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1 Henry's law constant of N,N-dichloromethylamine.

2 Application to the contamination of the atmosphere of
3 indoor swimming pools

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10 **RECEIVED DATE ()**

11 **Abstract**

12 The volatility of N,N-dichloromethylamine (DCMA), a disinfection by-product formed during
13 chlorination of swimming pool water, has been investigated in the present work. The Henry's law
14 constants for DCMA were experimentally determined at five temperatures (5, 15, 25, 35 and 45 °C)
15 using the single equilibrium technique. The volumic ratio between the gas and the water phases in
16 the headspace vessels ranged from 1 to 60 and the initial concentration of DCMA in the aqueous
17 solutions was ≈ 2 mM. The values obtained for the dimensionless Henry's law constant varied from
18 0.047 at 5 °C to 0.312 at 45°C. The temperature dependence of the Henry's law constants followed
19 the van't Hoff equation. Trace levels of DCMA ($16-70 \mu\text{g}\cdot\text{m}^{-3}$) were detected in the atmosphere of
20 an indoor swimming pool whereas the concentrations of DCMA in water pools were in the range
21 $8.8-15 \mu\text{g}\cdot\text{L}^{-1}$.

22 **KEYWORDS:** Henry's law constant, N,N-dichloromethylamine; Temperature dependence;
23 Headspace technique; Swimming pool.

24 **1. Introduction**

25 Chlorination with chlorine gas or sodium hypochlorite is the most common process used for the
26 disinfection of public swimming pool water. Along with its disinfectant action, chlorine also leads
27 to the formation of numerous disinfection by-products such as chloramines, trihalomethanes,
28 haloacetic acids, chloral hydrate and haloacetonitriles by the reaction with pollutants introduced by
29 bathers. It has been estimated that a bather introduces in the water 25-80 mL.h⁻¹ of urine and 200-
30 1000 mL.h⁻¹ of sweat (Gunkel and Jessen, 1988; Erdinger *et al.*, 1997). These human materials
31 contain nitrogenous compounds (urea, ammonia, creatinine, amino-acids, amines, ...) and the
32 amount of nitrogenous pollution released by a bather is about equal to 0.85 g N.h⁻¹ (Seux, 1988).

33 It is well-known that reactions of aqueous chlorine with ammonia at neutral pH lead to the
34 formation of monochloramine and dichloramine as intermediates and to nitrogen gas as end-product
35 (Jafvert and Valentine, 1992). In addition to N₂, NO₃⁻ is a stable end-product of reactions between
36 chlorine and ammonia. The reactions are largely controlled by the chlorine:ammonia nitrogen ratio
37 (Cl:N), pH, buffer and ionic strength . At Cl:N less than 7.6:1 by weight, chlorine is present as
38 combined chlorine (inorganic chloramines) and at Cl:N higher than 7.6:1, free chlorine is present in
39 water. Small amounts of nitrogen trichloride (or trichloramine) and nitrate ions are also produced.
40 The reactions of chlorine with nitrogenous components present in urine and sweat can also lead to
41 the formation of organic and inorganic chloramines, nitrate as well as many potentially harmful
42 DBPs (Judd and Bullock, 2003). By using a new analytical method (membrane introduction mass
43 spectrometry), Li and Blatchley (2007) have shown that nitrogen trichloride can also be formed by
44 chlorination of four model compounds present in urine (urea, creatinine, histidine and arginine). The
45 reaction of chlorine with creatinine leads to the formation of N,N-dichloromethylamine (CH₃NCl₂,
46 DCMA) (Tachikawa *et al.*, 2005; Li and Blatchley, 2007) and Li and Blatchley, (2007) first reported
47 the occurrence of CH₃NCl₂ in a swimming pool water.

