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Role of clothing in both accelerating and impeding dermal absorption of airborne SVOCs

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1 **Title**: Role of clothing in both accelerating and impeding dermal absorption of airborne

2 SVOCs

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25 **Running title:** Clothing enhances dermal uptake of airborne SVOCs

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Abstract

To assess the influence of clothing on dermal uptake of SVOCs, we measured uptake of

selected airborne phthalates for an individual wearing clean clothes or air-exposed clothes

and compared these results with dermal uptake for bare-skinned individuals under

otherwise identical experimental conditions. Using a breathing hood to isolate dermal from

inhalation uptake, we measured urinary metabolites of diethylphthalate (DEP) and di-n-

butylphthalate (DnBP) from an individual exposed to known concentrations of these

compounds for 6 hours in an experimental chamber. The individual wore either clean

(fresh) cotton clothes or cotton clothes that had been exposed to the same chamber air

concentrations for 9 days. For a 6-hour exposure, the net amounts of DEP and DnBP

absorbed when wearing fresh clothes were respectively 0.017 and 0.007 $\mu g/kg/(\mu g/m^3)$;

for exposed clothes the results were 0.178 and 0.261 $\mu g/kg/(\mu g/m^3)$ (values normalized

by air concentration and body mass). When compared against the average results for bare-

skinned participants, clean clothes were protective, while exposed clothes increased

dermal uptake for DEP and DnBP by factors of 3.3 and 6.5 respectively. Even for non-

occupational environments, wearing clothing that has adsorbed/absorbed indoor air

pollutants can increase dermal uptake of SVOCs by substantial amounts relative to bare

skin.

Introduction

Dermal absorption of organic compounds directly from air has been observed for some

volatile and semi-volatile compounds. In reviews by Rehal et al.[1] and Rauma et al.[2] a

handful of volatile organic compounds (VOCs) have been observed to have dermal uptakes

54 that are substantial compared to inhalation intakes. For example, Piotrowski[3,4] found that

55 nitrobenzene and phenol doses via dermal absorption were about 50% those due to

56 absorption by inhalation. Weschler and Nazaroff [5,6] argued that the dermal absorption dose

57 from air could also compare with or exceed the dose due to inhalation for semi-volatile

58 organic compounds (SVOCs) that meet specific criteria under steady-state conditions. In a

59 refinement of that model for non-steady-state conditions, Gong et al.[7] showed that timing of

60 exposure can significantly influence dose due to resistance and accumulation within the

61 dermis. In a test of the hypothesis that the dermal dose of SVOCs from air could be

62 significant, Weschler et al.[8] showed that dermal absorption was approximately equal to

63 inhalation dose for six bare-skinned male participants exposed to diethylphthalate (DEP)

64 and di n-butylphthalate (DnBP) for six hours in a chamber.

65

66 A few studies have evaluated how clothing may influence dermal uptake of organic

67 compounds from air or by transfer from treated fabrics. Piotrowski[3] found that clothing

68 reduced dermal uptake of airborne nitrobenzene by about 20-30% but had no observable

69 effect on phenol absorption.[4] Organics that have been applied to clothing can be also

70 absorbed. Blum et al.[9] observed metabolites of a flame retardant in the urine of children

71 who had worn clothing treated with this flame retardant. Similarly, subjects wearing

72 permethrin-impregnated battle dress uniforms absorbed this insecticide as evidenced by

73 urinary metabolites[10–12].

74

75 We hypothesize that sorption to clothing acts either to reduce or to increase dermal

76 uptake, depending on the extent to which the clothing has equilibrated with room air

4

77   contaminants prior to wearing. For some compounds, the boundary layer of air adjacent to

78   the skin presents greater resistance to transport than does the stratum corneum and viable

79   epidermis.[6] For such compounds uptake is sensitive to the magnitude of the boundary layer

80   permeability[7] and could be altered significantly by sorption to fabrics, especially for

81   compounds with high air-fabric partition coefficients.

82

83   For fabrics that are initially clean, adsorption to fabric fibers should decrease fabric

84   permeability, and lower overall dermal uptake, by reducing diffusional flux through the

85   fabric. With continued exposure, fabric permeability would increase as fabric surfaces

86   equilibrate with SVOCs. Fabrics that are exposed to building air for extended periods (e.g.

87   hanging up in a closet) may absorb a substantial quantity of SVOCs, or even reach

88   equilibrium, prior to wearing. For these clothes, we predict that dermal uptake will be

89   higher than uptake to bare skin.

90

91   Our objective is to test this hypothesis with two compounds that have been predicted, and

92   recently shown, to exhibit low dermal uptake resistance relative to mass-transfer

93   resistance through the layer of air adjacent to body surfaces. In this study, we measure

94   urinary concentrations and total excretion of DEP and DnBP metabolites during and after a

95   participant is exposed for 6 hours to known air concentrations of DEP and DnBP for 2

96   conditions: i) wearing freshly cleaned cotton clothing; ii) wearing previously clean cotton

97   clothing that had been exposed to the phthalates for at least one week. Inhalation uptake is

98   controlled with a breathing hood. Results are compared against results from six individuals

5

99   who wore only shorts but were subjected to nearly identical conditions (results reported in

100   Weschler et al.[8]).

101

Methods

103   The experiments reported here were integrated into the dermal uptake experiments

104   reported by Weschler et al.[8] and nearly all procedures, conditions and analytical methods

105   are therefore identical. The clothed individual was exposed to phthalates in the same

106   chamber at the same time as bare-skinned participants during two of the chamber

107   exposure intervals, specifically Wednesday of the 1st week and Tuesday of the 2nd week.

108

Exposure chamber

110   The 55 m^3 chamber housed two mixing fans, desks and chairs. The air exchange rate was

111   maintained at 0.7 1/h and the temperature was controlled at 30ºC. The relative humidity

112   was not controlled and ranged from 20 to 35% during the experiments. A breathing hood

113   (Amron International, Vista, CA, #8890 Oxygen Treatment Hood) was used so that the

114   participant in the clothing experiments could breathe clean air from outside the chamber,

115   thus allowing for the separation of dermal from inhalation dose. See Figure S.1 for an image

116   of the participant wearing test clothing and the hood while seated in the experimental

117   chamber. Air concentrations of DEP and DnBP were maintained by continuous emission

118   from aluminum panels (total area of 12 m^2) coated with Latex paint. The paint had been

119   formulated with 1% DEP and 10% DnBP (by weight), and was used to deliver these

120   phthalates into chamber air at a relatively constant emission rate.[8,13]

121

6

122   *Clothing and clothing preparation*

123   Clothing was purchased from two different clothing stores in Rolla, Missouri, USA. Each set

124   included a cotton undershirt, a pair of cotton jeans, a long-sleeved cotton tee shirt, cotton

