Title	Assessment of indirect inhalation exposure to formaldehyde evaporated from water
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Citation	Regulatory Toxicology and Pharmacology, 106, 43-49 https://doi.org/10.1016/j.yrtph.2019.04.019
Issue Date	2019-08
Doc URL	http://hdl.handle.net/2115/78997
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Type	article (author version)
File Information	01_AssessmentOfIndirectInhalationExposure.pdf

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1 **Short Communication for RTP (*Regulatory Toxicology and Pharmacology*)**

4 **Assessment of Indirect Inhalation Exposure to Formaldehyde Evaporated from Water**

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Abstract

Volatilization volumes and health risks associated with indirect inhalation exposure to formaldehyde evaporated from water have not been investigated quantitatively. We experimentally investigated formaldehyde volatility, compared with chloroform volatility, predicted formaldehyde inhalation exposure concentrations in Japanese bathrooms, and then re-evaluated drinking water quality standards. Although the Henry's law constant of formaldehyde is $1/10^4$ that of chloroform, with a 30-min exposure period, the formaldehyde non-equilibrium partition coefficient (K'_d) was 1/500th the chloroform value because of formaldehyde's faster volatilization rate. We used this ratio to estimate the cumulative probability distribution of formaldehyde concentrations in bathroom air. For a formaldehyde concentration in water of ≤ 2.6 mg/L-water (WHO tolerable concentration), the probability that the incremental formaldehyde concentration due to volatilization would exceed 100 $\mu\text{g}/\text{m}^3$ -air (WHO indoor air quality guideline) was low. However, major sources of formaldehyde in indoor air are building materials and furniture. We therefore calculated the allowable concentration in water by allocating a small percentage of the indoor air guideline value to indirect inhalation exposure via volatilization from tap water. With an allocation factor of 20% (10%), the allowable concentration was 0.52 (0.26) mg/L-water. These concentrations are similar to the Health Canada guideline concentration but they are 3 to 6 times the Japanese water quality standard.

Keywords:

Water quality standard

Partition coefficient

Shower

Volatility

Distribution

Chloroform

1. Introduction

Formaldehyde is a disinfection byproduct formed from anthropogenic chemicals as well as from natural organic matter during chlorination and ozonation processes (Glaze et al., 1989; Krasner et al., 1989; Becher et al., 1992; Weinberg et al., 1993; Mitch and Schreiber, 2008; Kobayashi et al., 2013) (National Research Council, 2011). The accidental contamination of tap water in 2012 by formaldehyde produced during purification of Tone River (Japan) water (Kosaka et al., 2014) has drawn attention to the importance of its control and risk management in water supply.

Because of the toxicity of formaldehyde, some countries and organizations have set standard or guideline values for formaldehyde concentrations in water and air, but they vary among countries and regions because of adjustment to take into account local sociocultural, economic and environmental/geological circumstances. Indoor-air formaldehyde concentration guideline values set by 16 countries and regions (summarized by Salthammer et al., 2010) range from 30 to 370 $\mu\text{g}/\text{m}^3$ -air for the average concentration during short-term exposure (30 min to 24 h). The short-term (30-min) exposure guideline value for the general population of 100 $\mu\text{g}/\text{m}^3$ -air recommended by WHO (2010) to prevent sensory irritation is the most common guideline value among these countries and regions (Salthammer et al., 2010)(Nielsen et al., 2017). This value of 100 $\mu\text{g}/\text{m}^3$ -air is lower than the chronic value of 0.2 mg/m^3 -air set by WHO. Thus the use of the short-term (30-minute) guideline of 0.1 mg/m^3 will also prevent long-term health effects, including cancer.