48 Chloramines and in particular inorganic chloramines have been suggested to largely contribute to
49 the typical smell and to the irritant properties of the atmosphere of indoor swimming pools (Héry *et*
50 *al.*, 1995). Nitrogen trichloride is the most volatile inorganic chloramine (Holzwarth *et al.*, 1984)
51 and is easily released into the air atmosphere of indoor pools. It has been shown to be a powerful

52 irritant for upper respiratory tracts (Gagnaire *et al.*, 1994). Therefore, most of the studies related to
53 the health risks associated with an exposure to DBPs present in the atmosphere of swimming pools
54 have focused on nitrogen trichloride. Published values for nitrogen trichloride concentrations in the
55 atmosphere of swimming pools range from below the detection limit ($\approx 0.05 \text{ mg.m}^{-3}$) to about 2
56 mg.m^{-3} (Jacobs *et al.*, 2007). For swimming pool workers, a dose/response relationship was
57 obtained for eye irritation, nasal and throat symptoms (Massin *et al.*, 1998a; Massin *et al.*, 1998b).
58 In France, NCl_3 concentrations in the atmosphere of indoor pools are not regulated. However, the
59 French institute of Occupational Health and Safety (INRS) has proposed a comfort limit value of 0.5
60 mg.m^{-3} (Héry *et al.*, 1995) even 0.3 mg.m^{-3} (Gérardin *et al.* 2005) for the concentration of NCl_3 in
61 the atmosphere of indoor pools. Carbonelle *et al.* (2002) have shown that trichloramine in air
62 increases the lung epithelium permeability at concentration levels as low as 0.3 mg.m^{-3} . In Belgium,
63 the Government of the Brussels-Capital Region has set a recommended maximum value of 0.3
64 mg.m^{-3} and a maximum admissible value of 0.5 mg.m^{-3} for the concentration of NCl_3 in the
65 atmosphere of indoor swimming pool (Gouvernement de la Région de Bruxelles-Capitale, 2002).

66 Organic chloramines formed by the reaction of chlorine with organic nitrogen contaminants may
67 i) contaminate the atmosphere of swimming pools, ii) give a positive interference in the
68 determination of NCl_3 concentration and iii) contribute to the irritant properties of the swimming
69 pool air. Among the organic chloramines, low molecular weight compounds such as DCMA might
70 be volatile. To our knowledge, the Henry's law constant of this chlorination by-product of creatinine
71 is unknown. Therefore, the main objective of the present work was to determine the Henry's law
72 constant of DCMA in the water/air system at various temperatures ranging between 5 and 55 °C. A
73 second objective of this work was to determine the concentration of DCMA in a pool water and in
74 the atmosphere of an indoor swimming pool of Poitiers.

75 **2. Material and methods**

76 **2.1. Reagents and preparation of standard solutions of DCMA**

77 All solutions were prepared from reagent-grade chemicals and purified water delivered by a
78 Millipore system (Milli RX75/Synergy 185). Stock solutions of methylamine (methylamine

79 hydrochloride, Acros Organics, 99%) and of free chlorine (prepared from sodium hypochlorite,
80 Acros Organics, 13 %) were stored in the dark at 4 °C.

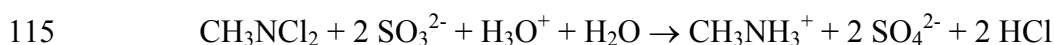
81 Stock solutions of N,N-dichloromethylamine (2 mmol.L^{-1}) were prepared a few minutes before
82 use by slowly adding free chlorine ($\text{pH} \approx 8$) to a solution of methylamine chloride in a well-stirred
83 reactor and using a chlorine:methylamine chloride molar ratio of 2:1. pH of the final solution was
84 adjusted to $\text{pH} 3.5 \pm 0.5$ with hydrochloric acid (37 % by weight). The change of the UV/Visible
85 absorbance with reaction time indicates that the reaction was achieved within a few seconds at $\text{pH} <$
86 4, in agreement with the previous works of Poncin *et al.* (1984).

