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Evidence of indoor sinks for formaldehyde through the field measurements using passive flux sampler and mass balance

Herve Plaisance¹ · Alodie Blondel² · Valerie Desauziers¹ · Pierre Mocho³

Abstract

A measurement campaign was conducted in 24 student rooms where formaldehyde emissions from all the indoor surfaces were measured using a passive flux sampler (PFS) parallel to monitoring of indoor and outdoor concentrations as well as the assessment of air exchange rate. Two mass balance models were used to predict indoor concentrations basing on input data recorded during this measurement campaign. The first model only takes into account the total emission from the indoor sources and the incoming and outgoing flows of compound brought by the air exchange rate. The second model added to these terms a further component related to the overall rate of removal processes (or “indoor sinks”) which was assessed in these same rooms during a previous field test campaign. A good agreement was found between the concentrations calculated by the model with the component relative to indoor removal processes and the measured concentrations. On the other hand, the predicted concentrations with a first model tend to highly overestimate the measured concentrations by a factor 1.9 on average. Apportionment of formaldehyde inputs and losses in the rooms was estimated and discussed. The results highlighted that indoor removal processes are a component to consider for formaldehyde budget indoors.

Keywords Formaldehyde · Building and furnishing materials · Indoor sources · Material emissions · Modeling

Introduction

Formaldehyde (HCHO) has been of special concern as an indoor air pollutant because of its abundance due to numerous indoor sources and the adverse health effects associated with the exposure to HCHO (Salthammer et al. 2010; Weschler 2009). HCHO emissions by indoor materials correspond to a major contribution to indoor contamination.

The indoor levels of HCHO in homes, schools, and work offices are generally in the range of 10–90 $\mu\text{g m}^{-3}$ (Langer et al. 2017; Dassonville et al. 2014; Mandin et al. 2017) while

the outdoor levels are typically 1–5 $\mu\text{g m}^{-3}$. However, the air/material exchanges on interior surfaces appear to play an important role in mass balance of HCHO indoors (Plaisance et al. 2013; Poulhet et al. 2014). Materials can act as HCHO sinks at first, then become emission sources for years when the environmental conditions are favorable to the emission process. Some studies (Liu et al. 2009; Xu et al. 2012; Xu and Zhang 2011) showed that the sink effect for HCHO on indoor materials (wallboards and carpets) increases slightly with the increase of humidity and its magnitude is higher compared to other compounds of nearby molecular weight (Plaisance et al. 2013). The mechanisms behind the sink effect for HCHO are not fully known. Many authors suggested that a fraction of HCHO may be transferred in water film formed on the material surfaces under the higher-humidity condition in relation to the highly water-soluble nature of compound (Xu et al. 2012). On the other hand, Ye et al. (2014) showed that the mass transfer of HCHO in some selected polymers could be partially irreversible. Indeed, even if the ATR-FTIR analysis did not reveal any formation of polymerized forms like paraformaldehyde on the material surfaces exposed to HCHO, it revealed the formation of aliphatic acids at 1734 cm^{-1} , suggesting that there is an irreversibility of the adsorption process that could

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be due to oxidation. The authors concluded that the observed mass-transfer irreversibility could be caused by formaldehyde molecules binding or reacting with the polymer matrix by chemisorption and that at least a part of the chemisorption processes were reversible.

