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Supplementary Information

Modeling Volatilization and Adsorption of Disinfection Byproducts in Natural Watersheds

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19 General Model Framework

20

21 The governing fate-and-transport model simulates a continuous input, point sourced, steady
22 state watershed (Equation 1)¹. The model is able to accounting for the effects of dilution
23 (e.g., unknown inflow), condensation (e.g., water evaporation), advection, dispersion,
24 transformation, and degradation among liquid, solid, and air interfaces. In general, it predicts
25 the content of DBP as a function of travel distance (x) and time (t).

26

$$\begin{aligned} V \frac{d[DBP]}{dt} = & [DBP]_{in_WWTP} \cdot Q_{in_WWTP} + [DBP]_{in_upstream} \cdot Q_{in_upstream} - Q_{out} \cdot [DBP] \\ & - V \cdot U_{water} \cdot \frac{d[DBP]}{dx} + V \cdot E_x \frac{d^2[DBP]}{dx^2} + r_T \cdot V \end{aligned} \quad 1$$

28

29 Where [DBP] represents the concentration of a DBP (mole/L); t refers to the time (hr); Q is
30 the water flow rate (m³/hr); U_{water} is the flow velocity in the flow direction (x-direction)
31 caused by advection (m/hr); E_x is the dispersive coefficient in the x direction (m²/hr); x is
32 the travel distance (m); r_T is the total loss rate of DBP (mole/L-hr); V is the volume of a
33 given watershed (m³). The subscript “in” indicates the inflows from WWTP and upstream;
34 and “out” indicates the outflow from the body of water.

35

36 In one cross-section or a specific point where the contaminant inflow DBP content equals to
37 the outflow DBP content, Equation 1 can be simplified as the following way²:

38

39
$$\frac{d[DBP]}{dt} = r_T - U_{water} \cdot \frac{d[DBP]}{dx} + E_x \frac{d^2[DBP]}{dx^2} \quad 2$$

40

41 Overall, the levels of DBP removal are affected by the degradation/transformation
42 processes (the first term, r_T), advection (the second term), and dispersion (the third term). r_T
43 determines the fates of the DBPs in the watershed, and U_{water} and E_x decide the transport
44 and spreading of the DBPs². r_T is the sum of a variety of DBP loss rates including
45 volatilization (r_V), photolysis (r_P), hydrolysis (r_H), biodegradation (r_B), adsorption (r_A), and
46 others (r_O) (Equation 3).

47

48
$$r_T = r_V + r_P + r_H + r_B + r_A + r_O \quad 3$$

49

50 In this study, emphases were placed on the capacities of r_V and r_A . Because loss rate is
51 usually described as a pseudo first-order reaction, the reduction rate of a DBP is a function
52 of its first-order rate constant (k_T) and concentration (Equation 4).

53

54
$$r_T = \frac{d[DBP]}{dt} = -k_T \cdot [DBP] \quad 4$$

55

56 DBP half-life ($T_{1/2}$) is calculated by k_T and is irrelevant to the initial concentrations of DBP
57 (Equation 5), which makes the data comparable across different labs and different types of
58 compounds.

59

60
$$T_{1/2} = \frac{\text{Ln}(2)}{k_T} \quad 5$$

61

62 The determination of the water flow velocity (U_{water}) in surface watersheds follows

63 Manning's equation:

64

65
$$U_{\text{water}} = \frac{R_H^{2/3} \cdot S^{1/2}}{n} \quad 6$$

66

67 Where R_H is the hydraulic radius (m) of the watershed, calculated as the cross-sectional
68 area (A , m^2) divided by the wetted perimeter (P , m); S is the hydraulic gradient or slope of
69 the watershed (unitless); and n refers to the roughness coefficient of the watershed
70 ($\text{hr}/\text{m}^{1/3}$).

71

72 For groundwater, the flow velocity of the water is determined by Darcy's law:

73

74
$$U_{\text{water}} = k_C \cdot S = k_C \cdot \frac{dH}{dx} \quad 7$$

75

76 Where k_C indicates the hydrological conductivity (m/hr) and H indicates the height from
77 the start to the end point.

