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Organophosphate esters in dust samples collected from Danish homes and daycare centers

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Highlights

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

Abstract

Organophosphates are used in a wide range of materials and consumer products and are ubiquitous in indoor environments. Certain organophosphates have been associated with various adverse health effects. The present paper reports mass fractions of organophosphates in dust samples collected from 500 bedrooms and 151 daycare centers of children living in Odense, Denmark. The identified compounds include: tris(isobutyl) phosphate (TIBP), tri-n-butyl phosphate (TNBP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), tris(2-butoxyethyl) phosphate (TBOEP), triphenylphosphate (TPHP), 2-ethylhexyl-diphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP) and tris(methylphenyl) phosphate (TMPP). Both the number of organophosphates with median values above the limit of detection and the median values were higher for samples from daycare centers than for samples from homes. Organophosphates with median mass fractions above the limit of detection were: TCEP from homes (6.9 µg g^{-1}), and TCEP (16 µg g^{-1}), TCIPP (5.6 µg g^{-1}), TDCIPP (7.1 µg g^{-1}), TBOEP (26 µg g^{-1}), TPHP (2.0 µg g^{-1}) and EHDPP (2.1 µg g^{-1}) from daycare centers. When present, TBOEP was typically the most abundant of the identified OPs. The sum of the organophosphate dust mass fractions measured in this study was roughly in the mid-range of summed mass fractions reported for dust samples collected in other countries. On a global scale, the geographical distribution of organophosphates in indoor dust is quite variable, with higher concentrations in industrialized countries. This trend differs from that for phthalate esters, whose geographic distribution is more homogeneous. Exposure to organophosphates via dust ingestion is relatively low, although there is considerable uncertainly in this assessment.

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

3

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 annd

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

2. Material and Methods

2.1 Study design

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

2.2 Dust collection

Dust was collected from non-floor surfaces in the children's bedrooms and daycares using ALK dust filters (ALK-Abelló A/S, Hørsholm, Denmark) mounted in a holder 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 ± 1

134   ^{o}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 ($\sim$ 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 (triamylphosphate (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 ± 0.09 and 0.99 ± 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   $0.1 - 5.0$ ng µL^{-1} with 2.0 ng µL^{-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 ± 0.05 µg/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 µg of the compound per gram of dust (µg g^{-}

190 ^{1}).

191

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, 90th percentile, and maximum mass fractions.

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 ½ 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 µg g^{-1}) was

220   more than twice as high as the concentration from homes (6.9 µg g^{-1}). The median mass

221   fractions of TCIPP and TDCIPP were noticeably different for the daycare center dust (5.6 µg

222   g^{-1} and 7.1 µg g^{-1}, respectively) and the home dust (0.5 µg g^{-1}and 0.6 µg g^{-1}, respectively; both

223   = ½ 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 µg g^{-1}) in a daycare center compared to the

236 average value for two homes (0.75 µg 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 µg g^{-1} *vs.* 9.1 µg 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 µg g^{-1}, max = 860 µg 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 µg 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 µg g^{-1}, max = 1

248 300 µg 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 ($k_{p\text{-}g} > 0.2$ 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 $\mu g\ g^{-1}$

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 $\mu g\ g^{-1}$ 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 µg 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 µg 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 ~ 500 µg 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

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 ½

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

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	Abbrevation*	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-etylhexyl) 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 (µg 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	**0.572***	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*	**0.593***	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*	**0.597***	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 (μg 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 (Mattrasses)	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

