Supplementary Information

Modeling Volatilization and Adsorption of Disinfection Byproducts in Natural Watersheds

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General Model Framework

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

\[
V \frac{d[DBP]}{dt} = [DBP_{in,WWTP}] \cdot Q_{in,WWTP} + [DBP_{in,upstream}] \cdot Q_{in,upstream} - Q_{out} \cdot [DBP] \\
- V \cdot U_{water} \cdot \frac{d[DBP]}{dx} + V \cdot E_x \cdot \frac{d^2[DBP]}{dx^2} + r_T \cdot V
\]

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

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

\[V \frac{d[DBP]}{dt} = [DBP_{in,WWTP}] \cdot Q_{in,WWTP} + [DBP_{in,upstream}] \cdot Q_{in,upstream} - Q_{out} \cdot [DBP] \]

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

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

\[
r_T = r_V + r_P + r_H + r_B + r_A + r_O
\]

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

\[
r_T = \frac{d[DBP]}{dt} = -k_T \cdot [DBP]
\]

DBP half-life \((T_{1/2})\) is calculated by \(k_T\) and is irrelevant to the initial concentrations of DBP (Equation 5), which makes the data comparable across different labs and different types of compounds.
The determination of the water flow velocity ($U_{\text{water}}$) in surface watersheds follows Manning’s equation:

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

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

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

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

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

Based on an empirical equation$^3$, the longitudinal dispersive coefficient $E_x$ in the surface watershed is associated with certain hydrogeological characteristics, as presented below:
\[ E_s = 3.4 \cdot 10^{-5} \cdot \frac{U_{\text{water}}^2 \cdot W^2}{H \cdot U_{\text{shear}}} \]

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

\[ U_{\text{shear}} = \left( g \cdot H \cdot S \right)^{1/2} \]

Where \( g \) is the gravity constant (9.8 m/sec\(^2\)).

In an aquifer system, there is significant dispersion primarily because of small- and large-scale mixing phenomena. Dispersivity \( (D_{\text{disp}}) \) dominates the dispersion effect (Equation 10), and its values range from 0.01 to 0.1 times of the travel distance\(^4\).

\[ E_s = D_t + D_{\text{disp}} \cdot U_{\text{water}} \]

Where \( D_t \) is the diffusivity for DBP, which is to be discussed in the following section and usually negligible in groundwater.

**Volatilization Model Development**

On the basis of the above-mentioned fate-and-transport model buildup and the
hydrogeological setups, volatilization and adsorption simulations were conducted. According to the classic two-film theory, volatilization refers to the transition of a compound from its liquid phase to its gaseous phase. The transfer rate \( \frac{dc}{dt} \) is associated with the mass-transfer coefficient \( k_l \), the water depth \( H \), and the concentration gradient between gaseous and liquid forms \(^2\) (Equation 11):

\[
\frac{dc}{dt} = \frac{k_{vol}}{H} \left( \frac{DBP_{gas}}{H_c} - [DBP] \cdot \alpha_0 \right)
\]

Where \( DBP_{gas} \) is the concentration of DBP in the gaseous phase (mole/L); \( k_{vol} \) is the volatilization rate coefficient (m/hr); \( \alpha_0 \) is the fraction of DBP in its non-ionized form (reason: the ionized species bonds strongly with water and therefore has little likelihood of detaching from water and transferring into air); \( H_c \) is the Henry's law constant (HLC) in unitless form, which is equal to:

\[
H_c = \frac{H_e}{R \cdot (273 + T)}
\]

Where \( R \) is a constant \( (8.02 \times 10^{-5} \text{ atm-m}^3/\text{mole-K}) \); \( T \) is the temperature in degrees Celsius \( (^\circ \text{C}) \); and \( H_e \) is the HLC in unit of atm-m\(^3\)/mole, which is positively correlated with the increase in temperature (Equation 13).
\[
H_{e1} = H_{e2} \cdot e^{\frac{-\Delta H}{R_C \left( \frac{1}{273 + T_1} - \frac{1}{273 + T_2} \right)}},
\]

\(H_{e1}\) and \(H_{e2}\) are the HLCs of two different temperatures (atm·m³/mole); \(R_C\) is the gas constant (8.314 J/mole·K), \(\Delta H\) is the enthalpy of vaporization (KJ/mole) of a DBP; \(T_1\) and \(T_2\) are temperatures (°C).