125   underwear and cotton socks. Details such as size, style and manufacturer can be found in

126   Table S.1.

127

128   Two sets of clothing were prepared by washing all pieces at the same time in a standard

129   clothes washer using unscented detergent. They were then dried in an electric dryer on the

130   "medium" setting and each set was packaged separately in two layers of clean aluminum

131   foil until use. During the first 6-hour exposure period, one set was worn directly from its

132   package and is denoted "fresh". Another set of clothing was exposed to chamber air for 9

133   days and denoted as "exposed". This exposure took place in the same chamber, under the

134   same conditions and at the same time as bare-skin dermal uptake experiments occurred;

135   the latter are described in Weschler et al.[8] The clothing was hung inside-out in the path of

136   fans to improve transfer of phthalates from air to the clothing. The air concentration was

137   measured during days 2 and 3 of the 9 day clothing-exposure interval. During these

138   periods, the average concentrations for DEP were 250 and 233 $\mu g/m^3$ and that of DnBP

139   was 123 and 114 $\mu g/m^3$.

140

141   *Preparation of participant*

142   Because there were a limited number of breathing hoods available in the exposure

143   chamber, it was only possible to study one clothed participant. The participant was a 48

144   year old Caucasian male, 192 cm tall weighing 91 kg. The participant followed the same

7

145 restricted diet and restricted use of personal care products protocol described in Weschler

146 et al.[8] These restrictions were intended to reduce background metabolites of DEP and

147 DnBP in the participants' urine. In brief, for 12 hours prior to exposure and 54 hours after

148 exposure began, the participant only ate Swedish dried bread and ate thick-rinded fruit

149 such as oranges, bananas and melons. He drank only tap water or tea made from tap water.

150 The participant showered without soaps or detergents 24 hours prior to the experiment

151 and showered without soaps again 48 hours after the beginning of an exposure. The

152 research protocol was approved by the Capital Region of Denmark Committee for Research

153 Ethics. The participant provided informed consent before participation and consented to

154 publication of his photo.

155

156 *Description of exposure periods*

157 The participant participated in two exposure experiments. The first took place on a

158 Wednesday coincident with the 2nd set of exposure experiments during the first week

159 described in Weschler et al.[8] The participant collected two urine samples on the morning of

160 the experiment. Immediately before entering the chamber the participant collected a urine

161 sample, changed into the "fresh" set of experimental clothes, donned a breathing hood and

162 entered the chamber at 11:00. The participant sat at a desk for most of the 6-hour exposure

163 period and left the chamber once briefly to collect a urine sample. At 17:00, the participant

164 left the chamber and changed into his normal clothing. Following this, the participant

165 maintained the restricted diet and personal product restrictions and collected all urine for

166 48 hours. The second exposure experiment took place on a Tuesday coincident with the 3rd

167 set of exposure experiments during the second week described in Weschler et al.[8] The

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168 procedure was identical to the first experiment except that the participant changed into the

169 "exposed" set of clothes before entering the chamber at 10:00 (leaving at 16:00).

170

171 *Analysis of air and urine*

172 Air concentrations of phthalates were determined by first collecting 6 L samples of air with

173 Tenax-TA filled thermal desorption tubes, and analyzing by thermal desorption followed by

174 gas chromatography using a mass selective detector. Phthalates were quantified using

175 original standards. The concentrations in air and other conditions are tabulated in

176 Weschler et al.[8]

177

178 Urine samples were weighed on the day of collection and stored in a freezer until they were

179 shipped overnight to the Institute for Prevention and Occupational Medicine of the German

180 Social Accident Insurance in Bochum, Germany. Urine samples were analyzed for mono-

181 ethyl phthalate (MEP), a metabolite of DEP, as well as mono-n-butyl phthalate (MnBP) and

182 3OH-mono-n-butyl phthalate (3OH-MnBP), metabolites of DnBP. The concentrations of

183 these metabolites were determined by two-dimensional high performance liquid

184 chromatography coupled to tandem mass spectrometry (LC/LC–MS/MS) using internal

185 isotope-labeled standards after enzymatic deconjugation of the phthalate metabolites from

186 the glucuronidated form following methods published by Koch et al.[14,15] Other details of

187 analytical methods can be found in Weschler et al.[8]

188

189 *Calculations*

9

190   Calculated total uptake of DEP or DnBP during the 6 hour exposure period was based on

191   methods described by Koch et al.[15–17] and outlined in Weschler et al. [8] Metabolite

192   concentrations were converted to mass excreted and then converted to parent molecule

193   uptake using predetermined metabolic conversion factors. In the "fresh clothes"

194   experiment there was very low overall dermal uptake of DEP and DnBP (see Results and

195   Discussion). To better quantify uncertainty in this case, background uptake has been

196   determined in a somewhat different manner than in Weschler et al.[8] For the present

197   participant, little residual uptake from the 6-hour experiment remained, relative to

198   background uptake, for the last four urinations of the fresh clothes experiment (collected

199   from 40.5 to 50.0 hours after exiting the chamber). Therefore, the average dose rate (total

200   dose/elapsed time) from these samples was subtracted from the dose rate calculated for

201   each post-exposure sample for both fresh and exposed clothes experiments. This was

202   multiplied by the sample time interval, and the result from each interval summed, to

203   determine the background-corrected total dose. Dermal uptake was also corrected for DEP

204   and DnBP measured in the breathing hood air (40.7 $\mu g/m^3$ and 5.7 $\mu g/m^3$, respectively)

205   using a breathing rate of 0.7 m^3/h. Dermal uptake was then normalized by the air

206   concentration during the 6 hours in the chamber and the participant's weight. Also

207   reported is the average flux for the 6-h exposure, corrected for background uptake and

208   hood air inhalation. Exposed surface area is taken as 2.06 m^2, estimated by equation 7A-7

209   of the Exposure Factors Handbook[18] and corrected for the area of the head (6.6% of total).

210   To compare the rate of uptake among exposure conditions and between phthalates, we

211   calculated a normalized metabolite excretion rate. First we calculated the slope of net

212   metabolite vs time from initial sample (after exposure begins) to the last sample that

10

213   includes no more than 75% of total net metabolite excreted. This slope divided by the total

214   mass excreted was defined as the normalized metabolite excretion rate. See Table S.2 for

215   additional details regarding the calculation methods.