87 **2.2. Henry's law constant determination**

88 Air/water partition coefficients or Henry's law constants were experimentally determined by using
89 a static method with variable headspace. This method can only be applicable for sufficiently volatile
90 compounds to be analytically admissible (McAullife, 1971; Gossett, 1987). In this study, a volume
91 V_L of a freshly prepared aqueous solution of DCMA ($C_{0,L} \approx 2 \text{ mmol.L}^{-1}$) was put into a vial (Total
92 volume : $V_T : 44 \pm 1 \text{ mL}$) or into a bottle ($V_T : 260 \pm 2 \text{ mL}$). The total volume of each vial or bottle
93 was exactly determined. The stock solution, the vessel and the air in the vessel were thermostated at
94 the desired temperature for at least one hour prior to the introduction of the DCMA solution. The
95 vessel was hermetically sealed with a PTFE-faced-silicone septum, immediately after introduction
96 of the DCMA solution. For each run, various ratios of inner gaseous headspace volume to the liquid
97 volume ($1 < V_G/V_L < 60$) were used in order to show the dependency of $C_{\text{eq},G}$ with $C_{\text{eq},L}$. The vessels
98 were set on a rotary tumbler for agitation in a thermostated room (Lovibond) for at least one hour.
99 Preliminary experiments demonstrated that the gas/liquid equilibrium was achieved within 10
100 minutes (Fig. S4 in Supplementary Content). After an agitation time of 1 hour, the vial or the bottle
101 was opened, the liquid phase was immediately transferred in a quartz cell (without using a pipette)
102 for a UV-spectroscopic determination of equilibrium DCMA concentration in the liquid phase
103 ($C_{\text{eq},L}$) at 302 nm. For each run, some vials were filled without headspace in order to confirm that
104 DCMA was not decomposed under our experimental conditions.

105 **2.3. Determination of DCMA level in the atmosphere of an indoor swimming pool**

106 An in situ measurement method was developed to determine DCMA level in the atmosphere of an
107 indoor swimming pool located at Poitiers (France). The sampler consisted of two 250-mL pyrex®
108 glass traps, containing 200 mL sodium sulfite (10 mmol.L⁻¹) and phosphate buffer (10 mmol.L⁻¹, pH
109 = 3.5-4) (Fig. S1 in Supplementary Content). The sampling flow rate was 1.5 L.min⁻¹ and the
110 sampling period varied from 2 to 4 h. The two traps were connected in series and no significant
111 breakthrough of DCMA from the first trap to the second one has been observed during any
112 sampling. Under these conditions, DCMA present in the atmosphere of the swimming pool is
113 absorbed in the traps and instantaneously reduced into the non volatile methylammonium ion (pKa
114 = 10.62; Hall, 1957) by sodium sulfite:



116 It should be noted that other volatile chloramines such as trichloramine can also be reduced by
117 sodium sulfite in the traps.

118 In order to determine the amounts of DCMA which have been trapped, the trapping solution was
119 transferred into a 200 mL volumetric flask and completed to 200 mL with purified water (Fig. S1 in
120 Supplementary Content). A volume of 20 mL of the trapping solution was introduced into a 25 mL
121 volumetric flask (five replicates for each trap). Methylammonium ion present in the trapping
122 solution was converted into DCMA with sodium hypochlorite in a 10 % molar excess (calculated
123 from initial sulfite concentration) and the solution was then adjusted to pH 3.5 ± 0.5. DCMA
124 concentration was then determined by HPLC and UV detection at 210 nm.

125

126 **2.4. Determination of DCMA in pool water**

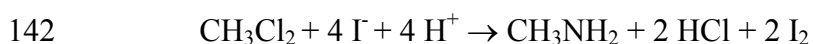
127 A volume of 10.0 L of water was collected from a spa and from a basin located in the indoor
128 swimming pool of Poitiers. DCMA was then stripped with an air flow rate of 1.5 L.min⁻¹ during 10
129 h at 45°C and the desorbed DCMA was then reduced into methylammonium ion with sodium sulfite
130 by passing the gas through the two same traps than those used for air sampling. It should also be

131 noted that a slow oxidation of sodium sulfite by oxygen occurred in the traps but the concentration
132 of sodium sulfite was always greater than 2 mmol.L⁻¹ after 10 h of air sparging.

