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# Field investigation on the removal of formaldehyde in indoor air

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## A B S T R A C T

The development of indoor air quality models requires to take into account the indoor removal processes (or “indoor sinks”) as accurately as the indoor concentrations. Field experiments were conducted in residential rooms to assess the indoor decay rate constant and deposition velocity of formaldehyde and to investigate the nature of these removal processes. The indoor decay rate constant and deposition velocity were respectively found to  $0.34 \pm 0.07 \text{ h}^{-1}$  and  $(2.53 \pm 0.51) \times 10^{-3} \text{ cm s}^{-1}$ , indicating a high potential of depletion and therefore a low persistence of this compound in indoor environment. Considering only the impact of indoor sinks, a short indoor half-life of 2 h for formaldehyde was assessed. This high removal of formaldehyde indoors in comparison with other volatile organic compounds and its dependence with the absolute humidity suggest that the adsorption on the indoor surfaces is not the only loss process for formaldehyde. The transfer of formaldehyde to the aqueous films present onto the indoor surfaces and on the surface of airborne particles was proposed as a possible removal pathway in real indoor conditions and discussed.

### Keywords:

Indoor air

Formaldehyde

Volatile organic compounds

Indoor sinks

Sorption

Building materials

## 1. Introduction

Assessing the potential impacts of air pollutant exposure on human health requires an understanding of not only the range of indoor levels but also the contributions of sources and indoor sinks on the concentrations under typical household conditions. Different types of miniature emission chambers, like the passive flux samplers [1,2] or standard FLEC<sup>®</sup> emission cell coupled with an active sampling method [3] or with solid-phase microextraction [4] are now available for in situ measurement of the flux of organic compounds emitted from various kinds of indoor materials. In contrast, few data exist on the removal of organic compounds from indoor sinks. The improvement of the prediction of indoor air quality models requires a better characterization of indoor sinks and of their impact on the concentration levels in real indoor conditions [5].

Most approaches to modeling pollutant concentrations in indoor air take into account four basic physical/chemical processes that describe the behavior of chemicals in a building interior. Two of these processes increasing indoor concentration levels are the flow of outdoor chemicals into the interior environment and the rate at which pollutants are emitted by indoor sources. Two other

processes decreasing indoor contaminant levels are the flow of indoor air out of the interior environment and the net rate of removal processes (or “indoor sinks”). These latter processes include heterogeneous and gas-phase chemical reactions which may produce secondary compounds of concern; changes in gas-particle partitioning; and sorptive interactions between gases and interior material surfaces. Understanding these dynamic processes and their contribution are essential for predicting indoor concentrations.

To simply set in equation all of these processes, Dockery and Spengler [6] proposed as a first approach to use a single mass balance model. This model assumes that the building interior is a single and well-mixed chemical volume. The secondary pollutants produced, for example, in photochemical reactions are not described by this simple mass-balance approach. The mathematical expression for the change in mass concentration of indoor contaminant is:

$$dC = PaC_{\text{out}}dt + \frac{Q}{V}dt - (a + k)Cdt \quad (1)$$

where  $C$ : average indoor contaminant concentration ( $\mu\text{g m}^{-3}$ );  $C_{\text{out}}$ : outdoor contaminant concentration ( $\mu\text{g m}^{-3}$ );  $P$ : fraction of outdoor contaminants that penetrates the shell (unitless) ( $1 = 100\%$  penetration);  $a$ : air exchange rate ( $\text{h}^{-1}$ ),  $Q$ : indoor source strength, i.e., the mass released per unit time from all indoor sources ( $\mu\text{g h}^{-1}$ ); and  $V$ : room volume ( $\text{m}^3$ ) and  $k$ : net rate of removal

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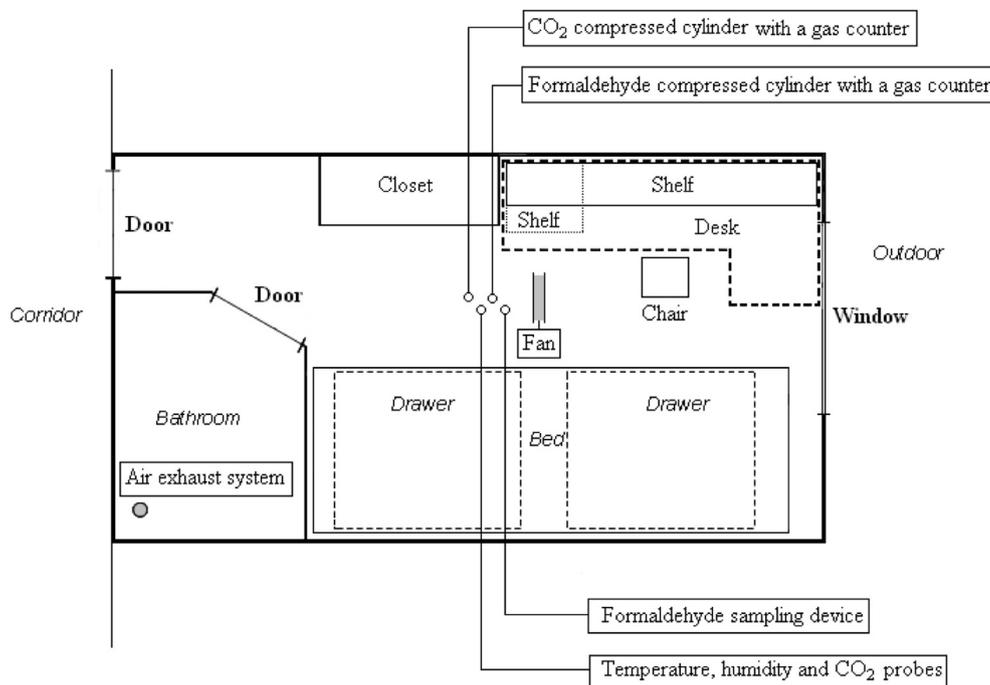