216

217   **Results and Discussion**

218   Major quantitative results are shown in Table 1. There is a striking difference between

219   results for fresh and exposed clothing experiments. The net metabolites excreted over the

220   54 hour period after initiation of exposure are far higher for exposed clothes than for fresh

221   clothes, indicating that parent compound uptake is much higher for exposed than for fresh

222   clothes When corrected for background uptake rate and inhalation from the breathing

223   hood and normalized by body mass and air concentration, wearing exposed clothes

224   resulted in DEP and DnBP uptakes that were 11 and 36 times greater, respectively, than

225   when wearing fresh clothes. The mass of metabolites excreted over the first 24 hours by

226   the volunteer wearing exposed clothes (3.6 mg MEP; 2.1 mg MnBP) approaches that due to

227   application of a 2% DEP/DnBP cream over most of the skin of subjects as reported by

228   Janjua et al.[19] (MEP range 2.5-85 mg; MnBP range 3.6-18 mg).

229

230   The ratio of the normalized uptake of DEP/DnBP was very different for the two scenarios.

231   For exposed clothing, normalized uptake of DEP is somewhat smaller than for DnBP

232   (DEP/DnBP = 0.7), but for fresh clothing it is much higher (DEP/DnBP = 2.3). This suggests

233   that fresh clothes retard uptake of DnBP more than DEP and/or that exposed clothes

234   enhance uptake of DnBP relative to DEP. Both mechanisms are consistent with a higher

235   cloth/air partition coefficient for DnBP, which has a higher molecular weight than DEP.

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236

237 Normalized dermal uptake for both fresh and exposed clothes differ substantially from

238 uptake to bare skin as described in Weschler et al.[8] For comparison, results for bare skin

239 and clothing experiments are shown in Figure 1. For exposed clothes, normalized uptake of

240 DEP and DnBP are 3.3 and 6.5 times greater, respectively, than the average of bare skin

241 results and 1.9 and 3.9 times higher than the highest uptake observed in the bare skin

242 experiments. For fresh clothes, uptake is 3.2 and 5.6 times lower than the average for bare

243 skin experiments. Based on a t-test, the probability, p, of the results stemming from random

244 variation was $<10^{-4}$ for exposed clothes and < 0.017 for fresh clothes. These findings are

245 consistent with the hypothesis that fresh clothes retard uptake and exposed clothes

246 increase uptake compared with bare skin.

247

248 A comparison of the results, accounting for participant age, is also enlightening. Weschler

249 et al.[8] observed a striking relationship between dermal uptake and age. Shown in Figure 2a

250 and 2b are plots of net amounts of MEP and MnBP excreted, from the time exposure began

251 until the end of urine sampling, for the two clothing experiments (worn by a 48 year-old

252 participant) and bare skin results from the 47 year-old participant reported by Weschler et

253 al.[8] For both phthalates, wearing exposed clothing increased the excretion rate and net

254 excretion. Wearing fresh clothes significantly reduced excretion rate and

255 net excretion.

256

257 In Figure 3, normalized clothing results for uptake of parent compounds are plotted against

258 age along with the normalized results for all six bare-skinned participants. The clothing

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259   results are clearly "off the line"; the exposed clothes result in much higher uptake and fresh

260   clothes much lower uptake than for bare skin. Again, using the 47 year-old participant from

261   Weschler et al.[8] as the best comparator, we observe that exposed clothes resulted in 2.3

262   and 3.4 times more uptake of DEP and DnBP respectively. Fresh clothes resulted in 4.5 and

263   11 times lower uptake.

264

265   The excretion rate of metabolites differs among conditions and between phthalate

266   metabolites. The difference between MnBP and MEP is apparent for exposed clothes in

267   Figure 2, with MEP rising faster than MnBP. The normalized excretion rate for both

268   conditions studied in this research and for the six bare skin participants is shown in Figure

269   4. To make the comparison more clear, the bare skin results for participants wearing

270   hoods are grouped with the clothed results. Qualitatively, clothed results are similar to

271   bare skin results: the normalized excretion rate of MEP is higher than for MnBP. For both

272   MEP and MnBP, the excretion rate is higher for exposed clothes than for fresh clothes. This

273   is consistent with the hypothesis that fresh clothes act as a barrier and delay transport

274   from air to skin. The difference is more pronounced for MnBP than for MEP, possibly due to

275   stronger sorption of DnBP to clothing.

276

277   The results support the hypotheses that 1) fresh clothes are protective, reducing uptake of

278   DEP and DnBP compared with bare-skinned participants and 2) exposed clothes increase

279   uptake. Although only one participant was tested (in two exposure periods), we believe the

280   results are compelling, especially when compared with the narrow range of results for six

281   bare-skinned participants. All results are significantly different from the six bare-skinned

13

282   participant results. When compared by age, the difference is even more apparent (Figure

283   3). However, replication of these results with a larger number of participants will be

284   valuable.

285

286   For both DEP and DnBP, the dose while wearing fresh clothes is small and could have come

287   from a combination of penetration through clothing and absorption by bare skin. The

288   participant in this study was not completely clothed: the hands were bare. We can estimate

289   the absorbed dose by hands assuming that hands are 4.7% of an average adult male's total

290   surface area.[18] We will use participant 2, the bare skinned participant closest in age to the

291   clothed participant, for comparison and will assume that the shorts worn by participant 2

292   covered approximately 5% of his total surface area. Correcting for the reduced total

293   exposed area due to hood (3.9% of total surface area) and shorts, the normalized dermal

294   uptake due to exposed hands for participant 2 would be approximately 0.004 and 0.003

295    $\mu g/kg /(\mu g/m^3)$ for DEP and DnBP respectively. These values can be compared with 0.017

296   and 0.007 $\mu g/kg /(\mu g/m^3)$ for DEP and DnBP for the fresh clothes experiment. Hence, for

297   DnBP, uptake by bare hands could represent a substantial fraction of total uptake from the

298   fresh clothing experiment. It is also interesting to note that the estimated DEP uptake by

299   bare hands accounts for only 25% of the observed uptake; therefore, penetration through

300   clothing may account for much of the uptake.

301

302   It is perhaps intuitive that fresh clothes should impede transfer from air to skin of airborne

303   contaminants. Clothing has been designed to protect workers from pesticide spray and

304   industrial toxic gases. A recent paper reported on the ability of "every-day" clothing[20] to

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305 reduce in vitro dermal penetration of chlorpyrifos from solution. But early human subject

306 studies of VOCs showed little influence of clothing on dermal absorption of nitrobenzene

307 and phenol.[3,4] This could be because sorption to cloth is weak for these low molecular

308 weight compounds. Higher molecular weight, low volatility organic compounds are known

309 to exhibit substantial air-fabric partitioning.[21,22] As volatility decreases, partitioning from

310 air to fabric increases and we would anticipate that retardation of transport across fabric

311 would also increase. Indeed, in this research we observed a lower normalized uptake of

312 DnBP relative to DEP, consistent with the roughly 25 times lower vapor pressure of DnBP.

313

314 Given the complicated geometry of fabric and skin, and the potential for air movement

315 through and under fabric, the data cannot be used to test more detailed models, to generate

316 exposure estimates or to identify compound/fabric combinations that would be most

317 protective or hazardous. Qualitatively, the transport of SVOCs into and out of clothing may

318 be described well by a model of transport of contaminants through porous media.[23] In the

319 context of this model, both advection and diffusion of contaminants through fabric would

320 be retarded by sorption. Key parameters influencing transport and dermal uptake are

321 likely to include the geometry and permeability of the fabric, how closely clothing fits, the

322 air-to-cloth partition coefficient, the dermal permeability of the contaminant, the elapsed

323 time the cloth is exposed to contaminated air after washing and the elapsed time clothing is

324 worn.

