# Indoor Residence Times of Semivolatile Organic Compounds: Model Estimation and Field Evaluation

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1   **ABSTRACT**

2        Indoor residence times of semivolatile organic compounds (SVOCs) are a major and

3   mostly unavailable input for residential exposure assessment. We calculated residence times for

4   a suite of SVOCs using a fugacity model applied to residential environments.  Residence times

5   depend on both the mass distribution of the compound between the "mobile phase" (air and dust

6   particles settled on the carpet) and the "non-mobile phase" (carpet fibers and pad) and the

7   removal rates resulting from air exchange and cleaning. We developed dust removal rates from

8   cleaning processes using an indoor-particle mass-balance model. Chemical properties determine

9   both the mass distribution and relative importance of the two removal pathways, resulting in

10  different residence times between compounds. We conducted a field study after chlorpyrifos was

11  phased out for indoor use in the U.S. in 2001 to determine the decreases in chlorpyrifos air

12  concentrations over a one year period. A measured average decrease of 18% in chlorpyrifos air

13  concentrations indicates the residence time of chlorpyrifos is expected to be 6.9 years and

14  compares well with model predictions. The estimates from this study provide the opportunity to

15  make more reliable estimates of SVOCs exposure in the indoor environment.

## 1. INTRODUCTION

Semivolatile organic compounds (SVOCs) are ubiquitous in the indoor environment and include plasticizers, brominated flame retardants, pesticides, and perfluorinated compounds [2-5]. As a result, they have been measured in indoor air and dust and it is evident there is human exposure as they have also been measured in biological samples as parent compounds in blood and as metabolites in urine [6, 7]. Some SVOCs have a strong tendency to bind to organic carbon in dust or to indoor surface materials. For these compounds that are primarily partitioned to dust or surface materials, residence times of indoor SVOCs are determined by both the removal rates resulting from air exchange and cleaning and the relative fraction of compounds in the air, dust, and surface reservoirs.

Chemical transformation or degradation by photolysis has little or no effect on SVOCs removal indoors because there is little direct sunlight [8]. In general, indoor SVOCs are resistant to biodegradation and only a few plasticizers are biologically degraded under specific environmental conditions [9, 10]. Thus, the dominant removal pathways for SVOCs from the home are expected to be either air exchange processes or removal of dust through surface cleaning, depending on the chemical properties of the SVOCs.

The air and dust are considered "mobile phases". There are also non-mobile phases such as carpet fibers that serve as reservoirs and there are no direct removal processes for a compound partitioned into surface reservoirs other than replacing surface materials. However, compounds in reservoirs can be redistributed by mass transfer to mobile phases and then removed. For example, when considering removal by cleaning, Hunt et al. found that mechanical cleaning did not completely remove SVOCs on surfaces because a significant portion of the compound was found in surface reservoirs such as carpet fibers or foam materials after a carpet vacuuming event

39  [11]. Therefore, we use the term "non-mobile phase" to represent the portion of the compound

40  partitioned into surface materials as opposed to the portion in dust or air.

41      In addition to determining the fraction in the mobile phase, specifically dust, the

42  residence time of dust needs to be quantified to assess the resulting residence time of SVOCs in

43  the home.  Few studies have characterized residence times of indoor dust. Qian et al. reported 81

44  days of residence time ($\tau$ = loss-rate$^{-1}$ (d)) for particles with a size of 2 $\mu$m in aerodynamic

45  diameter when vacuum cleaning was done once per week [12]. Allott et al. estimated  a mean

46  indoor residence time of 29 days from a house in the UK where vacuum cleaning occurred every

47  day [13]. Layton and Beamer estimated a mean residence time, $\tau$ (d), of 61 days for floor dust,

48  including a cleaning loss rate of 0.0053 d$^{-1}$ and a resuspension rate of 0.011 d$^{-1}$ [14].

49      SVOCs are fairly persistent in the indoor environment, as demonstrated by the presence

50  of many pesticides remaining in the indoor environment for years or decades after the chemical

51  was banned for indoor, or in some cases, outdoor use as well [15-17].  While studies have

52  focused on the air exchange rate of homes and the residence time of dust, these factors have not

53  been combined with the relative mass distribution between the mobile phase and the non-mobile

54  phase to address the residence time of SVOCs partitioned to surface materials.

55      Distinct from previous studies, the objectives of this study are to (1) estimate the

56  residence time of SVOCs in the indoor environment as a function of chemical partitioning and

57  removal rates resulting from air exchange and cleaning, (2) understand the fate and transport of

58  dust for three size ranges from an indoor dust model, (3) estimate a dust removal rate by surface

59  cleaning, and (4) conduct a limited model evaluation. We conducted two case studies. First,

60  based on removal rates and chemical properties, we estimated residence times for five chemicals

61  to compare the persistence and the primary removal pathway. Second, for model evaluation, we

62 used chlorpyrifos air samples from two time points collected in a field experiment. The phase out

63 of the indoor use of chlorpyrifos in the United States in 2001 [18] provides the opportunity for a

64 unique model evaluation exercise because we can compare the average annual decrease with the

65 modeled concentration changes.

66

## 2. METHODS

### 2. 1. Estimation of SVOCs residence times

69 For volatile organic compounds with a high vapor pressure and no indoor sources or

70 contributions from outdoors, the mass in a one-box system decreases based on the following

71 exponential decay equation:

$$M(t) = M_0 \cdot e^{-t/\tau} \tag{1}$$

73 And in the case of zero initial concentration and continuous indoor sources this mass balance

74 takes the form:

$$M(t) = S\tau \cdot (1 - e^{-t/\tau}) \tag{2}$$

76 where $M_0$ is the initial mass in the system (mg) and $\tau$ is the residence time due only to ventilation

77 (day) and $S$ is an emission rate of a continuous indoor source (mg/day). In both cases $\tau$ represents

78 the effective residence time of the system and depends on chemical and residential properties but

79 not on $M$ or $S$. However, in the case of SVOCs with low vapor pressure and high octanol-water

80 partition coefficient ($K_{ow}$) values, there can be significant mass partitioned to surface

81 compartments. Hence, at any time only a portion of the mass, including chemical desorption

82 from surface materials, is available for ventilation removal. In this case, the mass in the system

83 decreases more slowly:

$$M(t) = M_0 \cdot e^{-t/(\tau/\theta)} \tag{3}$$

4

85    where $\theta$ is the fraction of the compound in the mobile phase (in this case air) at equilibrium and

86    $\tau/\theta$ is the new residence time associated with $\theta$. It is apparent that the residence time increases as

87    the fraction in the mobile phase decreases.

88         Likewise, if we consider a chemical distributed between the dust and surface materials,

89    with the dust considered the mobile phase because it can be removed by cleaning, the residence

90    time of the compound will be longer than the residence time of the dust in the home due to the

91    large fraction partitioned to the carpet fibers, the non-mobile phase.