Fig. 1. Schematic of residential room (layout view) and instrumentation.

processes other than air flow, i.e., indoor decay rate constant ( $\text{h}^{-1}$ ) representing the sum of surface removal rate constant and reaction rate constant (both surface removal and reaction were assumed to follow the first order kinetics).

When a steady-state regime is achieved in the system, then  $C$ ,  $C_{\text{out}}$ ,  $P$ ,  $a$ ,  $k$  and  $Q$  are constant; equation (1) can be solved for  $C$  to give:

$$C = \left[ \frac{aP}{(a+k)} \right] C_{\text{out}} + \frac{Q}{V} \left[ \frac{1}{(a+k)} \right] \quad (2)$$

Data about indoor concentrations and application of mass-balance models suggest that for many pollutants, indoor sinks induce decay rates comparable to or greater than the air exchange rate [7]. Generally, the most reactive compounds have the highest decay rate constants, like ozone (from 1.44 to 2.6  $\text{h}^{-1}$ ) and nitrogen dioxide (from 0.8 to 1.3  $\text{h}^{-1}$ ) assuming a ratio Area of surfaces ( $A$ ) by room Volume ( $V$ ) equal to 2  $\text{m}^{-1}$  [7]. The  $k$  value of formaldehyde is poorly documented in the literature. Traynor et al. [8] reported a  $k$  value amounted to  $0.40 \pm 0.24 \text{ h}^{-1}$  ( $n = 5$  runs) deduced to the analysis of formaldehyde concentration decay from gas-stove emission experiments in an environmental chamber of high volume (27  $\text{m}^3$ ).

This value was largely used for indoor air quality modeling and numerous studies revealed that the formaldehyde concentration in real indoor air cannot be calculated only from indoor emission rates and air exchange rate. The concentration decay relative to indoor removal processes was taken into account to provide an accurate prediction of formaldehyde concentrations by modeling [9–11]. No data was reported to our knowledge about the assessment of this decay rate relative to indoor sinks in real indoor environments.

The objective of this study was to determine the decay rate constant for formaldehyde in several rooms by an experimental approach combining the measurement of air exchange rate and the follow-up of formaldehyde concentration decay in the rooms. The value obtained for this constant was discussed and compared with those of other indoor contaminants.

## 2. Experimental

### 2.1. Characteristics of rooms

The decay rate constant for formaldehyde was assessed in two similar unoccupied student rooms of a four-storeyed residence built in 1998. A schematic of these rooms is shown in Fig. 1. Their volume and surface area are 26  $\text{m}^3$  and 11  $\text{m}^2$ , respectively. The floor covering is linoleum. The walls are in sheet plaster that has been papered with painted fibre cloth. The ceiling is in painted sheet plaster. These rooms are furnished by a bed, a closet, a writing desk and a chair. The furnishing materials are plywood for the closet and particleboard for the writing desk, bed and chair. Each room has one window with an air entry, one front door leading out into a corridor and one inner door separating the room from the bathroom. Each room is filled with an air exhaust system located in the bathroom in continuous running during the field experiments.

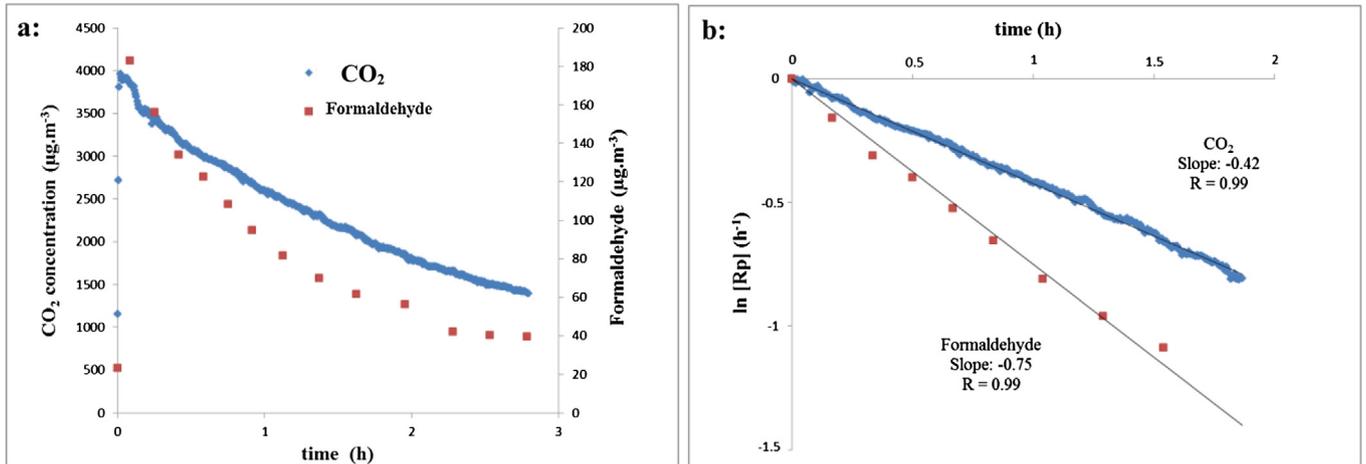
These rooms have as specific characteristic a high ratio of furniture area to the sum of building surfaces (sum of floor, walls, doors and ceiling) close to 0.8 by comparison with those of other indoor environments.

