Non-professional paint stripping, model prediction and experimental validation of indoor dichloromethane levels

Abstract We have experimentally quantified exposure to dichloromethane during non-professional paint stripping and validated the mathematical paint exposure model of van Veen et al. (1999). The model innovates the prediction of the dichloromethane evaporation rate and room concentration by accounting for transport in the paint stripper matrix. The experiments show that peak concentrations range from 600 to 1600 mg/m³, increasing to 2000 mg/m³ when direct sun radiation increases evaporation. A naive model prediction, using a priori parameter values from the experimental set-up and a previous experiment with alkanes, accurately predicts the upper range of the experimental values, but overpredicted four out of six experiments. Statistical fit of the two paint stripper layer parameters to the experimental data resulted in a good coincidence of predicted and experimental data. Model and experiment indicate that 10–30% of dichloromethane is immediately available for evaporation.

Introduction

Consumer products have long been recognized as important indoor sources of chemicals, some containing large amounts of volatile organic compounds. The use of consumer products with volatile components is expected to temporarily increase the indoor concentration of chemicals (Otson et al., 1981; van Veen et al., 1999; Wallace et al., 1987). Paint stripper is a regularly used product and many brands use dichloromethane as main ingredient (Otson et al., 1981; Riley et al., 2000). Although dichloromethane attracted much attention because of (near) fatal occupational accidents (Hall & Rumack, 1990; Shusterman et al., 1990) or surprisingly high peak levels (Anundi et al., 1993), hardly any studies on non-occupational exposure have been published (Girman & Hodgson, 1986; Hodgson & Girman, 1987; Riley et al., 2000).

The present study was initiated to validate a previously developed painting model (van Veen et al., 1999) for highly volatile chemicals and to predict risk during non-professional use of dichloromethane as paint stripper. The painting model has been added to the CONSEXPO package of consumer exposure models (van Veen, 1997). The study was started with two questions: in general how the paint model of van Veen et al. (1999) behaves for chemicals as volatile as dichloromethane and specifically what are the risks of non-occupational paint stripping with dichloromethane for consumers. We set up a paint stripping experiment to answer the above questions and to compare experimental results with model predictions. We recruited...
volunteers to perform the paint stripping, simulating a realistic, non-occupational situation for the use of the paint stripper.

**Materials and methods**

**Experiment**

Six volunteers were asked to apply a commercially available paint stripper to a surface of 1.28 m² by brush. We weighed out 400 g paint stripper in advance. The volunteers were instructed to apply all paint stripper onto the horizontal surface in their own pace, aiming at a uniform layer. The layer appeared to be a few millimetres thick after application. After application, the volunteers were instructed to stay in the room and walk around for 60 min. This is sufficiently long to make comparisons with model predictions. At the end of this period, they were asked to scrape the paint stripper with brush and scraper from the surface. Then, the volunteers left the room and the stripped surface and the temporary floor covering was taken out of the room to remove all dichloromethane sources. Two experiments were performed subsequently on a single day. In between experiments, the room was thoroughly ventilated until background level was reached.

Dichloromethane concentrations were measured at a single point at 1.60 cm height by infrared spectrometry (Miran, Foxboro Company, Foxboro, MA) and logged onto computer every minute. After 60 min, when the surface was removed from the room, the residual dichloromethane in room air was used to measure the ventilation rate of the room. As all sources were removed from the room, the decrease in dichloromethane concentration is directly related to ventilation rate via its exponential decrease.

Table 2 lists the parameters that could directly be measured from the room or had to be assumed based on van Veen et al. (1999). The duration of application was timed with a stopwatch. The start signal was given by the study director, the stop signal by the applicant. The applied amount of paint stripper was measured by weighing out the can before and after application.

**External exposure model**

The model described by van Veen et al. (1999) and van Veen (1997) was used to describe the paint stripping. The model is graphically described in Figure 1. In principle, the product is applied as a thin layer onto a surface and left to dry thereafter. The product layer is subdivided into two layers to simulate diffusion in the product layer. The chemical compound leaves the product by evaporation and leaves the room by ventilation. The model describes exposure during and after application in a single room.