92         A multi-compartment indoor fugacity model was used to determine the partitioning

93    between air, carpet, vinyl, carpet dust, and vinyl dust [19]. We used a boundary layer approach to

94    quantify diffusive transfer rates between compartments including carpet and vinyl flooring. The

95    surface-air partition coefficients ($K_{ja}$) for the surface $j$ were estimated as a function of vapor

96    pressure derived from existing laboratory experiments. Partitioning to dust associated with

97    surfaces was based on the relationship with the octanol-air partition coefficient ($K_{oa}$). SVOCs

98    partition strongly to various indoor surfaces such as particles, flooring, furniture, walls, and

99    ceilings. The impact of sorption to these surfaces was not included in our model due to the

100   limited partitioning information between the surface $j$ and air $a$. We summarized the model in the

101   Supporting Information and presented the mass distribution results in Table 2. As air exchange

102   and carpet cleaning are two primary removal pathways for various SVOCs from our preliminary

103   mass distribution analysis, the residence time in the home depends on both the mass distribution

104   and removal rates of two mobile phases, air and the dust settled on carpet. Then, the residence

105   time based on equilibrium partitioning is described by the following equation:

106
$$\tau_{sys} = \left( \theta_1 \cdot \frac{1}{\tau_{air}} + \theta_2 \cdot \frac{1}{\tau_c} \right)^{-1} = (\theta_1 \cdot a + \theta_2 \cdot k_c)^{-1} \qquad (4)$$

107    where $\tau_{sys}$ is the residence time of the system, $\tau_{air}$ is the residence time due to air exchange (=$1/a$),

108    $\tau_c$ is the residence time due to dust removal from carpet (=$1/k_c$), $\theta_1$ is the fraction of the

109    compound in the mobile phase in the air compartment [= (M $_{air}$+ M $_{air\ particles}$ )/(M $_{air}$ + M $_{air\ particles}$

110    + M $_{carpet}$ + M $_{carpet\ particles}$)], $\theta_2$ is the fraction of the compound in the mobile phase in the carpet

111    compartment [= M $_{carpet\ particles}$ /(M $_{air}$ + M $_{air\ particles}$ + M $_{carpet}$ + M $_{carpet\ particles}$)], $a$ is the air

112    exchange rate, and $k_c$ is the dust removal rate from carpet cleaning. As the fraction of the

113    compound in the mobile phase decreases, its residence time in the system increases. Derivation

114    of $\tau_{sys}$, $\theta_1$, and $\theta_2$ in terms of partition coefficients, which are dependent on chemical properties,

115    was based on an existing indoor fugacity model [19] and described in detail in the Supporting

116    Information.  Depending on the transfer rates between compartments relative to the removal rates,

117    the system may not reach equilibrium. The residence time based on a steady-state solution can

118    also be calculated and the equations can be found in the Supporting Information.

119

120    **2.2. Particle mass balance model**

121        We developed a particle mass balance model to describe the fate and transport of dust

122    indoors. Within this framework, we estimated the dust removal rate from surfaces and the indoor

123    emission rate as we identified these parameters as the least reliable values associated with

124    particle mass flows in the literature (see Supporting Information for parameter estimation and

125    uncertainty of these parameters). The model includes three compartments, air, carpet, and vinyl

126    flooring, as shown in Figure 1. Carpet and vinyl flooring were treated separately because of

127    differences in particle loading, track-in rates of outdoor soil, and removal rates through cleaning.

128    Although particles can build-up on walls, we did not include the walls as a model compartment

129    because the particles that land on the walls are those with an aerodynamic diameter less than 1

130    μm. Hence, only 0.9 % of the particles are estimated to be lost to walls (see Supporting

131    Information for more details on particle loss to walls). Infiltration and track-in of outdoor soil

132    (generally on shoes or by pets) were considered two primary pathways for outdoor particles to

133    enter the house, whereas ventilation and cleaning were the main removal processes of indoor

134    particles. Phase change, coagulation, and formation of particles in the air compartment can be

135    treated as gains and losses from various particle size fractions and may be an important process.

136    However, we did not have sufficient data to capture these processes independently, and rather

137    estimated a single source term from field data. The resulting particle mass balance in the air

138    compartment is

139
$$V\frac{dC_i}{dt} = C_o \cdot V \cdot a \cdot P + (C_c \cdot A_c + C_v \cdot A_v) \cdot R + S - C_i \cdot V \cdot (a + D) \tag{5}$$

140    where $V$ is the volume of house (m$^3$), $C_i$ is the particle concentration in indoor air (mg/m$^3$), $C_o$ is

141    the particle concentration in outdoor air (mg/m$^3$), $a$ is the air exchange rate (1/day), $P$ is the

142    penetration efficiency of outdoor particles reaching the indoors (unitless), $C_c$ is the particle

143    concentration on carpet (mg/m$^2$), $C_v$ is the particle concentration on vinyl flooring (mg/m$^2$), $A_c$ is

144    the area of carpet (m$^2$), $A_v$ is the area of vinyl flooring (m$^2$), $R$ is the resuspension rate from

145    carpet or vinyl (1/day), $S$ is the emission rate from indoor sources such as cooking (mg/day), and

146    $D$ is the deposition rate (1/day).

147         The particle mass balance for the surface compartment $j$ (c for carpet and v for vinyl) is

148
$$A_j\frac{dC_j}{dt} = C_i \cdot f_j \cdot V \cdot D + T_j - C_j \cdot A_j \cdot R - C_j \cdot A_j \cdot k_j \tag{6}$$

149    where $C_j$ is the particle concentration on the surface $j$ (mg/m$^2$), $A_j$ is the area of the surface $j$ (m$^2$),

150    $f_j$ is the fraction of the floor that is the surface $j$ (unitless), $T_j$ is the particle mass brought into the

151 surface $j$ through track-in (mg/day), and $k_j$ is the dust removal rate from the surface $j$ through

152 cleaning (1/day).

153 In reality, concentrations have short-term variability to events such as cooking

154 (increasing indoor air concentrations) or cleaning (reducing surface concentrations) at fixed

155 intervals rather than continuously. However, we assumed that the mass of dust in any

156 compartment would remain constant over the time scales relevant for SVOC residence times.

157 While there is a slight increase in the particle mass in carpet over time, exemplified by the fact

158 that carpets become dirtier over time, we assumed this rate of increase was negligible. When

159 keeping the mass constant over time, we expected for a long-term perspective that the sum of the

160 sources to surfaces due to deposition and track-in would be the same as the sum of the removals

161 from surfaces due to resuspension and cleaning. The fact that the mass of dust in any

162 compartment would remain constant over time allows us to rearrange equations (5) and (6) to

163 estimate any parameter value in each compartment based on published estimates of other

164 parameters in the equation. We used parameter values that were best derived from the literature

165 along with mass balance equations to estimate the parameter with the least reliable value

166 available from the literature for each compartment; specifically, the dust removal rates from

167 surfaces ($k_j$) and the emission rate from indoor sources to air ($S$). Although surface cleaning

168 including carpet vacuuming and sweeping hard floors are not actually expected to occur on a

169 daily basis, we assumed cleaning can be represented as a continuous process.

