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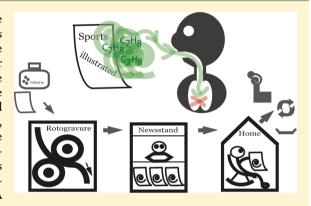


# Indoor Exposure to Toluene from Printed Matter *Matters:* Complementary Views from Life Cycle Assessment and Risk Assessment

Tobias Walser,\*,† Ronnie Juraske,† Evangelia Demou,‡ and Stefanie Hellweg†

Supporting Information

ABSTRACT: A pronounced presence of toluene from rotogravure printed matter has been frequently observed indoors. However, its consequences to human health in the life cycle of magazines are poorly known. Therefore, we quantified human-health risks in indoor environments with Risk Assessment (RA) and impacts relative to the total impact of toxic releases occurring in the life cycle of a magazine with Life Cycle Assessment (LCA). We used a one-box indoor model to estimate toluene concentrations in printing facilities, newsstands, and residences in a best, average, and worst-case scenario. The modeled concentrations are in the range of the values measured in onsite campaigns. Toluene concentrations can be close or even surpass the occupational legal thresholds in printing facilities in realistic worst-case scenarios. The concentrations in homes can surpass the US EPA reference dose (69  $\mu$ g/kg/day) in worst-case scenarios, but are still at



least 1 order of magnitude lower than in press rooms or newsstands. However, toluene inhaled at home becomes the dominant contribution to the total potential human toxicity impacts of toluene from printed matter when assessed with LCA, using the USEtox method complemented with indoor characterization factors for toluene. The significant contribution (44%) of toluene exposure in production, retail, and use in households, to the total life cycle impact of a magazine in the category of human toxicity, demonstrates that the indoor compartment requires particular attention in LCA. While RA works with threshold levels, LCA assumes that every toxic emission causes an incremental change to the total impact. Here, the combination of the two paradigms provides valuable information on the life cycle stages of printed matter.

#### ■ INTRODUCTION

Indoor Exposure and Health Effects from Toluene Emissions. Industrially produced chemical substances are a necessity of everyday life. Solvents are a prominent example with a worldwide production of close to 10 million metric tons per year. 1-3 The printing industry is the fifth largest industry worldwide in atmospheric solvent emissions, 4-6 which contribute, for example, to the formation of photochemical ozone and can cause adverse effects to human health.<sup>7-9</sup> The screening study of Demou et al. (2011)10 allowed the identification of troublesome compounds from a Life Cycle Assessment (LCA) and traditional Risk Assessment (RA) perspective, based on occupational exposure and hazard data. Toluene was ranked in the top 10 of the presented priority list using both methods. In addition, Caldwell et al. (2000) showed, in a comprehensive review of measured and modeled solvent concentrations at workplaces, that toluene is one of the most prominent emitted solvents, 11 large share of which originates from the printing industry. 12 In particular the rotogravure process is a significant emission source of toluene 11,13,14

because of the high toluene fraction in gravure ink (60–75 wt %). Toluene is emitted from the solvent components in the raw inks and related coatings used at the printing presses, with the main emission sources being the dryer exhaust vents (75–90%), fugitive printing vapors, and evaporation of solvent retained in the printing product. This has led to increased toluene workplace concentrations of up to 1900 mg/m<sup>32,3,5,6,9,17,18</sup> compared to a permissible workers exposure limit of 750 mg/m<sup>3.19</sup> While several studies investigated indoor concentrations of toluene in printing halls, <sup>20–25</sup> knowledge of elevated toluene concentrations and subsequent health impacts resulting from toluene emissions from printed matter downstream in the life cycle of magazines is still scarce. It has been recently shown by Caselli et al. <sup>26</sup> that average toluene indoor

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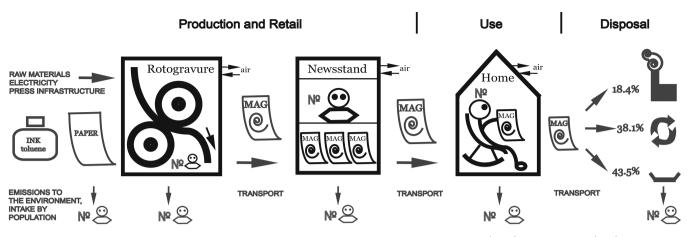


Figure 1. System boundaries of the LCA and the RA. The RA comprises the indoor compartments only (black) while the LCA (gray) also includes emissions from raw material production, transport, and disposal processes (incineration, recycling, landfill; numbers valid for EU-27<sup>2,53</sup>).

concentrations in newsstands can be up to  $1.5~\text{mg/m}^3$  and represent 70% w/w of the total VOCs measured.