### 2.2. Instrumentation, protocol and calculation

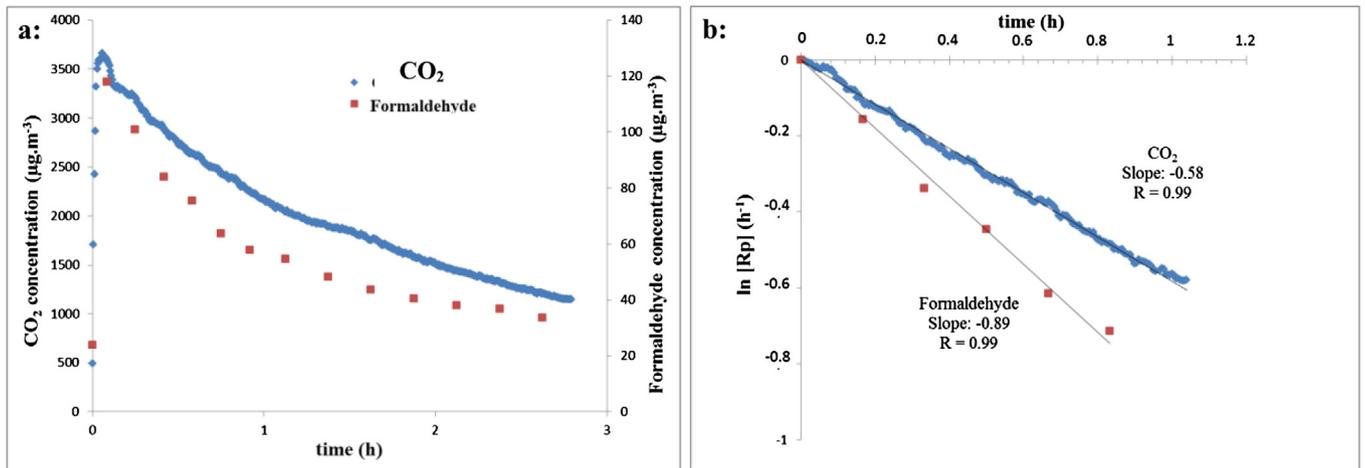
The measurement protocol was based on the simultaneous determination of air exchange rate ( $a$ ) and total rate of removal processes including air exchange rate ( $a + k$ ) in a room. The experiment was made in three steps:

Firstly, the injections of  $\text{CO}_2$  and formaldehyde were carried out at the center of the room at a height of approximately 1.2 m using a compressed cylinder of  $\text{CO}_2$  (at 99%) supplied by Air Liquide-company (Air Liquide, Loos, France) and another compressed gas cylinder containing 100 ppm of formaldehyde in nitrogen manufactured by Messer company (Messer, Mitry Mory, France). Some liters of each gas cylinder were injected using a gas counter in order to raise the  $\text{CO}_2$  and formaldehyde concentrations five to ten times.

