.491*	1								
TCEP	0.378*	0.253*	1							
TCIPP	0.436*	0.302*	0.478*	1						
TDCIPP	0.406*	0.204*	0.367*	<b>0.593*</b>	1					
TBOEP	0.281*	0.104	0.261*	0.282*	0.233*	1				
TPHP	0.219*	0.190*	0.313*	0.492*	0.407*	0.209*	1			
EHDPP	0.184*	0.193*	0.265*	0.438*	0.264*	0.178*	<b>0.597*</b>	1		
TEHP	0.041	0.079	-0.009	0.020	-0.066	0.027	0.085	0.083	1	
TMPP	0.222*	0.129	0.117	0.175*	0.071	0.039	0.231*	0.108	-0.019	1

\*p < 0.05

**Table 4.** Organophosphate mass fractions ( $\mu\text{g g}^{-1}$ ) in dust samples collected from residences and other indoor spaces as reported in relevant studies. Present results listed for comparison; the values in bold are organophosphates in this study with the median above LOD. All values are medians unless stated otherwise.

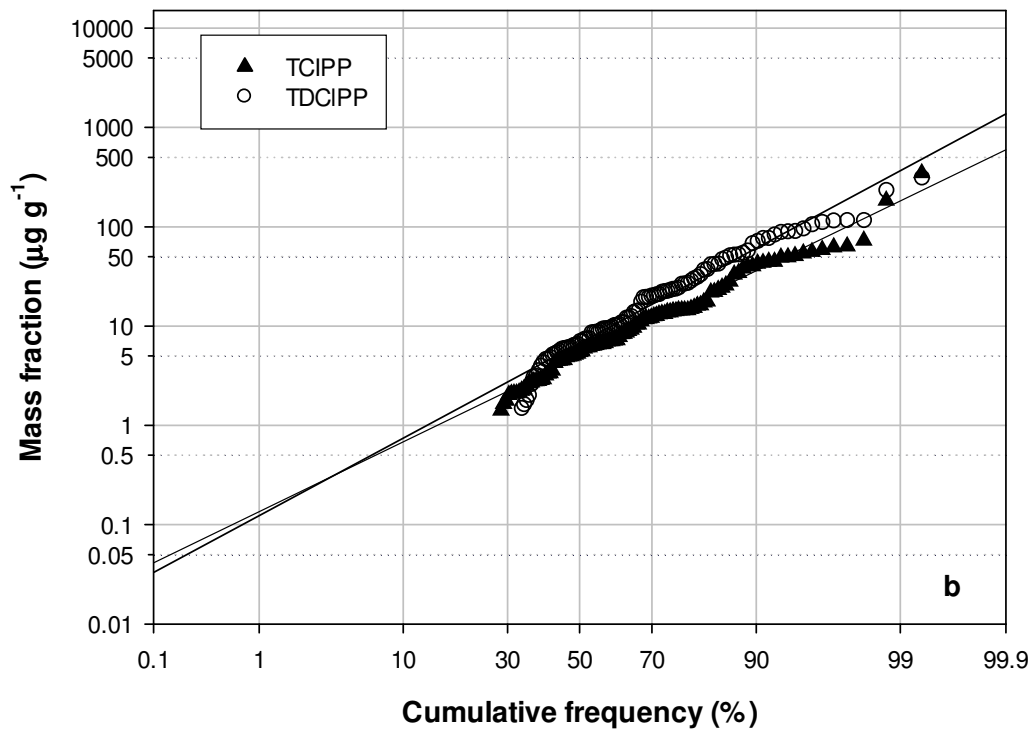
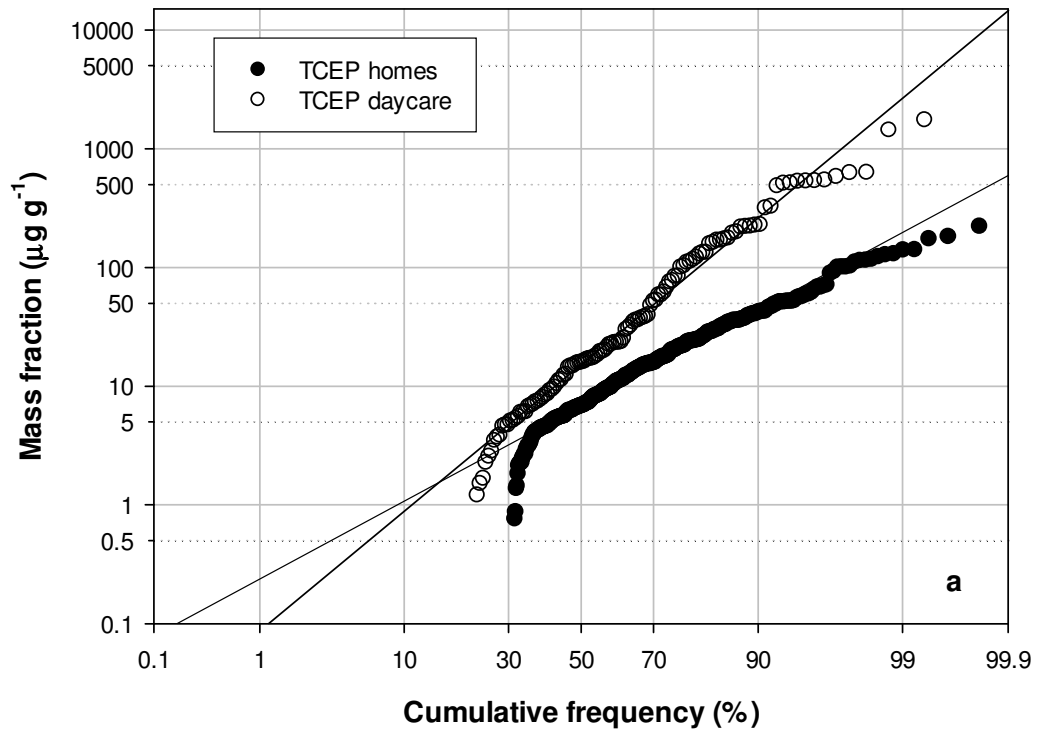
Reference	Country	Location	n	TIBP	TNBP	TCEP	TCIPP	TDCIPP	TBOEP	TPHP	EHDPP	TEHP	TMPP
Sagunski et al. (1997)	Germany	Homes	59	---	---	0.9	---	---	---	---	---	---	---
Ingerowski et al. (2001)	Germany	Homes	983	---	---	0.66	---	---	---	---	---	---	---
Ingerowski et al. (2001)	Germany	Homes	436	---	---	---	0.57	---	---	---	---	---	---
Becker et al. (2002)	Germany	Homes	199	---	---	< 0.1	---	---	5.8	0.3	---	< 0.1	< 0.1
Kersten and Reich (2003)	Germany	Homes	65	---	0.4	1.6	1.4	1.2	5	2.9	---	0.2	2.2
Marklund et al. (2003)	Sweden	Various indoor spaces	15	---	0.35	1.4	2.4	1.1	31	3.1	---	0.16	---