Not all organizations set a guideline value or maximum acceptable concentration for formaldehyde in drinking water because concentrations normally found in water supplies are much lower than the tolerable concentrations for ingestion of, for example, 2.6 mg/L -water, set by WHO (2014), and 0.35 mg/L -water, set by Health Canada (1997). In 2012, however, formaldehyde was detected at higher than the usual concentration of 0.001 mg/L -water or less on average (Ministry of Environment, 2001) in drinking water supplied from several water purification plants that draw raw water from Tone River, Japan (Kosaka et al., 2014). The maximum detected formaldehyde concentration was 0.168 mg/L -

water (Kosaka et al., 2014), which is 15% of the WHO (2014) tolerable concentration (2.6 mg/L-water), one-third of Australian guideline value for drinking water (= 0.5 mg/L-water; Australian NHMRC, NRMMC, 2011), about half the Canadian guideline value (= 0.35 mg/L-water; Health Canada, 1997), and twice the Japanese standard (0.08 mg/L-water; MHLWJ, 2003a). This formaldehyde detection event indicates that the difference between maximum acceptable concentrations and observed concentrations is actually not very large, and suggests that formaldehyde guidelines and standards for drinking water should be revisited.

The lower standard value in Japan compared with those of other countries is attributable to the difference in the way indirect inhalation exposure risk due to possible volatilization of formaldehyde from water is evaluated. WHO, which considers the indirect inhalation exposure risk to be low, established a tolerable concentration of 2.6 mg/L-water for formaldehyde in drinking water (WHO, 2014). In contrast, the Japanese Ministry of Health, Labour and Welfare set the Drinking Water Quality Standard to 0.08 mg/L-water, introducing an additional uncertainty factor of 10 to take the risk of indirect inhalation exposure into consideration (MHLWJ, 2003a). To the best of our knowledge, however, the only report on indirect inhalation exposure to formaldehyde due to volatilization is that of Owen et al. (1990), who estimated the amount of volatilized formaldehyde in indoor air due to the use of a humidifier containing a small amount of water. In contrast, several studies have reported on indirect exposure to chloroform, a typical volatile organic substance, due to volatilization from tap water during showering and bathing (Itoh and Asami, 2010; Jo et al., 2005; Kerger et al., 2000; Xu and Weisel, 2005; Akiyama et al., 2018)).

Here, it should be noted that the endpoints of toxicities for inhalation, oral and dermal exposures are different, and total exposure from multiple sources in multi-exposure assessments by methods such as the Leq approach is not applicable for formaldehyde. Formaldehyde is a route-dependent toxic substance because it has high reactivity (National Research Council, 2011). The endpoints of toxicities for inhalation and oral exposures are different. Formaldehyde reacts at the adsorption site but is not

delivered to distant sites and not available systemically in any reactive form; thus, the adsorption site becomes the toxicity endpoint (Heck and Casanova, 2004). For example, in animal experiments, pathological changes have been observed to the gastric epithelium on oral ingestion (Til et al., 1989) and to the nasal cavity and upper respiratory tract on inhalation (Kerns et al., 1983). Moreover, the formaldehyde concentration in blood of animals did not increase, even after inhalation exposure (Cassanova et al., 1988). Finally, the systemic delivery of formaldehyde is unlikely, and then the indirect inhalation exposure of water should be evaluated separately from the oral exposure of water.

The Henry's law constant for formaldehyde at 40 °C is 92.1 L·Pa/mol (Zhou and Mopper, 1990), which is about $1/10^4$ that for chloroform (7.66×10^5 L·Pa/mol; Gossett, 1987) (Table 1). Given this difference in the Henry's law constants, the volatility of formaldehyde is expected to be much smaller than that of chloroform. However, Henry's law applies to substances at air–water equilibrium, whereas when water is normally used in daily life, for example, for bathing, volatilization may occur under non-equilibrium conditions (Niizuma et al., 2013). Under these conditions, the volatilization rate, which is a function of molecular diffusivity and other factors, may also control the volatility of a substance. The diffusivity of formaldehyde is about twice that of chloroform in both air, calculated by the WL method (Wilke and Lee, 1955; Tucker and Nelken, 1990), and water, calculated by the HL method (Hayduk and Laudie, 1974; Tucker and Nelken, 1990) (Table 1). When the air–water contact time is limited, therefore, formaldehyde may have higher volatility than chloroform because of its higher diffusivity in air and water.

