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

2

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

5

6

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19

20 **Abstract**

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

37

38

39 **Keywords:**

40 Water quality standard

41 Partition coefficient

42 Shower

43 Volatility

44 Distribution

45 Chloroform

46

47 **1. Introduction**

48 Formaldehyde is a disinfection byproduct formed from anthropogenic chemicals as well as from  
49 natural organic matter during chlorination and ozonation processes (Glaze et al., 1989; Krasner et al.,  
50 1989; Becher et al., 1992; Weinberg et al., 1993; Mitch and Schreiber, 2008; Kobayashi et al., 2013)  
51 (National Research Council, 2011). The accidental contamination of tap water in 2012 by  
52 formaldehyde produced during purification of Tone River (Japan) water (Kosaka et al., 2014) has  
53 drawn attention to the importance of its control and risk management in water supply.

54

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

66

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

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

81

82 The lower standard value in Japan compared with those of other countries is attributable to the  
83 difference in the way indirect inhalation exposure risk due to possible volatilization of formaldehyde  
84 from water is evaluated. WHO, which considers the indirect inhalation exposure risk to be low,  
85 established a tolerable concentration of 2.6 mg/L-water for formaldehyde in drinking water (WHO,  
86 2014). In contrast, the Japanese Ministry of Health, Labour and Welfare set the Drinking Water Quality  
87 Standard to 0.08 mg/L-water, introducing an additional uncertainty factor of 10 to take the risk  
88 of indirect inhalation exposure into consideration (MHLWJ, 2003a). To the best of our knowledge,  
89 however, the only report on indirect inhalation exposure to formaldehyde due to volatilization is that  
90 of Owen et al. (1990), who estimated the amount of volatilized formaldehyde in indoor air due to the  
91 use of a humidifier containing a small amount of water. In contrast, several studies have reported on  
92 indirect exposure to chloroform, a typical volatile organic substance, due to volatilization from tap  
93 water during showering and bathing (Itoh and Asami, 2010; Jo et al., 2005; Kerger et al., 2000; Xu  
94 and Weisel, 2005; Akiyama et al., 2018)).

95

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

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

108

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

121

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

128

129

## 130 **2. Materials and methods**

131

### 132 *2.1. Air–water contact and sampling*

133 Twelve mixed solutions of formaldehyde (5 to 50 mg/L-water) and chloroform (5 to 50 µg/L-water)  
134 were prepared by diluting aqueous solutions of formaldehyde (37% w/w, Wako Pure Chemical Co.,  
135 Osaka, Japan) and chloroform (99% w/w, chloroform for trihalomethane analysis, Wako Pure  
136 Chemical Co.) with pure water (Milli-Q Advantage, Merck, Darmstadt, Germany). The prepared  
137 solutions had higher concentrations of formaldehyde than of chloroform because of formaldehyde's  
138 relatively low volatility at equilibrium, as indicated by the Henry's law constants. In each experiment,  
139 100 mL of mixed solution was first injected into an aluminum bag through a fitted sampling cock (GL  
140 Science, Tokyo, Japan), and then 10 L of ambient indoor air was introduced into the bag by using a  
141 pump (MP-Σ 300NII; Shibata Scientific Technology LTD., Saitama, Japan). The depth of the water  
142 was approximately 5 cm in the bag of the dimension (approximately 40 × 34 × 19 cm).

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

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

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

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

153

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

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

165

## 166 *2.2. Formaldehyde and chloroform analyses*

### 167 *2.2.1. Air-phase formaldehyde*

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

174

### 175 *2.2.2. Air-phase chloroform*

176 The activated carbon in the carbon cartridge was removed, and then the chloroform adsorbed on the  
177 carbon was extracted with 1 mL of carbon disulfide and analyzed in a gas chromatography/mass  
178 spectroscopy (GC/MS) system (Agilent 7890A gas chromatograph; Agilent 5975C mass spectrometer,  
179 Agilent Technologies) equipped with an Agilent DB-624 column (0.32 mm  $\times$  30 m, film thickness  
180 1.80  $\mu\text{m}$ ) according to the official Japanese air pollutant analysis method (Ministry of the Environment,  
181 2010).

182

183 *2.2.3. Liquid-phase formaldehyde*

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

189

190 *2.2.4. Liquid-phase chloroform*

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

196

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

198 
$$K'_d = \frac{C_{\text{air}}}{C_{\text{water}}}$$

199

(1)

200 where  $K'_d$  is the non-equilibrium partition coefficient,  $C_{\text{air}}$  is the air-phase concentration, and  $C_{\text{water}}$   
201 is the water-phase concentration.  $K'_d$  values were determined experimentally by fitting an equation  
202 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-  
203 squares method.