			N										
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
This work	**Denmark**	**Homes**	**497**	0.03	0.1	**6.9**	1.1	1.2	0.4	0.9	0.1	2.5	0.9
This work	**Denmark**	**Day-care centers**	**151**	0.03	0.1	**16.2**	**5.6**	**7.1**	**26.2**	**2.0**	**2.1**	2.5	0.9

n.d. not detected; --- not available/investigated; * mean values.
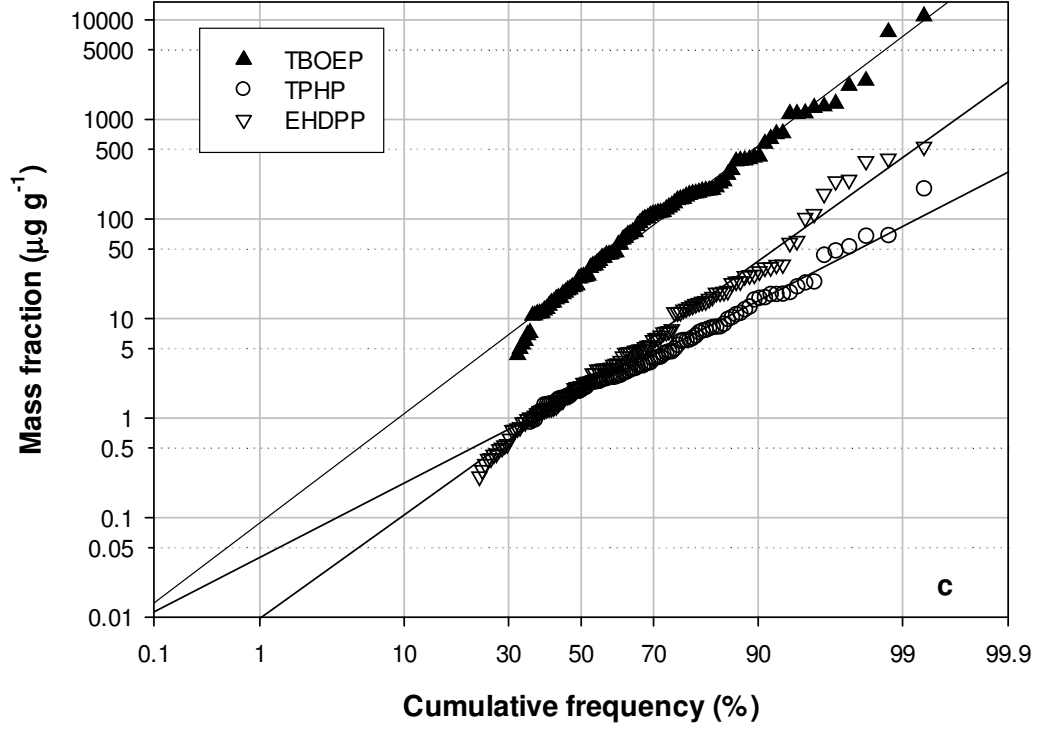