The three parameters describing the layered paint stripper matrix are difficult to measure, being the diffusional exchange rate between the layers, the relative size of the layers and the molecular weight of the matrix. We first applied the parameter values that worked well in the paint experiment of van Veen et al. (1999). We applied model sensitivity analysis to study model behavior as a function of these parameters.

The ACSL program was then used to statistically fit the paint stripper layer parameters to the experimental results. Because the molecular weight of the matrix appeared to be a very insensitive parameter, it was not taken into account in the fit procedure. Least squares fit was used to fit the fractional size of the upper layer and the exchange rate. The initial room concentration during fit was set to the measured initial concentration. The part of the concentration time series during removal of paint stripper, typically from 55 min after start, was omitted in the fit procedure. The fit for experiment 2a and 2b was only made for the first 30 min of the time series. Thereafter, the measured concentration quickly increased by incoming solar radiation, which is beyond the processes contained in the model.

**Results**

**Experimental results**

The experiment results in a stereotype pattern of the dichloromethane concentrations on days 1 and 3, while day 2 deviates in showing increasing concentrations after application (Figure 2a). During the day 1 and 3 application, concentrations quickly rise to levels between 600 and 1600 mg/m³. After the actual application, concentrations very slowly decline. At the moment of paint stripper removal, approximately 55 min after starting the experiment, concentrations increased again, adding 150–250 mg/m³ to the concentration before paint stripper removal. The measurements of day 3 showed sudden dips which were traced to a mismatch...
between Miran and data logger. Visual inspection of the output on Miran itself confirmed the main concentration profile. The concentrations on day 2 show increasing concentrations after actual application (Figure 2a). During this day, the first experiment had sun radiation on part of the surface, while indoor temperature was higher than on the other days.

Experiment specific parameters were measured during paint stripping (Table 2). The volunteers applied 372 g (s.d. 20.04) of paint stripper and left 26 g (s.d. 21.1) in the can, using on the average 94% of the presented amount. To apply the paint stripper, the volunteers needed 8.0 min (s.d. 4.20). The ventilation volume of the test room amounted to 0.25–0.3 air changes per hour during days 1 and 2. During day 3, ventilation was enhanced by opening a window 3 cm. The ventilation volume increased to 0.5–0.75 air changes per hour.

Comparison between experiment and model

The exposure pattern is reproduced by the model using initial parameter settings (Tables 1 and 2) at the level of the highest measurement series at experiment 1b (compare Figure 2a with 2b). The other experimental results are a factor of 1.5–2.5 lower than their model prediction. The increasing concentrations during experiment 2a and 2b were not reproduced by the model using the initial settings.

In order to explain the deviations between model prediction and experiment, we analyzed the model for the three parameters that could not be directly measured in the experiment, the fractional size of the upper layer, the exchange rate within the layers and the molecular weight of the matrix. These parameters define the paint stripper matrix. We expected that the matrix determines exposure because it restricts dichloromethane availability. The molecular weight of the matrix appeared to be a very insensitive parameter in the model because any value between 10 and 500 gives equal model output.

The relative size of the layers, in particular the size of the upper layer appears to determine the peak level just after application (Figure 3). Further analysis showed

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Duration of application (min)</th>
<th>Amount stripper used (g)</th>
<th>Temperature (°C)</th>
<th>Ventilation volume (l/h)</th>
<th>Ventilation rate (m³/h)</th>
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</thead>
<tbody>
<tr>
<td>1a</td>
<td>15</td>
<td>364</td>
<td>22.5</td>
<td>0.3107</td>
<td>14.81</td>
</tr>
<tr>
<td>1b</td>
<td>11</td>
<td>336</td>
<td>22.5</td>
<td>0.2981</td>
<td>12.30</td>
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<tr>
<td>2a</td>
<td>7</td>
<td>376</td>
<td>26 (sun on surface)</td>
<td>0.2901</td>
<td>13.82</td>
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<tr>
<td>2b</td>
<td>6</td>
<td>378</td>
<td>25</td>
<td>0.2576</td>
<td>12.28</td>
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<tr>
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<tr>
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<td>386</td>
<td>23</td>
<td>0.7473</td>
<td>35.61</td>
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</table>
that concentrations depend almost linearly on the relative size of the upper layer. Tripling the size of the upper layer, as in Figure 3, nearly triples dichloromethane concentrations. The diffusional exchange rate determines the time course of concentration after the peak. High exchange rates cause concentrations to rise in time by enabling rapid replenishment of dichloromethane in the upper layer. Low exchange rates cause concentrations to decrease, indicating insufficient replenishment of dichloromethane in the upper layer.