In light of these considerations, our objective in this study was to estimate the probability distribution of indirect inhalation exposure to formaldehyde due to volatilization from drinking water by experimentally comparing the volatility of formaldehyde with that of chloroform, using available data on chloroform volatility during showering and bathing. Then, we used these volatility results to re-evaluate drinking water quality standard values for formaldehyde in terms of indirect inhalation exposure.

2. Materials and methods

2.1. Air–water contact and sampling

Twelve mixed solutions of formaldehyde (5 to 50 mg/L-water) and chloroform (5 to 50 µg/L-water) were prepared by diluting aqueous solutions of formaldehyde (37% w/w, Wako Pure Chemical Co., Osaka, Japan) and chloroform (99% w/w, chloroform for trihalomethane analysis, Wako Pure Chemical Co.) with pure water (Milli-Q Advantage, Merck, Darmstadt, Germany). The prepared solutions had higher concentrations of formaldehyde than of chloroform because of formaldehyde's relatively low volatility at equilibrium, as indicated by the Henry's law constants. In each experiment, 100 mL of mixed solution was first injected into an aluminum bag through a fitted sampling cock (GL Science, Tokyo, Japan), and then 10 L of ambient indoor air was introduced into the bag by using a pump (MP-Σ 300NII; Shibata Scientific Technology LTD., Saitama, Japan). The depth of the water was approximately 5 cm in the bag of the dimension (approximately 40 × 34 × 19 cm).

. Air–water contact was carried out under the following three conditions (Table 2):

Condition A: The bag was partially submerged to about 10 cm under the water line for 30 min in a water bath maintained at 40 °C to warm the water in the bag.

Condition B: (1) The bag was first partially submerged to about 10 cm under the water line for 15 min in a water bath maintained at 40 °C. (2) The bag was removed from the bath and shaken for 2 min at a rate of 120 strokes per minute in a room with an ambient air temperature of 20 °C. (3) The bag was again partially submerged in the water bath for 1 min for warming. Steps 2 and 3 were repeated 5 times. The total air–water contact time was 30 min.

Condition C: The same as Condition B except that the water bath temperature was 60 °C. The total contact time was 30 min.

After the air–water contact period, the air in the bag was introduced into two sampling cartridges at a

flow rate of 0.5 L-air/min. One sampling cartridge was packed with silica gel coated with a derivatization reagent, 2,4-dinitrophenylhydrazine (DNPH) (Presep R-C DNPH, Wako Pure Chemical Co.), and used for formaldehyde analysis, and the other sampling cartridge was filled with granular activated carbon (Carbon bead active-standard type; Shibata Scientific Technology) and used for chloroform analysis. Vapor and steam as well as gaseous formaldehyde and chloroform, which could be potential inhalation exposure source, were captured by the cartridges. The dew condensation occurred only inside the pipe close the bag outlet and its volume was very small (<0.1 mL). The concentrations of formaldehyde and chloroform in the ambient indoor air, which was introduced into the bag, were 5–11 and 11–18 $\mu\text{g}/\text{m}^3$, respectively, which were much lower than the concentrations after volatilization in the bag.

2.2. Formaldehyde and chloroform analyses

2.2.1. Air-phase formaldehyde

Formaldehyde in the silica-gel cartridge was extracted with 10 mL of acetonitrile, and then analyzed in a high-performance liquid chromatography (HPLC) system (Agilent 1100, Agilent Technologies, California, USA) equipped with an Inertsil ODS-3 column (4.6 mm $\times$ 250 mm, particle diameter 3 μm , GL Science) and a variable wavelength detector (VWD; Agilent 1260, Agilent Technologies) according to the official Japanese air pollutant analysis method (Ministry of the Environment, 2010). The calibration line and CV are shown in Table 1S (Supplementary Information).