Toluene emissions from magazines extend beyond the workplace. Once the magazines are sold, additional human exposure occurs when the magazines are read and stored in homes until they are disposed. This also contributes to toluene indoor concentrations in homes being higher than respective outdoor concentrations. 8,26-28 Residential exposure time and human susceptibility are, on average, higher than in occupational settings,<sup>29</sup> and show high interpersonal variation. Toluene emissions in homes are less constant and influenced by the use pattern of magazines, that is, reading time, storage time, storage conditions, and the amount of magazines. Average indoor concentrations of toluene at homes are in the range of  $0.03 \text{ mg/m}^3$ , 28,30-33 (Figure 3) while the Oral Reference Concentration is 5 mg/m<sup>3</sup>.<sup>34</sup> The presence of toluene indoors partly results from the high use frequency of printed matter, in addition to other emission sources such as, for example, building materials and furniture.<sup>35</sup> Indoor concentrations are higher than outdoors also because of smaller air dilution volumes compared to outdoors and pollutant removal being limited by the air-exchange rates.<sup>36</sup> To a smaller extent, indoor solvent concentrations are also influenced by outdoor atmospheric conditions, human activities, and chemical reactions in air and on surfaces.37,38

Toluene emissions primarily affect the central nervous system (CNS) for both acute and chronic exposures. Toluene can cause dysfunctions and narcosis in humans after exposure to low or moderate levels by inhalation. Symptoms of toluene exposure include fatigue, sleepiness, headaches, and nausea. Severe cases of workplace exposure have also led to death. Epidemiological studies show that elevated toluene concentrations can also lead to long-term health effects, which resulted in governmentally defined threshold values (Supporting Information, Table S-1). However, holistic assessments on the health impact of increased indoor toluene concentrations at workplaces and in households are missing.

Risk Assessment and Life Cycle Assessment of Indoor Emissions and Exposure. Suitable methods to comprehensively evaluate the consequences on human health from increased pollutant concentrations are RA and LCA. LCA considers the entire life cycle of a product or service and evaluates the environmental burden and human health impacts from pollutant emissions related to a functional unit. 40 Because of this reference to the functional unit (e.g., the service of a

certain product), LCA assesses toxic effects of chemicals only relative to each other, and not on an absolute scale. In newer LCA methods, such as USEtox, 41 the product of emission, intake fractions, and effect factors is used to determine impact scores. Inhalation intake fractions are defined as the ratio of the amount of inhaled substance to the amount emitted. It has been demonstrated that indoor intake fractions of volatile substances are more than 2 orders of magnitude higher than outdoor values<sup>42</sup> owing to the extensive time that people spend indoors and because of the comparatively large pollutant concentrations indoors. 43-45 However, *indoor* emissions are seldom assessed with LCA even though they have been shown to be relevant. Skaar et al. 45 recently showed that the indoor impact of inhaled VOC emitted from wood products in the use stage is 4 orders of magnitude higher than the outdoor impact over the entire life cycle. The impact of indoor exposure may be even larger than reported, as this study only considered the indoor compartment in the use phase and neglected other stages in the life cycle. Studies that take into consideration both indoor and outdoor exposure and effects during the complete life cycle of a product are so far missing.