325

326 **Geometry and permeability of fabric**. Transport of air and moisture through fabric has

327 been extensively measured and modeled.[24–27]   Hydraulic permeability lumps geometric

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328   complexity of fabric into a parameter that characterizes fabric resistance to advective flux;

329   hydraulic permeability is defined as the volume flux of air due to a specific pressure

330   difference across the fabric in units of $cm^3/(cm^2\ s)$ (usually at a pressure difference equal

331   to 125 Pa). Hydraulic permeability can range over several orders of magnitude: very low

332   ($<0.1\ cm^3/(cm^2\ s)$) for dense or sealed materials and very high for loosely woven thin

333   fabrics ($>300\ cm^3/(cm^2\ s)$). SVOC transport is likely to be more influenced by advection in

334   loosely woven materials with a high hydraulic permeability; for tightly woven materials,

335   diffusive transport is expected to dominate. For intermediate materials, the relative

336   contributions of diffusion and advection will be influenced by pressure gradients, wind and

337   movement.

338

339   **How close clothing fits.** Some sorbed SVOCs may transfer from cloth to skin by contact.

340   However, since most of the surface area available for adsorption in a woven fabric is

341   internal, only a small fraction of the sorbed SVOC is likely a consequence of transfer by

342   direct contact with the outer fabric fibers. Instead, we believe that the more important

343   mechanism is desorption from fiber surfaces and diffusion across a thin air gap to skin. For

344   diffusion across a quiescent air gap, flux is proportional to the reciprocal of the air gap

345   distance. The air gap distance was not measured in this study but we estimate it ranged

346   from <0.1 cm to 0.5 cm. By comparison, a typical bare-skin concentration boundary layer is

347   about 0.2 to 0.4 cm, which can be estimated by dividing the gas diffusivity of the SVOC

348   ($0.056\ cm^2/s$)[28] by an air-to-skin deposition velocity (0.14-0.28 cm/s)[29]. Therefore, the

349   initial flux from fabric to skin could be smaller, or more than 4 times greater, than from

350   bulk air when wearing equilibrated clothing. Notably, this estimate overlaps the observed

16

351   ratio of uptake for exposed clothing to the average for bare skin (3.3 for DEP and 6.5 for

352   DnBP).

353

354   **Air-to-cloth partitioning**. The sorptive capacity of fabric will influence how it reduces or

355   enhances transport from air to skin. There is recognition that adsorption and desorption of

356   indoor-relevant gases on fabrics for tobacco smoke products[30–32] and pesticides[21]can

357   influence exposure. Several studies have shown that dry-cleaning solvents[33–36] and moth

358   repellants[37] can sorb to clothing and subsequently desorb, increasing indoor

359   concentrations. Specialty fabrics have been developed that sorb or react with chemical

360   warfare agents or pesticides to protect the wearer.[38] However, we have only identified two

361   papers[22,39] that report equilibrium partition coefficients for an indoor air contaminant and

362   commonly worn fabrics. In one paper[22] the investigators measured equilibrium partition

363   coefficients for airborne free-base methamphetamine and fabrics including cotton and

364   polyester. The partition coefficients were high enough that mouthing of these fabrics was

365   predicted to be the primary route of exposure for toddlers, similar to the observation by

366   Gurunathan et al.[21] for chlorpyrifos and plush toys.

367

368   **Dermal permeability**. We anticipate that the compounds that are most likely to exhibit

369   enhanced dermal uptake from exposed clothes are those that have high dermal

370   permeability coupled with gas-to-fabric partition coefficients in an intermediate range (not

371   too high, not too low). Uptake of compounds with low dermal permeability is limited by

372   resistance across skin; modest changes in mass-transfer conditions external to skin will

373   likely have little impact on overall uptake. Dermal permeability of compounds typical of

17

374 indoor air have been estimated by Weschler and Nazaroff.[6] They identified more than 30

375 common indoor pollutants that are predicted to have high dermal uptake relative to

376 inhalation uptake. If a compound has too high a gas-to-fabric partition coefficient, this will

377 retard transfer from the fabric to skin. On the other hand, if a compound has too small a

378 gas-to-fabric partition coefficient, then exposed clothes have sorbed very little of the

379 compound and there will be concomitantly little enhancement. It is in the intermediate

380 range of gas-fabric partitioning that sorption to clothes prior to wear will have the greatest

381 enhancement on uptake.

382

383 **Elapsed time clothing sorbs contaminants and time clothing is worn.** It takes time for

384 fabric to adsorb airborne contaminants and approach equilibrium with gas phase

385 concentrations. It also takes time for contaminants to desorb and transfer to skin. As an

386 example, consider a tight-fitting shirt that has been washed, stored in the presence of a

387 contaminant (in air) and then worn. If we assume that the characteristic time for the fabric

388 to equilibrate (τ_e) is independent of the air concentration, then we can qualitatively

389 compare this time to the actual time stored in the presence of a contaminant (t_s) or the time

390 clothing is worn after storage (t_w). *Scenario 1: $t_s < \tau_e$.* For this scenario, the fabric has not

391 equilibrated with the contaminant concentration in the air and may in fact continue to sorb

392 contaminants even while worn. Regardless of the chemical, enhanced flux from cloth to

393 skin will be limited. *Scenario 2: $t_s \geq \tau_e$ and $t_w < \tau_e$.* For this scenario the fabric is well

394 equilibrated with a contaminant before wearing, but the time worn is short relative to the

395 time it takes for the contaminant to reach a new steady-state. During the time worn, flux to

396 skin will be enhanced but the mass adsorbed to fabric will not change substantially. This

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397 scenario could be represented by a shirt worn for a short time that had adsorbed a

398 relatively more volatile, low partition coefficient chemical; it could also be represented by a

399 shirt worn for a longer period of time that had adsorbed a less volatile, higher partition

400 coefficient chemical. *Scenario 3: $t_s \geq \tau_e$ and $t_w > \tau_e$.* Here, the shirt has been worn long enough

401 that a substantial fraction of the contaminant has desorbed. While the initial flux to skin

402 may be high, the time-averaged flux will be lower than for *Scenario 2* (all else being equal).