170 The household properties used in the model are listed in Table S1. Both equations (5) and

171 (6) are applicable to any particle size ranges. We used three particle size ranges including $0 - 2.5$

172 μm, $2.5 - 10$ μm, and $10 - 150$ μm in aerodynamic diameter because of distinct physical

173 properties resulting from particle size and associated health related concerns. First, the deposition

174    rate of particles smaller than 2.5 µm is 4 times smaller than that of particles between 2.5 and 10

175    µm [20]. In addition, only particles smaller than 2.5 µm may penetrate deeply into the lung [21],

176    while any particles smaller than 10 µm are accessible for inhalation exposure [22]. Third, we

177    restricted our analysis up to 150 µm because particles larger than 150 µm do not adhere to skin

178    [23]. When assessing model parameter values, we also consider the relationship between those

179    values, such as estimating that 30 – 50 % of floor dust is due to tracked soil from outdoors [24]

180    and 20 – 43% of particles in indoor air are due to indoor sources [25].  The mean and coefficient

181    of variation (CV) for each model parameter are listed in Table 1 and the rationale for parameter

182    value selection and associated uncertainties are summarized extensively in the Supporting

183    Information. We arbitrarily assigned a value of 1 for the CV of $k_j$, and $S$ as there was insufficient

184    information in the literature to determine the value of the CV and we felt the assigned mean

185    value was reasonable considering the limited available data.

186

187    **2. 3. Case study – application to a suite of SVOCs**

188        We estimated both the equilibrium and steady-state residence times for diazinon,

189    chlorpyrifos, permethrin, polybrominated diphenyl ethers (PBDE)-47, and PBDE-99 using both

190    chemical partitioning between the mobile and non-mobile phases and removal rates resulting

191    from air exchange and cleaning. We also compared the importance of the primary loss

192    mechanisms between the compounds. Chemical properties for these compounds are listed in

193    Table S2 in the Supporting Information. We also performed a first-order uncertainty analysis to

194    compute the relative contribution of input variances to the resulting variance of the equilibrium

195    residence times for each studied chemical. The first-order uncertainty analysis estimates the

196    variance in an output variable from the first-order term of the Taylor series approximation[52].

197    The variance of each input variable was estimated by multiplying the sum of input variances by

198    the square of first-order derivatives of output for each input variable. The mean and CV for each

199    model parameter used in the uncertainty analysis are listed in Table S3 in the Supporting

200    Information. The estimated CVs used in the uncertainty analysis included uncertainty due to the

201    limited available data and variability due to differences between homes.

202

203    **2.4. Case study – chlorpyrifos field study**

204        We used chlorpyrifos air samples from a field study to evaluate our modeled residence

205    time in the indoor environment. We recruited 38 families from 22 counties in Northern

206    California and collected passive air samples at two time periods approximately one year apart in

207    2008 and 2009 ($\mu = 347$ days and $\sigma = 62$ days) [53]. All recruitment and data collection

208    protocols were approved by the institutional review board at the University of California at Davis

209    and informed consent for participation was obtained upon enrollment into the study [53]. Passive

210    indoor air samplers were deployed for approximately 30 days ($\mu = 31$ days and $\sigma = 3.4$ days).

211    We assumed that no chlorpyrifos was applied in the home between the two measurement points,

212    such that the home could be considered a single system with a first-order loss rate in order to

213    provide an observed residence time of chlorpyrifos by computing the change in air

214    concentrations. We also assumed that chlorpyrifos concentrations in air and surface

215    compartments were in equilibrium at the time of air sampling. Based on the $K_{ow}$ and Henry's law

216    constant for chlorpyrifos, the majority (>99 %) of the compound in the air compartment would

217    be associated with the vapor phase, rather than the particle phase (see Supporting Information for

218    more details on sampling and partitioning between air and particles) [54].

219

## 3. RESULTS AND DISCUSSION

### 3.1. Particle mass flows

We determined the mass flow rate to and from each compartment based both on the initial literature-based parameter values and on values obtained from balancing the emission rate of indoor sources and the floor dust removal rates using equations (5) and (6). The particle mass flow rates for each pathway and particle size range are presented in Figure 2. The five particle flow pathways include resuspension/deposition (dependent on the flow direction), track-in, infiltration/ventilation, indoor sources, and cleaning. For the smallest particle size range of 0 – 2.5 μm, the relative amount of particles resuspended from the surface compartments to the air compartment is much smaller than deposition as compared to other size ranges. For the largest size range of 10 – 150 μm, particles moving from outdoors into the air compartment through infiltration are almost negligible due to the low penetration efficiency. The mass of particles moving to the indoor air compartment through infiltration and out through ventilation are different because particle concentrations in indoor air and outdoor air are different and penetration efficiency applies only in the estimation of the particle mass flow by infiltration. We also included the particle sources to the house and the particle removals from the house to compare the contribution of each flow pathway for the house. As particle size increased, cleaning the surface compartment is a dominant removal pathway and track-in becomes a primary flow pathway into the house. The re-adjusted dust removal rates ($k_j$) and emission rates ($S$) for each particle size range are summarized in Table 1 and the re-adjusted dust removal rates for all particle size ranges for carpet and vinyl flooring from the particle mass balances are 0.008 and 0.06 day$^{-1}$, respectively. We carried out an uncertainty analysis on three parameters including $k_c$, $k_v$, and $S$ (see Figure S2 of the Supporting Information). For both $k_c$ and $k_v$, particle

243  concentrations in indoor air and on surfaces as well as the deposition rate are the three most

244  influential parameters on the outcome uncertainties for all particle size ranges. Moreover, track-

245  in and the area of carpet were other parameters contributing to the uncertainties of $k_c$. For $S$, as

246  particle size increased, the contribution of the air exchange rate to the uncertainties became small

247  and that of the deposition rate became the most significant.

248

249  **3.2. Residence times of SVOCs**

250      We computed the equilibrium mass distribution, removal rates through each pathway,

251  percent of compounds removed in one year, and both steady-state and equilibrium overall

252  residence times for diazinon, chlorpyrifos, permethrin, PBDE-47, and PBDE-99 (Table 2). We

253  note that the different chemical properties of these compounds resulted in different mass

254  distributions among the mobile phases (that include air, air particles, and carpet dust) and in the

255  relative contribution of ventilation and carpet cleaning on total removal. For example, even

256  though only a very small fraction of mass (0.01%) was in the air compartment compared to

257  carpet particles (0.1%), the primary removal pathway for diazinon and chlorpyrifos was

258  ventilation, because the ventilation rate (12.7 day$^{-1}$) was about three orders of magnitude larger

259  than the dust removal rate from carpet cleaning (0.008 day$^{-1}$).  As the amount of compound that

260  can be eliminated through ventilation was limited by the amount of compound that can be

261  transferred from carpet to air, the steady-state residence time was significantly longer than the

262  equilibrium residence time.