Reactions in indoor air and on the indoor surfaces may act as secondary sources and sinks of HCHO. The reaction of unsaturated compounds (e.g., alkenes, terpenes) with O_3 was identified as a way of production of HCHO indoors (Weschler and Shields 1996). This production of HCHO was particularly highlighted in the cases of significant introduction of reactive chemicals (O_3 , NO_x , and organics) most often linked to occupant activities such as cleaning, cooking, or smoking (Weschler and Carslaw 2018). Impact of indoor chemistry on the potential formation of HCHO was evaluated by Mendez et al. (2015) according to different realistic scenarios and concluded that oxidation processes contribute with 1–11.2% to the total emission. Concerning the reactions on the indoor surfaces, secondary emission of HCHO was identified from carpets containing unsaturated compounds exposed to low O_3 concentrations of 30 to 50 ppb. The increase in the HCHO concentration induced by these reactions remains low around +2 ppb in the 20- m^3 chamber (Weschler 1992). Recent photocatalytic indoor wall paints incorporating modified TiO_2 to work as a catalyst under indoor daylight or artificial light were developed. Organic binders like acrylic blends, vinyl acetate, styrene, and unsaturated fatty acids, which are also sensitive to photoreactions, are typical constituents of wall paint. Contrasted results on the action of sink or source of these paints for HCHO were obtained depending on the experimental conditions and should be deepened (Salthammer and Fuhrmann 2007).

This paper examined the removal rate of HCHO in indoor air from the application of two mass balance models to data of on-site measurement campaign carried out in 24 unoccupied student rooms. In the absence of potential sources associated with occupant activities, only HCHO amount released from materials were considered. In this campaign, the HCHO emission rates from the indoor surfaces of rooms were measured using a passive flux sampler (PFS) in parallel to monitoring of indoor and outdoor concentrations and the measurements of air exchange rate. The contribution of the sink effect to HCHO budget in indoor air will be estimated by the comparison between the prediction of two simple models, one with and the other without the term relative to indoor removal processes. This paper complements two previous articles (Blondel and Plaisance 2011; Plaisance et al. 2013) on this measurement campaign providing a view of HCHO inputs and loss apportionment in the rooms. Previous field studies of Shinohara et al. (2007, 2009) using PFS allowed to identify and rank the indoor sources, but the number of sampled rooms was insufficient to investigate the contribution of sinks to HCHO indoors.

Materials and methods

Description of sample sites and measurements of environmental factors

Measurement campaign was carried out from September 2009 to March 2010 in 24 unoccupied rooms belonging to three student residences. The buildings are close to each other in a radius of 500 m. They are located in the city center of Douai, a small French city of 40,000 inhabitants. Except the contribution of known outdoor sources of HCHO (urban heating and road traffic), no major outdoor source was identified nearby the buildings.

This was confirmed by the low outdoor HCHO concentrations measured in this campaign comprised between 0.7 and 5.7 $\mu g m^{-3}$. The selected rooms were unoccupied, and there was no HCHO emission from combustion and related activities like tobacco smoking, cooking, and fireplaces during the sampling period. The rooms are filled with electric heating.

Eight rooms per residence were selected for sampling. A schematic of these rooms is shown in Fig. 1. Their volume and surface area are 26 m^3 and 11 m^2 on average. The dates of building construction are 1998, 1975, and 1991 for H1, H2, and H3 residences, respectively. The H2 residence was renovated in 2003, the walls and ceiling were painted and furniture changed in all the rooms. The floor covering is linoleum or parquet. The walls are plasterboard that has been papered with painted fiber cloth. The ceiling is painted cement. Each room has a window, a front door leading out into a corridor, and an inner door separating the room from the bathroom. These rooms are furnished by a closet in plywood, a writing desk, a bed, and a chair in particleboard. The furniture dates are from 1998, 2003, and 1991 for the H1, H2, and H3 residences, respectively. Each sampled room has an exhaust ventilation system located in the bathroom. The incoming air in the room mainly comes from outdoors through a vent hole placed on the window frame and for a minor part from the corridor through the leakages of the front door. This minor part is not considered in the mass balance of HCHO which are done afterwards. A multifunction probe was used to continually monitored and recorded temperature and absolute humidity in the rooms during sampling. The door and window were kept closed for at least 3 days before the sampling period.