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

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

The non-ionized fraction of a chemical, \(\alpha_0\), is a function of its acid-base dissociation constant (pK\(_a\)), and calculated by pK\(_a\) and the hydrogen ion content [H\(^+\)] in a designated pH

\[
\alpha_0 = \frac{[H^+]}{[H^+] + 10^{-pK_a}}
\]

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

\[
k_{vol} = \left( k_{liquid} + \frac{1}{k_{gas} \cdot H_C} \right)^{-1}
\]
The liquid-film exchange coefficient $k_{\text{liquid}}$ (m/hr) can be further estimated by an empirical equation related to DBP chemical properties:\(^2\):

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

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

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

Where the diffusivity of an organic compound in water ($D_l$) is computed via an equation proposed by USEPA:\(^6\):

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

Where $\rho_{\text{DBP}}$ is the density of DBP.

In terms of the DBP transfer in a gas-film, the coefficient $k_{\text{gas}}$ mainly depends on DBP diffusivity in gas ($D_g$) and wind velocity ($U_{\text{wind}}$):\(^2\):
\[ K_g = 0.001 \cdot \left( \frac{D_g}{U_g} \right)^{2/3} \cdot U_{wind} \]

Where \( v_g \) is the kinematic viscosity constant of air (0.15 cm\(^2\)/s). Like \( D_l \), \( D_g \) can also be estimated by the chemical properties of MW, density, and temperature, based on the following equations (Equations 21 and 22):

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

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

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

**Adsorption Model Development**

Similar to volatilization, the removal of DBPs via adsorption in surface watersheds also involves two steps: first, DBPs in dissolved forms are partitioned into suspended particles (SP) coated with organic matter, forming particulate DBPs (Equation 23). Next, the adsorbed DBPs settle down to the waterbed along with SP via the force of gravity. The first
step decides the adsorptive potentials of the DBPs in the SP, and the second step controls the settling kinetics of the DBPs and SP. The adsorption equilibrium is assumed to be linear, which is true for relatively low concentrations of DBPs (ng/L or μg/L levels) in the environment. The adsorption kinetics are assumed rapid and instantaneous by assigning a high adsorption rate constant \( k_{\text{adsorption}} = 25000/\text{hr} \). Sediment comes only from upstream suspended particles (SPs) in a watershed if there are no soil movements, riverbank erosion, or other types of renewal; this assumption serves as the basis of this study. Before SP settles down and becomes sediment, SP adsorbs and equilibrates with DBPs as much/fast as possible, during which SP and DBP have sufficient opportunity in contacting with each other and reaches its adsorption capacity. Once settled, SP, along with the adsorbed DBP, are kept in waterbed and termed sediment. Because the sediment adsorbs DBP already, its adsorption ability is much lower than initial SP, if not zero. In addition, sediment in waterbed is not fully in contact with DBP in water, so its adsorption ability can be compromised. Under such condition, the exchange of DBPs between the water and the waterbed sediment becomes relatively insignificant.

\[
\frac{d[DBP_{\text{sorbed}}]}{dt} = k_{\text{adsorption}}(K_P \cdot [DBP] - [DBP_{\text{sorbed}}])
\]

Where \( K_P \) is the partition coefficient (L/kg) as defined in Equation 24. For a compound with reversible adsorption and desorption, \( K_P \) is estimated by its octanol-water partitioning constant \( (K_{ow}) \), SP concentration \( ([SP], \text{mg/L}) \), and the fraction of organic matter \( (f_{oc}) \) coated in SP.
\[ K_p = \frac{[DBP_{\text{sorbed}}]}{[DBP_{\text{dissolved}}]} = \frac{2.8 \cdot f_{OC} \cdot K_{OW}}{1.4 + [SP] \cdot f_{OC} \cdot K_{OW}} \cdot \alpha_0 \]