263      As the mass fraction in air decreases and the mass fraction in carpet dust increases, as

264  was the case for the other three compounds (permethrin, PBDE-47, PBDE-99), the primary

265  removal process was through carpet cleaning.  For these compounds, the percent difference

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266 between the equilibrium and steady-state residence times was lower because the transfer rate

267 between the carpet to the air was less limiting. Diazinon is removed most quickly, followed by

268 permethrin, chlorpyrifos, PBDE-47, and PBDE-99.

269        In Figure 3, we present the concentration profiles of diazinon and PBDE-99 under two

270 sets of removal mechanisms, carpet cleaning with ventilation and carpet cleaning only.  As the

271 gap between solid lines and dotted lines increases, the contribution of surface cleaning on

272 SVOCs removals compared to ventilation decreases. For example, the amount of PBDE-99

273 removed by carpet cleaning (red dotted line) was much larger than that of diazinon by carpet

274 cleaning (black dotted line). However, the total amount of PBDE-99 removed by both carpet

275 cleaning and ventilation (red solid line) was smaller than that of diazinon (black solid line).

276 These results indicate the dependence of the primary removal pathway and the residence time for

277 SVOCs on chemical properties.

278        We carried out an uncertainty analysis on the residence time estimates in order to assess

279 the sensitivity of our results to model inputs. Figure 4 illustrates results from the first-order

280 uncertainty analysis and shows that the relative contribution to overall uncertainty in the

281 residence time is attributable to key model inputs. For both diazinon and chlorpyrifos, a primary

282 removal pathway was ventilation; vapor pressure and the air exchange rate were the two most

283 influential parameters on the outcome. For the other three compounds, a primary removal

284 pathway was carpet cleaning; therefore, the contribution of dust-related parameters including

285 embedded dust ratio, particle loading on carpet, dust removal rate from carpet, Henry's law

286 constant, and $K_{ow}$ became significant to the residence time.

287

288 **3.3. Comparison of field studies to model predictions**

289     We used our field samples to evaluate the change in chlorpyrifos air concentrations

290     collected from 38 homes after adjusting for the time difference between two air samples. This

291     provided a basis for our model evaluation. All but one field-sample pair had levels above the

292     method detection limit (MDL) at both time points. We assigned the half value of MDL (0.016

293     ng/m$^3$) to the non-detected sample. In 25 homes, chlorpyrifos concentrations either decreased

294     (average of 18% ($\sigma$=18%)) or stayed relatively constant (i.e., less than 5% change). We

295     hypothesized that although our field homes should overall have average parameter values of air

296     exchange rate and cleaning rate, variability between homes may result in different values for the

297     decreases in chlorpyrifos air concentrations. In Figure 5, we plot our estimated percent

298     distribution of initial chlorpyrifos concentrations associated with different fractions in the non-

299     mobile phase of the carpet compartment under equilibrium distribution. As the fraction of

300     chlorpyrifos in the non-mobile phase of the carpet compartment increases, the amount removed

301     from the house by ventilation and carpet cleaning decreases following equation (1) with the

302     residence time defined as in equation (4).

303     Based on the average decrease of 18% over the year from the chlorpyrifos air samples in

304     the majority (25/38) of the homes, we anticipated just over 98% of the chlorpyrifos to be

305     associated with the non-mobile phase of carpet.  This value compares to the fugacity-based

306     model estimate of 98.8% of chlorpyrifos in the non-mobile phase including carpet, pad, and

307     deeply embedded dust with only 0.1% in the mobile phase including air and carpet surface dust

308     (Table 2). The modeled fraction of the compound in the non-mobile phase is also consistent with

309     the measured values reported by Fortune et al. [48]. They collected pesticide samples from dust

310     (including surface dust and more deeply embedded dust) and carpet components (including

311     fibers and pad) from six homes in North Carolina to determine the distribution of pesticide

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312  residues between dust, carpet fibers, and pad compartments. They found that approximately 98%

313  of total chlorpyrifos household mass was partitioned into carpet fibers and pad.

314  The steady-state residence time appears to over-predict as compared to the field data.

315  This may indicate that the model assumptions for the boundary layer resistance were not accurate,

316  and that the true boundary layer resistance was much less than that in the model.

317  We note that our analysis was limited by the uncertainties associated with the increase in

318  concentrations over time for 13 of the homes.   We excluded one case where air concentrations

319  increased dramatically from 1.9 to 35.1 $ng/m^3$, due to an unknown chlorpyrifos source.  In the

320  remaining 12 homes chlorpyrifos concentrations increased an average of 97%. We hypothesized

321  that increases may result from changes in experimental conditions, such as air exchange rate or

322  indoor temperature during sampling periods.  If this were the case, other compounds with long

323  residence times would also be impacted.  We compared the air sample concentrations of

324  chlorpyrifos and simultaneously measured PBDE-47 in those 12 homes with increasing

325  chlorpyrifos concentrations to see if PBDE-47 concentrations also increased.  We found that both

326  chlorpyrifos and PBDE-47 air concentrations increased in 6 of the 12 homes, suggesting that air

327  exchange rate or other experimental conditions differed significantly between the two sampling

328  times. In the other 6 homes where chlorpyrifos concentrations increased and PBDE-47 decreased,

329  we believe measurement error may result in misinterpretation of the concentration changes. This

330  is plausible because 5 homes had samples with concentrations under the estimated limit of

331  quantification (ELOQ) for both chlorpyrifos and PBDE-47 and 1 additional home had

332  concentrations under the ELOQ for chlorpyrifos.  The average concentration change and the

333  number of homes with values between the MDL and ELOQ for chlorpyrifos and PBDE-47 are

334  summarized in the Supporting Information, Table S4.

335

### 3.4. Implications/Limitations

This study has several implications in terms of SVOCs exposure in residential and commercial areas. First, dust removal rates derived from the particle mass balance model provide insight on the residence time of SVOCs partitioned to dust, which serves as an important medium of mass transport for SVOCs in homes. Although indoor multimedia models based on fugacity have been considered useful tools to understand the behavior of SVOCs [19, 54], the role of dust removal was not well quantified in previous models. Second, the fraction of SVOCs in the non-mobile phase supports the premise that SVOCs are persistent in the indoor environment. Although chlorpyrifos was phased out for most indoor uses in 2001, the analysis of samples collected in 2008-2009 supports our determination that the equilibrium residence time (i.e., the half-life divided by ln (2)) of chlorpyrifos partitioned onto the surface materials is 6.9 years. This observation is consistent with the assumption that these compounds partition primarily into the non-mobile phase of the surface materials. The steady-state residence time is much greater, indicating that chemicals may transfer more easily between phases within the indoor environment than estimated. Third, we demonstrated that the residence times and the removal rates of each pathway are strongly dependent on chemical properties. This reveals the importance of chemical properties in predicting variations of exposure relative to source levels among a range of SVOCs. As permethrin and PBDE-99 are assumed to have their removals driven by cleaning, field data is needed to evaluate the effectiveness of the model for these types of compounds.

