(Draft) Exposure Workflow for DnBP in Vinyl Flooring

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1. Details on chemical/product selection

- Di(n-butyl) phthalate (DnBP or DBP) is one of the better studied semivolatile organic compounds (SVOCs) that is present in many consumer products and that has been frequently found in indoor environments. The following references are examples of peer-reviewed publications concerning DnBP:
  - Salthammer and Goss (2019)
  - Eftekhari and Morrison (2018)
  - Cao, Weschler et al. (2016)
  - Morrison, Weschler et al. (2016)
  - Weschler, Bekö et al. (2015)
  - Bi, Liang et al. (2015)
  - Liang and Xu (2014)
- PFAS are a very diverse group of chemicals. While some are SVOCs or behave similarly to SVOCs, others are more or less volatile. DnBP is an example of a higher-volatility SVOC, and is in the range of many PFAS precursor compounds, such as monoPAPs, diPAPs, and FTOHs. However, many of the chemical characteristics necessary to categorize PFAS as SVOCs (primarily vapor pressure and boiling point) are only available as predictions, and where experimental data are available, they often differ greatly from the predicted values:
  - Vapor pressure of DnBP: 5.9e-03 Pa (USEPA 2019) to 6.7e-03 Pa (Wu, Eichler et al. 2016) at 25°C
  - Boiling point of DnBP: 340°C
  - Vapor pressure range of PFAS (predicted): 8.03×10^{-8} Pa to 9.19×10^{3} Pa at 25°C (USEPA 2019)
  - Boiling point range of PFAS (predicted): 95°C to 376°C (USEPA 2019)
- Much of the work of Dr. Little's group at Virginia Tech has included research on DnBP, including following peer-reviewed publications:
  - Eichler, Cao et al. (2019)
  - Eichler, Wu et al. (2018)
  - Cao, Zhang et al. (2017)
  - Wu, Eichler et al. (2016)
  - Xie, Wu et al. (2015)
  - Wu, Xie et al. (2015)
  - Benning, Liu et al. (2013)
  - Little, Weschler et al. (2012)
- DnBP is an SVOC that is mainly used as a plasticizer in PVC products. The most relevant properties for this exposure workflow analysis are:
  - Molecular weight MW = 278.3 g mol^{-1} (USEPA 2019)
  - Octanol-air partition coefficient $\log_{10}(K_{oa})$ = 9.83 (Salthammer and Goss 2019)
  - Vapor pressure p_s = 6.70e-03 Pa (Wu, Eichler et al. 2016)

2. Decision Context and Life Cycle Implications

- The Alternatives Analysis (AA) for Priority Products and Chemicals of Concern is documented in a 2017 guide (DTSC 2017) published by the California Department of Toxic Substances Control (DTSC).
- The AA framework includes two stages:
  - During the first stage, the goal, scope, legal, functional, and performance requirements of the Priority Product and the Chemical of Concern are identified by the responsible entity. This information is used to identify possible alternatives.
  - The second AA stage contains an in-depth analysis that refines the relevant factors and product function descriptions of the first stage and expands the analysis to consider additional impacts, including life cycle and economic effects.
- An important aspect of the AA is to incorporate a life cycle perspective and to consider all stages from manufacture to disposal.
- Life cycle stages as described in the guide are (DTSC 2017):
  - Raw materials
  - Intermediate
  - Manufacture
  - Packing
  - Transportation
  - Distribution
  - Use
  - Operations & maintenance
  - Waste
  - Reuse & recycling
  - End-of-life
- Environmental impacts of interest include air quality, ecological, soil quality and water quality (DTSC 2017).
- Figure 1 highlights the life-cycle stages that are relevant for the presented chemical/product selection of DnBP in vinyl flooring and relevant exposure routes and receptors.