Air exchange rate and air flow incoming into the room

The air exchange rate was determined by the injection of CO_2 in the room and follow-up of its decay according to the standard method ASTM E 741-00 (2006). CO_2 was injected at the center of the room by means of a compressed gas cylinder of pure CO_2 (Air Liquide), and a fan was used to mix air and achieve an initial uniform concentration in the room up to around 3500 ppm. Temporal decay of CO_2 concentration is continuously monitored for 2 h by means of a CO_2 probe (Data logger Testo term 400,

CO₂ sensor 0632.1240, Testo, France). Here, CO₂ is considered as an inert gas, and therefore, the concentration decay in the room follows a first-order kinetic only attributable to air exchange. Solving this first-order equation leads to assess the air exchange rate (expressed in h⁻¹) given by Plaisance et al. (2013). Air exchange rate was assessed twice in each room, the days before or after the HCHO sampling period.

Measurements of indoor emissions

The HCHO emissions from building and furnishing materials were measured on-site using a PFS previously developed and described in Blondel and Plaisance (2010). Its performance for the measurement of HCHO emissions from materials was documented in this previous article. PFS consists of a tinted glass Petri dish (inner diameter 35.4 mm, depth 20 mm) at the bottom of which is put a quartz fiber filter coated with 2,4-dinitrophenylhydrazine (DNPH). HCHO emitted from the material diffuses through the air into the sampler volume following the concentration gradient that develops between the material and the filter area. HCHO is trapped by reaction with DNPH doped on the filter.

The formed DNPH-formaldehyde hydrazone was then extracted from the filter using acetonitrile (HPLC grade, Waters, France) and analyzed by high performance liquid chromatography (Waters 2695 HPLC, Waters, France). The sampled HCHO mass was converted into the emission rate using the empirical linear relationship between the passive sampler and emission test chamber (used as reference method) which was previously set up analyzing a large selection of indoor materials. Detection limit was estimated to 1.2 µg m⁻² h⁻¹ for a 6-h sampling time and the precision of replicate measurements to 7.8% (expressed in relative standard deviation). The details on the conservation tests, analytical conditions, conversion of collected HCHO mass into emission rate, and performance of PFS are given in previous articles (Blondel and Plaisance 2010; Blondel and Plaisance 2011; Plaisance et al. 2014).

In each room, 13 to 15 passive samplers were placed on all the materials present in the indoor environment to assess their emission rates (Fig. 1): the floor, walls, ceiling, desks, doors, closets, shelves, bed, and chair. Around 20% of the emission rate measurements were above the detection limit of 1.2 µg m⁻² h⁻¹. These values were replaced by the detection limit. The surface area of each sampled material was systematically measured. The window and doors were maintained closed before each sampling for at least 12 h in order to attain a steady state of concentration and emissions.

Indoor and outdoor concentration measurements

The HCHO concentrations in each room and outdoors were simultaneously measured by the conventional active sampling of air through DNPH cartridges (Waters, WAT037500), according

to ISO 16000-3 (2002). The sampling device consisted of a pump (N86KN18, KNF, Germany), a mass flow meter, and a DNPH cartridge. The sampling flow rates were regulated to 200 mL min⁻¹ and checked before and after each pumped sample with a certified flowmeter (DryCal DC-Lite). The sampling period was 6 h and coincides with the one of PFS. The indoor sampling point was made at the height of around 1.2 m, in the middle of the room. The outdoor sampling point was set near the window air entry at least 20 cm from the surfaces. These cartridges were eluted with acetonitrile and analyzed by HPLC according to the same method for analysis of PFS. Detection limit was estimated to be 0.2 µg m⁻³ for the sampling conditions described above.