In contrast to LCA that provides a relative assessment, RA provides the framework for investigating risks of human-health effects on an absolute scale and for this detailed local information is often required. The resulting spatial specificity in combination with the necessary temporal resolution distinguishes RA from LCA.<sup>46</sup> RA has been widely applied to assess chemical releases indoors and outdoors.<sup>47–49</sup> In RA, the actual dose (predicted daily intake, PDI) is commonly put into relation to the respective acceptable daily intake (ADI).<sup>50</sup> Some risk assessment studies have considered the number of people exposed as a weighting factor,<sup>51</sup> but in most cases individual exposure is assessed in relation to no-effect doses.<sup>52</sup>

A complementary assessment of human-health impacts with LCA and RA along the life cycle of a toluene emitting product has not been performed so far. Demonstrations of the affinities such as similar fate and exposure modeling, but at the same time accounting for different temporal and spatial details are scarce. For both LCA and RA, a one-box model may be used for the indoor exposure assessment in relatively small rooms under well mixing conditions. A more detailed analysis of human exposure indoors and associated toxic impacts, both in terms of RA and LCA, would improve the assessment of exposures to high toluene concentrations found at different stages in the life cycle of rotogravure printed magazines.

Table 1. Parameter Values for the Scenarios<sup>a</sup>

|            | emission<br>rate                      | room           | air exchange<br>rate, k <sub>tot</sub> | magazines in stock | storage | indoor<br>exposure time | breathing<br>rate | modeled<br>concentration | exposed                |   |               |
|------------|---------------------------------------|----------------|--|--------------------|---------|-------------------------|-------------------|--------------------------|------------------------|---|---------------|
|            | g/h                                   | m <sub>3</sub> | 1/h                                    | amount             | days    | fraction of a day       | m³/day            | mg/m <sup>3</sup>        | number per<br>facility | comments  | references    |
| Pressrooms | ıs                                    |                |  |                    |         |                         |                   |                          |                        |   |               |
| best       | $8.83 \times 10^{4}$                  | 19300          | 9                                      | 15530              | 1       | 0.11                    | 20                | 381                      | S                      | 3/8 printing, 5/8 idle low  |               |
| average    | $1.53 \times 10^5$                    | 16600          | 4.6                                    | 25890              | П       | 0.21                    | 20                | 613                      | 15                     | 5/8 printing, 3/8 idle high   | 3,17,58,64,65 |
| worst      | $2.22 \times 10^5$                    | 5755           | 1.3                                    | 41420              | П       | 0.25                    | 24                | 686                      | 30                     | continuous printing   |               |
| Newsstands | ds                                    |                |  |                    |         |                         |                   |                          |                        |   |               |
| best       | 0.19                                  | 80             | 3.6                                    | 800                | 7       | 0.11                    | 12                | 0.65                     | 1.5                    | a small number of stapled magazines with high ventilation                                     |               |
| average    | 1.48                                  | 7.5            | 2.2                                    | 1000               | 2       | 0.21                    | 16                | 8.91                     | 7                      | standard newsstand  | 26,58,59,64   |
| worst      | 4.45                                  | 30             | 1.3                                    | 1500               | 1       | 0.25                    | 20                | 1111                     | 8                      | small newsstand with many magazines   |               |
| Households | ds                                    |                |  |                    |         |                         |                   |                          |                        |   |               |
| best       | 0.0011                                | 188            | 2.5                                    | 0.45               | 14      | 0.58                    | 12                | 0.002                    | 1                      | few readings in a well- ventilated house, reading time 2 $\ensuremath{\mathrm{h}}/$ magazine  |               |
| average    | 0.0078                                | 63             | 9.0                                    | 1.59               | 10      | 0.58                    | 12                | 0.21                     | ю                      | average European household, reading time 6 h/magazine (several persons)                       | 58,64,66,67   |
| worst      | 0.0541                                | 38             | 0.5                                    | 5.58               |         | 1                       | 12                | 2.9                      | s                      | many magazines are read in one room, reading time 10 $\mathrm{h}/$ magazine (several persons) |               |
| backgrour  | background concentrations (mg/m³, SD) | ons (mg/m³,    | SD)                                    |                    |         | 0.013 (0.004)           |                   | 0.015 (0.013)            |                        |   | 26,28         |

"The number of exposed persons is required for the LCA, and the number of magazines constantly in stock is required for the RA, while all other parameters are required for both the LCA and the RA. The emission rate is adapted to "one magazine" for the LCA. SD = standard deviation.