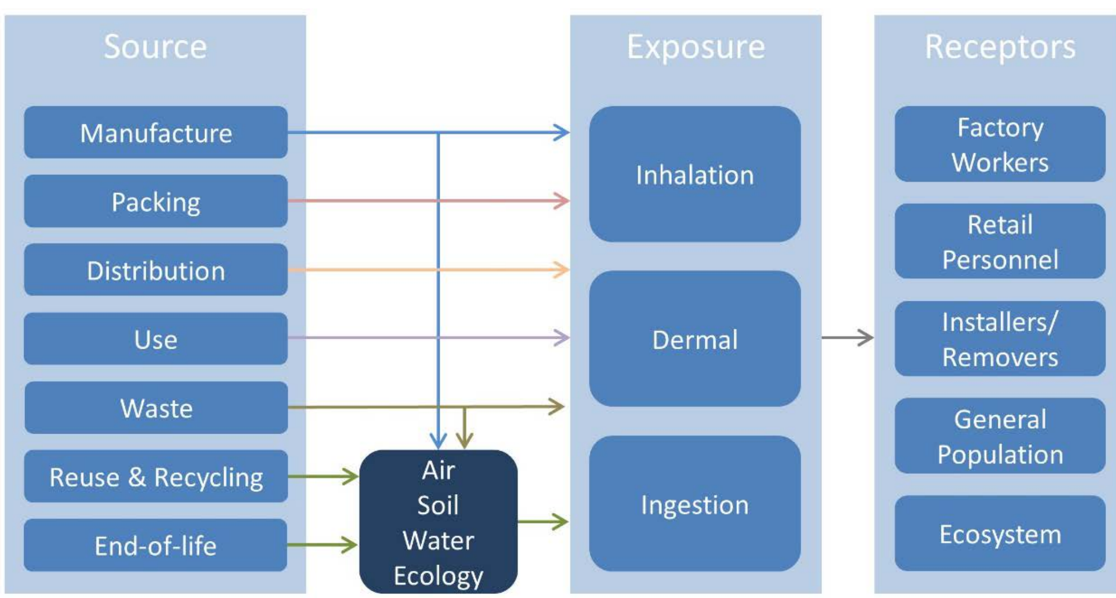

Figure 1: Important life cycle stages, exposure routes, and receptors for DnBP in vinyl flooring.

3. Suggested Exposure Workflow

- The suggested exposure workflow can be directly used to evaluate exposure of the general population/consumer to the selected chemical/product combination during the use stage of the product. It can also be adapted to evaluate exposure of factory workers, retail personnel and floor installers/removers during the manufacture, packing, distribution and waste stages of the product.
- It can be used to identify relevant factors within the DTSC AA.
- The workflow is based on a mechanistic framework for rapid exposure estimation which has been developed over the past year by Dr. Little, Clara Eichler and an international team of researchers (Eichler, Xu et al. 2020).
- A simplified schematic of the framework can be found in Figure 2. Here, the aspect of the framework focusing on solid products is highlighted. See Eichler, Xu et al. (2020) for a description of the complete framework.
- Figure 3 shows the workflow. In the following sections, the example of DnBP in vinyl flooring at the Use stage is applied to this workflow.
- Data sources:
    - Chemical properties: EPA CompTox Chemistry Dashboard (https://comptox.epa.gov/dashboard) and NIH PubChem (https://pubchem.ncbi.nlm.nih.gov/)
    - Product properties: Product labels, manufacturer information, experimental data
    - Properties of the indoor environment: Peer-reviewed literature data and/or specific data for a given exposure scenario
    - Occupant characteristics: Information about who is exposed (adults, children, their ages, etc.), which is needed to select relevant exposure factors (see below)
    - Models: Direct use of models accompanying the framework and/or other models that reflect the exposure scenario and selected exposure pathways
    - Assumptions: Generally reflected mathematically in the models as simplifications
    - Model parameters: Peer-reviewed literature, databases, other models, predictive relationships and tools such as SPARC or EPI Suite
    - Exposure factors: EPA exposure factors handbook, peer-reviewed literature or specific available data
- Missing data and data selection:
    - Scripts or source code implementing those steps are not openly available to date.
    - Data is expected to be missing. In those cases, we suggest to either use data for compounds with similar properties or to use predictive relationships/tools to estimate the missing information. In any case, data sources should be clearly indicated, especially if a parameter has been estimated. It is also possible to use a range of parameters to derive a worst-case scenario and a possible range of exposure estimates for different assumptions.
    - Multiple data sets should be compared and their applicability to the case study should be evaluated. Averages and medians can be used, possibly including upper and lower bounds.
    - Experimental data is generally preferred over modeled or estimated data, as long as the experiments reflect the given scenario well. Comparisons with data for other compounds and products may yield additional information on the suitability of a specific data set.
- Outputs: The result of this exposure workflow is a pathway-specific concentration per kg body weight per day for the selected exposed individual in a given exposure scenario. Example: A 6-year-old may inhale about 3 µg DnBP per kg body weight per day in a house that has vinyl flooring in all rooms.