Our approach for estimating a key set of exposure-relevant residential parameters offers the opportunity to reduce important contributions to overall uncertainties in household exposure

16

358    assessments. We note two important findings. First, the assumption that the mass of dust in any

359    compartment will remain constant over a long period of time makes our indoor-particle mass-

360    balance model less sensitive to input parameters that are measured during short-term

361    experimental periods. Our concern is whether these short-term measurements reflect long-term

362    averages appropriate to the model. Second, the use of three particle size ranges reduces the

363    uncertainties in model prediction by avoiding the mischaracterization of particle transport

364    properties, which vary widely by particle size.

365        The results here provide useful insights for future work. Based on our observation that

366    some chlorpyrifos air samples increased over the year even though its indoor use was banned

367    many years ago, future observational measurement studies may want to have better control over

368    housing parameters such as air exchange rate, as the change in concentration may have also

369    resulted from differences in the air exchange rate during the sampling period. Model predictions

370    could be improved if the uncertain model input parameters shown in Figures 4 and S2 were

371    measured in the same experimental conditions over a long period of time with the involvement

372    of human activities. Chemicals with low vapor pressure and high octanol-water partition

373    coefficient values were expected to strongly sorb to other interior surfaces including furniture,

374    electronics, fabrics, walls, and ceilings, but the impact of sorption to these surfaces was not

375    included in our model due to the limited partitioning information between the surface $j$ and air

376    ($K_{ja}$).  Thus, accounting for sorption to these interior surfaces in the model may improve future

377    work.

378

379    **ACKNOWLEDGMENTS**

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384

**Supporting Information Available**

386    The fraction of the SVOCs in the mobile phases and the residence time based on

387    chemical properties are derived in the Supporting Information. The rationale for parameter

388    selection and estimation, chemical properties, particle loss to walls, and results of uncertainty

389    analysis are also described in the Supporting Information. This material is available free of

390    charge via the Internet at http://pubs.acs.org.

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**Table 1. Properties of Dust in Three Size Fraction Ranges**

| Property name (units) | symbol | Particle size ranges (µm) | | | References |
|---|---|---|---|---|---|
| | | 0 - 2.5 Mean (CV) | 2.5 - 10 Mean (CV) | 10 - 150 Mean (CV) | |
| Fraction of organic carbon (--) | $f_{oc}$ | 0.65 (0.30) | 0.28 (0.30) | 0.06 (0.30) | [26] |
| Indoor air particle concentration (mg/m$^3$) | $C_i$ | $1.3 \times 10^{-2}$ (0.58) | $1.2 \times 10^{-2}$ (0.88) | $4.3 \times 10^{-3}$ (0.75) | [27-35] |
| Outdoor air particle concentration (mg/m$^3$) | $C_o$ | $7.3 \times 10^{-3}$ (0.65) | $6.9 \times 10^{-3}$ (0.41) | $1.6 \times 10^{-2}$ (0.59) | [27-31] |
| Particle concentration on carpet (mg/m$^2$) | $C_c$ | 20 (0.30) | 61 (0.30) | 300 (0.30) | [27,36,37 ] |
| Particle concentration on vinyl (mg/m$^2$) | $C_v$ | 3 (0.30) | 6 (0.30) | 49 (0.30) | [27,36,37 ] |
| Deposition loss rate (1/d) | $D$ | 9 (0.47) | 34 (0.36) | 166 (1.00) | [27,29,32,38,39] |
| Resuspension rate (1/d) | $R$ | $4.3 \times 10^{-4}$ (0.50) | $2.7 \times 10^{-3}$ (0.50) | $4.8 \times 10^{-3}$ (1.00) | [27,40] |
| Penetration efficiency (--) | $P$ | 0.82 (0.13) | 0.65 (0.35) | 0.10 (0.50) | [41-46] |
| Track-in to carpet (mg/d) | $T_c$ | 10 (0.70) | 31 (0.70) | 171 (0.70) | [14,27,47] |
| Track-in to vinyl (mg/d) | $T_v$ | 1.0 (0.70) | 3.1 (0.70) | 17.1 (0.70) | [14,27,47] |
| Initial removal rate from carpet cleaning (1/d) | $k_c$ | $5.0 \times 10^{-3}$(1.00) | $5.0 \times 10^{-3}$(1.00) | $5.0 \times 10^{-3}$(1.00) | [14,48] |
| Initial removal rate from vinyl cleaning (1/d) | $k_v$ | $2.5 \times 10^{-2}$(1.00) | $2.5 \times 10^{-2}$(1.00) | $2.5 \times 10^{-2}$(1.00) | [14,48] |
| Initial emission rate to indoor air (mg/d) | $S$ | 75 (1.00) | 20(1.00) | - | [49-51] |
| *Removal rate from carpet cleaning (1/d)* [a] | $k_c$ | *$1.8 \times 10^{-2}$(0.69)* | *$1.8 \times 10^{-2}$(0.91)* | *$5.0 \times 10^{-3}$(1.64)* | |
| *Removal rate from vinyl cleaning (1/d)* [a] | $k_v$ | *$1.1 \times 10^{-1}$(0.79)* | *$1.8 \times 10^{-1}$(0.98)* | *$4.5 \times 10^{-2}$(1.25)* | |
| *Emission rate to indoor air (mg/d)* [a] | $S$ | *104 (1.27)* | *188(1.35)* | *93.4(3.18)* | |

[a] Re-adjusted values from particle mass balances.

**Table 2. Summary of Mass Distributions, Removals, Initial Concentration Changes after 1 Year, and Residence Times for Five SVOCs**

| | Diazinon | Chlorpyrifos | Permethrin | PBDE-47 | PBDE-99 |
|---|---|---|---|---|---|
| Mass distribution (%) | | | | | |
| air | 0.01 | 0.003 | 0.00001 | 0.001 | 0.0001 |
| air particles | 0.00002 | 0.00003 | 0.001 | 0.0002 | 0.0003 |
| carpet + pad + deeply embedded particles | 98.7 | 98.8 | 93.0 | 97.8 | 97.4 |
| carpet particles | 0.1 | 0.2 | 6.6 | 1.3 | 2.0 |
| vinyl flooring | 1.2 | 1.0 | 0.4 | 0.8 | 0.6 |
| vinyl particles | 0.001 | 0.001 | 0.04 | 0.01 | 0.01 |
| Removal (%) | | | | | |
| ventilation | 99.1 | 96.0 | 19.9 | 57.5 | 24.3 |
| carpet cleaning | 0.9 | 3.9 | 76.9 | 40.9 | 72.8 |
| vinyl cleaning | 0.0 | 0.2 | 3.1 | 1.7 | 3.0 |
| Initial concentration change after 1 year (%) | | | | | |
| Carpet cleaning only | 0.4 | 0.6 | 18.7 | 3.9 | 5.8 |
| Ventilation only | 36.5 | 13.0 | 4.2 | 5.2 | 1.9 |
| Ventilation + carpet cleaning | 36.8 | 13.5 | 22.9 | 9.1 | 7.7 |
| Equilibrium Residence time (year) | 2.2 | 6.9 | 3.8 | 10.5 | 12.5 |
| Steady state residence time (year) | 6.7 | 19 | 3.9 | 16.2 | 13.7 |