2.2.2. Air-phase chloroform

The activated carbon in the carbon cartridge was removed, and then the chloroform adsorbed on the carbon was extracted with 1 mL of carbon disulfide and analyzed in a gas chromatography/mass spectroscopy (GC/MS) system (Agilent 7890A gas chromatograph; Agilent 5975C mass spectrometer, Agilent Technologies) equipped with an Agilent DB-624 column (0.32 mm $\times$ 30 m, film thickness 1.80 μm) according to the official Japanese air pollutant analysis method (Ministry of the Environment, 2010).

2.2.3. Liquid-phase formaldehyde

DNPH (Wako Pure Chemical Co.) was diluted with acetonitrile to 0.1% w/w. Phosphoric acid (Wako Pure Chemical Co.) was diluted with pure water to 20% w/w. Diluted DNPH (0.5 mL) and diluted phosphoric acid (0.2 mL) were added to 10 mL of sample solution containing formaldehyde. This solution was analyzed by the HPLC-VWD system according to the official Japanese drinking water quality analysis method (MHLWJ, 2003b).

2.2.4. Liquid-phase chloroform

Hydrochloric acid (400 µL, 1 mol/L) (Kanto Chemical Co., Tokyo, Japan) was added to 50 mL of sample solution containing chloroform. This solution was analyzed by a Purge and Trap GC/MS system (AQUA PT 5000J PLUS; JEOL, Tokyo, Japan; GC-2010, Shimadzu corporation, Kyoto, Japan) equipped with an Inertcap® AQUATIC column (0.25 mm × 60 m, film thickness 1.0 µm, GL Science) according to the official Japanese drinking water quality analysis method (MHLWJ, 2003b).

Volatility is represented by the non-equilibrium partition coefficient K'_d , defined by equation (1).

$$K'_d = \frac{C_{\text{air}}}{C_{\text{water}}}$$

(1)

where K'_d is the non-equilibrium partition coefficient, C_{air} is the air-phase concentration, and C_{water} is the water-phase concentration. K'_d values were determined experimentally by fitting an equation of the form $C_{\text{air}} = K'_d C_{\text{water}}$ (i.e., slope = K'_d and intercept = 0) to the observed data by the least-squares method.

3. Results and Discussion

3.1. Chloroform

We plotted the observed relationship between the concentration of chloroform in water (C_a) and its concentration in air (C_w) under each condition (Fig. 1). In Condition A, the water temperature in the bag reached 40 °C in 5 min. In Condition B, the water temperature in the bag after the final shaking was 25 °C, and in Condition C, it was 30 °C after the final shaking. Thus, the water temperatures in the air–water contact experiments were all higher than 20 °C, and the temperature at which the equilibrium relationship shown in Fig. 1 was calculated. If chloroform had reached air–water equilibrium in the experiments, the observed air-phase concentrations would be higher than the concentrations calculated using the Henry’s law constant for chloroform at 20 °C (Fig. 1, solid line). However, all of the experimentally obtained air-phase concentrations were lower than the calculated values. This result indicates that chloroform did not reach air–water equilibrium in any of our experiments.

In all three conditions, the observed relationship between C_a and C_w of chloroform was linear; thus, there was no concentration effect on the K'_d value. We calculated K'_d for chloroform by fitting equation (1) to the experimental data by least squares (Table 3). We also used actual air-phase and water-phase chloroform concentrations in bathrooms in Japan (Itoh and Asami, 2010; Niizuma et al., 2013) to calculate the cumulative probability distribution of K'_d in bathrooms (Fig. 2). The large distribution range of K'_d for chloroform suggests that the increase of chloroform in air due to volatilization varies individually from house to house depending on lifestyles and bathroom structures etc. The K'_d values obtained in our study fall within the 60th to 80th percentile range of the cumulative distribution in actual bathrooms (Fig. 2); this result suggests that the volatilization of chloroform from water to air in our study may be similar to conditions that can occur as a result of people showering and bathing in actual bathrooms.