78

79 Based on an empirical equation³, the longitudinal dispersive coefficient E_x in the surface
80 watershed is associated with certain hydrogeological characteristics, as presented below:

81

$$E_x = 3.4 \cdot 10^{-5} \cdot \frac{U_{water}^2 \cdot W^2}{H \cdot U_{shear}} \quad 8$$

83

84 Where W means the width of the watershed (m) and U_{shear} refers to the shear velocity
85 (m/hr), which can be estimated by the following equation:

86

$$U_{shear} = (g \cdot H \cdot S)^{1/2} \quad 9$$

88

89 Where g is the gravity constant (9.8 m/sec²).

90

91 In an aquifer system, there is significant dispersion primarily because of small- and
92 large-scale mixing phenomena. Dispersivity (D_{disp}) dominates the dispersion effect
93 (Equation 10), and its values range from 0.01 to 0.1 times of the travel distance⁴.

94

$$E_x = D_l + D_{disp} \cdot U_{water} \quad 10$$

96

97 Where D_l is the diffusivity for DBP, which is to be discussed in the following section and
98 usually negligible in groundwater.

99

100 **Volatilization Model Development**

101

102 On the basis of the above-mentioned fate-and-transport model buildup and the

103 hydrogeological setups, volatilization and adsorption simulations were conducted.
104 According to the classic two-film theory, volatilization refers to the transition of a
105 compound from its liquid phase to its gaseous phase. The transfer rate (dc/dt) is associated
106 with the mass-transfer coefficient (k_l), the water depth (H), and the concentration gradient
107 between gaseous and liquid forms²(Equation 11):

$$109 \quad r_v = \frac{d[DBP]}{dt} = \frac{k_{vol}}{H} \cdot \left(\frac{[DBP]_{gas}}{H_c} - [DBP] \cdot \alpha_0 \right) \quad 11$$

110
111 Where DBP_{gas} is the concentration of DBP in the gaseous phase (mole/L); k_{vol} is the
112 volatilization rate coefficient (m/hr); α_0 is the fraction of DBP in its non-ionized form
113 (reason: the ionized species bonds strongly with water and therefore has little likelihood of
114 detaching from water and transferring into air); H_c is the Henry's law constant (HLC) in
115 unitless form, which is equal to:

$$117 \quad H_c = \frac{H_e}{R \cdot (273 + T)} \quad 12$$

118
119 Where R is a constant (8.02×10^{-5} atm-m³/mole-K); T is the temperature in degrees Celsius
120 (^oC); and H_e is the HLC in unit of atm-m³/mole, which is positively correlated with the
121 increase in temperature (Equation 13).

122

$$H_{e1} = H_{e2} \cdot e^{\frac{-\Delta H}{R_C} \left(\frac{1}{273+T_1} - \frac{1}{273+T_2} \right)} \quad 13$$

124

125 H_{e1} and H_{e2} are the HLCs of two different temperatures ($\text{atm}\cdot\text{m}^3/\text{mole}$); R_C is the gas
126 constant ($8.314 \text{ J/mole}\cdot\text{K}$), ΔH is the enthalpy of vaporization (KJ/mole) of a DBP; T_1 and
127 T_2 are temperatures ($^{\circ}\text{C}$).

128

129 In an open system for which gaseous DBP is immediately dispersed, equation 11 can be
130 simplified to include the aqueous DBP only:

131

$$r_v = \frac{d[DBP]}{dt} = -\frac{k_{vol}}{H} \cdot [DBP] \cdot \alpha_0 \quad 14$$

133

134 The non-ionized fraction of a chemical, α_0 , is a function of its acid-base dissociation
135 constant (pK_a), and calculated by pK_a and the hydrogen ion content $[\text{H}^+]$ in a designated
136 pH^5 :

137

$$\alpha_0 = \frac{[\text{H}^+]}{[\text{H}^+] + 10^{-\text{pK}_a}} \quad 15$$

139

140 The parameter k_{vol} is determined by the gas-film exchange coefficient (k_{gas}) and the
141 liquid-film exchange coefficient (k_{liquid}), according to the two-film theory (Equation 16):

142

$$k_{vol} = \left(\frac{1}{k_{liquid}} + \frac{1}{k_{gas} \cdot H_C} \right)^{-1} \quad 16$$

144

145 The liquid-film exchange coefficient k_{liquid} (m/hr) can be further estimated by an empirical
146 equation related to DBP chemical properties²:

147

$$148 \quad k_{\text{liquid}} = k_{\text{exchange}} \cdot \left(\frac{32}{MW}\right)^{1/4} \quad 17$$

149

150 Where k_{exchange} is the coefficient of a DBP in exchange with water (m/hr); MW refers to the
151 molecular weight (g/mole). k_{exchange} of a DBP can be calculated by its diffusivity (D_l), water
152 velocity (U_{water}), and water depth (H)²:

153

$$154 \quad K_{\text{exchange}} = \left(D_l \cdot \frac{U_{\text{water}}}{H}\right)^{1/2} \quad 18$$

155

156 Where the diffusivity of an organic compound in water (D_l) is computed via an equation
157 proposed by USEPA⁶:

158

$$159 \quad D_l = 1.518 \cdot 10^{-4} \cdot \left(\frac{T + 273}{298}\right) \cdot \left(\frac{MW}{\rho_{\text{DBP}}}\right)^{-0.6} \quad 19$$

160

161 Where ρ_{DBP} is the density of DBP.

162

163 In terms of the DBP transfer in a gas-film, the coefficient k_{gas} mainly depends on DBP
164 diffusivity in gas (D_g) and wind velocity (U_{wind})²:

165

166
$$K_g = 0.001 \cdot \left(\frac{D_g}{\nu_g}\right)^{2/3} \cdot U_{wind}$$
 20

167

168 Where ν_g is the kinematic viscosity constant of air ($0.15 \text{ cm}^2/\text{s}$). Like D_l , D_g can also be
169 estimated by the chemical properties of MW, density, and temperature, based on the
170 following equations (Equations 21 and 22)⁶.

171

172
$$D_g = \frac{2.29 \cdot 10^{-3} \cdot (T + 273)^{1.5} \cdot \sqrt{0.034 + 1/MW} \cdot 0.4}{((MW/2.5/\rho_{DBP})^{1/3} + 1.8)^2} \quad \text{if } (1 - 1.5 \cdot 10^{-5} \cdot MW^2) \leq 0.4$$
 21

173
$$D_g = \frac{2.29 \cdot 10^{-3} \cdot (T + 273)^{1.5} \cdot \sqrt{0.034 + 1/MW} \cdot (1 - 1.5 \cdot 10^{-5} \cdot MW^2)}{((MW/2.5/\rho_{DBP})^{1/3} + 1.8)^2} \quad \text{if } (1 - 1.5 \cdot 10^{-5} \cdot MW^2) > 0.4$$
 22

174

175 Overall, the volatilization rate constant (k_{vol}) is determined by approximately twelve
176 variables, including watershed hydrogeological characteristics (U_{water} , W , H , S , and n),
177 environmental conditions (T and U_{wind}), and chemical-specific properties (HLC , pK_a , ρ_{DBP} ,
178 ΔH , and MW). By selecting the hydrogeological and environmental settings, estimating the
179 relative loss of different classes of DBPs becomes possible.

180

181 **Adsorption Model Development**

182

183 Similar to volatilization, the removal of DBPs via adsorption in surface watersheds also
184 involves two steps: first, DBPs in dissolved forms are partitioned into suspended particles
185 (SP) coated with organic matter, forming particulate DBPs (Equation 23). Next, the
186 adsorbed DBPs settle down to the waterbed along with SP via the force of gravity. The first

187 step decides the adsorptive potentials of the DBPs in the SP, and the second step controls
188 the settling kinetics of the DBPs and SP⁷. The adsorption equilibrium is assumed to be
189 linear, which is true for relatively low concentrations of DBPs (ng/L or µg/L levels) in the
190 environment. The adsorption kinetics are assumed rapid and instantaneous by assigning a
191 high adsorption rate constant ($k_{\text{adsorption}} = 25000/\text{hr}$). Sediment comes only from upstream
192 suspended particles (SPs) in a watershed if there are no soil movements, riverbank erosion,
193 or other types of renewal; this assumption serves as the basis of this study. Before SP settles
194 down and becomes sediment, SP adsorbs and equilibrates with DBPs as much/fast as
195 possible, during which SP and DBP have sufficient opportunity in contacting with each
196 other and reaches its adsorption capacity. Once settled, SP, along with the adsorbed DBP,
197 are kept in waterbed and termed sediment. Because the sediment adsorbs DBP already, its
198 adsorption ability is much lower than initial SP, if not zero. In addition, sediment in
199 waterbed is not fully in contact with DBP in water, so its adsorption ability can be
200 compromised. Under such condition, the exchange of DBPs between the water and the
201 waterbed sediment becomes relatively insignificant.