Mass balance models

The concentration of an indoor air pollutant is a function of numerous processes including indoor emissions, exchange with outdoors, deposition to indoor surfaces, removal by filtration, and indoor chemistry. The most approaches to modeling pollutant concentrations in indoor air take into account a reduced number of the main production and loss processes acting on the behavior of chemical indoors. Here, a simple one-box model based on mass conservation was used to estimate the part of indoor sinks to HCHO mass balance. The room is assumed to be a well-mixed chemical volume and the potential input of secondary pollutants produces, for example, by reactivity is not considered in this simple approach. Two production processes were considered: the indoor emissions evaluated by PFS measurements and the flow of outdoor contaminants incoming into the indoor environment evaluated by the air exchange rate of the room and outdoor concentrations. Two loss processes were taken into account: the flow of indoor air out of the interior environment and the net removal rate of indoor contaminants induced by various removal processes (or indoor sinks) that occur in the interior environment. The mass balance can be expressed by the differential equation as follows:

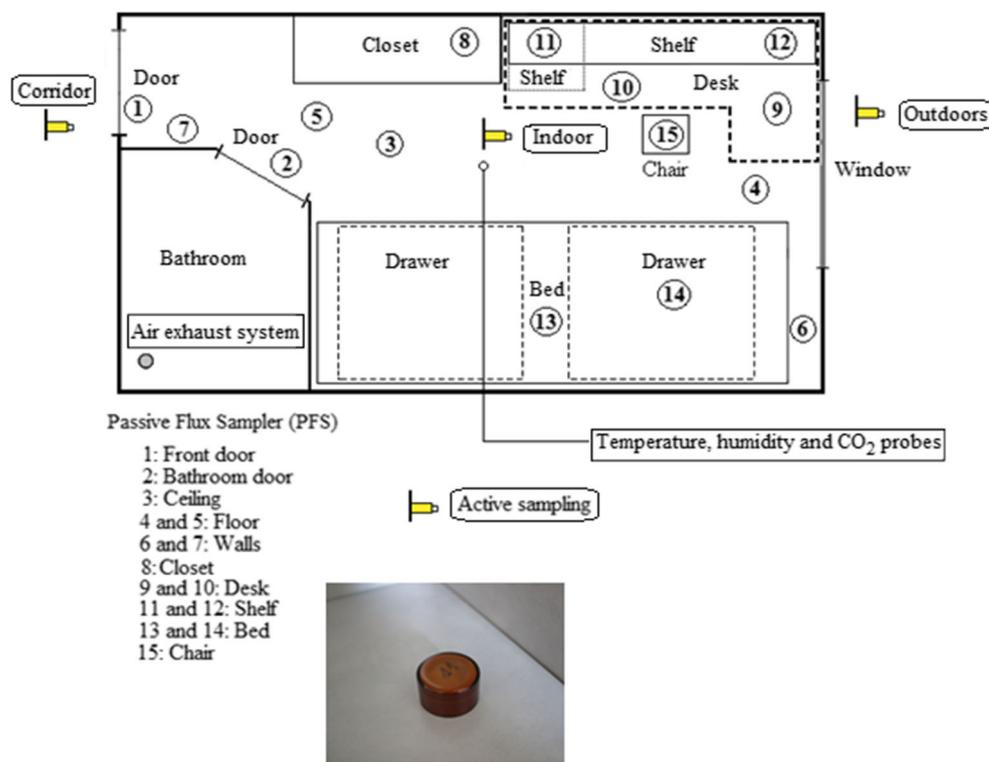
$$dC = PaC_{\text{ext}}dt + \left(\sum_i Q_i \cdot S_i / V \right) dt - (a + k)Cdt \quad (1)$$

where C is the indoor contaminant concentration (µg m⁻³), t is the time (h), C_{ext} is the contaminant concentration of air coming from outdoors (µg m⁻³), P is the fraction of outdoor contaminant that penetrates the shell (unitless) ($1 = 100\%$ penetration), a is the air exchange rate (h⁻¹), Q_i is the i th indoor source emission (µg m⁻² h⁻¹), S_i is the surface emission of the i th indoor source (m²), V is the room volume (m³), and k is the net rate of removal processes other than air flow (h⁻¹).