403

404 Since DnBP is anticipated to have a higher partition coefficient than DEP, we would

405 anticipate that τ_e would be greater for DnBP than DEP. We observe a normalized dermal

406 uptake that is higher for DnBP than DEP from exposed clothes. If the 6-hour period that the

407 participant wears the exposed clothing is similar or longer than τ_e for DEP, then it may fall

408 under *Scenario 3*, while DnBP falls under *Scenario 2*.

409

410 **Conclusions**

411 Clothing acts as a barrier to exposure, but also as a reservoir for recently adsorbed

412 chemicals; the latter can increase dermal uptake. Not only are people subjected to airborne

413 SVOCs while at home, they are also exposed to "home pollutants" outside of their residence

414 when they wear clothing that has been stored in the presence of various SVOCs at home.

415 Given the very large increase in the normalized dermal uptake of DEP and DnBP observed

416 for exposed fabric in this study, we believe clothing-mediated dermal uptake is an under-

417 recognized exposure pathway that could be a substantial or even a dominant exposure

418 route for many chemicals. This is of potential importance in occupational as well as non-

419 occupational settings.

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Acknowledgements

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References

1   Rehal B, Maibach H. Percutaneous absorption of vapors in human skin. *Cutan Ocul Toxicol* 2011; **30**: 87–91.

2   Rauma M, Boman A, Johanson G. Predicting the absorption of chemical vapours. *Adv Drug Deliv Rev* 2013; **65**: 306–314.

3   Piotrowski J. Further investigations on the evaluation of exposure to nitrobenzene. *Br J Ind Med* 1967; **24**: 60–65.

4   Piotrowski J. Evaluation of exposure to phenol: absorption of phenol vapour in the lungs and through the skin and excretion of phenol in urine. *Br J Ind Med* 1971; **28**: 172–178.

5   Weschler CJ, Nazaroff WW. SVOC exposure indoors: Fresh look at dermal pathways. *Indoor Air* 2012; **22**: 356–377.

6   Weschler CJ, Nazaroff WW. Dermal uptake of organic vapors commonly found in indoor air. *Environ Sci Technol* 2014; **48**: 1230–1237.

7   Gong M, Zhang Y, Weschler CJ. Predicting dermal absorption of gas-phase chemicals: Transient model development, evaluation, and application. *Indoor Air* 2014; **24**: 292–306.

8   Weschler CJ, Beko G, Koch HM, Salthammer T, Schripp T, Toftum J *et al.* Transdermal uptake of diethyl- and di(n-butyl) phthalate directly from air: experimental verification. *Environ Health Perspect* 2015; doi:10.1289/ehp.1409151.

9   Blum A, Gold MD, Ames BN, Jones FR, Hett EA, Dougherty RC *et al.* Children absorb tris-BP flame retardant from sleepwear: urine contains the mutagenic metabolite, 2,3-dibromopropanol. *Science* 1978; **201**: 1020–1023.

10 Appel KE, Gundert-Remy U, Fischer H, Faulde M, Mross KG, Letzel S *et al.* Risk assessment of Bundeswehr (German Federal Armed Forces) permethrin-impregnated battle dress uniforms (BDU). *Int J Hyg Environ Health* 2008; **211**: 88–104.

11 Rossbach B, Appel KE, Mross KG, Letzel S. Uptake of permethrin from impregnated clothing. *Toxicol Lett* 2010; **192**: 50–55.

12 Kegel P, Letzel S, Rossbach B. Biomonitoring in wearers of permethrin impregnated battle dress uniforms in Afghanistan and Germany. *Occup Environ Med* 2014; **71**: 112–117.

21

458 　13　Schripp T, Salthammer T, Fauck C, Beko̎ G, Weschler CJ. Latex paint as a delivery
459 　　　　vehicle for diethylphthalate and di-n-butylphthalate: Predictable boundary layer
460 　　　　concentrations and emission rates. *Sci Total Environ* 2014; **494**: 299–305.

461 　14　Koch HM, Gonzalez-Reche LM, Angerer J. On-line clean-up by multidimensional liquid
462 　　　　chromatography-electrospray ionization tandem mass spectrometry for high
463 　　　　throughput quantification of primary and secondary phthalate metabolites in human
464 　　　　urine. *J Chromatogr B Analyt Technol Biomed Life Sci* 2003; **784**: 169–182.

465 　15　Koch HM, Christensen KLY, Harth V, Lorber M, Brüning T. Di-n-butyl phthalate (DnBP)
466 　　　　and diisobutyl phthalate (DiBP) metabolism in a human volunteer after single oral
467 　　　　doses. *Arch Toxicol* 2012; **86**: 1829–1839.

468 　16　Koch HM, Becker K, Wittassek M, Seiwert M, Angerer J, Kolossa-Gehring M. Di-n-
469 　　　　butylphthalate and butylbenzylphthalate - Urinary metabolite levels and estimated
470 　　　　daily intakes: Pilot study for the German Environmental Survey on children. *J Expo Sci
471 　　　　Environ Epidemiol* 2007; **17**: 378–387.

472 　17　Koch HM, Lorber M, Christensen KLY, Pälmke C, Koslitz S, Brüning T. Identifying
473 　　　　sources of phthalate exposure with human biomonitoring: Results of a 48h fasting
474 　　　　study with urine collection and personal activity patterns. *Int J Hyg Environ Health*
475 　　　　2013; **216**: 672–681.

476 　18　USEPA. Exposure Factors Handbook: 2011 Edition. US Environmental Protection
477 　　　　Agency: Washington D.C, 2011.

478 　19　Janjua NR, Frederiksen H, Skakkebæk NE, Wulf HC, Andersson A-M. Urinary excretion
479 　　　　of phthalates and paraben after repeated whole-body topical application in humans. *Int
480 　　　　J Androl* 2008; **31**: 118–129.

481 　20　Moya J, Howard-Reed C, Corsi RL. Volatilization of chemicals from tap water to indoor
482 　　　　air from contaminated water used for showering. *Environ Sci Technol* 1999; **33**: 2321–
483 　　　　2327.

484 　21　Moore CA, Wilkinson SC, Blain PG, Dunn M, Aust GA, Williams FM. Use of a human skin
485 　　　　in vitro model to investigate the influence of 'every-day' clothing and skin surface
486 　　　　decontamination on the percutaneous penetration of organophosphates. *Toxicol Lett*
487 　　　　2014; **229**: 257–264.