Nagorka and Ulrich (2003)	Germany	Homes	28	---	2.5	2.5	---	1.7	16.1	6.5	0.8	0.8	---
García et al. (2007)	Spain	Homes	8	0.22	0.23	0.51	3.8	---	9.4	1.9	---	---	---
Stapleton et al. (2009)	USA	Homes	50	---	---	---	0.57	1.9	---	7.4	---	---	---
Kanazawa et al. (2010)	Japan	Homes	41	---	1.4	7.5	18.7	4	1 570	5.4	---	4.3	---
Meeker and Stapleton (2010)	USA	Homes	50	---	---	---	---	1.8	---	5.5	---	---	---
Van den Eede et al. (2011)	Belgium	Homes	33	3.0	0.13	0.23	1.4	0.36	2.0	0.50	---	---	0.20
Van den Eede et al. (2011)	Belgium	Shops	15	1.0	0.21	0.59	2.9	0.76	3.6	2.0	---	---	0.02
Bergh et al. (2011)	Sweden	Home	10	1.1	0.3	2.1	1.6	10	4	1.2	0.5	n.d.	---
Bergh et al. (2011)	Sweden	Day-care centers	10	0.7	1.2	30	3.1	9.1	1 600	1.9	0.8	0.1	---
Bergh et al. (2011)	Sweden	Work	10	1.3	0.2	6.7	19	17	87	5.3	1.0	n.d.	---
Ali et al. (2012a)	New Zealand	Homes (Floor dust)	34	---	0.08	0.11	0.35	---	4.02	0.6	---	---	0.1
Ali et al. (2012a)	New Zealand	Homes (Mattresses)	16	---	0.07	0.04	0.25	---	1.55	0.24	---	---	0.2
Ali et al. (2012b)	Pakistan	Homes	31	---	0.014	---	---	---	0.027	0.094	---	---	---
Brommer et al. (2012)*	Germany	Homes	6	---	0.13	0.20	0.74	< 0.080	0.73	0.38	---	---	0.1
Brommer et al. (2012)*	Germany	Offices	10	---	0.22	0.12	3.0	0.15	7.0	2.5	---	---	0.4
Dirtu et al. (2012)	Romania	Homes	47	0.39	0.045	0.10	0.86	0.06	1.5	0.50	---	---	0.50
Dodson et al. (2012)	USA 2006	Homes	16	0.084	0.032	5.1	2.1	2.8	12	---	0.61	<0.2	1
Dodson et al. (2012)	USA 2011	Homes	16	< 0.080	< 0.080	2.7	2.2	2.1	11	---	0.56	<0.2	0.68