204

205

206 **3. Results and Discussion**

207

208 *3.1. Chloroform*

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

220

221 In all three conditions, the observed relationship between  $C_a$  and  $C_w$  of chloroform was linear; thus,  
222 there was no concentration effect on the  $K'_d$  value. We calculated  $K'_d$  for chloroform by fitting  
223 equation (1) to the experimental data by least squares (Table 3). We also used actual air-phase and  
224 water-phase chloroform concentrations in bathrooms in Japan (Itoh and Asami, 2010; Niizuma et al.,  
225 2013) to calculate the cumulative probability distribution of  $K'_d$  in bathrooms (Fig. 2). The large  
226 distribution range of  $K'_d$  for chloroform suggests that the increase of chloroform in air due to  
227 volatilization varies individually from house to house depending on lifestyles and bathroom structures  
228 etc. The  $K'_d$  values obtained in our study fall within the 60th to 80th percentile range of the cumulative  
229 distribution in actual bathrooms (Fig. 2); this result suggests that the volatilization of chloroform from  
230 water to air in our study may be similar to conditions that can occur as a result of people showering  
231 and bathing in actual bathrooms.

232

### 233 3.2. Formaldehyde

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

236 tended to slightly increase the concentration of formaldehyde in air. In Conditions B and C, the water  
237 temperature in the bag at the end of the air–water contact experiments was 25 and 30 °C, respectively,  
238 and the air–water concentration relationships observed in these conditions were close to those  
239 predicted from the Henry’s law constants for formaldehyde at 25 and 35 °C (Zhou and Mopper, 1990)  
240 (Fig. 3). Therefore, in Conditions B and C, the formaldehyde state may have been close to air–water  
241 equilibrium. In Condition A (water temperature = 40 °C with no shaking), formaldehyde  
242 concentrations in air were lower than those predicted by the Henry’s law constant for formaldehyde at  
243 40 °C, indicating that equilibrium was not attained.

244

245 We fitted equation (1) to the observed air–water concentration relationships to determine the  $K'_d$  value  
246 for each condition (Table 3). The  $K'_d$  values of formaldehyde were about 1/500 those of chloroform  
247 in all three conditions, irrespective of whether air–water equilibrium was attained: air–water  
248 equilibrium of formaldehyde was not reached in Condition A, but it was in Conditions B and C. Table  
249 3 also shows the Henry’s law constants and transfer efficiencies for formaldehyde and chloroform in  
250 the three conditions. The transfer efficiency is a measure of the volatilization rate per unit time from  
251 aqueous solution and can be calculated from a substance’s Henry’s law constant and its diffusion  
252 coefficients in water and air (McKone, 1987). The Henry’s law constants of formaldehyde were about  
253  $1/10^4$  times those of chloroform. In contrast, the transfer efficiency of formaldehyde was between  
254 about 1/20 and 1/50 of chloroform. Thus, in each condition the difference in the transfer efficiency  
255 was much less than the difference in the Henry’ law constant. Because of the higher diffusivities of  
256 formaldehyde in both air and water (Table 1), its volatilization rate should be expected to be higher  
257 than that of chloroform. Therefore, the  $K'_d$  values of formaldehyde were about 1/500 times that of  
258 chloroform, although the Henry’s law constants of formaldehyde were about  $1/10^4$  times those of  
259 chloroform. We estimated the  $K'_d$  value distribution of formaldehyde in bathrooms by multiplying the  
260  $K'_d$  value distribution of chloroform in actual bathrooms (solid line in Fig. 2) by the ratio of the  $K'_d$   
261 values of formaldehyde to those of chloroform, which were obtained by the bag experiments (using  
262 the average of the  $K'_d$  values obtained under the three conditions).