Assuming the system is in a steady state, C , C_{ext} , P , a , k , and Q are constant and Eq. 1 can be solved for C to give:

$$C = \frac{aP}{a+k} \cdot C_{\text{ext}} + \frac{\sum_i Q_i S_i}{V} \cdot \frac{1}{a+k} \quad (2)$$

Fig. 1 Schematic of room (layout view) and sampling design and a picture of PFS



Previous studies on the relationship between indoor/outdoor HCHO concentrations (Lewis and Zweidinger 1992; Liu et al. 2006) showed that there is no significant losses when the outdoor compound penetrates the building envelop and enters into the room. In consequence, a value of $P=1$ was considered in this study. To solve C for each sampled room, it requires knowing the decay rate constant k for HCHO indoors. This constant corresponds to the overall contribution of all the removal processes in indoor environment other than that of the air exchange rate. Field experiments were carried out in these same rooms to assess this k constant by simultaneous injection of HCHO and CO_2 and monitoring the decay of two compound concentrations in the room (Plaisance et al. 2013). A decay rate constant k of $0.34 \pm 0.07 \text{ h}^{-1}$ was deduced from this study that is consistent with the k value of $0.40 \pm 0.24 \text{ h}^{-1}$ found previously by Traynor et al. (1982). The decay rate of HCHO is higher compared to other compounds of near-by molecular weight and comparable to that of fine particles having a diameter $< 0.5 \mu\text{m}$ (Nazaroff and Cass 1986). As described by Plaisance et al. (2013) and modeled by Mendez et al. (2015), the reactions of HCHO with ozone and OH and NO_3 radicals and photolysis in indoor air are too slow to be the cause of this removal. Several studies (Liu et al. 2009; Xu et al. 2012; Xu and Zhang 2011) tend to demonstrate that the main origin of this loss is the interaction of

HCHO with interior surfaces and its magnitude is strongly increased under high humidity conditions. Consequently, a decay rate constant k of 0.34 was considered in Eqs. 1 and 2 and can be expressed as a full deposition velocity of $0.092 \pm 0.019 \text{ m h}^{-1}$ considering the ratio of the room volume to the total area covered by materials ($\frac{V}{S} = 0.27 \text{ m}$). In this case, the k value and deposition velocity cover all removal processes occurring on the surfaces including sorption and reactions.

The contribution of the indoor sinks was assessed by comparing the results of the application of mass balance with and without the k constant (Eq. 2).

Results and discussion

Indoor concentrations, indoor emissions, and air exchange in the rooms

Table 1 summarizes the results obtained in the 24 student rooms and reports the HCHO inputs (material emissions and air inlet). The indoor HCHO concentrations are comprised between 6.6 and $49.9 \mu\text{g m}^{-3}$. These concentration levels are consistent with those reported in France as part of a national campaign carried out by the Observatory on Indoor Air Quality (OQAI 2006) in 554 dwellings where the median concentration was $19.6 \mu\text{g m}^{-3}$ with a range from 1.3 to $86.3 \mu\text{g m}^{-3}$. The mean

Table 1 Summary of measurements obtained in the three student residences and apportionment of HCHO inputs