Ali et al. (2013)	Kuwait	Homes	15	0.054	0.058	0.71	1.46	0.36	0.86	0.43	0.19	0.065	0.16
Ali et al. (2013)	Pakistan	Homes	15	0.025	<0.020	0.015	<0.020	<0.005	0.017	0.175	0.067	0.02	0
Kim et al. (2013)	Philippines	Homes (Malate)	37	---	0.019	0.034	---	---	---	0.089	0.11	0.14	0
Kim et al. (2013)	Philippines	Homes (Payatas)	20	---	0.020	0.016	---	---	---	0.074	0.034	0.041	0
Araki et al. (2014)	Japan	Homes (Floor)	148	---	1.0	5.8	8.7	2.8	508	4.5	---	2.1	<4.0
Araki et al. (2014)	Japan	Homes (Multi-surface)	120	---	1.2	8.3	25.8	10.8	111	11.5	---	1.5	<4.0
Tajima et al. (2014)	Japan	Homes (Floor)	48	---	< 0.36	< 0.65	0.74	< 0.59	31	0.9	---	< 0.67	<4.0
Tajima et al. (2014)	Japan	Homes (Upper surfaces)	128	---	0.74	1.17	2.23	< 0.59	26.55	3.13	---	< 0.67	<4.0
Abdallah and Covaci (2014)	Egypt	Homes	20	0.023	0.017	0.022	0.028	0.072	0.018	0.067	0.042	---	---
Abdallah and Covaci (2014)	Egypt	Offices	20	0.028	0.023	0.031	0.080	0.049	0.143	0.073	0.048	---	---
Cequier et al. (2014)	Norway	Homes	48	---	0.06	0.41	2.68	0.50	13.4	0.98	0.62	---	0.31
Cequier et al. (2014)	Norway	Classrooms	6	---	0.04	1.21	2.04	1.49	87.2	1.54	2.34	---	0.06
Fan et al., 2014	Canada	Homes (fresh dust)	134		0.25	0.80	1.4	2.7	31.9	1.70	0.54	---	2.60
Fromme et al., 2014	Germany	Day-care centers	63	<0.30	<0.30	0.40	2.68	---	225	0.50	1.10	0.50	---
Shin et al., 2014	USA	Homes	30	---	---	0.50	---	3.6	---	2.0	---	---	---
Brommer & Harrad, 2015	UK	Homes (living rooms)	32	---	<0.03	0.81	21	0.71	---	3.3	1.6	---	0
Brommer & Harrad, 2015	UK	Offices	61	---	<0.03	0.87	33	0.48	---	4.3	5.3	---	<0.01
Brommer & Harrad, 2015	UK	Schools, day-care centers	28	---	0.12	0.86	16	0.51	---	4.1	29	---	<0.01
He et al., 2015	China	Rural homes	25	---	0.14	1.93	1.22	0.15	0.20	1.09	0.31	0.19	---
He et al., 2015	China	Urban homes	11	---	0.08	3.78	0.75	0.13	0.32	0.15	0.36	0.14	---
Hoffman et al., 2015	USA	Homes	49	---	---	---	---	1.39	---	1.02	---	---	---
Luongo and Östman, 2015	Sweden	Homes	62	5.3	5.6	4.0	11	2.0	11	4.3	2.7	---	2.7
<b>This work</b>	<b>Denmark</b>	<b>Homes</b>	<b>497</b>	0.03	0.1	<b>6.9</b>	1.1	1.2	0.4	0.9	0.1	2.5	0.9
<b>This work</b>	<b>Denmark</b>	<b>Day-care centers</b>	<b>151</b>	0.03	0.1	<b>16.2</b>	<b>5.6</b>	<b>7.1</b>	<b>26.2</b>	<b>2.0</b>	<b>2.1</b>	2.5	0.9