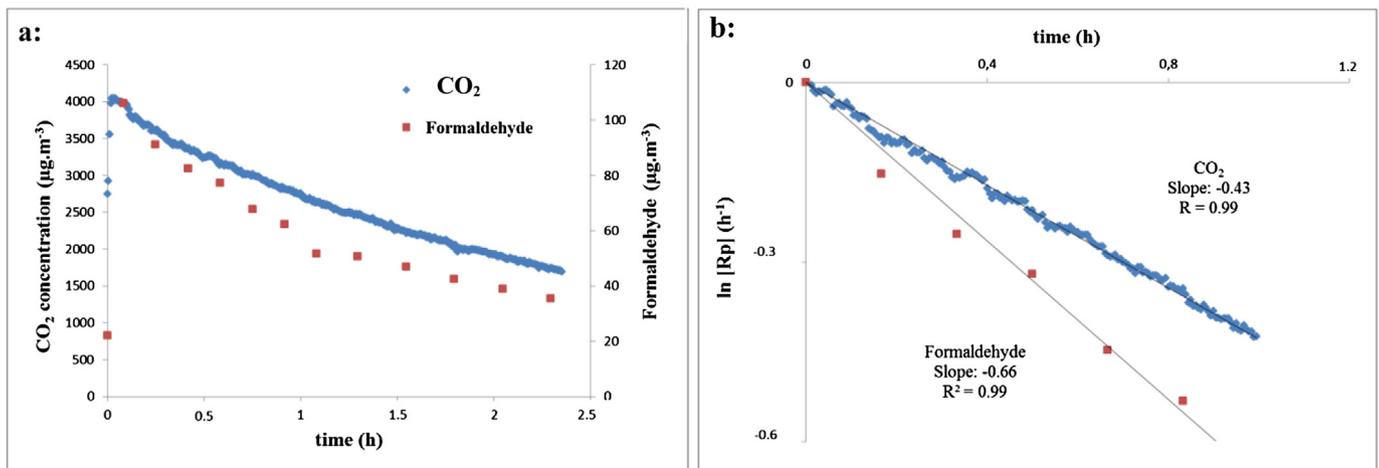
**Run 3:**



**Run 6:**



**Run 2:**



**Fig. 2.** Formaldehyde concentration versus time (a) and Neperian logarithm of Rp versus time (b) for three experiments. With  $R_p = (a + k)C - aC_{out}/(a + k)C_0 - aC_{out}$

Secondly, a fan was run in the room for 5 min to mix air and achieve uniform concentrations of CO<sub>2</sub> and formaldehyde.

Thirdly, CO<sub>2</sub> and formaldehyde were monitored for 3 h at the center of the room at a height of 1.2 m by means of a CO<sub>2</sub> probe (Data logger Testo term 400, CO<sub>2</sub> sensor 0632.1240, Testo, France) and a conventional DNP<sub>H</sub>-derivatization active method, respectively. For

formaldehyde, successive air samples were pumped through cartridges (Sep-Pack cartridges, Waters, Guyancourt, France) filled with silica impregnated with 2,4-dinitrophenylhydrazine (DNPH) producing hydrazone which itself was extracted with 5 mL of acetonitrile and analyzed by high performance liquid chromatography with UV detection at a wavelength of 365 nm. The sampling device

consisted of a pump (N86KN18, KNF, Germany), a mass flow meter (25068 SPF, MKS Instruments, Inc., Le Bourget, France) and DNP cartridges. More details on this method were given in Ref. [1]. The flow sampling rate was maintained constant to  $1 \text{ L min}^{-1}$  as recommended by the ISO 16000-3 standard [12] and checked before and after each experiment with a flow meter (DryCal DC-Lite) certified against the national reference standard of Laboratoire National d'Essais (LNE). The sampling duration was 10 min for the first hour and 15 min for the two following hours.

Temperature and relative humidity were continuously monitored and recorded by means multifunction probes (Datalogger Testo term 400 and sensor 0635.1540) during the experiments. The materials used for gas injection (gas counters and gas cylinders) as well as the device for monitoring of temperature, humidity and  $\text{CO}_2$  were left in the room during the tests. The sampling device of formaldehyde was placed outside the room. A sampling line through the air entry of window was set to allow a formaldehyde sampling at the center of the room.

The  $\text{CO}_2$  concentration decay into the room after the injection was used to determine air exchange rate ( $a$ ). For this,  $\text{CO}_2$  is considered as an inert gas for which the concentration variation in the room follows a first order kinetic only attributable to air exchange ( $k = 0$ ).

The methodology for determining the air exchange rate ( $a$ ) and the indoor decay rate constant ( $k$ ) was detailed in the following paragraph.

### 2.3. Theoretical approach for determining $a$ and $k$

The principle is expressed as a mass balance that accounts for all sources and sinks of a compound that passes in and out a well-mixed volume ( $V$ ). This can be expressed for formaldehyde as:

$$\frac{dC}{dt} = aC_{\text{out}} - (a + k)C \quad (3)$$

where  $C_{\text{out}}$  was defined previously as the outdoor contaminant concentration entering the controlled volume by ventilation. Just after the time of injection and air mixing by fan, the formaldehyde concentration decay versus time results from both air exchange and indoor removal processes or "indoor sinks". This calculation assumes that the contribution of indoor sources to the change in concentration is relatively minor compared to that resulting from removal processes. This assumption is verified when the rise in the concentration subsequent to the injection is high enough in order that the removal processes are prevailing.

Indoor sinks are quantified by the constant  $k$ , assuming a first order kinetic for the variation of  $C$  versus time.

The integration of Eq. (3) leads to:

$$\ln \frac{(a + k)C - aC_{\text{out}}}{(a + k)C_0 - aC_{\text{out}}} = -(a + k)t \quad (4)$$

with  $C_0$  the initial formaldehyde concentration in the studied volume.

In the case of  $\text{CO}_2$ , the Eq. (4) is also available and can be simplified by assuming  $k$  value closed to 0. Then, this equation can be written as:

$$\ln \frac{C - C_{\text{out}}}{C_0 - C_{\text{out}}} = -at \quad (5)$$

A linear relation is obtained between the logarithmic term and time. By plotting this relation, the air exchange rate ( $a$ ) is directly deduced from the slope of the plot.

**Table 1**

Results on the decay rate constant of formaldehyde and its deposition velocity in the rooms.