488 　22　Gurunathan S, Robson M, Freeman N, Buckley B, Roy A, Meyer R *et al.* Accumulation of
489 　　　　chlorpyrifos on residential surfaces and toys accessible to children. *Environ Health
490 　　　　Perspect* 1998; **106**: 9–16.

491 　23　Morrison GC, Shakila N, Parker K. Accumulation of gas-phase methamphetamine on
492 　　　　clothing , toy fabrics and skin oil. *Indoor Air* 2014; **doi: 10.1111/ina.12159**.

22

493 24 Fetter CW. *Contaminant Hydrogeology*. MacMillan Publishing Company: New York,
494   1993.

495 25 Mavruz S, Ogulata RT. Investigation of air permeability of single jersey fabrics with
496   different relaxation states. *J Text Inst* 2011; **102**: 57–64.

497 26 Ogulata RT, Mavruz S. Investigation of porosity and air permeability values of plain
498   knitted fabrics. *Fibres Text East Eur* 2010; **82**: 71–75.

499 27 Gibson WB, Keller PR, Foltz DJ, Harvey GJ. Diethylene glycol mono butyl ether
500   concentrations in room air from application of cleaner formulations to hard surfaces. *J
501   Expo Anal Environ Epidemiol* 1991; **1**: 369–383.

502 28 Ghaddar N, Ghali K, Harathani J, Jaroudi E. Ventilation rates of micro-climate air
503   annulus of the clothing-skin system under periodic motion. *Int J Heat Mass Transf* 2005;
504   **48**: 3151–3166.

505 29 Lyman W, Reehl W, Rosenblatt D. *Handbook of Chemical Property Estimation Methods*.
506   Ameican Chemical Society, 1990.

507 30 Weschler CJ, Salthammer T, Fromme H. Partitioning of phthalates among the gas phase,
508   airborne particles and settled dust in indoor environments. *Atmos Environ* 2008; **42**:
509   1449–1460.

510 31 Noble RE. Environmental tobacco smoke uptake by clothing fabrics. *Sci Total Environ*
511   2000; **262**: 1–3.

512 32 Chien Y-C, Chang C-P, Liu Z-Z. Volatile organics off-gassed among tobacco-exposed
513   clothing fabrics. *J Hazard Mater* 2011; **193**: 139–148.

514 33 Ueta I, Saito Y, Teraoka K, Miura T, Jinno K. Determination of volatile organic
515   compounds for a systematic evaluation of third-hand smoking. *Anal Sci* 2010; **26**: 569–
516   574.

517 34 Tichenor BA, Sparks LE, Jackson MD, Guo Z, Mason Plunket MACM, Rasor SA. Emissions
518   of perchloroethylene from dry cleaned fabrics. *Atmospheric Environ - Part Gen Top*
519   1990; **24 A**: 1219–1229.

520 35 Chao CYH, Tung TCW, Niu JL, Pang SW, Lee RYM. Indoor perchloroethylene
521   accumulation from dry cleaned clothing on residential premises. *Build Environ* 1998;
522   **34**: 319–328.

523 36 Thomas KW, Pellizzari ED, Perritt RL, Nelson WC. Effect of dry-cleaned clothes on
524   tetrachloroethylene levels in indoor air, personal air, and breath for residents of several
525   New Jersey homes. *J Expo Anal Environ Epidemiol* 1991; **1**: 475–490.

23

526 37 Sherlach KS, Gorka AP, Dantzler A, Roepe PD. Quantification of perchloroethylene
527   residues in dry-cleaned fabrics. *Environ Toxicol Chem* 2011; **30**: 2481–2487.

528 38 Guerrero PA, Corsi RL. Emissions of p-dichlorobenzene and naphthalene from
529   consumer products. *J Air Waste Manag Assoc* 2012; **62**: 1075–1084.

530 39 Schreuder-Gibson H, Truong Q, Walker J, Owens J, Wander J, Jones W. Chemical and
531   Biological Protection and Detection in Fabrics for Protective Clothing. *MRS Bull* 2003;
532   **28**: 574–578.

533 40 Piadé JJ, D'Andrés S, Sanders EB. Sorption phenomena of nicotine and ethenylpyridine
534   vapors on different materials in a test chamber. *Environ Sci Technol* 1999; **33**: 2046–
535   2052.

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5   538   **Table legend**
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7   539   **Table 1**. Net amount of metabolites excreted during the time period from entering the chamber
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9   540   until 54 hours later, as well as parent compound uptake calculated from the metabolite levels;
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12   541   details regarding the calculation of the listed values are presented in Supporting Information.
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544　**Figure legends.**

545　**Figure 1**. Normalized mass of DEP and DnBP absorbed for fresh and exposed clothes

546　experiments. Also shown for comparison are results from the 6 bare-skinned participants

547　(boxplot) reported in Weschler et al.[8] The line within the box represents the median; the

548　bottom and top of the box, the 25th and 75th percentiles; the upper and lower whiskers, the

549　10th and 90th percentiles.

550　**Figure 2**. Net amount of MEP (2a) and MnBP (2b) excreted from beginning of exposure

551　until last urine sample. Results for fresh and exposed clothes are compared against the bare

552　skin results of the closest aged participant in Weschler et al.[8]

553　**Figure 3**. Normalized dermal uptake of DEP and DnBP versus age. Shown are results from

554　this research (clothes) and results for six bare skin participants reported by Weschler et

555　al.[8]

556　**Figure 4**. Normalized metabolite excretion rate for MEP and MnBP. Shown are results from

557　this research (clothes) and results for six bare-skinned participants reported by Weschler

558　et al.[8] The line within the box represents the median; the bottom and top of the box, the

559　25th and 75th percentiles; the upper and lower whiskers, the 10th and 90th percentiles.