133 To assess this method, 10.0 L of a standard aqueous solution of DCMA ([DCMA] = 1.9 μmol.L⁻¹)
134 has been analyzed under identical conditions. The data showed that DCMA was quantitatively
135 desorbed and trapped in the first absorption vessel. The recovery yield was 104 ± 3 % and DCMA
136 was not detected in the second trap.

137 **2.5. Analytical methods**

138 Free chlorine and DCMA concentrations in the stock solutions were determined iodometrically by
139 using the US Standard Method 4500B (APHA, 2005) with sodium thiosulfate 0.01 mol.L⁻¹
140 (Prolabo, > 99.9%). In the case of DCMA, two moles of free iodine is liberated by the reaction with
141 KI :



143 pH was measured with a MeterLab PHM 250 pH-meter (Radiometer) equipped with a glass
144 electrode (Radiometer, CL114 JB).

145 UV spectra of DCMA were recorded from 200 to 350 nm with a Cary 50 (Varian) and treated
146 with WinUV 3.0 software (Varian). DCMA concentrations in dilute solutions (0.35-3.5 mmol.L⁻¹)
147 were determined iodometrically in order to confirm the concentrations of DCMA.

148 DCMA concentration in the traps was determined by HPLC because of the possible presence of
149 other chloramines. HPLC analyses were performed with a Waters system (W600 controller;
150 W717plus Autosampler) equipped with a Zorbax 300Extend-C18 column and a UV detector at 210
151 nm (Waters W486). DCMA was eluted with a methanol (20%) / phosphate buffer (0.1 mol.L⁻¹; pH
152 = 4) (80%) mobile phase at a flow rate of 0.8 mL.min⁻¹. All HPLC analyses were made on five
153 replicates with a sampling volume of 200 μL. Under these analytical conditions, the absolute
154 detection and quantification limits were evaluated as 3 x 10⁻¹² and 9 x 10⁻¹² mol, respectively.
155 Relative quantification limit depends on the concentration factor applied during sampling collection
156 and on the volume of reactants added before analyses.

157 3. Background and expressions used

158 3.1. Data format

159 The two-phase equilibrium between air and water phases for a volatile solute in a dilute aqueous
160 solution can be represented by Henry's law coefficients or by air/water partition coefficients. Since
161 these coefficients can be expressed by a multitude of forms and associated units, Table 1 reports the
162 symbols and the expressions that will be used in this study.

163 3.2. Calculations of Henry law coefficients for DCMA

164 If DCMA is not decomposed under our experimental conditions, equilibrium concentration in the
165 gas phase ($C_{i,G}$) can be deduced from the mass balance expression :

$$166 \quad C_{i,G} = \frac{V_L}{V_G} (C_{0,L} - C_{i,L}) \quad (1)$$

167 The molar fractions of DCMA in water and in air were calculated as follows:

$$168 \quad x_i = \frac{C_{i,L}}{C_{i,L} + \rho_L/MW_L} = \frac{C_{i,L}}{\rho_L/MW_L} \text{ for dilute aqueous solutions} \quad (2)$$

$$169 \quad y_i = \frac{C_{i,G}}{P_T/RT} = \frac{RTV_L}{P_T V_G} (C_{0,L} - C_{i,L}) \quad (3)$$

170 where ρ_L is approximately equal to 1000 kg.m^{-3} for the temperature range studied in this work,
171 MW_L is the molecular weight of water ($0.018 \text{ kg.mol}^{-1}$), R is the universal gas constant ($R = 8.314$
172 $\text{Pa.m}^3.\text{mol}^{-1} \text{ K}^{-1} = 8.206 \times 10^{-5} \text{ atm.m}^3.\text{mol}^{-1}.\text{K}^{-1}$).