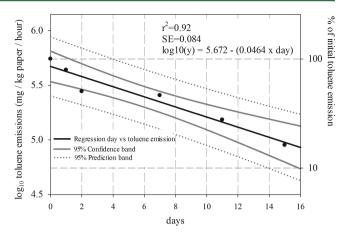
Aim of the Study. The aim of this study is to quantify potential impacts to human health caused by toluene emissions from rotogravure printed magazines over their entire life cycle, with a particular focus on the indoor environment, including both workplaces and homes. Therefore, this paper will integrate workers as well as consumer exposure indoors into LCA, something which has not been done before. Health impacts are assessed in two ways: Toxic impacts of toluene are quantified over the entire life cycle of printed magazines and then compared to the total human toxicity of a magazine, calculated with LCA. These results allow for a relative quantification of human toxicity on a population basis. On the other hand, we conducted a RA for printing facilities, newsstands, and residences, in order to determine the absolute individual health risk associated to toluene emissions.

#### MATERIALS AND METHODS

Scope of the Study. The system boundaries are shown in Figure 1, with the geographical scope being Europe. In a first step, total emissions of toluene were quantified in three different settings (press rooms, newsstands, and households) and for three scenarios (realistic best, average and worst-case scenarios, Table 1). The risk of these emissions was then evaluated in the RA for the three indoor environments and the three scenarios.

The Functional Unit (FU) in the LCA was defined as "reading one magazine". Therefore, the toluene emissions in press rooms, newsstands, and households were all adjusted to one magazine. For other emissions, we covered all life cycle stages of a magazine, which contains 50 A4 sheets of rotogravure printed, supercalendered paper (60 g/m²); 35.5 g of toluene is required per magazine. Existing processes have been used from ecoinvent v2.2, and the detailed inventory for the newly developed processes, including raw materials, transport, energy use, and emissions is shown in Supporting Information, Table S2. The UCTE electricity mix was used if no other information was available. The USEtox method to assess human toxic effects from indoor toluene emissions in the Life Cycle Impact Assessment (LCIA).

Toluene Emissions from Printed Matter. The consumption of printed matter, such as weekly and monthly magazines, journals, periodicals, and unaddressed mail is approximately 61 kg per household per year or 1.2 kg per week in Europe. 58 Rotogravure is 18% of the total volume. Thus the average weekly consumption of rotogravure printed matter per household is approximately 0.2 kg. The emission from exposed surfaces of printed matter over time is shown in Figure 2. Once printed, it is assumed that the weekly published magazines with a total surface area of 6.45 m<sup>2</sup> are printed and delivered to retailers within one day. In the newsstands, approximately 160 cm<sup>2</sup> of the front pages of each magazine in stock is unveiled and volatilization of toluene is hence limited. Newsstands are modeled as single rooms with the salespersons as primarily exposed subjects. Weekly published magazines are sold after two days on average, 59 and we assumed that the magazines are read and stored at home for a further 14 days. For the average case it is assumed that two persons read the magazine for 3 h each, and they are exposed to all the pages of the magazine during that time (Table 1). For the rest of the time only emissions from the front page are included in the LCIA. We included outdoor emissions from landfills and assumed that toluene is completely transformed to CO<sub>2</sub> in



**Figure 2.** Toluene emission profile of exposed surface printed with rotogravure (primary data from ref 58). The regression was used to estimate toluene emission from the magazines over time (paper weight:  $60~g/m^2$ ).

waste incineration plants. The cut-off approach was applied for recycling, and, hence, no environmental impacts were attached to recycling activities.

Assessing the Effects of Indoor Toluene Emissions. We used a one-box indoor model with complete mixing for the printing facility, the newsstand, and the households (eq 1). Furthermore, we assumed steady-state conditions for the toluene concentrations indoors:

$$C_{\infty} = \frac{E}{Vk_{\text{tot}}} \tag{1}$$

with emission rate E (mg/h), volume V (m³), and the total removal rate  $k_{\rm tot}$  (h¹), which includes ventilation, adsorption to walls, and degradation in air ( $t_{1/2}=3$  days). Emoval by human uptake is negligible and hence not included. The outdoor concentration of toluene is much lower than that indoors (Table 1) and was not considered. The models were parametrized as shown in Table 1 and the Supporting Information (SI). The air exchange is influenced by mechanical ventilation, opening windows, and permeable walls. Further, we compared the modeled concentrations with minimum, arithmetic mean, and maximum values from measurement campaigns reported in peer-reviewed studies  $^{2,3,5,6,9,17,18,61,62}$  and calculated the predicted daily intake (PDI, mg/kg/day, eq 2) of toluene:

$$PDI = f_{\text{day}} \frac{C \cdot IR}{BW}$$
 (2)

where  $f_{\rm day}$  is the average daily exposure time (fraction of one day, unitless), and C is the indoor concentration (mg/m<sup>3</sup>). We also varied inhalation rate (IR, m<sup>3</sup>/day) and body weight (BW, kg) within realistic ranges (Table 2).