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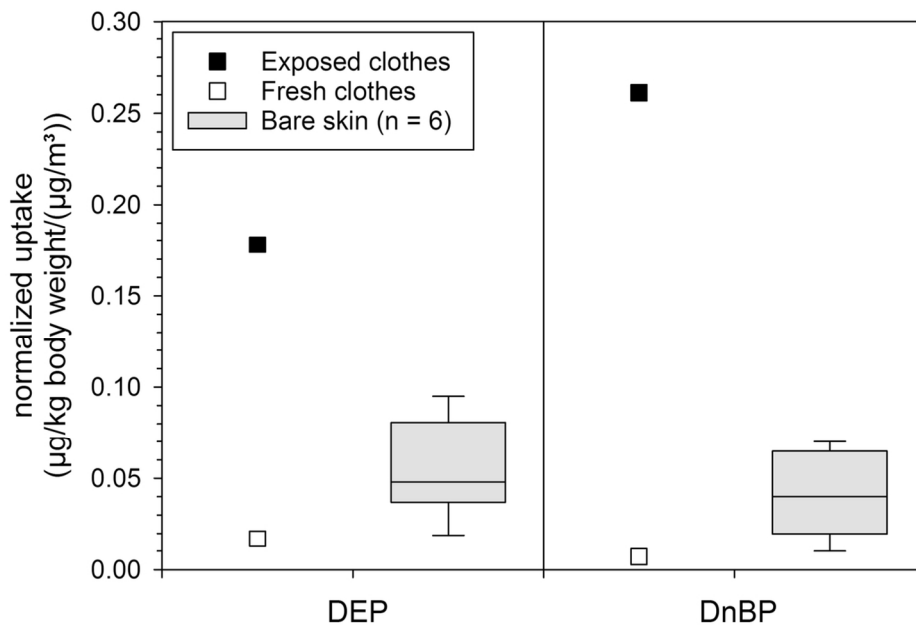Figure 1. Normalized mass of DEP and DnBP absorbed for fresh and exposed clothes experiments. Also shown for comparison are results from the 6 bare-skinned subjects (boxplot) reported in Weschler et al.[8] The line within the box represents the median; the bottom and top of the box, the 25th and 75th percentiles; the upper and lower whiskers, the 10th and 90th percentiles.
114x80mm (300 x 300 DPI)
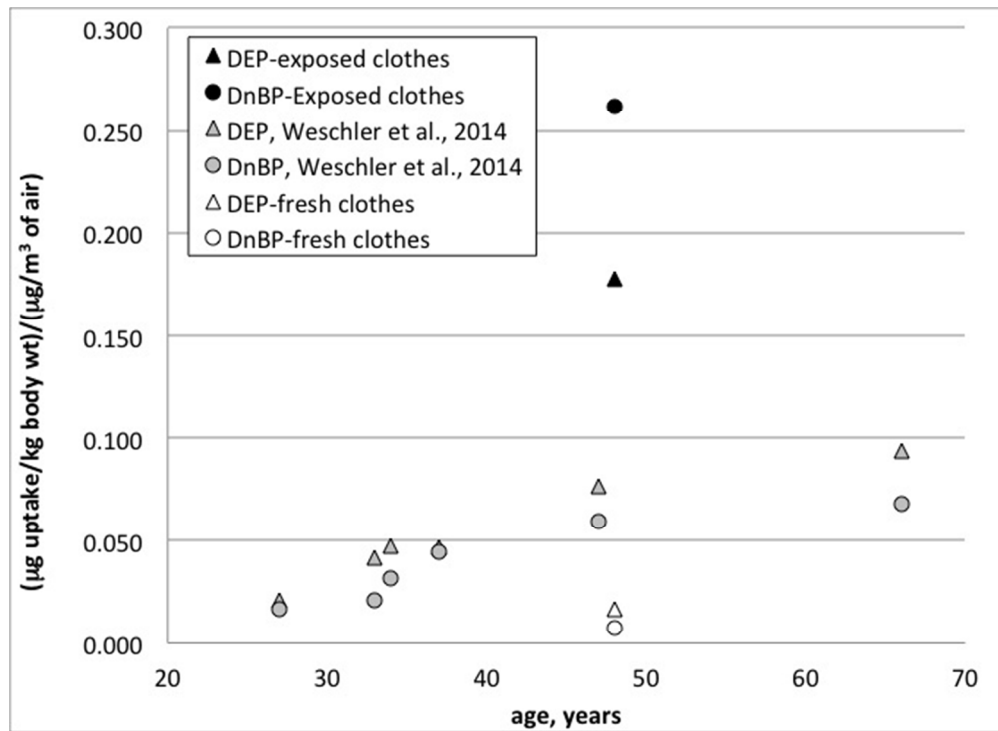
Figure 3. Normalized dermal uptake of DEP and DnBP versus age. Shown are results from this research (clothes) and results for six bare skin subjects reported by Weschler et al.[8]
241x175mm (72 x 72 DPI)

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Figure 2. Net amount of MEP (2a) and MnBP (2b) excreted from beginning of exposure until last urine sample. Results for fresh and exposed clothes are compared against the bare skin results of the closest aged subject in Weschler et al.[8]
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Normalized metabolite excretion rate for MEP and MnBP. Shown are results from this research (clothes) and results for six bare-skinned subjects reported by Weschler et al.[8] The line within the box represents the median; the bottom and top of the box, the 25th and 75th percentiles; the upper and lower whiskers, the 10th and 90th percentiles.
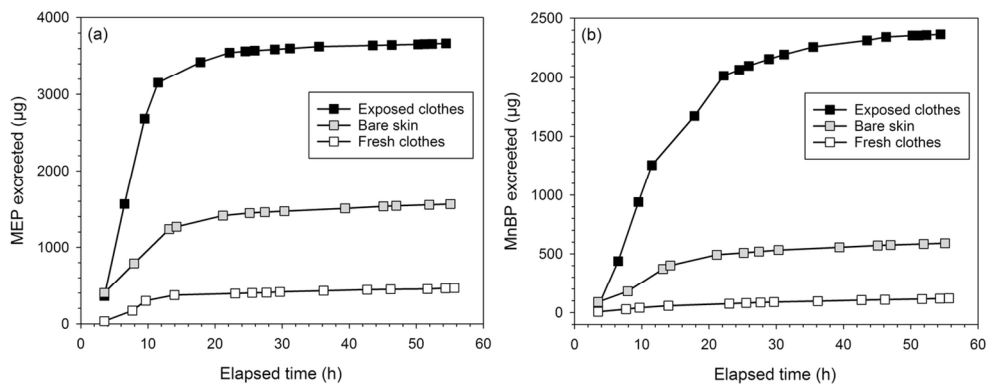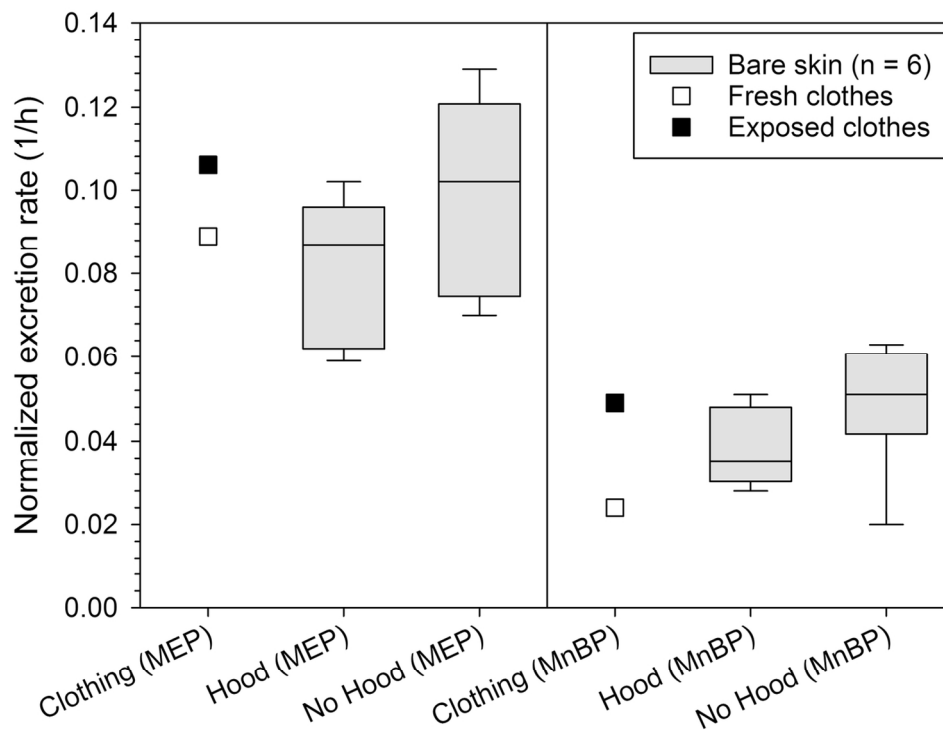129x108mm (300 x 300 DPI)