## FIGURES
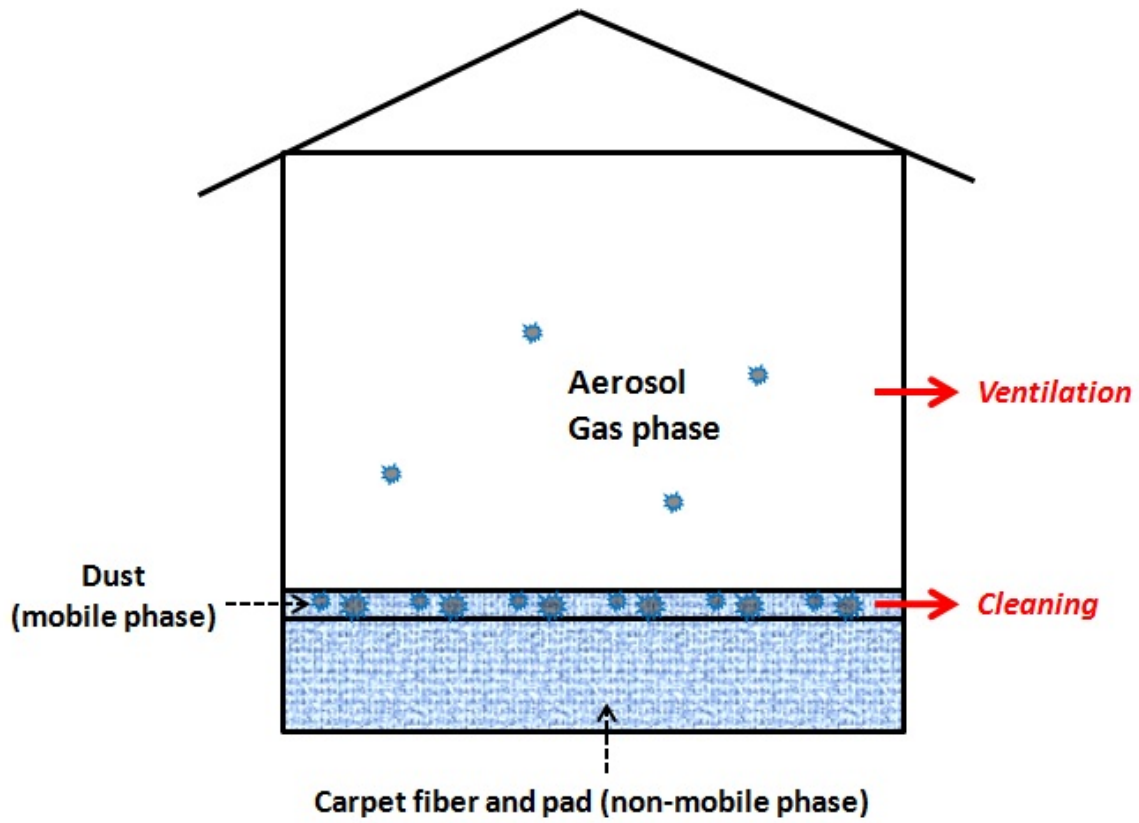


**TOC and Abstract Art**
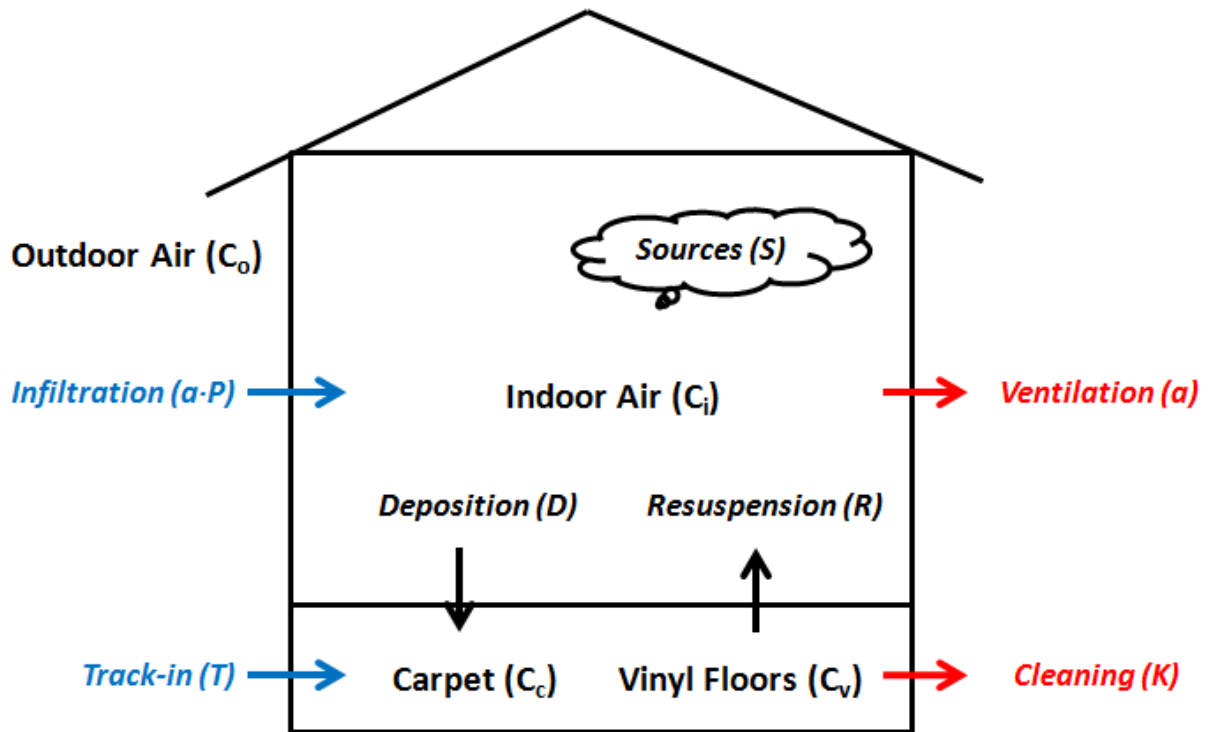
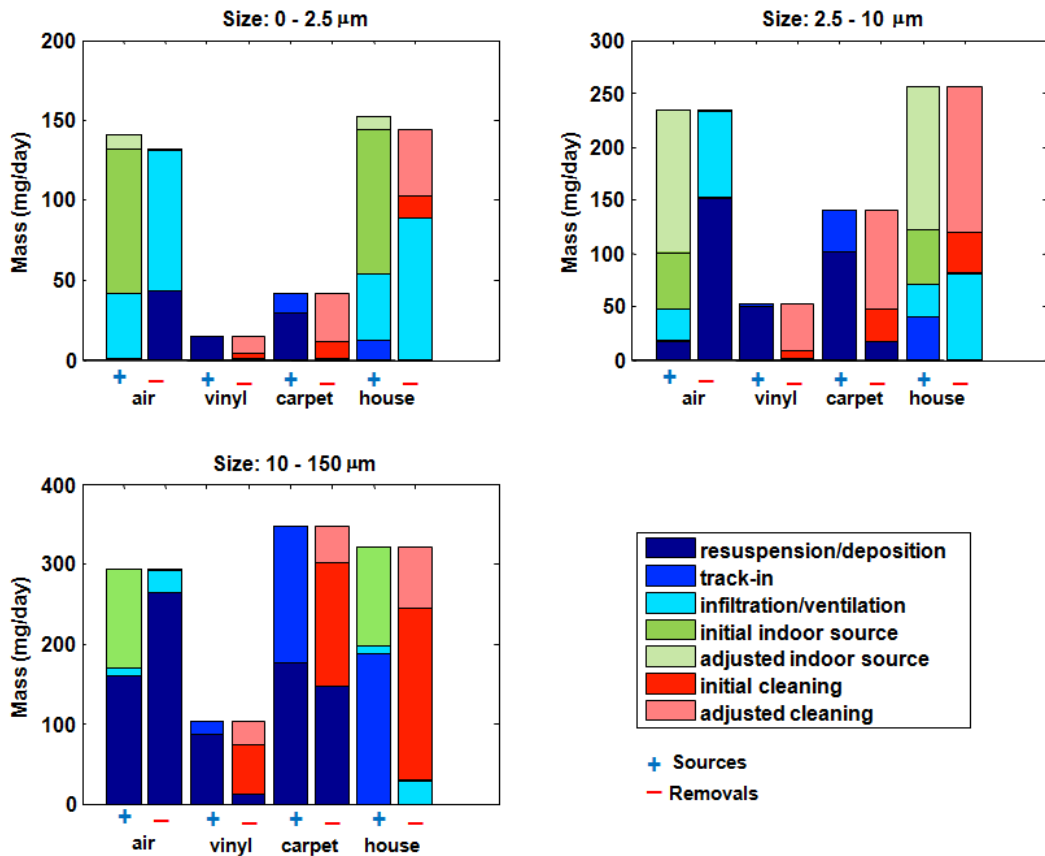**Figure 1.** Model framework for indoor dust model.