Run	Room	T (°C) <i>RH (%)</i>	$C_0/C_{\text{background}}$	$a$ ( $\text{h}^{-1}$ )	$k$ ( $\text{h}^{-1}$ )	Dep ( $\text{cm s}^{-1}$ ) $\times 10^3$
1	1	19.6 <i>50.6</i>	2.9	0.62	0.40	3.00
2	1	22.2 <i>33</i>	4.8	0.43	0.23	1.73
3	1	22 <i>33</i>	7.9	0.42	0.33	2.48
4	1	28.2 <i>32</i>	4.2	0.85	0.37	2.78
5	2	22.1 <i>34</i>	5.4	0.64	0.29	2.18
6	2	21.6 <i>36</i>	5.0	0.58	0.31	2.33
7	1	20.8 <i>44</i>	3.4	0.64	0.43	3.23
Average $\pm$ SD:				0.34 $\pm$ 0.07		2.53 $\pm$ 0.51

$C_0$ : maximum formaldehyde concentration obtained after injection of formaldehyde in the room.

$C_{\text{background}}$ : background formaldehyde concentration in the room before injection. The relative humidity ( $RH$ ) is shown in italics in this table.

From the knowledge of the air exchange rate using Eq. (5) applied to  $\text{CO}_2$ , it is possible to calculate the formaldehyde constant  $k$  from Eq. (4). Eq. (4) was solved by a Newton–Raphson method, implemented in Microsoft Excel software, to determine the  $k$  value of each experiment point. When  $k$  is known, the logarithmic term of Eq. (4) is quantified and by plotting this term versus time for all experiments, we can estimate the mean value of the constant  $k$  from the slope of the plot which is equal to  $a + k$ .

The indoor deposition velocity in  $\text{cm s}^{-1}$  ( $Dep$ ) is often preferred to the decay rate constant ( $k$ ) because the latter takes into account the characteristics of the room, i.e. the ratio of total indoor surfaces (including building and furniture) to the room volume. It is defined as shown:

$$Dep = \frac{V}{S} \times k \quad (6)$$

For both rooms of this study,  $S/V$  ratio is equal to  $3.7 \text{ m}^{-1}$ .

## 3. Results and discussion

Seven experiments were conducted in two different rooms. Fig. 2 shows three examples of the  $\text{CO}_2$  and formaldehyde concentrations as a function of time as well as the linear relationships obtained between the logarithms of these concentrations and time used for estimating air exchange rate and the decay rate constant of formaldehyde. Table 1 gathers the results of these seven trials and the environmental conditions in the rooms. These seven experiments gave consistent estimates of the decay rate constant with an average value of  $0.34 \pm 0.07 \text{ h}^{-1}$  in agreement with the value previously published by Traynor et al. [8] deduced from laboratory experiments ( $0.40 \pm 0.24 \text{ h}^{-1}$ ). This good agreement suggests that the removal is weakly dependent on the nature and surfaces of indoor materials. Indeed, if we compare the deposition velocity  $Dep$  (in  $\text{cm s}^{-1}$ ), our assessment of  $(2.53 \pm 0.51) \times 10^{-3} \text{ cm s}^{-1}$  differs from the value of  $(5.0 \pm 3.0) \times 10^{-3} \text{ cm.s}^{-1}$  provided by Traynor et al. [8] because of a surface-to-volume ratio different between both test sets ( $S/V = 3.7 \text{ m}^{-1}$  for our study against  $2 \text{ m}^{-1}$  for Traynor et al. [8]).

Moreover, if the adsorption on the indoor surfaces was the only loss process for formaldehyde, the increase of temperature should change the solid-air partition in favor of gas phase and cause a decrease of decay rate. No dependence clearly appears between the decay rate of formaldehyde and temperature in these results. It

**Table 2**

Comparison of decay rate constants, deposition velocities and half-lives of several contaminants indoors.

Contaminant	$k$ ( $\text{h}^{-1}$ )	$Dep$ ( $\text{cm s}^{-1}$ ) $\times 10^3$	Half-life (h)	Description of experiments
Ozone	$2.8 \pm 1.3$	$49 \pm 17$	0.2	$n = 43$ Decay rate after introduction of outdoor air more concentrated ozone in dwellings; $S/V = 1.6 \text{ m}^{-1}$ [13]
$\text{NO}_2$	$1.3 \pm 0.6$	$18 \pm 9$	0.7	$n = 5$ Decay rate from gas-stove emission experiment in environmental chamber of $27 \text{ m}^3$ ; $S/V = 2 \text{ m}^{-1}$ [8]
Particles $<10 \mu\text{m}$	$1.0 \pm 0.6$	$11 \pm 6$	0.7	$n = 6$ Decay rate of concentration in rooms
Particles $<1 \mu\text{m}$	$0.5 \pm 0.3$	$5.6 \pm 3.6$	1.4	$a = 1,28 \text{ h}^{-1}$ ; $S/V = 2.5 \text{ m}^{-1}$ [14]
Particles $<0.5 \mu\text{m}$	$0.48 \pm 0.21$	$6.7 \pm 2.9$	1.4	$n = 5$ Decay rate from gas-stove emission experiment in environmental chamber of $27 \text{ m}^3$ ; $S/V = 2 \text{ m}^{-1}$ [8]
Formaldehyde	$0.40 \pm 0.24$	$5.0 \pm 3.0$	1.7	$n = 5$ Decay rate from gas-stove emission experiment in environmental chamber of $27 \text{ m}^3$ ; $S/V = 2 \text{ m}^{-1}$ [8]
Acrolein	$0.34 \pm 0.07$	$2.53 \pm 0.51$	2.0	$n = 7$ This study; $S/V = 3.7 \text{ m}^{-1}$
3-Methylbutanal	$0.05 \pm 0.01$	–	14.4	$n = 4$ (acrolein, $n = 3$ ) Decay rate resulting from domestic cooking events in a room. $a = 0.063 \text{ h}^{-1}$ , $S/V$ not reported [15]
Hexanal	$0.02 \pm 0.01$	–	32	
2-Heptenal	$0.06 \pm 0.06$	–	12	
2-Heptenal	$0.14 \pm 0.02$	–	4.8	