Building	Air exchange rate (a), temperature (T), relative humidity (HR), and outdoor HCHO concentration (C_{ext}) Mean (min–max)	Indoor HCHO concentration ($\mu\text{g m}^{-3}$) Mean (min–max)	Highest HCHO emission rates ($\mu\text{g m}^{-2} \text{h}^{-1}$) in descending order Mean (min–max)	Sum of HCHO inputs $\sum S_i \times Q_i + a \times V \times C_{\text{ext}}$ ($\mu\text{g h}^{-1}$) Mean (min–max)	Apportionment of HCHO inputs
H1 ($n = 8$)	a (h^{-1}) = 0.52 (0.31–0.87) T ($^{\circ}\text{C}$) = 18.6 (15.0–22.0) HR (%) = 49 (38–60) C_{ext} ($\mu\text{g m}^{-3}$) = 2.3 (0.7–3.5)	17.9 (9.5–27.3)	Bathroom door 4.6 (1.2–7.9) Closet/shelf 4.5 (1.2–7.6) Bed 4.2 (1.2–9.4) Ceiling 3.7 (1.2–5.5) Walls 3.6 (1.2–7.5) Door 3.4 (1.2–6.7)	382 (150–579)	Closet/shelf 30% Walls 28% Ceiling 11% Air inlet 9% Floor 7% Other sources ($n = 6$) 15%
H2 ($n = 8$)	a (h^{-1}) = 1.36 (0.87–2.17) T ($^{\circ}\text{C}$) = 20.9 (19.0–22.2) HR (%) = 50 (24–82) C_{ext} ($\mu\text{g m}^{-3}$) = 3.1 (0.9–5.7)	10.9 (6.6–21.6)	Closet/shelf 4.3 (1.2–9.5) Ceiling 3.6 (1.2–8.6) Bed 3.5 (1.2–8.3) Desk 3.2 (1.2–6.4) Walls 2.7 (1.2–5.7)	393 (261–660)	Air inlet 27% Walls 26% Closet/shelf 18% Bed 8% Ceiling 8% Desk 5% Other sources ($n = 5$) 8%
H3 ($n = 8$)	a (h^{-1}) = 0.54 (0.35–0.91) T ($^{\circ}\text{C}$) = 23.3 (18.4–26.0) HR (%) = 40 (28–52) C_{ext} ($\mu\text{g m}^{-3}$) = 2.5 (1.3–3.6)	35.2 (14.3–49.9)	Bed 87.3 (21.3–131.3) Ceiling 10.1 (3.7–13.0) Bathroom door 9.2 (2.5–28.2) Walls 7.6 (1.2–11.6) Floor 5.3 (2.5–13.0) Desk 5.3 (1.3–12.1)	807 (327–1053)	Bed 32% Walls 25% Ceiling 14% Closet/shelf 12% Floor 7% Other sources ($n = 6$) 10%

concentrations found in the rooms of three residences are higher than the indoor air quality guideline value for a long-term exposure to HCHO fixed to $10 \mu\text{g m}^{-3}$ in France (ANSES 2007). The high concentrations found in the rooms of H3 residence are mainly explained by the presence of a strong emitter of HCHO (bed material) with high emission rates recorded from 21 to $131 \mu\text{g m}^{-2} \text{h}^{-1}$. The bed in the rooms of H3 residence mainly consists of plywood and has been set up in the rooms on delivery of the building, i.e., in 1991. After 18 years of setting up, the emission of the bed material remains high. Note also that the emission rates of other indoor surfaces (ceiling, walls, and floor) are higher in the rooms of H3 residence than in those of two other residences. This might be the result of transfer of a HCHO fraction emitted by the bed material to other surrounding indoor surfaces. Nevertheless, all the emission rates recorded in the rooms of H1 and H2 residences are low below $10 \mu\text{g m}^{-2} \text{h}^{-1}$. The HCHO inputs for the rooms of these two residences are similar, only the air exchange rate explains the difference in concentration. Outdoor concentrations are low ($2.5 \mu\text{g m}^{-3}$ in average). In consequence, the contribution of outdoor air to HCHO inputs remains low ($\leq 10\%$) in cases of rooms where there is the presence of a major indoor source (rooms of H3 residence) and of rooms with a low air exchange rate ($\sim 0.5 \text{h}^{-1}$) combined to low indoor emissions below $10 \mu\text{g m}^{-2} \text{h}^{-1}$ (rooms of H1 residence). Outdoor air can be a significant contributor to HCHO budget when the air exchange rate is high ($\sim 1.36 \text{h}^{-1}$) combined to low indoor emissions below $10 \mu\text{g m}^{-2} \text{h}^{-1}$ (rooms of H2 residence).