These PDIs were compared to measurement results and legal threshold values. The risk quotient RQ was calculated as the ratio of the PDI to the acceptable daily intake (ADI), as conventionally done in RA (eq 3):

$$RQ = \frac{PDI}{ADI}$$
 (3)

For the ADI, the following values were taken (see Figure 3b): RfD (US EPA),  $6.86\cdot10^{-2}$  mg/kg/day; OSHA-PEL,  $1.29\cdot10^{2}$  mg/kg/day; NIOSH-REL,  $6.45\cdot10^{1}$  mg/kg/day; ACGIH-TLV,  $3.22\cdot10^{1}$  mg/kg/day.

Table 2. Parameter Values for the Sensitivity Analysis <sup>12,26,59,64-66</sup> and Own Assumptions. Doses Based on the Parameter Deviation from the Average Case (One Parameter Changed, the Others Held Constant)

|                         | press room                    | newsstand               | household          |
|-------------------------|-------------------------------|-------------------------|--------------------|
| removal ra              | ate (h <sup>-1</sup> )        |                         |                    |
| min                     | 0.5                           | 0.5                     | 0.5                |
| max                     | 10                            | 5                       | 5                  |
| room volu               | ime (m³)                      |                         |                    |
| min                     | 500                           | 30                      | 30                 |
| max                     | 390000                        | 190                     | 190                |
| exposure                | period (h∙day <sup>-1</sup> ) |                         |                    |
| min                     | 1                             | 1                       | 1                  |
| max                     | 10                            | 10                      | 24                 |
| body weig               | ght (kg)                      |                         |                    |
| min                     | 40                            | 40                      | 10 (children       |
| max                     | 130                           | 130                     | 130                |
| inhalation              | rate (m³·day⁻¹)               |                         |                    |
| min                     | 6                             | 6                       | 6                  |
| max                     | 24                            | 24                      | 24                 |
| emission 1              | rate (kg·h <sup>-1</sup> )    | amount of n<br>(number) | nagazines in stock |
| min                     | 1                             | 50                      | 0.5                |
| max                     | 2000                          | 2500                    | 50                 |
| emitting a<br>magazine) | rea (m² per                   |                         |                    |
| min                     |                               | 0.32                    | 0.32               |
| max                     |                               | 64.5                    | 64.5               |

In LCA, characterization factors (CF) describe the potential additional human health impact related to the emission of a mass unit of pollutant. The CF for indoor exposure to toluene in the LCA was calculated by multiplying the intake fraction (iF) and effect factor (EF), the latter taken from the USEtox database. The CF is used to determine the relative importance of emissions in an environmental compartment. Outdoor toluene emissions were assessed with the CFs of the USEtox method. The CF multiplied with the actual emissions per functional unit provides the impact score for human toxicity (IS<sub>h</sub>) in terms of comparative toxic units (CTU) as follows:

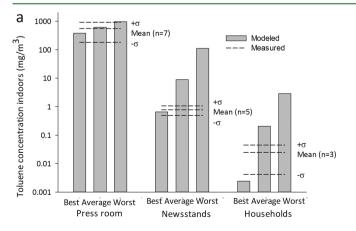
$$IS_{h} = E \cdot \frac{N \cdot IR}{Q} \cdot EF$$
(4)

where *E* is the emitted toluene per functional unit (kg), IR is a breathing rate of  $12-24 \text{ m}^3/\text{day}$  (depending on the activity), <sup>64</sup> *N* is the average number of persons in the investigated indoor compartment, *Q* is the constant volumetric ventilation rate of the indoor environment (m³/day), and the EF is the effect factor for toluene inhalation (3.64 ×  $10^{-3}$  cases/kg<sub>inhaled</sub> <sup>41</sup>).