173 The various Henry's law constants listed in Table 1 were then calculated from $C_{i,L}$, $C_{i,G}$, x_i and y_i
174 values. Assuming that $P_T = 1 \text{ atm}$, the relationship between the various Henry's law constants
175 (Staudinger and Roberts, 2001) are the following:

$$176 \quad H_{cc} = H_{yx} \frac{0.2194}{T} = H_{px} \frac{2.165 \times 10^{-6}}{T} = H'_{px} \frac{0.2194}{T} = H_{pc} \frac{0.120}{T} = H'_{pc} \frac{12187}{T} \quad (4)$$

177 4. Results

178 4.1. Purity, stability and UV spectrum of aqueous solutions of DCMA at $\text{pH } 3.5 \pm 0.5$

179 The HPLC chromatograms of stock solutions of DCMA prepared at pH 3.5 ± 0.5 with a
180 chlorine:methylamine molar ratio of 2:1 showed only one peak corresponding to DCMA (Fig. S2 in
181 Supplementary Content). Iodometric titrations showed no loss of oxidants because the total amount
182 of chlorine was equal to the amount of free chlorine which has been introduced into the solutions of
183 methylamine. These data indicate that stock solutions of DCMA only contain DCMA and that the
184 concentration of DCMA is equal to the half of the initial concentration of free chlorine. (1 mole of
185 DCMA is equivalent to 2 moles of free chlorine).

186 UV/Visible spectra of dilute solutions of DCMA ($3.4 \times 10^{-4} \text{ M} < [\text{DCMA}] < 3.5 \times 10^{-3} \text{ M}$) were
187 recorded by using quartz cells (optical length: 1, 5 or 10 cm). As shown the spectrum presented in
188 Fig. S3 in Supplementary Content, DCMA absorbs in the UV region. The spectrum presents an
189 absorption band at 302 nm with a molar extinction coefficient equal to $\epsilon_{302\text{nm}} = 309 \pm 18 \text{ mol}^{-1}$
190 $\cdot \text{L}\cdot\text{cm}^{-1}$ (mean value of 39 absorbance values determined from different standard solutions of
191 DCMA). Spectrophotometric analyses also demonstrated that the UV spectra of DCMA solutions
192 stored in hermetically closed vials and filled without headspace did not change over a storage time
193 of 15 h at 5 - 55 °C and pH 3.5 ± 0.5 . These results confirm that DCMA did not decompose in water
194 under our experimental conditions.

195 Fig. S3 in Supplementary Content also shows that the UV/visible spectrum of DCMA is similar to
196 the spectrum of dichloramine (NHCl_2) which presents an absorption band at 293 nm ($\epsilon_{293\text{nm}} = 289 \pm$
197 $5 \text{ mol}^{-1} \cdot \text{L}\cdot\text{cm}^{-1}$, mean value of 9 UV-absorbance values).

198 **4.2. Henry's law constant of N,N-dichloromethylamine**

199 The Henry's law constant was determined at five different temperatures by measuring the
200 equilibrium concentration of DCMA in the aqueous phase ($C_{i,L}$). All the experimental conditions
201 ($C_{0,L}$, V_L , V_G , T) and the equilibrium concentrations ($C_{i,L}$ and $C_{i,G}$) have been reported in
202 Supplementary Content (Tables S1-S5 and Fig. S5).

203 From the experimental data, the various forms of the Henry's law constants reported in Table 1
204 (H_{cc} , H'_{px} , H'_{pc} and H_{yx}) have been calculated by linear regression analysis. As shown the data in

205 Fig. 1, straight lines were obtained for the dependence of $C_{i,G}$ with $C_{i,L}$ at 288 and 308 K as well as
206 for the other temperatures studied (Tables S1-S5 in Supplementary Content).

207 Values of Henry's law constants determined in this work are reported in Table 2. The values
208 obtained for the air-to-water concentration ratio (H_{cc}) vary from 0.048 at 5 °C to 0.335 at 45 °C. The
209 temperature dependence of Henry's law constants is correctly described by the van't Hoff equation
210 (Fig. 2):

$$211 \quad \ln(H) = A + \frac{B}{T}$$

212 where $B = 4298.11$ K (excepted for H_{cc}) and A , a constant which depends on the unit used for the
213 Henry's law constants. Values of A and B have been reported in Table 2.