263

264

265 *3.3. Indirect exposure to formaldehyde*

266 We calculated the probability distribution of the formaldehyde concentration in air due to volatilization  
267 by multiplying the  $K'_d$  value distribution curve by an arbitrary concentration of formaldehyde in tap  
268 water. We searched for appropriate formaldehyde concentrations in tap water which would not cause  
269 health effect due to volatilization. Figure 4 shows the probability distribution of the formaldehyde  
270 concentration in bathroom air due to volatilization of tap water when the formaldehyde concentration  
271 in the tap water is assumed to be 2.6 mg/L-water (tolerable concentration; WHO, 2014). The 5th and  
272 95th percentiles of the formaldehyde concentration in air were 1.7 and 100  $\mu\text{g}/\text{m}^3$ -air, respectively,  
273 and the mean and median concentrations were 25 and 27  $\mu\text{g}/\text{m}^3$ -air. The 95th percentile concentration  
274 is close to the equilibrium concentration calculated by using the Henry's law constant for formaldehyde  
275 at a water temperature of 40 °C (Fig. 4, vertical dashed line). This high concentration in air might be  
276 attained during long showers or in an insufficiently ventilated bathroom (Niizuma et al., 2013). The  
277 median concentration, 27  $\mu\text{g}/\text{m}^3$ -air, can be interpreted to mean that the probability that up to 1/4 of  
278 the equilibrium concentration of formaldehyde in air at 40 °C is volatilized is 50%.

279

280 When the tap water concentration was 2.6 mg/L-water or less, the increment of the concentration in  
281 air due to volatilization was mostly less than 100  $\mu\text{g}/\text{m}^3$ -air [short-term (30-min) exposure guideline  
282 value for indoor air quality; WHO, 2010]. Note: the short-term exposure guideline was used for  
283 comparison because the time spent in bath room is not long [the 5, 50 and 95 percentiles of the time  
284 spent in bath room are 7, 18, and 40 min, respectively (Niizuma et al., 2013)]. If the criterion that the  
285 95th percentile value of the in-air formaldehyde concentration distribution should be equal to 100  
286  $\mu\text{g}/\text{m}^3$ -air is regarded as protecting the majority of a population, then the tap water concentration  
287 criterion for formaldehyde due to volatilization would be 2.6 mg/L-water, which is incidentally equal  
288 to the WHO (2014) guideline value for drinking water.

289

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

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

321

322

#### 323 **4. Conclusion**

324

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

341

342

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346 by the granting organization and does not necessarily reflect its opinion; therefore, no official  
347 endorsement should be inferred.

348

#### 349 **Appendix.**

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

351

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498 **List of Figure and Table Captions**

499

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

503

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

507

508 Fig. 3. Experimentally observed formaldehyde concentrations in air ( $C_a$ ) vs. those in water ( $C_w$ )  
509 compared with equilibrium relationships calculated by using values from Zhou and Mopper  
510 (1990) for the Henry's law constant for formaldehyde at 25, 30, and 40 °C.

511

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

515

516 Fig. 5. Schematics of formaldehyde exposure sources.

517

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

520

521 Table 2. Air–water contact conditions.

522

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

524

Fig. 1.

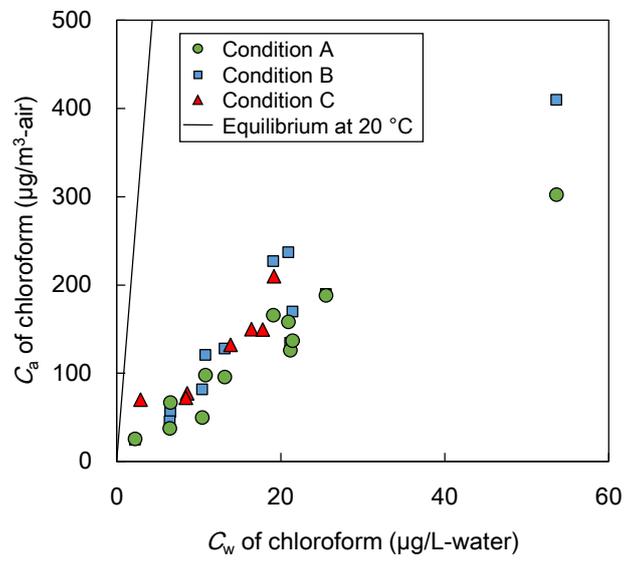


Fig. 2.