**Figure 2.** Summary of the average daily particle mass balance in the three size classes with (+) indicating sources and (-) removals. Indoor sources and cleaning-rate removals have been adjusted up or down relative to measurements of dust to achieve steady-state; these adjustments are indicated by lighter shading.
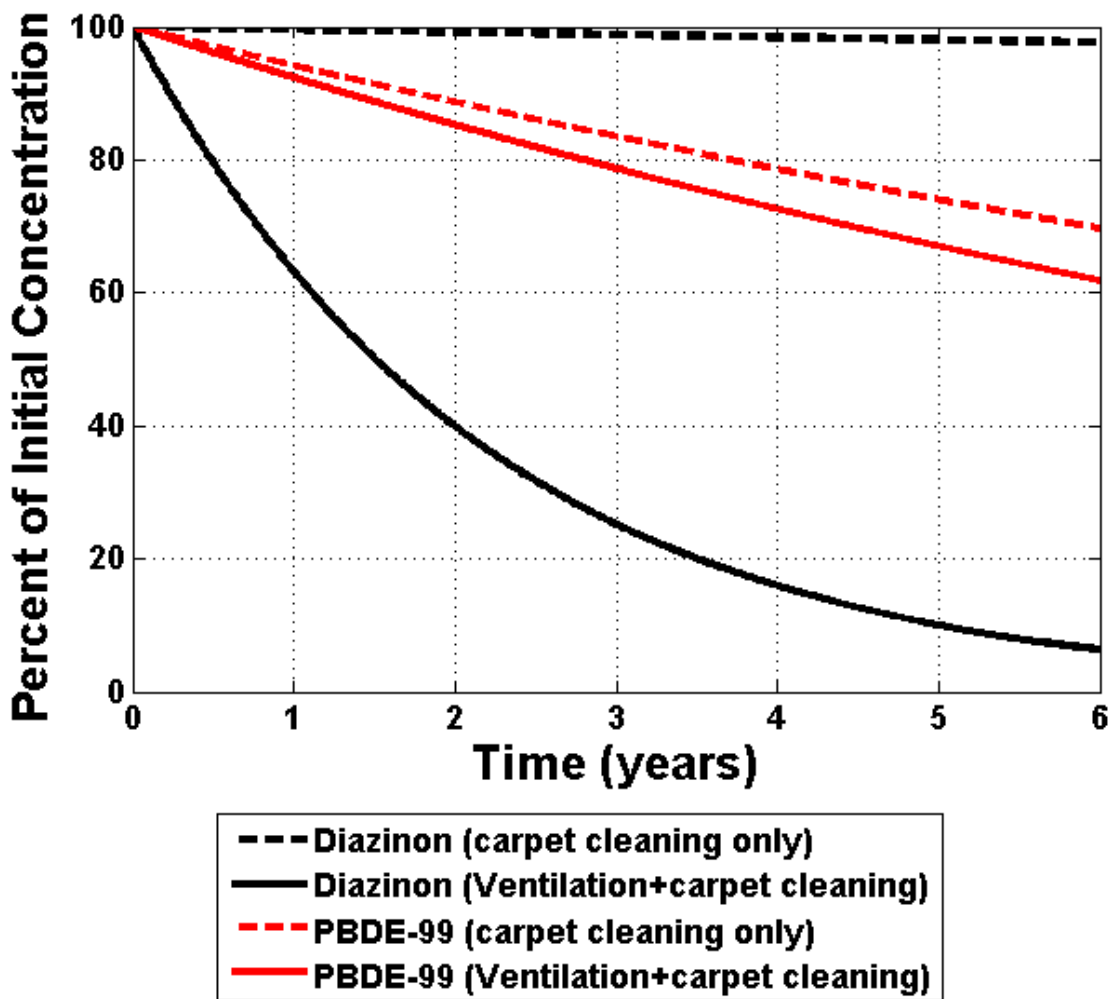
**Figure 3.** Concentration change of diazinon and PBDE-99 indoors as a result of different residence times from ventilation and carpet cleaning. The gaps between solid lines and dotted lines indicate the relative contribution of ventilation on SVOCs removals.
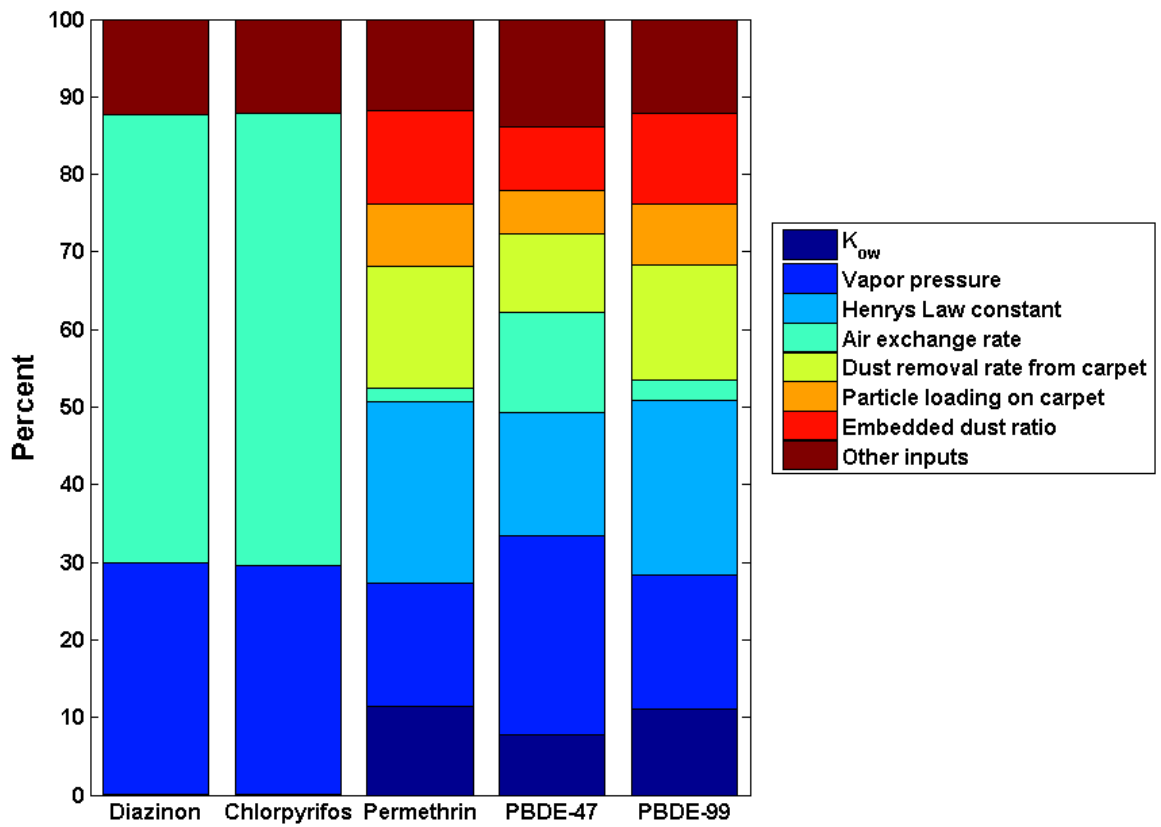