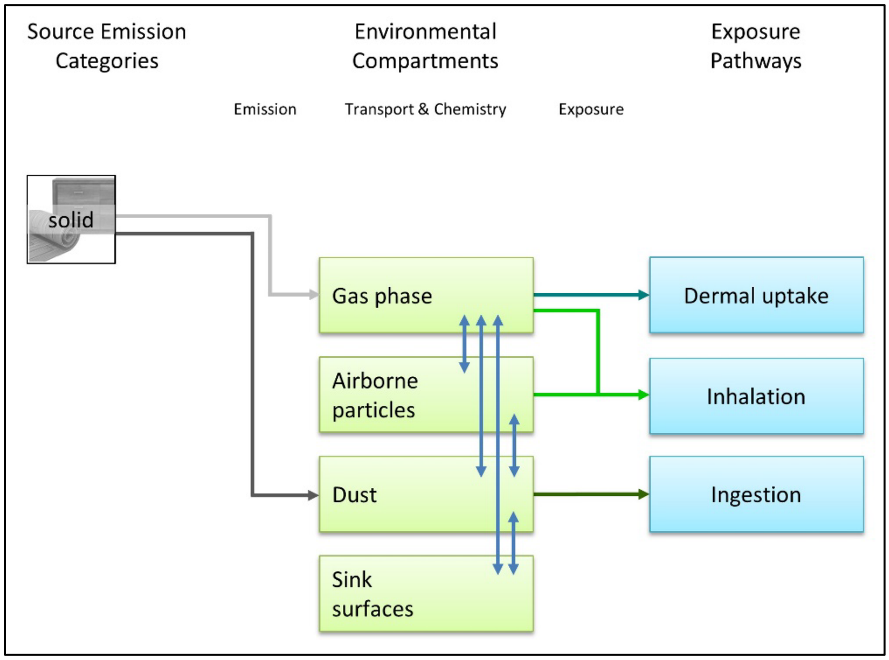

Figure 2: The modular mechanistic framework for rapid exposure estimation of SVOCs emitted from solid products (Eichler, Xu et al. 2020).

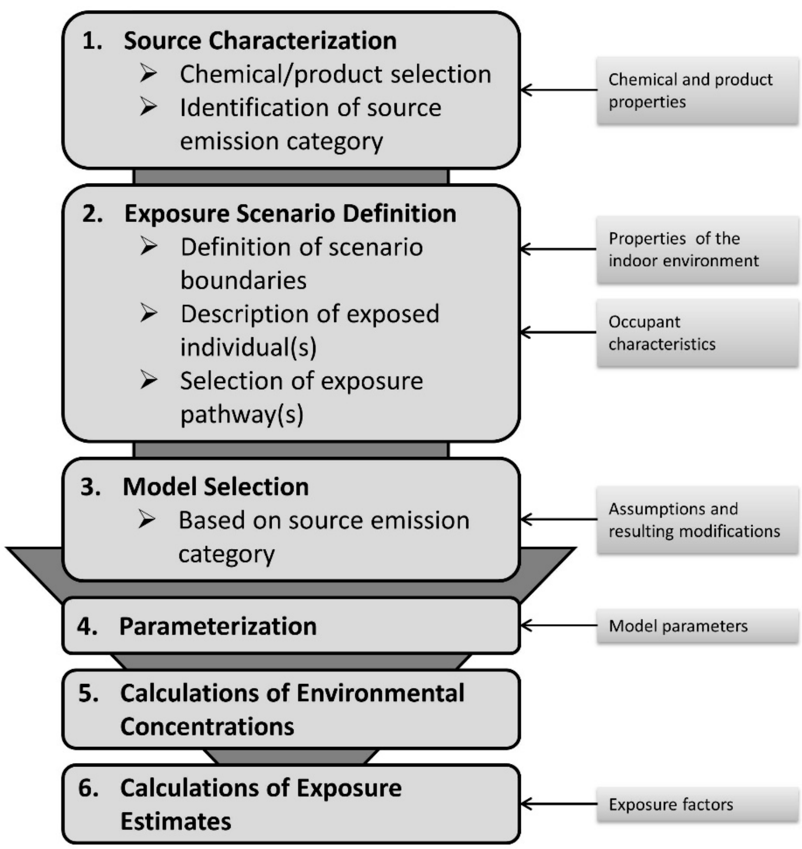

Figure 3: Flow chart showing suggested exposure workflow and inputs.