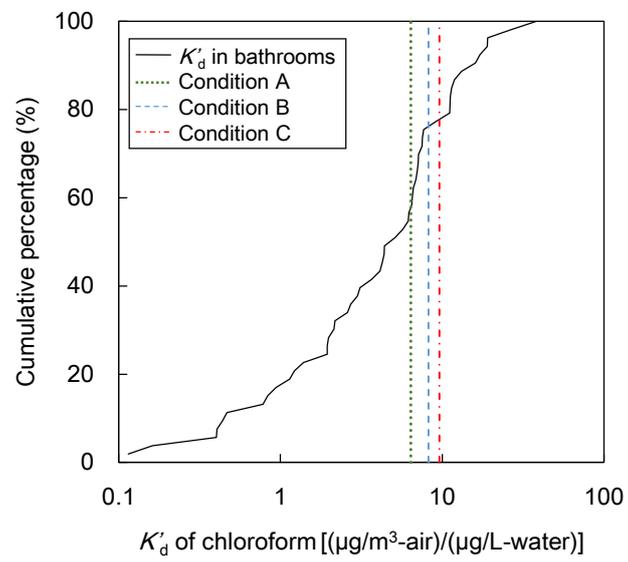


Fig. 3.

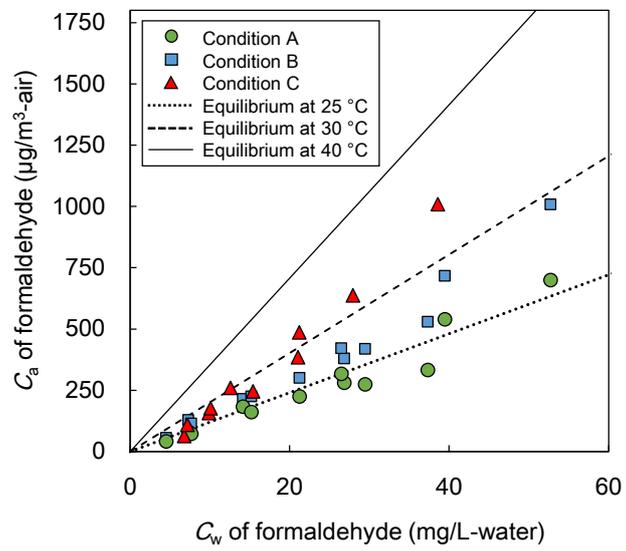


Fig. 4.

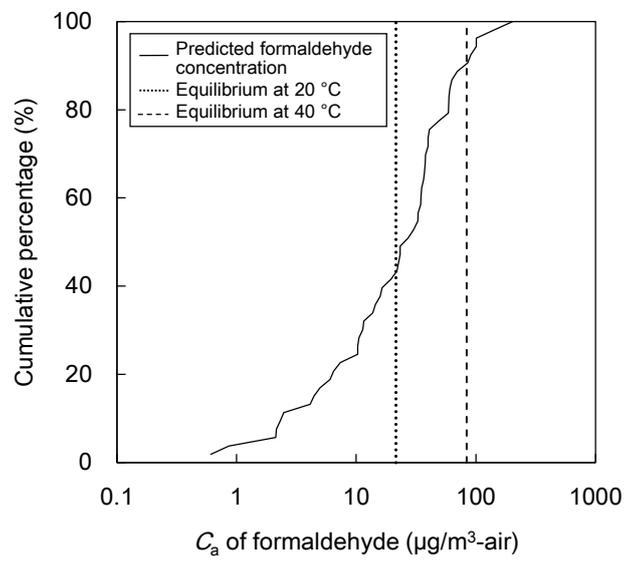
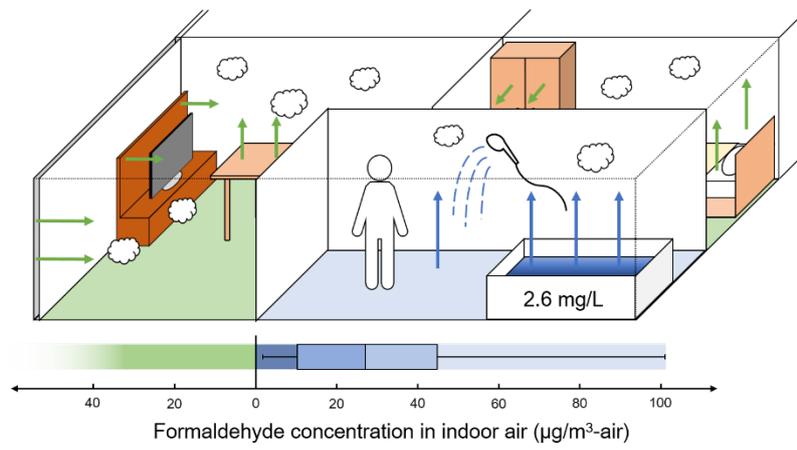


Fig. 5.