**Scenarios.** We developed three scenarios for the press room by changing the daily periods for printing, room volumes, ventilation, number and activity of exposed persons, and different types of printing activities (Table 1). For printing activities and associated emissions and concentrations, the publication of Wadden et al. 17 provided a robust data set. Further, we developed three scenarios for the newspaper stands and homes (Table 1). Realistic best case scenarios and worst case scenarios were built with parameters from the upper and lower end of the collected reference values (Table 1). However, the most extreme values were not always used for the scenarios because the combination of these values would have led to unrealistic scenarios. The average individual daily intake of toluene at home was added to the daily dose of employees in newspaper stands or in the printing industry. All scenarios were fed into the LCA and/or the RA. Modeled concentrations and subsequent exposure to toluene are compared in the RA with threshold values for indoor concentrations and maximum allowed daily doses. In the LCA, scenario based toxicity on human health from indoor emissions of toluene are compared with the total impact score of the functional unit.

# **■** RESULTS

Risk Assessment. The modeled indoor concentrations for the press room calculated with the one-box model corresponded well with the measurement data from literature (Figure 3a). Modeled concentrations are the highest in the press room for all scenarios, followed by newsstands and residences. The realistic worst-case scenarios show that the toluene concentrations can rise above legal threshold values in both occupational and residential settings. The respective toluene doses of the average scenario were 40 mg/kg/day



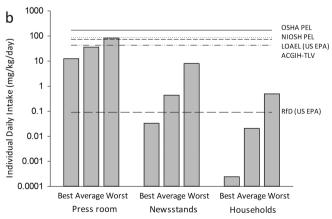
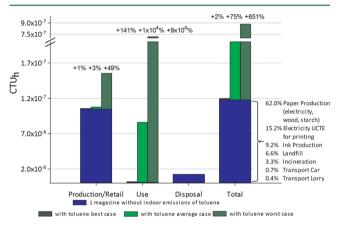


Figure 3. (a) Modeled and measured toluene concentrations indoors. <sup>2,3,5,6,9,17,18,61,62</sup> (b) Respective doses are highest in press rooms, followed by newspaper stands and households. A selection of legal threshold doses is added to Figure 3b for comparison: PEL, permissible exposure limit; LOAEL, lowest observed adverse effect level; TLV, technical limit value; OSHA, Occupational Safety and Health Administration; NIOSH, National Institute for Occupational Safety and Health; ACGIH, American Conference of Governmental Industrial Hygienists; RfD, reference dose.

(press room), 0.5 mg/kg/day (newsstands), and 0.022 mg/kg/day (household). RQs for the most stringent occupational threshold (ACGIH-TLV, 32 mg/kg/day) are surpassed for the worst case scenario in the pressroom (256%) and close to 1 in the average scenario (112%). By contrast, scenarios for the newsstands resulted in a risk quotient below 1 (RQ = 0.001–0.25). In the worst-case scenario, the RfD (0.07 mg/kg/day, US EPA) based RQ for people at home is up to 7.2 while under average conditions, this RQ is 0.3. Reasons for the high RQ in the worst-case scenario are the assumptions about the large number of stored magazines read in a small living room with a small air exchange. Lowering the body weight in the worst-case scenario can further increase the RQ up to 12 (BW 40 kg).

Life Cycle Assessment. In contrast to RA, LCA includes the number of exposed people in the calculation of the intake fraction (eq 3). The results of the LCIA are proportionally influenced by the number of people exposed, and hence the number of workers and residents indoors is a sensitive parameter. Moreover, a large part of the toluene emissions from a magazine occur in the use phase. Thus, with LCA, the use stage becomes the prominent life cycle stage regarding human health impacts from inhaled toluene (Figure 4).

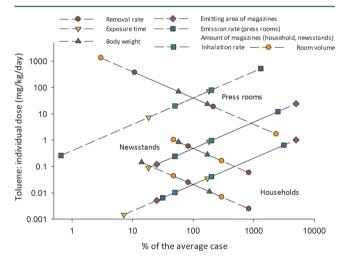


**Figure 4.** Human health impacts (comparative toxic units  $CTU_h$ ) over the life cycle of one magazine, calculated with the USEtox method. The green bars show the absolute  $CTU_h$  and relative (%) additional human toxicity because of indoor exposure to toluene. The relative contribution of the most important processes to the  $CTU_h$  is shown on the right.