Table 1. Net amount of metabolites excreted during the time period from entering the chamber until 54 hours later, as well as parent compound uptake calculated from the metabolite levels; details regarding the calculation of the listed values are presented in Supporting Information.

	Metabolites excreted (µg)			Total uptake parent (µg)		Background corrected uptake parent (µg)		Dermal only uptake parent (corrected for concentration in hood) (µg)		Normalized dermal uptake (µg/kg/(µg/m³))		Average flux based on 6 hour exposure (µg /m²/h)	
	MEP	MnBP	3OH-MnBP	DEP	DnBP	DEP	DnBP	DEP	DnBP	DEP	DnBP	DEP	DnBP
Fresh clothing	466	121	7.7	634	176	522	98	352	74	0.017	0.007	28	6
Exposed clothing	3666	2367	136	4995	3432	4882	3355	4712	3331	0.178	0.261	381	270

For Peer Review Only

Supplemental Material

Role of clothing in both increasing and decreasing dermal absorption of airborne SVOCs

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Table S1. Clothing characteristics determined from product packaging or labels

Clothing	Composition	Size	Manufacturer	Description
Undershirt	100% cotton	M/M, 38-40" (97-102 cm)	Gildan	Short sleeve, crew neck, color: white Estimated cloth area = 0.91 m^2
Underwear	100% cotton with elastic band	L/G, 36-38" (91-97 cm)	Hanes	Boxer style briefs, color: grey Estimated cloth area = 0.24 m^3
Shirt	100% cotton	M	Gildan	Long sleeve tee-shirt, crew neck, color: dark green Estimated cloth area = 1.03 m^3
Pants	100% cotton	36" (91 cm) waist 36" (91 cm) inseam	Wrangler	Jeans, slim fit, color: dark blue Estimated cloth area = 1.10 m^2
Socks	85% cotton 12% polyester 1% elastic 1% nylon 1% spandex	12W-15	Starter	Tube socks that rise ~20 cm above ankle, color: white Estimated cloth area (pair) = 0.07 m^2

Figure S1. Male subject shown wearing full set of test clothing and the breathing hood while seated in the test chamber.

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Table S2. Net amount of metabolites excreted during the time period from entering the chamber until 54 hours later, as well as parent compound uptake calculated from the metabolite levels. This Table is identical to Table 1, but is included here with detailed explanations of calculation methods.

	Metabolites excreted (µg)[1]			Total uptake parent (µg)[2]		Background corrected uptake parent (µg)[3]		Dermal only uptake parent (corrected for concentration in hood) (µg)[4]		Normalized dermal uptake (µg/kg/(µg/m³)[5]		Average flux (µg /m²/h)[6]	
	MEP	MnBP	3OH-MnBP	DEP	DnBP	DEP	DnBP	DEP	DnBP	DEP	DnBP	DEP	DnBP
Fresh clothing	466	121	7.7	634	176	522	98	352	74	0.017	0.007	28	6
Exposed clothing	3666	2367	136	4995	3432	4882	3355	4712	3331	0.178	0.261	381	270

1. The mass of metabolites excreted is determined by multiplying the concentration of each metabolite by the volume of urine collected for each sample and summing over all samples collected during the 54 hour period after the exposure started.

2. Total parent uptake is calculated by converting mass from metabolite to parent and using a metabolic conversion factor.

Compound	Abbreviation	CAS-no.	Molecular weight (g/mol)	Metabolic conversion factor
Diethylphthalate	DEP	84-66-2	222.24	NA
Di-n-butylphthalate	DnBP	84-74-2	278.34	NA
Monoethylphthalate	MEP	2306-33-4	194.18	0.84
Mono-n-butylphthalate	MnBP	131-70-4	222.24	0.84
3OH-mono-n-butylphthalate	3OH-MnBP	57074-43-8	238.24	0.07

DEP = [(MEP /194.18) * 222.24]/0.84
DnBP = [(MnBP /222.24)* 278.34]+ [(3OH-MnBP /238.24) * 278.34] / (0.84+0.07)

3. Background-corrected uptake of the parent compound is determined by subtracting out the background concentration of metabolites, integrating the resulting mass, then applying the conversion described in (2) above. Background is defined as the pre-exposure urine concentration.

4. Dermal uptake of parent compounds is calculated by subtracting from background-corrected uptake the inhaled mass of DEP and DnBP based on concentrations in breathing air of the hood (40.7 and 5.7 µg/m³, respectively). Inhalation rate is assumed to be 0.7 m³/h. Therefore, the mass subtracted is 170 and 24 µg for DEP and DnBP respectively.

5. Normalized uptake is calculated by dividing the dermal uptake by average exposure air concentration and the subject body mass. Average air concentrations during the fresh clothing experiment were 230 µg/m³ DEP and 113

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$\mu g/m^3$ DnBP. Average air concentrations during the exposed clothing experiment were 291 $\mu g/m^3$ DEP and 140 $\mu g/m^3$ DnBP.

6. The average flux is estimated from the "Dermal only" corrected parent compound uptake, divided by exposed surface area of the participant and the exposure period (6 hours). Exposed surface area is taken as 2.06 m^2, estimated by equation 7A-7 of the Exposure Factors Handbook[18] and corrected for the area of the head (6.6% of total).

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