3.2. Formaldehyde

The relationships between the observed concentrations of formaldehyde in air and water were also linear (Fig. 3). Both shaking (Conditions B and C) and a higher water bath temperature (Condition C)

tended to slightly increase the concentration of formaldehyde in air. In Conditions B and C, the water temperature in the bag at the end of the air–water contact experiments was 25 and 30 °C, respectively, and the air–water concentration relationships observed in these conditions were close to those predicted from the Henry’s law constants for formaldehyde at 25 and 35 °C (Zhou and Mopper, 1990) (Fig. 3). Therefore, in Conditions B and C, the formaldehyde state may have been close to air–water equilibrium. In Condition A (water temperature = 40 °C with no shaking), formaldehyde concentrations in air were lower than those predicted by the Henry’s law constant for formaldehyde at 40 °C, indicating that equilibrium was not attained.

We fitted equation (1) to the observed air–water concentration relationships to determine the K'_d value for each condition (Table 3). The K'_d values of formaldehyde were about 1/500 those of chloroform in all three conditions, irrespective of whether air–water equilibrium was attained: air–water equilibrium of formaldehyde was not reached in Condition A, but it was in Conditions B and C. Table 3 also shows the Henry’s law constants and transfer efficiencies for formaldehyde and chloroform in the three conditions. The transfer efficiency is a measure of the volatilization rate per unit time from aqueous solution and can be calculated from a substance’s Henry’s law constant and its diffusion coefficients in water and air (McKone, 1987). The Henry’s law constants of formaldehyde were about $1/10^4$ times those of chloroform. In contrast, the transfer efficiency of formaldehyde was between about 1/20 and 1/50 of chloroform. Thus, in each condition the difference in the transfer efficiency was much less than the difference in the Henry’ law constant. Because of the higher diffusivities of formaldehyde in both air and water (Table 1), its volatilization rate should be expected to be higher than that of chloroform. Therefore, the K'_d values of formaldehyde were about 1/500 times that of chloroform, although the Henry’s law constants of formaldehyde were about $1/10^4$ times those of chloroform. We estimated the K'_d value distribution of formaldehyde in bathrooms by multiplying the K'_d value distribution of chloroform in actual bathrooms (solid line in Fig. 2) by the ratio of the K'_d values of formaldehyde to those of chloroform, which were obtained by the bag experiments (using the average of the K'_d values obtained under the three conditions).

3.3. Indirect exposure to formaldehyde

We calculated the probability distribution of the formaldehyde concentration in air due to volatilization by multiplying the K'_d value distribution curve by an arbitrary concentration of formaldehyde in tap water. We searched for appropriate formaldehyde concentrations in tap water which would not cause health effect due to volatilization. Figure 4 shows the probability distribution of the formaldehyde concentration in bathroom air due to volatilization of tap water when the formaldehyde concentration in the tap water is assumed to be 2.6 mg/L-water (tolerable concentration; WHO, 2014). The 5th and 95th percentiles of the formaldehyde concentration in air were 1.7 and 100 $\mu\text{g}/\text{m}^3$ -air, respectively, and the mean and median concentrations were 25 and 27 $\mu\text{g}/\text{m}^3$ -air. The 95th percentile concentration is close to the equilibrium concentration calculated by using the Henry's law constant for formaldehyde at a water temperature of 40 °C (Fig. 4, vertical dashed line). This high concentration in air might be attained during long showers or in an insufficiently ventilated bathroom (Niizuma et al., 2013). The median concentration, 27 $\mu\text{g}/\text{m}^3$ -air, can be interpreted to mean that the probability that up to 1/4 of the equilibrium concentration of formaldehyde in air at 40 °C is volatilized is 50%.