The toluene emission rate of an open magazine is approximately 140 mg/h during reading, 17 opening all pages of the magazine (total area: 6.45 m<sup>2</sup>). The emission rate of closed magazines at home decreases from 60 mg to 20 mg per magazine per hour over 14 storage days. In total and on a population basis, inhaled toluene in the use phase results in 10 times higher human health impacts than in the production and retail (press rooms and newsstands). Inhaled toluene in press rooms and newsstands (average scenario) adds 3% to the total human health impacts of the production and retail stage. However, depending on the parameter values chosen, toluene emissions can become a major contributor to human toxicity, adding up to 49%. The influence of the scenario assumptions on the use phase is much larger: the additional CTU<sub>h</sub> contributed by inhaled toluene varies by 4 orders of magnitude (Figure 4) and can become higher than the previous life cycle stage, in absolute terms. Regarding the end-of-life of magazines, volatilized toluene from landfill to the outdoor atmosphere

(13.1 g per magazine) contributes 14% to the  $CTU_h$  of the disposal phase. Over the entire life cycle and calculated with the parameters of the *average* scenarios, indoor toluene emissions contribute 43% to the total  $CTU_h$ . The next highest contribution (34%) to the total  $CTU_h$  of one magazine arises from the emissions of paper production, and more specifically from the emissions of wood chips production, electricity generation, and potato starch production.

**Sensitivity Analysis.** Toluene concentrations, duration of exposure, number of exposed persons, and other parameters show a high variability. Therefore, a sensitivity analysis was also performed by varying each input parameter within best and worst case values while holding the others constant (Figure 5).



**Figure 5.** Sensitivity analysis for body dose from exposure to toluene emissions indoors from magazines in press rooms, households, and newspaper stands. The parameters are independent of each other and influence the dose in a linear manner. The parameter values are varied for each parameter within realistic ranges, with the maximum and minimum value indicated (numeric values in Table 2). The line crossing indicates the estimated individual dose of the *average* scenario. An example of the calculation procedure is shown in Supporting Information, eq S1.

The varied parameters are linked linearly and show the same slope. The sensitivity analysis demonstrates that the emission rates, removal rates, and room volume are critical parameters for maintaining an acceptable toluene level in occupational settings. For instance, if toluene emissions in printing facilities are difficult to reduce, ventilation becomes particularly important in maintaining workers' safety. The assumed emitting exposed surface of a magazine is an influencing parameter on the estimated toluene concentration in newsstands and households. Also, the number of stocked magazines in newsstands and households is influencing indoor concentrations to a large degree. In contrast, human parameters such as body weight and inhalation rate vary less and affect the internal dose by less than 1 order of magnitude. Also average exposure time is relatively constant and rather difficult to individually reduce in the different indoor settings.

#### DISCUSSION

The one-box model performed well against the measured indoor concentrations for which the building parameters were known. For toluene, which is volatile and persistent (degradation rate,  $1.63 \cdot 10^{-3}$  per hour), ventilation dominates

adsorption and degradation by more than 10 orders of magnitude ( $10^{-1}$  vs  $10^{-18}$ ) and therefore the latter two were negligible. The variability of indoor conditions was covered with worst, average, and best case scenarios as taken from the peer-reviewed and gray literature, and from databases. The scenario parameters and the model results have the advantage of allowing for an extensive sensitivity analysis (Figure 5) and identifying drivers of exposure and impact. Models are also low cost, adaptable to specific workplace or residence conditions, and they provide concentration ranges for screening assessments. For LCA in particular, accuracy within 1 order of magnitude is acceptable in view of the larger uncertainty of the effect factors, and hence the use of models instead of measurement values is acceptable.

To our knowledge, this is the first LCA study tracking indoor and outdoor exposure along the life cycle of a product including workplace and consumer exposure. It becomes apparent that indoor exposure to toluene largely contributes to the overall human toxicity when comparing the various stages in the life cycle of a magazine. Hence, this study confirms the findings of previous papers 42,44,69 that the indoor compartment requires inclusion in the LCA framework. In contrast to RA, the functional unit approach of LCA shifts the focus from the pressrooms and newsstands to consumer exposure in the households. Toluene emissions from a magazine have a higher relative impact on the population during the use phase than in production and retail, even though these latter compartments exhibit higher indoor concentrations. This is because of the potentially larger population being exposed in the use phase and the inherent assumption in LCA of linearity in dose and effect; that is, any increase in concentration leads to an increase in effect. The high relevance of consumer exposure during the use phase further strengthens the need for LCAs to include this exposure pathway. The application of this augmented approach may also be recommendable for other LCAs, such as those of cosmetics and other chemicals, which are generally assessed without consideration of inhalation or dermal exposure during the use phase.