## Supplementary Information

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

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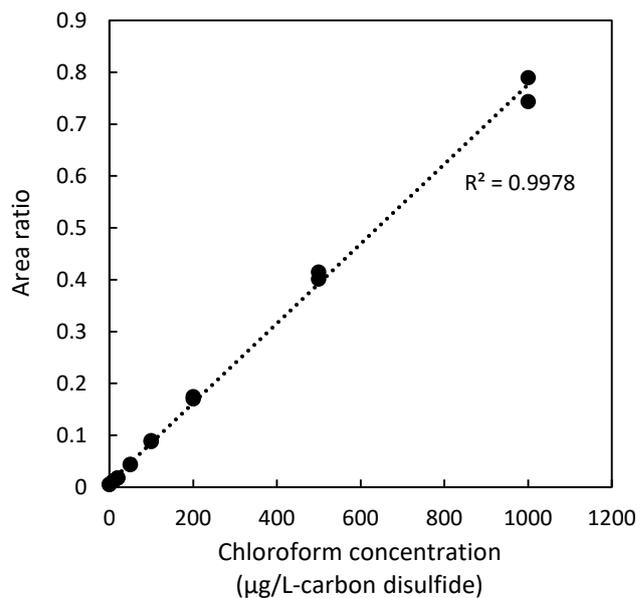


Figure 1S. Calibration line of chloroform in carbon disulfide obtained by GC/MS-ALS (Agilent technologies)

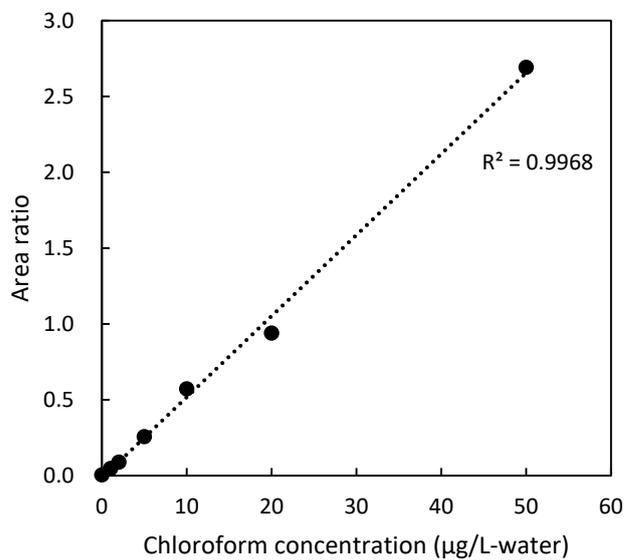


Figure 2S. Calibration line of chloroform in water obtained by PT&GC/MS (Shimadzu)

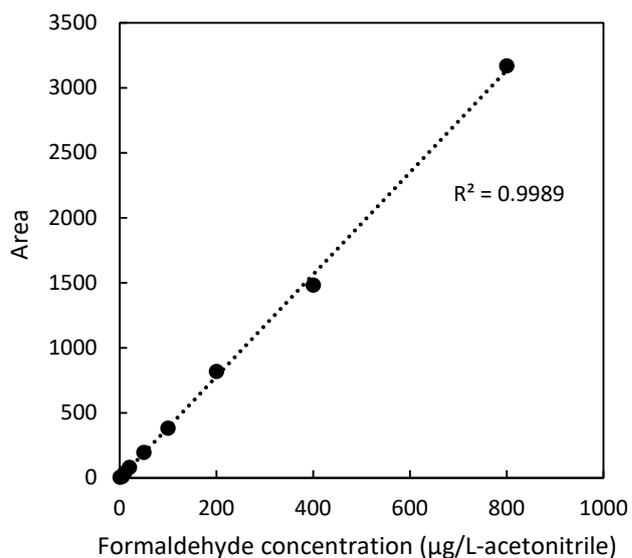


Figure 3S. Calibration line formaldehyde in acetonitrile obtained by HPLC-VWD (Agilent technologies)

Table 1S. Conforming the recoveries of air-phase formaldehyde (100 µg/m<sup>3</sup>-air) and chloroform (100 µg/m<sup>3</sup>-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/m <sup>3</sup> -air              | 10.8 to 21.4 µg/L-water                        | 15.2 to 39.5 µg/L-water                        |
| Coefficient of variation | 9.99×10 <sup>-6</sup> to 4.43×10 <sup>-2</sup> | 6.86×10 <sup>-2</sup> to 1.37×10 <sup>-1</sup> | 1.02×10 <sup>-3</sup> to 8.37×10 <sup>-3</sup> |