214 The solvation enthalpy (ΔH°_{sol}) can be calculated from the slope of the $\ln(H) = f(1/T)$ straight
215 line (for H constant other than H_{cc}) :

$$216 \quad \Delta H^{\circ}_{sol} = B R \text{ with } R = 8.314 \text{ Pa.m}^3 \cdot \text{mol}^{-1} \text{ K}^{-1}$$

217 The solvation enthalpy of $-35.7 \text{ kJ.mol}^{-1}$ obtained for DCMA is very close to the values
218 published for NH_2Cl , NHCl_2 and NCl_3 (Sander, 1999) which are in the range $34.2\text{-}39.9 \text{ kJ.mol}^{-1}$
219 (Table 3).

220 A comparison of the Henry's law constants (Table 3) or of the air-water partition coefficient (Fig.
221 3) of some disinfection by-products formed during chlorination of swimming pool water shows that
222 DCMA is a little less volatile than chloroform, about 3 times less volatile than trichloramine but far
223 much volatile than monochloramine and dichloramine. At the average temperature of recreation
224 pools ($\approx 30^\circ\text{C}$), the air-water coefficients (H_{cc} values) of trichloramine, chloroform, DCMA,
225 dichloramine and monochloramine are equal to 0.504, 0.195, 0.135, 1.75×10^{-3} and 5.58×10^{-4}
226 respectively. If DCMA is produced in water pools at concentration levels of about $0.1 \mu\text{mol.L}^{-1}$ (10
227 $\mu\text{g.L}^{-1}$), the theoretical concentration of DCMA in air in a closed system should be $\approx 1.9 \text{ mg.m}^{-3}$.
228 This concentration might cause irritation to bathers and to pool attendance.

229 **4.3. Concentration levels of DCMA in water pools and in the atmosphere of an indoor**
230 **swimming pool.**

231 The DCMA levels in water and in the atmosphere of an indoor swimming pool located at Poitiers
232 have been determined between February 2009 and May 2009. The swimming pool has a 25 meter
233 pool (436 m³), a leisure pool (190 m³), a children pool (10 m³), a toboggan pool (26 m³) and a spa
234 (5 m³). The total volume of the atmosphere of the indoor pool (15 000 m³) can be contaminated by
235 volatile compounds that escape from the five basins. Table 4 reports the main operating conditions
236 of the swimming pool for the four campaigns (C1 to C4) made in this study.

237 DCMA was determined in water collected from the spa (campaigns C1 and C2) and from the 25
238 meter pool (campaigns C3 and C4). The spa water is totally renewed every night in order to
239 maintain the concentration of combined chlorine below 0.6 mg Cl₂.L⁻¹. The mean residence time of
240 water in the 25 meter pool is 10 days. Analyses showed that the concentrations of DCMA in water
241 samples ranged from 88 to 150 nmol.L⁻¹ (8.8 and 15 µg.L⁻¹) (Table 4) and that about 3 % of the
242 combined chlorine concentration can be accounted for DCMA (Table 4). Our concentrations of
243 DCMA in water are of the same order of magnitude than those obtained by Weaver *et al.* (2009)
244 using membrane introduction mass spectrometry (MIMS) for the determination of DCMA in 11
245 water pools (1.6 µg.L⁻¹ < [DCMA] < 50.5 µg.L⁻¹). It should be noted that about 80 % of the spa
246 water is renewed every night and there is always about 12-13 bathers in the spa.

247 The water samples collected from the 25 meter pool were chlorinated at an arbitrary dose of 14
248 mg Cl₂.L⁻¹ in a 10 L headspace-free bottle in order to show if the DCMA concentration could
249 increase by increasing free chlorine concentration and reaction time. After a reaction time of 72 h,
250 analyses showed that this postchlorination step led to a chlorine consumption of about 8 mg Cl₂.L⁻¹
251 and to an increase of the DCMA concentration by a factor of 2.5-3. The DCMA concentrations were
252 in the range 230-270 nmol.L⁻¹ (23-27 µg.L⁻¹). This increase of the concentration of DCMA suggests
253 that reactions leading to the formation of DCMA are not very fast, in agreement with the kinetic
254 data obtained by Li and Blatchley (2007) for the formation of DCMA from creatinine. Methylamine
255 and creatinine are known to produce DCMA by chlorination (Poncin *et al.*, 1984; Li and Blatchley,
256 2007). As the concentration of methylamine in urine is about 10 times less than the concentration of
257 creatinine (Mitchell and Zhang, 2001) most of the DCMA formed in swimming pool is probably