Fractional size of the upper layer and exchange rate in the layers were statistically fit to the experimental data to achieve their best fitting value (Table 3). The fractional size of upper layer varies between 0.2 and 0.3 for the experiments on day 1, while it is 0.1 for all other experiments. The exchange rate varies between 0.23 and 0.36 for the experiments on days 1 and 3. It is 0.44–0.85 on day 2, where room temperature was higher and the first experiment suffered from direct radiation on the paint stripper.

Sensitivity analysis of room size and ventilation rate

The sensitivity of the model outcomes for the parameters room size and ventilation rate is shown in Figure 4. The analysis was based on the parameter values derived for experiment 1b (Tables 1 and 2). As one parameter was varied, the other was fixed at its value in experiment 1b. Mean predicted dichloromethane concentration decreases with increasing room size and ventilation rate. Surprisingly, the effect of room size is stronger than that of ventilation rate below 50 m³ room size and 50 m³/h ventilation rate. Decreasing room size causes the ventilation volume (ventilation rate divided by room size) to increase, while decreasing ventilation rate has the opposite effect. The sensitivity analysis shows that the effect of decreasing room size, as initial volume of distribution,
is stronger than the effect of increasing ventilation volume.

Discussion

The experiment was started with two questions, in general how the exposure model of Van Veen et al. (1999) behaves for chemicals as volatile as dichloromethane and specifically what are the risks of non-occupational paint stripping with dichloromethane for consumers. To start with the latter question on paint stripping, the experimental results indicate that dichloromethane concentrations of 600–1600 mg/m³ can be expected during paint stripping in residential, low ventilation rooms. During scraping the stripper of the surface, levels increase with 150–250 mg/m³, as also observed by Girman and Hodgson (1986) and Hodgson and Girman (1987). When the stripped surface was heated by sun rays, levels increased to 2000 mg/m³. These levels agree with the 0–60 min Time weighed average (TWA) levels of 750–2530 mg/m³ in an unventilated room reported by Otson et al. (1981). It also agrees with peak levels of 400–1200 mg/m³ for days 1 and 3, in agreement with the higher temperatures that day. During experiment 2a, sun rays directly heated the surface in the second half of the experiment, accounting for the quick increase in dichloromethane concentrations in the second half. This part was not used for the fitting and the exchange rate is expected to be larger than 0.85/min during the second half. The fractional size of the upper layer is 0.1 for days 2 and 3, while it is 0.2–0.3 for day 1. An explanation might be the duration of application, which is 4–7 min during days 2 and 3, while it was 11–15 min on day 1. During slow application, more of the paint stripper matrix is apparently exposed to air. In conclusion, more dichloromethane is expected to be released during slow than during quick application.

The question is if the model can generally be applied for exposure assessment of all types of paint stripper. The critical question is whether all paint strippers make 10–30% of the total amount of dichloromethane directly available for evaporation. If more is available, the model will underpredict exposure. In agreement with our results, Riley et al. (2000) assume that 25% of the dichloromethane immediately evaporates, and find a good fit between predicted and observed peak values. A second question is if the model would be able to predict exposure to other chemicals from paint stripper. Exposure to chemicals that have a comparable vapour pressure might be predicted by the parameters as presented here. Chemicals with a much lower vapour pressure might be better predicted with the parameters described by van Veen et al. (1999), where n-decane was the subject of measurements.

In conclusion, the model presented by van Veen et al. (1999) could successfully be applied to paint stripping. The model fit to the experimental data indicates that 10–30% dichloromethane is directly available for evaporation. This amount, divided by room size, approximates the observed peak level.

References


Experimental validation of indoor dichloromethane levels