When the tap water concentration was 2.6 mg/L-water or less, the increment of the concentration in air due to volatilization was mostly less than 100 $\mu\text{g}/\text{m}^3$ -air [short-term (30-min) exposure guideline value for indoor air quality; WHO, 2010]. Note: the short-term exposure guideline was used for comparison because the time spent in bath room is not long [the 5, 50 and 95 percentiles of the time spent in bath room are 7, 18, and 40 min, respectively (Niizuma et al., 2013)]. If the criterion that the 95th percentile value of the in-air formaldehyde concentration distribution should be equal to 100 $\mu\text{g}/\text{m}^3$ -air is regarded as protecting the majority of a population, then the tap water concentration criterion for formaldehyde due to volatilization would be 2.6 mg/L-water, which is incidentally equal to the WHO (2014) guideline value for drinking water.

The most prevalent sources of formaldehyde in indoor air, however, are building materials and furniture made of pressed-wood products, insulation materials, and coating materials (Fig. 5) (Salthammer et al., 2010) (Shinohara et al., 2007; Shinohara et al., 2009). Uchiyama et al. (2015) conducted a nationwide survey of indoor air quality in Japan and reported that the mean (maximum) formaldehyde concentrations in summer and winter were 34 (222) and 13 (58) $\mu\text{g}/\text{m}^3$ -air, respectively. Matsumura et al. (2012) analyzed a nationwide survey of the year 2006 and reported that 50 and 75 percentiles are 0.042 and 0.085 ppm (~ 53 and ~ 110 $\mu\text{g}/\text{m}^3$ -air), respectively. Concentrations that exceeded 100 $\mu\text{g}/\text{m}^3$ -air (guideline value for indoor air quality set by WHO) were also reported by Yamashita et al. (2012). Given these values, a concentration of 100 $\mu\text{g}/\text{m}^3$ -air due to the volatilization from water alone is not an appropriate criterion. Because volatilization from tap water is not expected to be the major source of exposure, only a portion of the indoor air guideline value should be allocated to the indirect inhalation exposure to formaldehyde from tap water via volatilization. If 20% of the WHO guideline value of 100 $\mu\text{g}/\text{m}^3$ -air is allocated to indirect inhalation exposure due to volatilization from tap water, then the corresponding in-air concentration from that source is 20 $\mu\text{g}/\text{m}^3$ -air, which can be achieved by volatilization from tap water with a formaldehyde concentration of <0.52 mg/L-water. With an allocation rate of 10%, the corresponding concentration in tap water is <0.26 mg/L-water. These values are similar to the Health Canada guideline value of 0.35 mg/L-water (Health Canada, 1997), which was derived by allocating a fraction of the oral tolerable daily intake of formaldehyde to drinking water given an average daily water intake of 2 L/d, but they are respectively about 6 and 3 times higher than the Drinking Water Quality Standard value of Japan of 0.08 mg/L-water (MHLWJ, 2003a), which is lower than the guideline values of other countries. The Drinking Water Quality Standard value of Japan was conservatively derived by applying an additional uncertainty factor of 10 to the fraction of the TDI allocated to drinking water to account for the indirect inhalation risk, but it may be too protective. Indirect inhalation exposure estimates, like estimates of intake via food, are generally lifestyle-specific. Therefore, the results of this study are based on the exposure probability associated with Japanese lifestyles, which include bathing and showering habits. However, the approach employed in this study can be applied to the determination of indirect exposure

in other circumstances, irrespective of lifestyle. In this study, we assumed the conservative low allocation factor values. The allocation factor could change upward or downward depending upon the concentration of formaldehyde from these other indoor sources, however, if the concentration of formaldehyde from other sources is known in a home or building ahead of time,