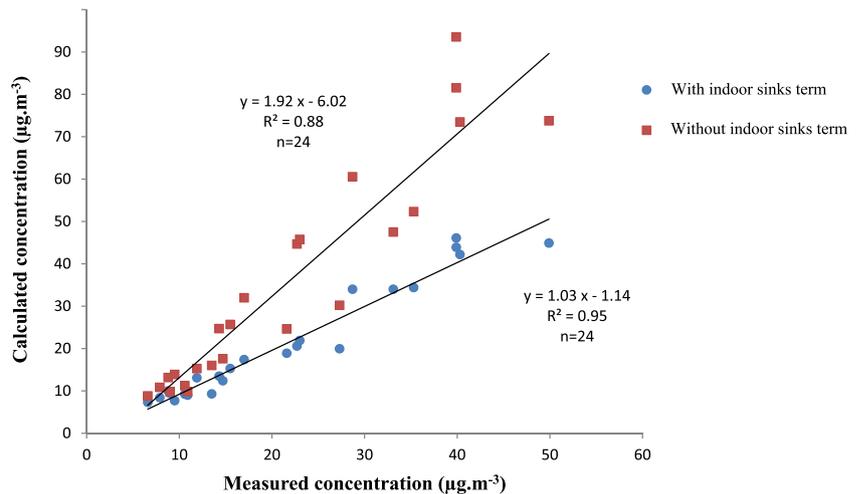
So, the HCHO concentration levels in the rooms are highly dependent on the characteristics specific to each building (emission levels of building and furnishing materials and air exchange rate). As shown here, the decrease over time of HCHO emission from wood-based material is often very slow and its impact on indoor concentration can be significant over many years (like the bed material in the rooms of H3 residence).

Comparison between the concentrations predicted by mass balance and the measured concentrations and HCHO loss apportionment

Equation 2 describing the mass balance of the room is used to calculate the indoor concentrations with and without taking into account the term k relating to indoor sinks. Figure 2 shows the comparison between the concentrations predicted by these two ways and the measured concentrations. A clear difference is observed between the two prediction methods. A good agreement is found between the predictions with the term k relating to indoor sinks and the measured concentrations. Twenty-two out of 24 values predicted with the term k have a relative deviation lower than -30% compared to the measured concentrations. There is no systematic bias between these two concentrations as shown by the slope close to 1.

On the other hand, the prediction without the term k relating to indoor sinks leads to an overestimate of the concentration by a factor 1.9 on average. The indoor sinks appear as a

Fig. 2 Concentrations predicted by mass balance with and without taking into account the term k relating to indoor sinks versus the measured concentrations



major component to consider in the budget of HCHO indoors. This result is consistent with several recent studies (Liu et al. 2009; Xu et al. 2012; Xu and Zhang 2011) on the sorption of HCHO which showed a high affinity and retention of this compound on the building materials.

Table 2 summarizes the apportionment of HCHO losses in the rooms of three student residences. The part due to indoor sinks represents from 24 to 41% depending on the type of rooms. For an air exchange rate of 0.5 h^{-1} typically encountered in indoor environments, this same part is about 40%. Mendez et al. (2015) evaluated the impact of deposition processes on HCHO concentrations in the indoor environment. The authors modeled 20 different scenarios and came to the conclusion that HCHO deposition processes contribute with 13–73% and a geometric mean of 27% to the total removal.

Previous works showed that vapor pressure (P_0) is a reasonably good predictor of the adsorption capability of volatile organic compounds spanning the mostly chemical classes on the materials (Plaisance et al. 2013). In this article, a relationship between the Neperian logarithm of k ($\ln k$) and the Neperian logarithm of P_0 was reported for about thirty volatile

organic compounds from the results of various field experiments. HCHO does not follow this overall relationship. The k value of HCHO should be close to zero when this relationship is used. This high sink effect for HCHO is not explained by its vapor pressure, suggesting that the process involved is not only physisorption for this compound.

Previous studies demonstrated that the material/air partition of HCOH for calcium silicate board (Xu and Zhang 2011), gypsum wallboards and carpets (Xu et al. 2012), and painted gypsum wallboard (Liu, 2009) increases with high humidity conditions. At the scale of a room, the field experiments (Plaisance et al. 2013) also showed that the first-order loss rate of HCOH also increases for high humidity conditions.