n.d. not detected; --- not available/investigated; \* mean values.

Figure 1.



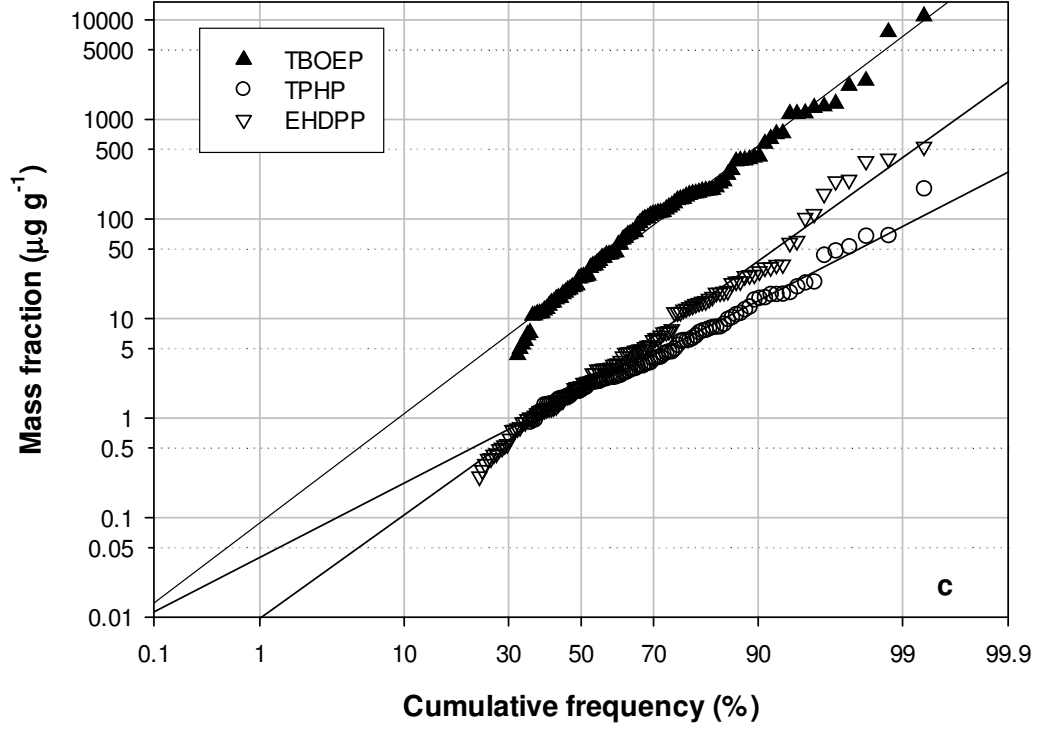
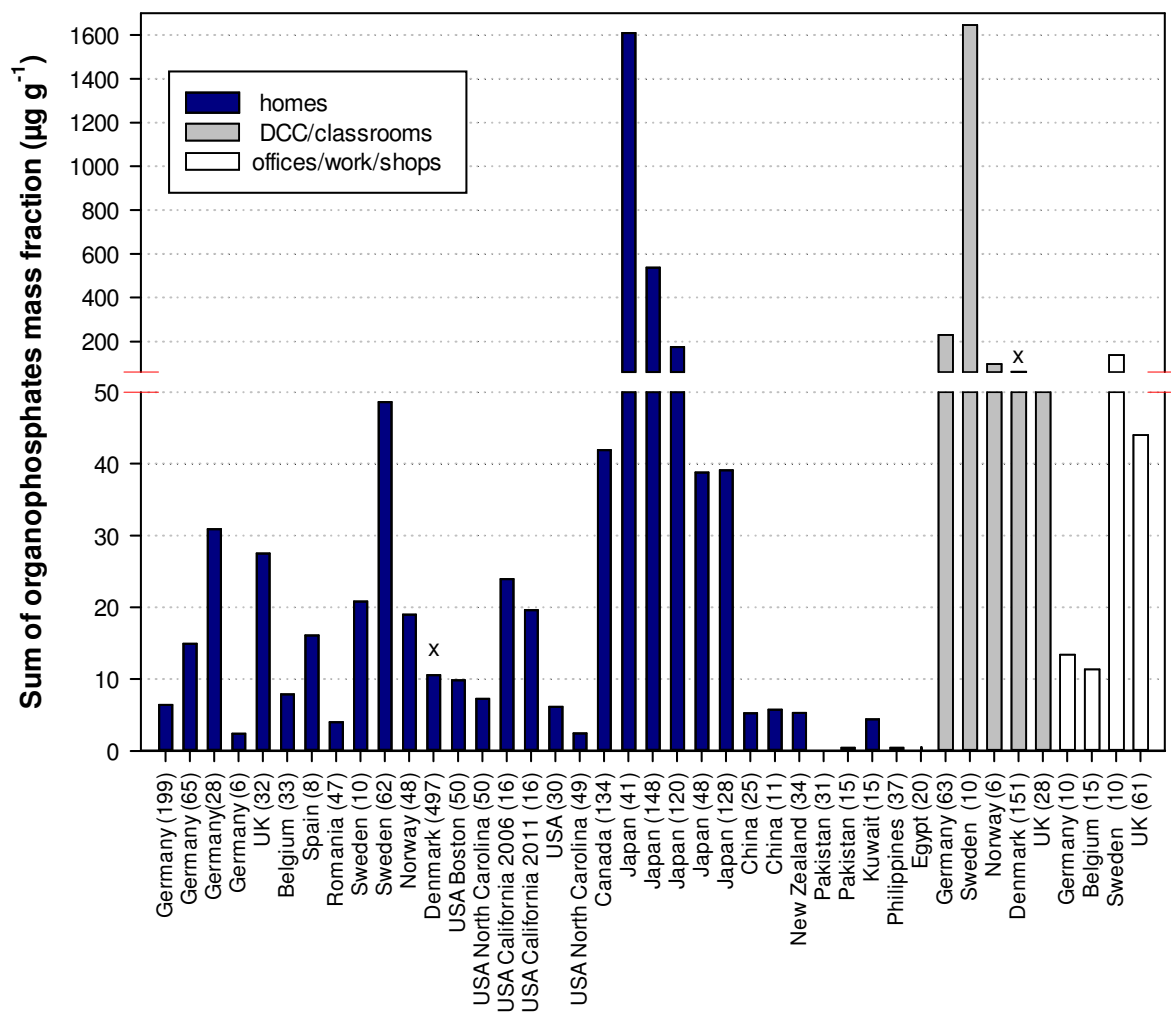


Figure 2.



## Figure Captions

**Figure 1.** Cumulative frequency distributions of measured mass fractions of a) TCEP in dust from homes (filled circle) and daycare centers (open circles); b) TCIPP (filled triangles) and TDCIPP (open circles) in dust from daycare centers; c) TBOEP (filled triangles), TPHP (open circles) and EHDPP (open triangles) in dust from daycare centers.

**Figure 2.** Geographic distribution of the sum of organophosphates reported in indoor dust from homes, daycare centers (DCC), classrooms (school) and various work environments (offices, shops, work). The data are selected from Table S1; entries with two or more individual organophosphates are included. The references can be identified by mapping country and number of samples with corresponding information in Table 4. Results from this work are marked with an “x”.