4. Case Study

- Considered chemical/product combination: DnBP in vinyl flooring
- Considered life cycle stage: Use
- Considered receptors: General population/consumer
- Emphasized aspects of decision context: Derivation of exposure estimates to be used in combination with toxicity data for rapid risk assessment and risk screenings

1. *Source Characterization*
   - Source: Vinyl flooring containing one plasticizer, DnBP
   - DnBP concentration: 9 wt%
   - Source emission category (Eichler, Xu et al. 2020): solid (see Figure 3)

2. *Exposure Scenario Definition*
   - Definition of scenario boundaries of the indoor environment in which exposure occurs:
     - Scenario A: Vinyl flooring in the kitchen only
     - Scenario B: Vinyl flooring throughout average US house
     - Assumptions:
       - Steady state/equilibrium has been reached
       - SVOC emissions are externally controlled
       - The indoor air is well mixed
       - Outdoor contributions are negligible
     - Also:
       - No particle generation indoors (but particles are present at certain concentration, see below)
       - “Clothing” and respective interactions are not considered
       - Dust is equally distributed on source and sink surfaces
       - Dust removal (e.g. by vacuuming) occurs once per week
     - Determination of parameters needed to describe scenarios: see Table 1

Table 1: Parameters describing the indoor environment in which exposure occurs

Parameter	Scenario A: Kitchen	Scenario B: House	References
Source surface area *A* (m^2)	19	250	Manuja, Ritchie et al. (2019) and census.gov
Ceiling height (m)	2.4		Manuja, Ritchie et al. (2019)
Volume *V* (m^3)	600		calculated
Total surface area *A* (m^2)	1080		calculated* based on Manuja, Ritchie et al. (2019)
Sink surface area A_s (m^2)	1061	830	calculated
Air change rate λ (h^{-1})	0.4		Jayjock and Havics (2018)
Total suspended particles TSP ($\mu g\ m^{-3}$)	20		Little, Weschler et al. (2012)
*Surface-area-to-volume ratio w/o contents = 1.8 m^{-1}			

- Exposed individuals:
  - Child (2-6 years)
  - Adult (> 21 years)
- Exposure pathways:
  - Dermal uptake from the gas phase
  - inhalation of air and airborne particles
  - Ingestion of dust from both source and sink surfaces

3. *Model Selection*
   - Based on source emission category → here: solid
   - Relevant mechanisms: Summarized in the following general mass balance for indoor SVOCs

$$V\frac{dy}{dt}+V\frac{dF}{dt}=Q\cdot(y_{out}+F_{out})-Q\cdot(y+F)+h_m\cdot A\cdot(y_0-y)-h_{m,s}\cdot A_s\cdot(y-y_s)-\ v_d\cdot F\cdot(A+A_s)+\ R_p\cdot M\cdot P_{dust}\cdot A+\ R_p\cdot M_s\cdot P_{dust,s}\cdot A_s$$

4. *Parameterization*
   - Simplifications incorporating assumptions and scenario boundaries
     - Assumption: steady state → $V\frac{dy}{dt}+V\frac{dF}{dt}=0$
     - Assumption: no contributions from outdoors → $Q\cdot(y_{out}+F_{out})=0$
     - Assumption: equilibrium has been reached, no further loss to surfaces → $y_s=y$
     - Assumption: mass loading on source and sink surfaces is equal → $M_s=M$
   - Calculations
     - Particle phase concentrations: $F=K_p\cdot TSP\cdot y$
     - Dust phase concentrations: $P_{dust}=K_{dust}\cdot y_0$ (source surfaces) and $P_{dust,s}=K_{dust}\cdot y_s$ (sink surfaces)
   - The mass balance (Step 3) now can be simplified to:

$$y=\frac{y_0\cdot A\cdot(h_m+R_p\cdot M\cdot K_{dust})}{Q+Q\cdot TSP\cdot K_p+v_d\cdot TSP\cdot K_p\cdot(A+A_s)-R_p\cdot M\cdot K_{dust}\cdot A_s}$$

   - Flow rate: $Q=\lambda\cdot V$
     - λ and V given as part of scenario definition
   - Air-particle partition coefficient: $K_p=\frac{f_{om\_part}\cdot K_{oa}}{\rho_{part}}$ (Finizio, Mackay et al. 1997)
   - Air-dust partition coefficient: $K_{dust}=\frac{f_{om\_dust}\cdot K_{oa}}{\rho_{dust}}$ (Finizio, Mackay et al. 1997)
   - Dust loading: $\frac{dM}{dt}=v_d\cdot TSP-R_p\cdot M$
     - Dust removal every 7 days as given in scenario definition → differential equation has to be solved for t = 168 h
     - Particle concentration TSP: see Table 1 (part of scenario definition)
   - See Table 2 for list of remaining parameters needed to solve mass balance
   - See Table 3 for calculated results

5. *Calculation of Environmental Concentrations*
   - DnBP concentrations in the gas phase, particle phase and source and sink dust phases
   - Results see Table 4