An assumption is that HCOH could be transferred in water film formed on the material surfaces in relation to its highly water-soluble nature. In aqueous phase, HCHO is hydrated to form methanediol ($\text{CH}_2(\text{OH})_2$) and then different polymerized forms like paraformaldehyde depending on concentration (Seyfioglu and Odabasi 2006; Allou et al. 2011; Hanoune et al. 2011). However, this assumption has not been confirmed experimentally, and these reaction products have so far not

Table 2 Apportionment of HCHO losses in the rooms of three student residences

Building	Air exchange rate (a), temperature (T), and relative humidity (HR) Mean (min–max)	Indoor HCHO concentration ($\mu\text{g m}^{-3}$) Mean (min–max)	Apportionment of HCHO losses
H1 ($n = 8$)	a (h^{-1}) = 0.52 (0.31–0.87) T ($^{\circ}\text{C}$) = 18.6 (15.0–22.0) HR (%) = 49 (38–60)	17.9 (9.5–27.3)	Air outlet 59% Indoor losses 41%
H2 ($n = 8$)	a (h^{-1}) = 1.36 (0.87–2.17) T ($^{\circ}\text{C}$) = 20.9 (19.0–22.2) HR (%) = 50 (24–82)	10.9 (6.6–21.6)	Air outlet 76% Indoor losses: 24%
H3 ($n = 8$)	a (h^{-1}) = 0.54 (0.35–0.91) T ($^{\circ}\text{C}$) = 23.3 (18.4–26.0) HR (%) = 40 (28–52)	35.2 (14.3–49.9)	Air outlet 61% Indoor losses 39%

been identified on the material surfaces exposed to HCHO. Ye et al. (2014) rather identified some oxidized forms like aliphatic acids on some polymers exposed to HCHO. These results suggest that there is the copresence of the reversible and irreversible fractions of HCHO molecules on polymer surfaces due to physisorption and chemisorption. Additional extraction/fluorimetry testing indicated that at least some of the chemisorbed formaldehyde on polycarbonate was reversible (Ye et al. 2014). It seems likely that several processes are responsible for indoor sinks of HCHO. More studies are needed to identify the reaction mechanisms involved, especially by the use of advanced physical analysis techniques for material surface.

Limitations of the study

The study and modeling are limited to the case of unoccupied indoor environments. There is no contribution of occupant activities known to be indoor sources of HCHO like tobacco smoking, cooking, and other combustions that are often present in indoor living spaces.

The rooms have a specific characteristic of having a high ratio of indoor surfaces to room volume equal to 3.7 m^{-1} on average. It is due to a larger amount of furniture in the room than in a usual room. This characteristic may favor the interactions between air and materials and raise the contribution of indoor sinks.

Another limitation is the study scale (room) that does not allow to determine the nature of removal processes involved. It is only possible to assess the overall impact of indoor sinks to HCHO budget at the scale of room. As shown in this study, the contribution of indoor sinks cannot be neglected.

Conclusions

The contribution of indoor sinks to HCHO budget was investigated by on-site measurements of emissions and concentrations carried out in 24 student rooms. Mass balance was calculated with and without term relative to indoor sinks. The results showed that it is required to consider the contribution of indoor sinks. Without term relative to indoor sinks, the prediction leads to a high overestimate of the concentration by a factor 1.9 on average compared to the measured concentration. Conversely, using a deposition velocity of $0.092 \pm 0.019 \text{ m h}^{-1}$ estimated by previous field experiments carried out in the same rooms corrects this deviation and a high level of agreement is achieved between calculated and measured concentrations. These results highlight the singular behavior of HCHO indoors with a high assumed retention of this compound on the building materials. Although the mechanisms behind the indoor sinks of HCHO are not fully known, this

study suggests that the process is not only physisorption for this compound as for a large majority of other VOCs.

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