202

$$203 \quad \frac{d[DBP_{\text{sorbed}}]}{dt} = k_{\text{adsorption}} (K_p \cdot [DBP] - [DBP_{\text{sorbed}}]) \quad 23$$

204

205 Where K_p is the partition coefficient (L/kg) as defined in Equation 24. For a compound
206 with reversible adsorption and desorption, K_p is estimated by its octanol-water partitioning
207 constant (K_{ow}), SP concentration ($[SP]$, mg/L), and the fraction of organic matter (f_{oc})
208 coated in SP².

209

$$210 \quad K_p = \frac{[DBP_{sorbed}]}{[DBP_{dissolved}]} = \frac{2.8 \cdot f_{OC} \cdot K_{OW}}{1.4 + [SP] \cdot f_{OC} \cdot K_{OW}} \cdot \alpha_0 \quad 24$$

211

212 Where α_0 is the percentage of a specific DBP in non-ionized form (reason: the ionized
213 species bonds strongly with water and therefore has little likelihood of detaching from
214 water and absorbing on adsorbent). The particulate and dissolved fractions of DBPs are
215 calculated with the following equations²:

216

$$217 \quad f_p = \frac{K_p \cdot [SP]}{1 + K_p \cdot [SP]} \quad 25$$

$$218 \quad f_d = 1 - f_p \quad 26$$

219

220 Where f_p is the fraction of DBP in particulate form, or the absorbable fraction (%); f_d is the
221 fraction of DBP in dissolved form (%).

222

223 At the second step, SP and DBPs settle simultaneously. Under constant temperature, the
224 nominal settling velocity of SP is mainly determined by the particle size and the difference
225 in density between water (ρ_{water}) and particle ($\rho_{particle}$), according to Stokes' law (Equation
226 27):

227

$$228 \quad v_s = \frac{g}{18} \cdot \left(\frac{\rho_{solid} - \rho_{water}}{\mu} \right) \cdot d_i^2 \quad 27$$

229 Where: v_s is the settling velocity of the suspended particle (m/hr); ρ_{solid} is the density of

230 suspended particles (g/cm^3); ρ_{water} is the density of water (assumed to be constant at
231 $1\text{g}/\text{cm}^3$); d_i refers to the diameter of the suspended particle (μm); ν is the viscosity of water
232 at a certain temperature ($= 0.1 \text{ cm}^2/\text{s}$ at 25°C) and decreases with temperature (T); and g is
233 the gravity acceleration constant ($9.8 \text{ m}/\text{sec}^2$). The density of a SP has been shown to
234 roughly correspond with its diameter (Equation 28) in some case studies²:

235

$$236 \quad \rho_{\text{solid}} = 2 \cdot d_i^{-0.15} \quad 28$$

237

238 Overall, the removal of SP follows a first-order reaction rate (Equation 29) in which water
239 depth (H) serves as an important factor in determining the SP settling rate². The removal of
240 DBPs also follows a seemingly first-order reaction rate (Equation 30). If a DBP exists
241 primarily in non-ionized form (i.e., $\alpha_0=1$), the DBP rate can be converted to be Equation 31,
242 in which the reduction rate constant of the DBP (k_{settling}) decreases with the declining SP
243 content (Equation 32).

244

$$245 \quad \frac{d[\text{SP}]}{dt} = -k_{\text{SP}} \cdot [\text{SP}] = -\frac{\nu_s}{H} \cdot [\text{SP}] \quad 29$$

$$246 \quad \frac{d[\text{DBP}]}{dt} = -\frac{\nu_s}{H} \cdot [\text{DBP}_p] = -\frac{\nu_s}{H} \cdot [\text{DBP}] \cdot \alpha_0 \cdot f_p \quad 30$$

$$247 \quad \frac{d[\text{DBP}]}{dt} = -\frac{\nu_s}{H} \cdot [\text{DBP}] \cdot \frac{K_p \cdot [\text{SP}]}{1 + K_p \cdot [\text{SP}]} = -k_{\text{SP}} \cdot \frac{K_p \cdot [\text{SP}]}{1 + K_p \cdot [\text{SP}]} \cdot [\text{DBP}] \quad 31$$

$$248 \quad k_{\text{settling}} = \frac{K_p \cdot [\text{SP}]}{1 + K_p \cdot [\text{SP}]} \cdot k_{\text{SP}} \quad 32$$