The half-life of formaldehyde ( $t_{1/2}$ ) is the time required for the concentration to fall to half its initial value ( $C_0$ ) because of indoor removal processes. It is directly deduced from the decay rate constant ( $k$ ) using the followed equation:  $t_{1/2} = -\ln(2)/k$ .

would seem that the adsorption on material surfaces is not the only depletion pathway for formaldehyde.

The decay rate constant and deposition velocity for formaldehyde are quite high. These indoor sinks can be as important as air exchange rate in removing indoor formaldehyde, especially when the air exchange rate is low. For the tested rooms having air exchange rates comprised between  $0.42$  and  $0.85 \text{ h}^{-1}$ , indoor removal processes represent between 27 and 44% of total depletion of formaldehyde in indoor environments.

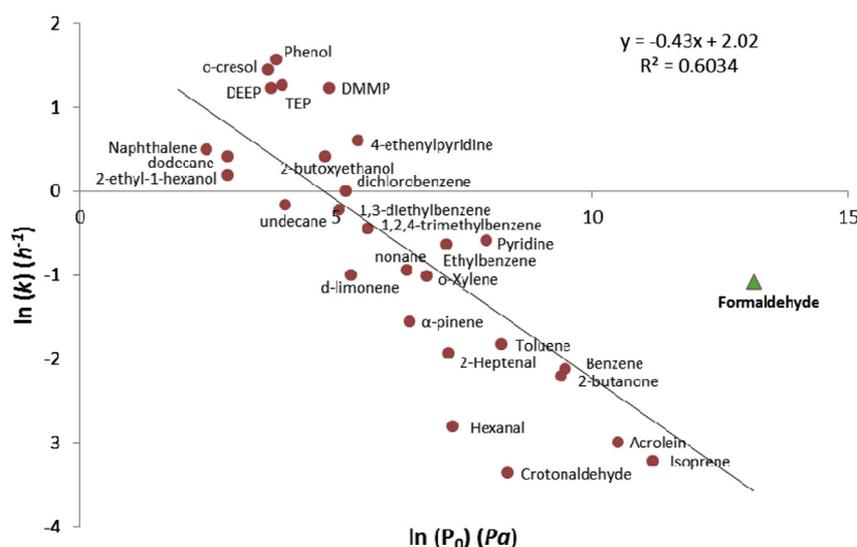
From the decay rate constant, the half-life of formaldehyde associated to indoor removal processes was calculated. In Table 2, it is compared to indoor half-lifetime of other chemicals, especially the carbonyls, reported in previous studies. A relatively short indoor half-life of 2 h for formaldehyde is obtained which is ranged between the values found for the atmospheric oxidants like  $\text{O}_3$ ,  $\text{NO}_2$  and  $\text{NO}$  (below 1 h) and those of other carbonyls (above 4 h). The decay rate of formaldehyde is comparable to that of fine particles having a diameter  $<0.5 \mu\text{m}$ . Formaldehyde also appears to have the least indoor persistence ability among the carbonyls.

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 [16]. Fig. 3 presents the relationship between the Neperian

logarithm of  $k$  ( $\ln k$ ) and the Neperian logarithm of  $P_0$  ( $\ln P_0$ ) reported in various experimental studies [15–17]. It should be noted that the analysis is limited to volatile organic compounds. Consequently, some organic compounds in these experimental studies (tetradecane, 1-methyl-naphthalene, 2,3-dimethylnaphthalene, nicotine, methyl salicylate and 2-hexyloxy-ethanol) were not considered. The  $k$  value of formaldehyde stands out from the general trend found for the whole of other compound data. If formaldehyde was only removed by adsorption, its  $k$  value should be close to 0 (applying the linear equation found in Fig. 3). Its behavior also seems to differ from those of other polar compounds like phenol, 2-butoxyethanol and o-cresol. This result suggests that the adsorption on material surfaces is not the only depletion process for formaldehyde.