258 formed from creatinine. On the basis of a production of 0.66 mole of DCMA per mole of creatinine
259 (Li and Blatchley; 2007), the DCMA formation potentials measured in our study ($250 \pm 20 \text{ nmol.L}^{-1}$)
260 ¹) should correspond to a concentration of creatinine in the water samples of 350-400 nmol.L^{-1} . This
261 is fully consistent with the concentrations of creatinine which can be estimated from the
262 concentrations of urea of 30-50 $\mu\text{mol.L}^{-1}$ (1.8-3.0 mg.L^{-1}) which have been measured in this
263 swimming pool water (unpublished data) and from a mean molar ratio of urea to creatinine of about
264 100 in urine.

265 As far as air analyses are concerned, air was sampled at a distance of about 4 m from the two
266 main basins and at a height of 1.5 m. DCMA concentrations in air were in the range 0.16-0.70
267 $\mu\text{mol.m}^{-3}$ (16-70 $\mu\text{g.m}^{-3}$) and far below the theoretical DCMA concentration in air (1.5-2.0 mg
268 DCMA m^{-3}) that should be in equilibrium with the aqueous concentrations of DCMA at 30 °C (11-
269 15 $\mu\text{g.L}^{-1}$) at 30 °C (Table 4). The concentration of DCMA was higher for the first campaign ($70 \pm$
270 $30 \mu\text{g.m}^{-3}$) than for the second one ($16 \pm 2 \mu\text{g.m}^{-3}$). This was consistent with the observations made
271 by the attendant pools who reported that the atmosphere was found to be more irritant during the
272 first campaign of analyses. It should also be noted that the lowest value of DCMA concentration
273 obtained during the second campaign might be attributed to the fact that the ventilation rate was
274 higher and that all the roof windows were opened.

275 Nowadays, the concentrations of DCMA in water and in the atmosphere of indoor swimming
276 pools are not controlled. As trichloramine exposure is considered to be at the origin of eye and
277 airway irritations, only trichloramine concentrations have been determined in the atmosphere of
278 indoor pools (Massin *et al.*, 1998b; Jacobs *et al.*, 2007). In these studies, the analytical method used
279 for the determination of trichloramine in the atmosphere of indoor pools is based on the reduction of
280 trichloramine by arsenic trioxide and subsequent determination of the chloride ion formed (Héry *et*
281 *al.*, 1995). The concentration of trichloramine in water pools can also be determined by this method
282 after a gas/liquid desorption of trichloramine. The data obtained in the present work suggest that the
283 use of this method might lead to an overestimation of the concentration of trichloramine in the
284 presence of other volatile organic chloramines such as DCMA. The membrane introduction mass

285 spectrometry (MIMS) is a more convenient method for the differentiation and the quantification of
286 inorganic and organic chloramines in water and in air (Weaver *et al.*, 2009).

287 **6. Conclusion**

288 The Henry's law constants determined in the present work show that N,N-dichloromethylamine
289 (DCMA) is quite as volatile than trichloramine. This work confirms the presence of DCMA in pool
290 water previously reported by Li and Blatchley (2007) and Weaver *et al.* (2009) and this work
291 demonstrates for the first time the presence of DCMA in the atmosphere of indoor swimming pools.
292 These data suggest that the health risks associated with the formation of this volatile organic
293 chloramine during chlorination of swimming pool water must be considered in further
294 epidemiological studies. Additional research is also needed in order to develop specific analytical
295 methods for the determination of DCMA and trichloramine and to evaluate the irritant properties for
296 eyes and the respiratory tracts of DCMA and for mixture of DCMA and trichloramine.

297 **Acknowledgments**

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300 **Appendix A : Supplementary Content**

301 Supplementary data associated with this article can be found in the online version at DOI ...

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