The RA showed that these higher concentrations can lead to potential health risks for workers. In worst-case scenarios, workers in newsstands and in printing halls can be exposed to >200 mg/m<sup>3</sup>. These concentrations can cause headache or other adverse health effects over the long-term. 70 The ACGIH-TLV is surpassed in the average and worst-case scenarios for the press room, but not in the scenarios for the newsstands. The toluene uptake rate of 100% might overestimate the real dose, albeit this conservative approach is conventionally applied in risk assessments. In the literature the uptake of toluene has been estimated to be 40-60% of the total amount inhaled, 71,72 which would reduce the estimated doses by half. At home, people are exposed to much lower toluene concentrations, although the RfC for toluene (0.38 mg/m<sup>3</sup>) can be surpassed in homes in worst-case scenarios (Figure 3). While we only considered one, but a prominent source of toluene, other emission sources might also contribute to indoor concentrations, increasing the actual total toluene concentration to which people are exposed. Examples are toluene emissions from materials in new homes, and painting and decorating.<sup>30</sup> As a consequence, long-term health effects may not be limited to only susceptible persons.

The unknown likelihood of parameter values and their combination in the exposure model did not allow carrying out a robust uncertainty analysis. However, the results of the

sensitivity analysis confirmed that toluene exposure tends to be higher in newsstands than in residences (Figure 5). It was shown that a critical parameter in the model is the exposed surface area of the magazines. Assuming the entire surface of a magazine is exposed to ambient air, an almost complete volatilization (>90%) of toluene would occur during production and use (16 days, Figure 2). As a consequence, much higher indoor concentrations would have been calculated by the models for newsstands and for homes. In reality, a very limited part of the magazines is exposed to the air because they are closed most of the time and thus retain the toluene. Therefore, we assumed that 60% of the toluene is still in the printed matter once the magazines are disposed. The resulting modeled concentrations are in agreement with the measurement results but are influenced by numerous additional parameters. The consumer scenarios show a large variability of possible exposure to toluene, because of the many different reading habits and living conditions of the general public. Quick disposal and hence limiting the number of magazines lying about at home and adequate ventilation can reduce the toluene exposure substantially (Figure 5). Occupational exposure can be limited by installing ventilation systems close to the toluene emission sources, by the adoption of activated carbon filters, or more difficult, by reducing the toluene content in the ink.

LCA and RA results provide two perspectives on the risk and human health impacts of toluene emissions indoors. While the individual risk quotients of the RA are at least 2 orders of magnitude higher in the worker scenarios compared to the consumer scenarios, the LCA results highlighted the importance of the consumer stage regarding the total human health impacts of a magazine. RA works with threshold values, suggesting that there is no effect below a certain pollutant dose. In contrast, LCA adds linearly a marginal human toxicity impact per additional emitted toxicant, arguing that even a small increase in toxic burden may affect human health on a population basis. Moreover, LCA accounts for a vast amount of emissions in the life cycle of printed matter and juxtaposes their effects in relation to each other. Therefore, LCA provides a more holistic assessment than RA but usually lacks spatial, temporal, and legal threshold information. This is complemented with RA which focuses foremost on single substances and individual, absolute thresholds levels. Short and long-term effects are commonly determined by complex investigations that account for, for example, reversibility, synergistic effects, and nonlinear dose-response relationships. Margins of safety are accounted for and vary between countries, explaining the variety of different (occupational) threshold levels. Local information is also incorporated into the RA to determine site specific health risks. All these fundamental differences promote the combination of both methods for holistic analyses of products or services in order to provide multifaceted answers which would not be possible by working in silos. This case study of toluene in printed matter which includes the development of indoor specific assessment data provides an ideal example of such a methodological combination.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Additional data tables as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### **Notes**

The authors declare no competing financial interest.

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