Indoor chemistry may be one of the decay pathways of formaldehyde. But, the reactions have to be fast compared to the air exchange rate to take part in the variation of formaldehyde concentration. Various chemical processes can contribute to the variation of formaldehyde concentration in indoor air:

- formaldehyde oxidation by ozone or hydroxyl radical ( $\text{OH}^\cdot$ ) or nitrate radical ( $\text{NO}_3^\cdot$ ),
- formaldehyde removal by photolysis,



**Fig. 3.** Relationship between saturation vapor pressure at  $25^\circ\text{C}$  ( $P_0$  (Pa)) and decay rates of 31 VOCs determined from room experiments by Singer et al. [16,17], Seaman et al. [15] and in this study. DMMP = dimethylmethylphosphonate; DEEP = diethylethylphosphonate; TEP = triethylphosphonate.

**Table 3**  
Dependence of decay rate and deposition velocity with respect to absolute humidity.

Absolute humidity ( $\text{g m}^{-3}$ )	Decay rate constant ( $\text{h}^{-1}$ )	Deposition velocity ( $\text{cm s}^{-1}$ ) $\times 10^3$	Run
6.4	0.33	2.48	3
6.5	0.23	1.73	2
6.6	0.29	2.18	5
6.8	0.31	2.33	6
7.9	0.46	3.23	7
8.5	0.40	3.00	1
8.8	0.37	2.78	4

- interaction between formaldehyde and water (absorption and/or reaction).

The reactions of formaldehyde with OH and  $\text{NO}_3$  radicals and  $\text{O}_3$  have very slow kinetics (the reaction constants  $\text{kOH}$ , 298 K =  $8.5 \cdot 10^{-12} \text{ cm}^3 \text{ radical}^{-1} \text{ s}^{-1}$ ,  $\text{kNO}_3$ , 298 K =  $5.6 \cdot 10^{-16} \text{ cm}^3 \text{ radical}^{-1} \text{ s}^{-1}$  and  $\text{kO}_3$ , 298 K =  $2 \cdot 10^{-24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and lead to various products as formic acid by oxidation with  $\text{NO}_3$  and  $\text{HO}_2$  and oxide carbon and dioxide carbon by reaction with OH [18–20]. The indoor concentrations of radicals and ozone are known to be significantly lower than outdoors. However, if we consider the case where the indoor concentrations of these oxidants are similar to those commonly found in ambient air ( $[\text{OH}] = 2 \cdot 10^6 \text{ radicals.cm}^{-3}$ ,  $[\text{NO}_3] = 5 \cdot 10^8 \text{ radicals cm}^{-3}$  and  $[\text{O}_3] = 7 \cdot 10^{11} \text{ molecules.cm}^{-3}$ ), the half-life for formaldehyde will be 1.2, 80 days and >4.5 years, respectively [21]. So, it is unlikely that these reactions lead to significant losses during the sampling time.

Photolysis of formaldehyde outdoors is a loss process faster. The half-life for formaldehyde was assessed from 1.6 to 6 h based on these photolysis reactions [22]. It follows two main reaction pathways:



This process is much more limited in indoor air because the light spectrum is changed with a reduction of 80% for wavelengths below 360 nm. This value is the upper boundary for the photolysis of formaldehyde, so the degradation by photolysis indoors is limited.

Other possible removal pathway is the transfer of gaseous formaldehyde into the aqueous phases present indoors. Formaldehyde is known to have a high affinity with water [23]. Its Henry's law constant, calculated from Arrhenius expressions were estimated to  $5020 \pm 1170 \text{ M atm}^{-1}$  at 293 K [24]. In aqueous phase, formaldehyde can be easily hydrated to form methanediol ( $\text{CH}_2(\text{OH})_2$ ) [25].

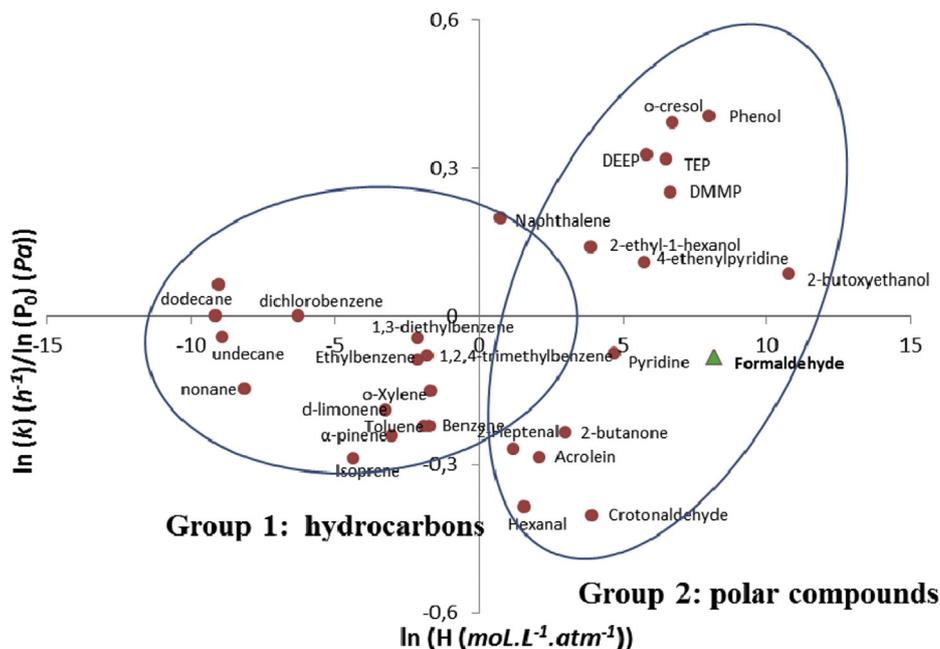
Interaction between formaldehyde and humidity is first examined following the results shown in Table 3. In this table, the results of experiments are classified in increasing order of absolute humidity. The formaldehyde deposition velocity seems to increase with the absolute humidity. Regression analysis gives a significant correlation ( $r = 0.77$ ,  $p = 0.046$ ) between the deposition velocity and absolute humidity at the 95% confidence level. However, other rooms will be tested to consolidate this result.