249

250 Where k_{SP} is the first-order reduction rate constant (1/hr) of SP.

251

252 Theoretically, the settled DBPs may diffuse into soils, undergoing biodegradation and
253 hydrolysis in the sediment. These subsequent processes are nonetheless beyond the scope
254 of this study and therefore are not emphasized.

255

256 In well-confined aquifer, soil occupies most of the space and serves as an absorbent. The
257 adsorption rate of DBPs on soils also follows Equation 23, but unlike the surface watershed,
258 the content of particles in aquifer is much larger (in 1,000,000 mg/L level), which is
259 determined by the product of the particle density (ρ_{solid} , kg/L) and the aquifer porosity (Φ)
260 (Equations 33 and 34).

261

$$262 \quad \rho_{bulk} = \rho_{solid} \cdot (1 - \phi) \quad 33$$

$$263 \quad [SS] = 10^6 \cdot \rho_{bulk} \quad 34$$

264

265 Because the amount of DBP loss in water is equal to the amount of DBP gain in soil
266 (Equation 35)⁷, the fate and transport of DBPs in aquifer are influenced by the adsorption
267 (the first term of Equation 36) and degradation/transformation processes (the second term
268 of Equation 36)

269

$$270 \quad d[DBP] \cdot V \cdot \phi = d[DBP_{sorbed}] \cdot V \cdot \rho_{solid} \cdot (1 - \phi) \quad 35$$

$$271 \quad \frac{d[DBP]}{dt} = - \frac{d[DBP_{sorbed}]}{dt} \cdot \frac{\rho_{solid} \cdot (1 - \phi)}{\phi} - k_T \cdot [DBP] \quad 36$$

272

273 Retardation in groundwater systems does not reduce DBPs directly, but provides DBPs
274 with more time to be degraded or transformed by other removal mechanisms. The
275 retardation coefficient (R) is defined as the ratio of the volume of water needed to transport
276 a pollutant completely through the aquifer (V_{req}) to the unit volume (V_{unit} , namely pore
277 volume) of the aquifer (Equation 35). In other words, a pollutant may reside ($R-1$) times of
278 period longer than pure water. Quantification of R is a function of aquifer bulk density
279 (ρ_{bulk}), K_P , and Φ (Equation 35)

280

$$281 \quad R = \frac{V_{req}}{V_{unit}} = 1 + \frac{\rho_{bulk} \cdot K_P}{\phi} \quad 37$$

282

283 In brief, the removal of DBPs via the adsorption process occurs differently in surface
284 watershed and underground watersheds: one process occurs through settling and the other by
285 prolonging the retention time to allow other mechanisms to degrade the DBPs. However,
286 both processes depend heavily on the partitioning ability of the DBPs, expressed as K_P or
287 K_{ow} , and the adsorbent concentration (i.e., $[SP]$). In addition to the environmental factors
288 (such as T , $[SP]$, f_{oc} , Φ , and ρ_{solid}), certain hydrogeological parameters including water level
289 height (H) and dispersivity (D_{disp} , from Equation 10) are also critical to the fate and transport
290 of DBPs.

291

292 In order to compare the relative importance of different types of mechanisms, a list of
293 reaction rate constants were extracted from earlier studies. The rate of photolysis is subject
294 to adjustment for water depth according to Equation 38⁸.

295

$$296 \quad k_{\text{photolysis}} = k_{\text{surface}} \cdot e^{-k_{\lambda} \cdot H} \quad 38$$

297

298 Where $k_{\text{photolysis}}$ denotes the solar photolysis rate constant of a DBP at a depth of H (1/hour),

299 k_{surface} denotes the photolysis rate constant near the surface of the watershed or at a depth of

300 zero (1/hour). k_{λ} is a constant with average value of 0.1/cm, and D is the average depth of

301 watershed (in unit of cm).

302

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