**Figure 4.** Percent contribution of model inputs on the uncertainty of residence times for diazinon, chlorpyrifos, permethrin, PBDE-47, and PBDE-99.
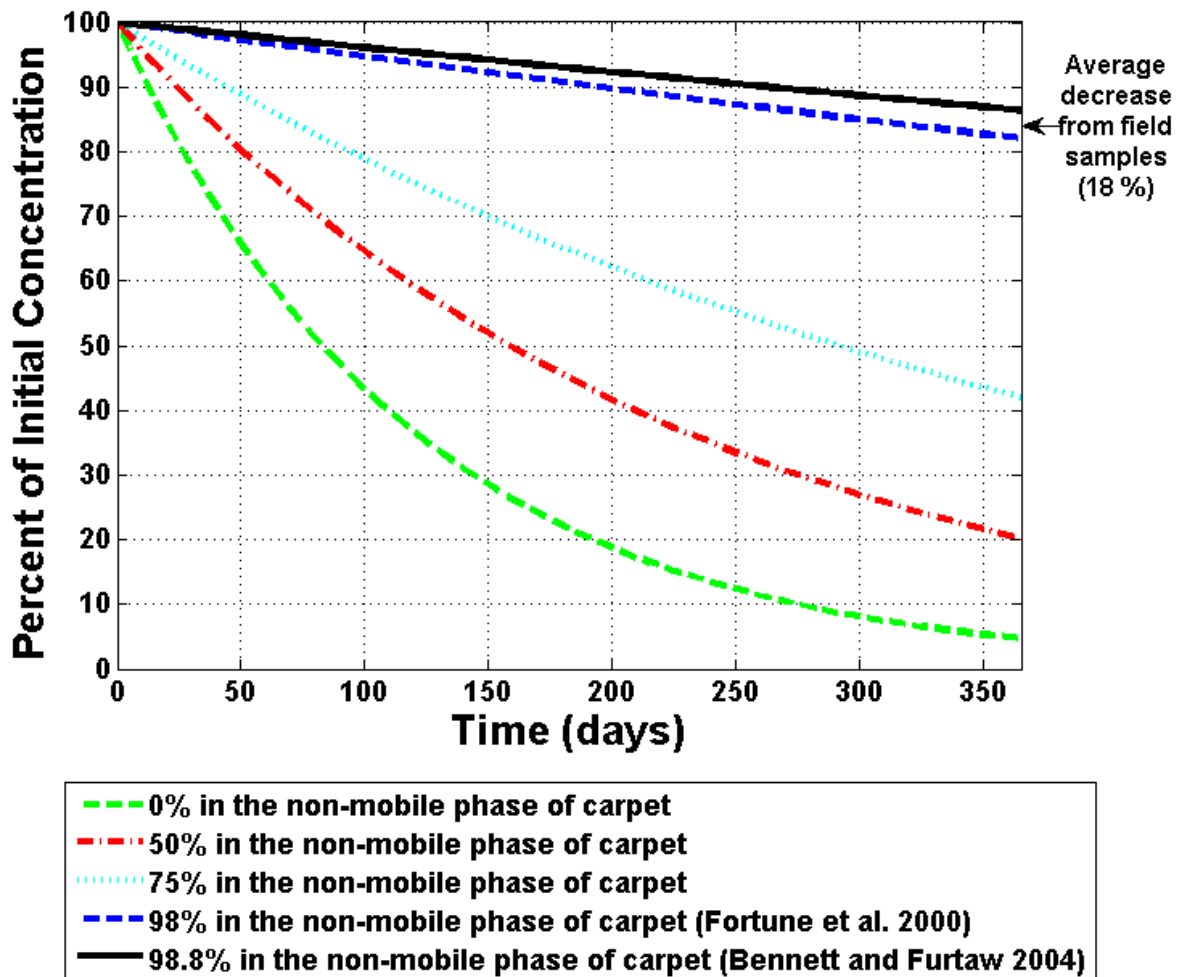
**Figure 5.** Chlorpyrifos concentration changes in the indoor environments by different fractions in the non-mobile phase of carpet.

**Brief**

Residence times are estimated by chemical partitioning between the mobile and non-mobile phases and the removal rates resulting from air exchange and cleaning.