Adsorption of compounds on the indoor materials is the major process in the indoor removal as evidenced by the high dependence found between  $\ln k$  and  $\ln P_0$  shown in Fig. 3. To highlight potential secondary factors that could contribute to indoor removal, it is necessary to define a new indicator of indoor removal which is free from the contribution of adsorption. Therefore,  $\ln k/\ln P_0$  is chosen as new indicator. It is intended to reflect a part of indoor removal unexplained by adsorption.

Fig. 4 shows the  $\ln k/\ln P_0$  ratio versus the Neperian logarithm of Henry's constant ( $\ln H$ ) for the same series of compounds that in Fig. 3.

In this Fig. 4, the compounds are distributed into two groups:

- the hydrocarbons (alkanes, alkenes and aromatics) for which no correlation is found between the removal indicator ( $\ln k/\ln P_0$ ) and  $\ln H$ ,
- the polar compounds (alcohols, ethers, aldehydes, phosphonates...) for which the removal indicator increases with  $\ln H$ . For polar compounds, more the compound has affinity with water ( $\ln H$ ), more its indoor removal will tend to increase ( $\ln k$ )



**Fig. 4.** Variation of  $\ln k/\ln P_0$  ratio with respect to the Neperian logarithm of Henry's constant ( $\ln H$ ) for 31 VOCs determined from room experiments by Singer et al. [16,17], Seaman et al. [15] and in this study. DMMP = dimethylmethylphosphonate; DEEP = diethylethylphosphonate; TEP = triethylphosphonate.

In  $P_0$ ). This is a secondary trend only observed for polar compounds.

The  $k$  value of formaldehyde seems to follow this trend contrary to the relationship between  $\ln k$  and  $\ln P_0$  shown in Fig. 3. Formaldehyde is rather classified in the second category of compounds, i.e. those for which indoor removal is dependent on the affinity of the compound with water.

These results show that the affinity with water plays a role in the removal of polar compounds (like formaldehyde) indoors. An assumption can be made to explain the ability of formaldehyde to remove indoors. The sorbed water to indoor surfaces and/or on the airborne particles could be indoor sinks. Its amount is variable depending on the media surface properties (porosity, surface tension) leading to the formation of aqueous surface films when the relative humidity increases. These aqueous surface films could be the site of formaldehyde hydrolysis reaction and contribute to the depletion of this compound indoors.

These results should be supplemented by additional experiments in order to check if this high removal velocity of formaldehyde due to indoor sinks is found with the same magnitude in other buildings with different characteristics (air exchange rate, ratio of building surfaces to room volume, indoor materials, building age...).

The significant finding of this research was the high ability of formaldehyde to be removed from indoor air with a decay rate constant of  $0.34 \pm 0.07 \text{ h}^{-1}$  and a relatively short indoor half-life of 2 h.

In consequence, it appears essential to consider indoor sinks as a key process for any modeling approach of formaldehyde in indoor air.

Another consideration, the high indoor levels of this contaminant recorded in various measurement campaigns cannot be explained by its ability of persistence in air. It is rather the result of large amounts of this compound emitted by indoor sources and perhaps the effect of gas-phase reactions for example between terpenes or alkenes and ozone with production of formaldehyde.

#### 4. Conclusion

This study highlights the uniqueness behavior of formaldehyde as indoor contaminant which combines a high volatility (high vapor pressure) and a high removal due to indoor sinks. The results show the importance of taking into account the contribution of indoor sinks for the modeling of formaldehyde in indoor air. The parameters assessed in this study, the indoor decay rate constant ( $k = 0.34 \pm 0.07 \text{ h}^{-1}$ ) and deposition velocity ( $Dep = (2.53 \pm 0.51) \times 10^{-3} \text{ cm s}^{-1}$ ), may be used as input data for integration of indoor sinks in modeling.

These results give an assessment of the overall indoor removal at the scale of a room. In a further approach, the removal could be determined at the scale of material by carrying out specific field tests with on-site emission cells on the capability of each indoor surface to remove formaldehyde.

Data analysis tends to focus on the transfer of gaseous formaldehyde into the aqueous phases present indoors (water sorbed to indoor surfaces and/or on the airborne particles) as a possible removal pathway.

More investigation is necessary to get detailed information about nature of these removal processes and examine the variation in their impact according to indoor surfaces and environmental conditions. Especially, it would be useful to further investigate the interaction between formaldehyde and water present on the indoor surfaces and on airborne particles.

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