Table 2: Parameters needed to solve mass balance

Parameter	Scenario A: Kitchen	Scenario B: House	References
Organic fraction particles f_{om_part} (-)	0.4		Weschler and Nazaroff (2010)
Density particles ρ_{part} (g cm^{-3})	1		Weschler and Nazaroff (2010)
Organic fraction dust f_{om_dust} (-)	0.2		Weschler and Nazaroff (2010)
Density dust ρ_{dust} (g cm^{-3})	2		Weschler and Nazaroff (2010)
Deposition rate v_d (m h^{-1})	4.9		Shi and Zhao (2012)
Resuspension rate R_p (h^{-1})	7.2e-05		Thatcher and Layton (1995)
Gas-phase concentration immediately adjacent to the source material y_0 (µg m^{-3})	25.9		Liang and Xu (2014)
Mass transfer coefficient h_m (m h^{-1})	1.44		Xu, Liu et al. (2012)

Table 3: Calculated parameters needed for solving mass balance

Parameter	Scenario A: Kitchen	Scenario B: House	References
Q (m^3 h^{-1})	240		calculated
K_p (m^3 g^{-1})	2704		calculated
K_{dust} (m^3 g^{-1})	676		calculated
M (µg m^{-2})	1.63e+04		calculated

Table 4: Resulting environmental concentrations

Concentration	Scenario A: Kitchen	Scenario B: House
Gas phase y (µg m^{-3})	0.34	5.38
Particle phase F (µg m^{-3})	0.019	0.291
Dust phase source surfaces P_{dust} (µg g^{-1})	17511	17511
Dust phase sink surfaces $P_{dust,s}$ (µg g^{-1})	232	3638

6. *Calculation of Exposure Estimates*
   - Considered exposure pathways:
     - Dermal uptake of DnBP from the gas-phase: $Ex_{gas\_d} = y \cdot k_{p\_g} \cdot A_{exp}/BW$
     - Inhalation of gas- and particle-phase DnBP: $Ex_{inh} = (y + F) \cdot IR_{inh} \cdot ED/BW$
     - Ingestion of dust-phase DnBP: $Ex_{dust\_ing} = P_{dust} \cdot IR_{dust}/BW$
   - Relevant data from EPA Exposure Factors Handbook (see Table 5)
   - Transdermal permeability coefficient k_{p_g} = 4.8 m h^{-1} (Weschler and Nazaroff 2012)
   - Resulting daily exposure estimates: see Table 6

Table 5: Parameters needed for calculation of exposure estimates

	Child (2-6 yrs)	Adult (> 21 yrs)
Inhalation rate IR_{inh} (m^3 h^{-1})	0.396	0.660
Exposure duration *ED* (h d^{-1})	21.8	19.2
Dust ingestion rate IR_{dust} (µg d^{-1})	30000	20000
Exposed skin area A_{exp}* (m^2)	0.089	0.223
Body weight *BW* (kg)	16.2	80
*Assumption: Only head and hands are exposed		

Table 6: Resulting exposure estimates of DnBP in vinyl flooring per kg body weight per day

	Child (2-6 yrs)		Adult (> 21 yrs)		
	Scenario A: Kitchen	Scenario B: House	Scenario A: Kitchen	Scenario B: House	
Inhalation	0.193	3.03	0.057	0.90	µg kg^{-1} d^{-1}
Dust ingestion*	0.993	12.68	0.134	1.71	µg kg^{-1} d^{-1}
Dermal uptake gas phase**	0.216	3.39	0.110	1.73	µg kg^{-1} d^{-1}
*Accounts for fraction of source and sink surfaces of total surface area **Only head and hands are exposed					

5. Generalization of the Proposed Exposure Workflow

- Using the mechanistic framework (Eichler, Xu et al. 2020), chemical/product combinations that can be placed into one of the source emission categories may be used.
- The workflow can be adapted for exposure estimation for other life cycle stages resulting in human exposure.
- The framework and associated models have been developed for SVOCs; depending on the chemical of interest, assumptions and calculations have to be adopted to accommodate different vapor pressures and behavioral characteristics. In these cases, the framework serves more as a guideline for further research and data acquisition and exposure estimates may become more uncertain.
- The most important gaps impeding the application of this workflow are
    1. Availability of data: Relevant mechanistic data to describe emission and partitioning of chemicals is missing entirely or only available in journal articles, but cannot be found in databases. Thus, connecting scenario data with exposure factors is very difficult. This is in particular true for PFAS, which have not been well studied regarding their behavior in indoor environments.
    2. Scripts implementing these workflows are not readily available. Researchers working on these topics have scripts/spreadsheets to use within their models, but these are usually not available to others.

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