Where \( \alpha_0 \) is the percentage of a specific DBP in non-ionized form (reason: the ionized species bonds strongly with water and therefore has little likelihood of detaching from water and absorbing on adsorbent). The particulate and dissolved fractions of DBPs are calculated with the following equations:

\[ f_p = \frac{K_p \cdot [SP]}{1 + K_p \cdot [SP]} \]
\[ f_d = 1 - f_p \]

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

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

\[ v_s = \frac{g}{18} \left( \frac{\rho_{\text{solid}} - \rho_{\text{water}}}{\mu} \right) d_i^2 \]

Where: \( v_s \) is the settling velocity of the suspended particle (m/hr); \( \rho_{\text{solid}} \) is the density of
suspended particles (g/cm³); \( \rho_{\text{water}} \) is the density of water (assumed to be constant at 1g/cm³); \( d_i \) refers to the diameter of the suspended particle (µm); \( u \) is the viscosity of water at a certain temperature (= 0.1 cm²/s at 25 °C) and decreases with temperature (T); and \( g \) is the gravity acceleration constant (9.8 m/sec²). The density of a SP has been shown to roughly correspond with its diameter (Equation 28) in some case studies:

\[
\rho_{\text{solid}} = 2 \cdot d_i^{-0.15}
\]

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

\[
\frac{d[SP]}{dt} = -k_{SP} \cdot [SP] = -\frac{v_s}{H} \cdot [SP]
\]

\[
\frac{d[DBP]}{dt} = -\frac{v_s}{H} \cdot [DBP] \cdot \frac{1}{[DBP]} \cdot [SP] = -k_{SP} \cdot \frac{K_p \cdot [SP]}{1 + K_p \cdot [SP]} \cdot [DBP]
\]

\[
k_{\text{settling}} = \frac{K_p \cdot [SP]}{1 + K_p \cdot [SP]} \cdot k_{SP}
\]

Where \( k_{SP} \) is the first-order reduction rate constant (1/hr) of SP.
Theoretically, the settled DBPs may diffuse into soils, undergoing biodegradation and hydrolysis in the sediment. These subsequent processes are nonetheless beyond the scope of this study and therefore are not emphasized.

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

\[
\rho_{\text{bulk}} = \rho_{\text{solid}} \cdot (1 - \phi)
\]

\[
[SS] = 10^5 \cdot \rho_{\text{bulk}}
\]

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

\[
d[DBP] \cdot V \cdot \phi = d[DBP_{\text{sorbed}}] \cdot V \cdot \rho_{\text{solid}} \cdot (1 - \phi)
\]

\[
\frac{d[DBP]}{dt} = - \frac{d[DBP_{\text{sorbed}}]}{dt} \cdot \frac{\rho_{\text{solid}} \cdot (1 - \phi)}{\phi} - k_T \cdot [DBP]
\]
Retardation in groundwater systems does not reduce DBPs directly, but provides DBPs with more time to be degraded or transformed by other removal mechanisms. The retardation coefficient (R) is defined as the ratio of the volume of water needed to transport a pollutant completely through the aquifer ($V_{\text{req}}$) to the unit volume ($V_{\text{unit}}$, namely pore volume) of the aquifer (Equation 35). In other words, a pollutant may reside (R-1) times of period longer than pure water. Quantification of R is a function of aquifer bulk density ($\rho_{\text{bulk}}$), $K_P$, and $\phi$ (Equation 35)

$$R = \frac{V_{\text{req}}}{V_{\text{unit}}} = 1 + \frac{\rho_{\text{bulk}} \times K_P}{\phi}$$

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

In order to compare the relative importance of different types of mechanisms, a list of reaction rate constants were extracted from earlier studies. The rate of photolysis is subject to adjustment for water depth according to Equation 38^8.
$k_{\text{photolysis}} = k_{\text{surface}} \cdot e^{-k_{\lambda}H}$

Where $k_{\text{photolysis}}$ denotes the solar photolysis rate constant of a DBP at a depth of $H$ (1/hour), $k_{\text{surface}}$ denotes the photolysis rate constant near the surface of the watershed or at a depth of zero (1/hour). $k_{\lambda}$ is a constant with average value of 0.1/cm, and $D$ is the average depth of watershed (in unit of cm).

**References:**