4. Conclusion

Although the Henry's law constant of formaldehyde is $1/10^4$ that of chloroform, formaldehyde volatility, as indicated by its non-equilibrium partition coefficient (K'_d), after a limited (30-min) contact period was 1/500th the volatility of chloroform. The probability distribution of formaldehyde concentrations in air due to volatilization in bathrooms in Japan was estimated by measuring and comparing the volatilities of formaldehyde and chloroform from water. For tap water containing a formaldehyde concentration of 2.6 mg/L-water, the tolerable concentration recommended by WHO, the 5th percentile, median value, and 95th percentile of the formaldehyde concentration in air due to volatilization was 1.7, 27, and 100 $\mu\text{g}/\text{m}^3$ -air, respectively. Thus, volatilization from tap water alone would result in a concentration in air of 100 $\mu\text{g}/\text{m}^3$ -air in 5% of cases. However, formaldehyde released from building materials and furniture containing formaldehyde is the major source of formaldehyde inhalation exposure in indoor air; thus, if 20% (10%) of the WHO guideline value is allocated to indirect inhalation exposure via volatilization from water, then the acceptable tap water concentration is just 0.52 (0.26) mg/L-water. These concentrations are similar to the guideline value for formaldehyde of Health Canada (0.35 mg/L-water), but they are larger than the Drinking Water Quality Standard value of Japan (0.08 mg/L-water), which takes the additional risk of indirect exposure into account. This result suggests that the Japanese standard value may be too protective.

Acknowledgments

This study was supported by a Health and Labour Sciences Research Grant (H28-Kenki-Ippan-005) from the Ministry of Health, Labour, and Welfare of Japan. However, this work has not been evaluated by the granting organization and does not necessarily reflect its opinion; therefore, no official endorsement should be inferred.

Appendix.

Supplementary Information is available in the online version at #####.

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List of Figure and Table Captions

Fig. 1. Experimental data for the concentration of chloroform in air (C_a) vs. that in water (C_w). The solid line shows the equilibrium relationship at 20 °C calculated by using the Henry's law constant (Gosset, 1987).

Fig. 2. Comparison of the cumulative probability distribution of K'_d values for chloroform in actual bathrooms, calculated using data from Itoh and Asami (2010), with the K'_d values obtained in this study for each condition.

Fig. 3. Experimentally observed formaldehyde concentrations in air (C_a) vs. those in water (C_w) compared with equilibrium relationships calculated by using values from Zhou and Mopper (1990) for the Henry's law constant for formaldehyde at 25, 30, and 40 °C.

Fig. 4. Predicted formaldehyde concentrations in bathroom air due to its evaporation from tap water containing 2.6 mg/L of formaldehyde (solid line). The dotted and dashed lines indicate formaldehyde concentrations at equilibrium with water at 20 and 40 °C, respectively.

Fig. 5. Schematics of formaldehyde exposure sources.

Table 1. Diffusion coefficients in air and water and Henry's law constants of formaldehyde and chloroform.

Table 2. Air–water contact conditions.

Table 3. K'_d values, Henry's law constants, and transfer efficiencies of formaldehyde and chloroform.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Supplementary Information

Assessment of Indirect Inhalation Exposure to Formaldehyde Evaporated from Water

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Figure 1S. Calibration line of chloroform in carbon disulfide obtained by GC/MS-ALS (Agilent technologies)

Figure 2S. Calibration line of chloroform in water obtained by PT&GC/MS (Shimadzu)

Figure 3S. Calibration line formaldehyde in acetonitrile obtained by HPLC-VWD (Agilent technologies)

Table 1S. Conforming the recoveries of air-phase formaldehyde (100 µg/m³-air) and chloroform (100 µg/m³-air) by the silica gel and carbon cartridges, respectively.

Formaldehyde	Chloroform
98 %	113 %

Table 2S. Measurement accuracy tests

	Chloroform in air	Chloroform in water	Formaldehyde in water
Concentrations	18.1 to 400µg/m³-air	10.8 to 21.4 µg/L-water	15.2 to 39.5 µg/L-water
Coefficient of variation	9.99×10^{-6} to 4.43×10^{-2}	6.86×10^{-2} to 1.37×10^{-1}	1.02×10^{-3} to 8.37×10^{-3}