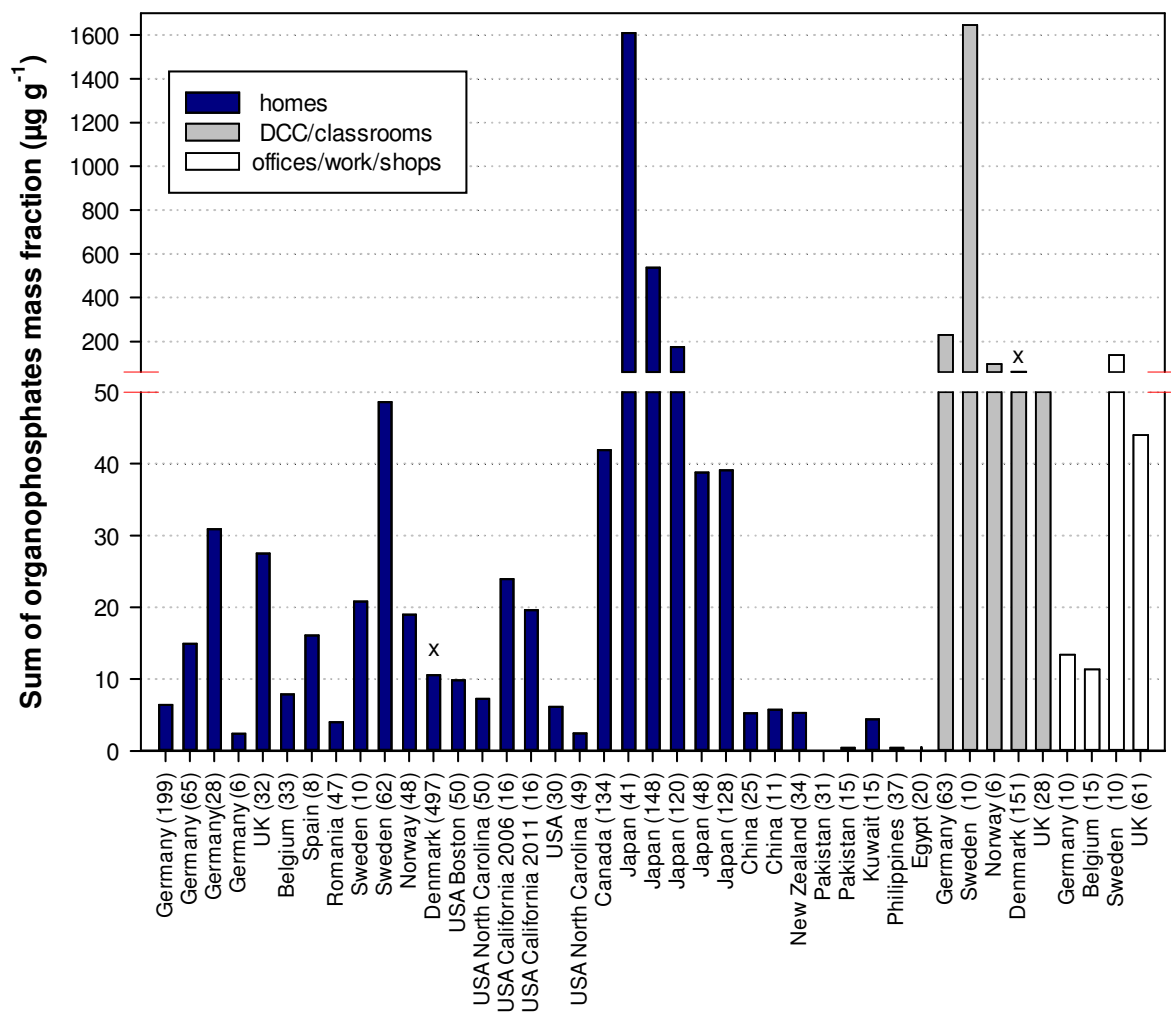
Figure 1.
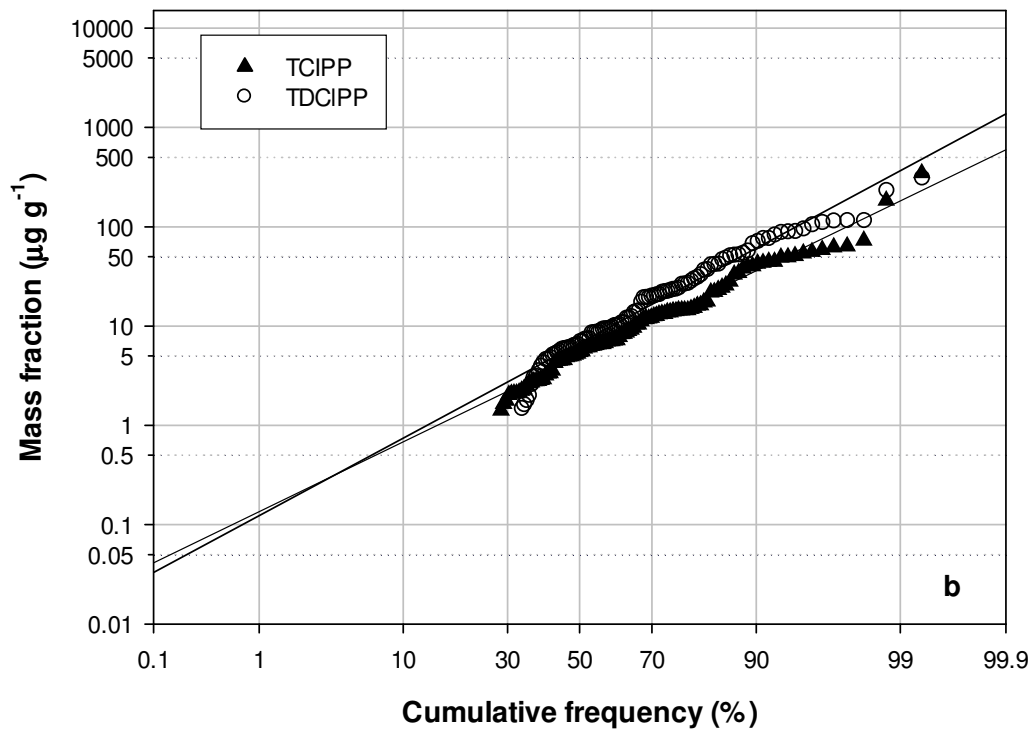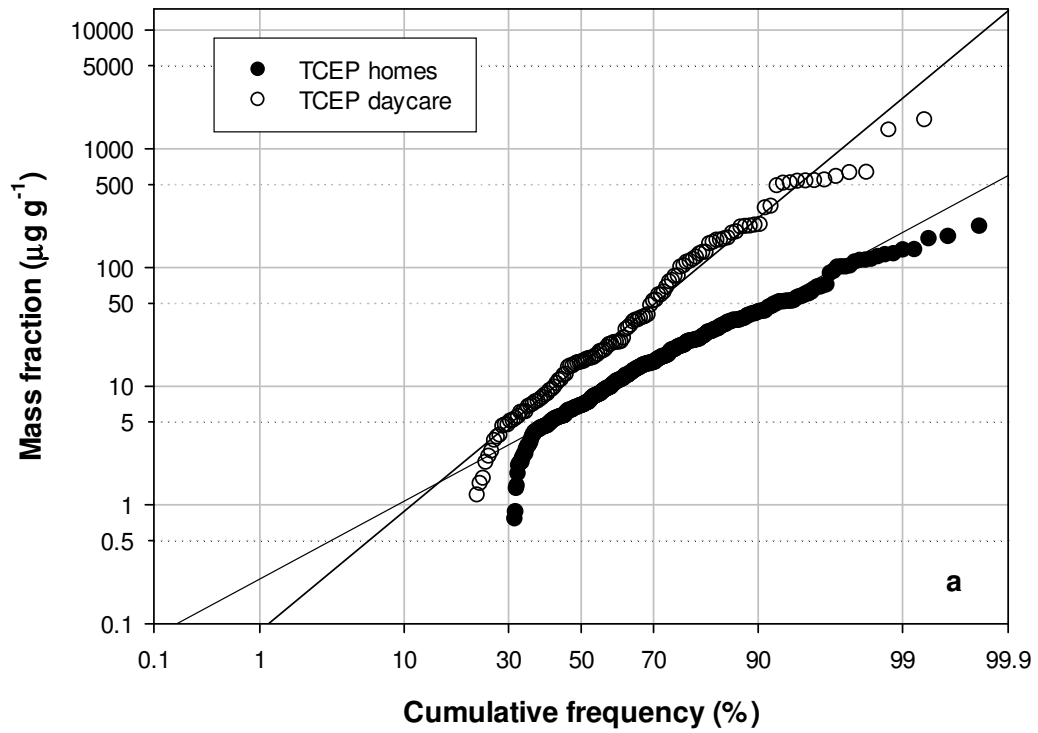
Figure 2.

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".