Evaluating Henry’s law constant of
N-Nitrosodimethylamine (NDMA)

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ABSTRACT

N-Nitrosodimethylamine (NDMA), a potential carcinogen, may contaminate the groundwater when
the reclaimed wastewater is used for irrigation and groundwater recharge. Henry’s law constant is a
critical parameter to assess the fate and transport of reclaimed wastewater-borne NDMA in the soil
profile. We conducted a laboratory experiment in which the change of NDMA concentration in water
exposed to the atmosphere was measured with respect to time and, based on the data, obtained the
dimensionless Henry’s law constant ($K_{H}'$) of NDMA, at $1.0 \times 10^{-4}$. The $K_{H}'$ suggests that NDMA has a
relatively high potential to volatilize in the field where NDMA-containing wastewater is used for
irrigation and the volatilization loss may be a significant pathway of NDMA transport. The experiment
was based on the two boundary-layer approach of mass transfer at the atmosphere-water interface.
It is an expedient method to delineate $K_{H}'$ for volatile or semi-volatile compounds present in water at
low concentrations.

Key words | boundary-layer model, mass transfer, volatilization, water reuse

INTRODUCTION

N-Nitrosodimethylamine (NDMA) is a member of the carcino
gen family, the N-nitrosamines, and is a disinfection by-
product of great concerns (Mitch & Sedlak 2002a, b). The
treated wastewater usually contains relatively high concen-
trations of NDMA. For instances, the mean concentration
of NDMA in the chlorinated effluents of a publicly owned
treatment work in California was approximately 1,000 ng/L
(Gan et al. 2006) and, in a separate case, Pehlivanoglu &
Sedlak (2004) found 500 ng/L of NDMA in the reclaimed
water delivered for landscape irrigation. The reported
NDMA concentrations in the water are considerably
higher than the 10 ng/L notification level and higher than
the 500 ng/L response level set by the California Department
of Health Services (CDHS 2006).

The leaching risks of NDMA with reclaimed wastewater
irrigation are of concern due to its water solubility and
low soil adsorption capacity (Gunnison et al. 2000; Yang
et al. 2005). Gan et al. (2006) found that the soils of
established turfgrass were not effective at retaining NDMA
applied through the reclaimed wastewater irrigation.
Haruta et al. (2008) assessed the leaching risk of NDMA
in soil receiving reclaimed wastewater based on the model
simulation results from HYDRUS. The results showed that
while the risk of NDMA to reach the ground water was
slim under the customary conditions for landscape irriga-
tion, the risk could be significantly increased under
extreme conditions. The NDMA leaching risks are highly
dependent on the biodegradation and volatilization
processes. Oliver (1979), Arienzo et al. (2006) and Gan et al.
(2006) demonstrated that volatilization was likely a major
pathway for NDMA disappearance in unsaturated soil.

Henry’s law constant ($K_H$) is a distribution coefficient
representing the equilibrium of a volatile or semi-volatile
substance between the atmospheric and aqueous phases. It
is an important physicochemical parameter that governs
the volatilization process. A high $K_H$ suggests that volatil-
ization may be a significant transport process for a chemical
contaminant in unsaturated soil (Jury et al. 1984).

There is not sufficient data on the $K_H$ of NDMA. Mirvish et al. (1976) estimated that dimensionless Henry’s
law constant ($K_{H}'$) of NDMA was $1.1 \times 10^{-5}$ while the Inter-
national Programme on Chemical Safety (IPCS 2002) cited
$1.4 \times 10^{-3}$ as the $K_{H}'$ of NDMA. There would be significant
discrepancies in the outcomes, depending on which $K_{H}'$ is
employed in the transport and risk assessment. At $K_{H}' = 1.4 \times 10^{-3}$, the vapor phase diffusion of NDMA would be a dominating process in unsaturated soils and the chemical’s transport through the voids would be rapid (Jury et al. 1984).

The Henry’s law constant is generally determined under the equilibrium conditions and there is a lack of reliable and consistent $K_{H}$ measurement for potentially harmful trace chemical contaminants due to cumbersome experimental procedures. Often, it results in estimations derived from other physicochemical attributes of the compound. The equilibrium conditions are not representative of the field environment from which the volatilization takes place. Simple and straightforward methods to measure $K_{H}$ of chemicals present in dilute aqueous solutions will be useful. In this study, we devised a laboratory method to determine the dimensionless Henry’s law constant ($K_{H}'$) of volatile and semi-volatile chemicals in water, based on a two boundary-layer approach, and used it to determine the $K_{H}'$ of NDMA under the dynamic conditions. Factors affecting the outcomes were evaluated.

MATERIALS AND METHODS

Experiment setup

The methyl-14C labeled NDMA (specific activity 57 mCi/mmole; radioactive purity 99%) was acquired from Mora- vek Biochemicals, USA. Stock solutions were prepared by dissolving $^{14}$C-NDMA in 0.01 M CaCl$_2$ solution. 200 ml of the 70 μg/L NDMA aqueous solution was transferred into a 125 mm (diameter) by 65 mm (depth) glass dish and immediately placed in a fume hood operating at the room temperature ($20 \pm 1$ °C). At 0, 0.5, 1, 2, 4, 8, 24 and 48 h following the treatment, 1.0 mL aliquots were withdrawn using a micro syringe and immediately added into 6 mL of Ultima Gold scintillation cocktail. The samples were then measured for their radioactivity on a Beckman LS 1800 Liquid Scintillation Counter. The experiment was replicated three times. During the course of the experiment, the solution was continuously stirred, at 300 r/min by a magnetic stirring bar. The NDMA concentrations remaining at the preset sampling times were calculated using the measured radioactivity and the specific activity. At the same time, the weight of each glass container was determined, from which the corresponding depth of the remaining water was calculated.

Mathematical modeling of $K_{H}$

The partition of a volatile or semi-volatile compound between the atmospheric and aqueous phases may be delineated by the two boundary-layer mass transfer model (Liss & Slater 1974). This model depicts the transfer of a compound across the atmosphere–water interface and its validity has been demonstrated by experiments in laboratory as well as observations made in natural environments including lakes, rivers and oceans (Richard 1981). In the model scheme, there is bulk water, and bulk atmosphere separated by two interfacial layers: a liquid film and a gas film.

Based on Fick’s first law and assuming that transport across the gas and aqueous interfaces is a steady-state process, the flux of chemical passing through the interfacial layer ($F$, g/cm$^2$/h) may described as:

$$F = k_g(C_g - C_{sg}) = k_l(C_{sl} - C_l)$$

(1)

where $k_g$ and $k_l$ is the gas and aqueous phase exchange coefficient (cm/h), respectively, $C_g$ and $C_l$ is the concentration at the outer edge of the gas and aqueous film (g/cm$^3$), respectively, $C_{sg}$ and $C_{sl}$ is the concentration in the gas and aqueous phase at the interface (g/cm$^3$), respectively.

The dimensionless Henry’s law constant ($K_{H}'$) is given as:

$$K_{H}' = C_{sg}/C_{sl}$$

(2)

Therefore, $C_{sg}$ and $C_{sl}$ in Equation (1) can be obtained as:

$$C_{sg} = [C_g + (k_l/k_g)C_l] * k_gK_{H}' / k_l + k_gK_{H}'$$

(3a)

$$C_{sl} = [C_l + (k_g/k_l)C_g]/(1 + K_{H}')$$

(3b)

Substituting Equation (3a) and (3b) into Equation (2), we can get:

$$F = (C_g - K_{H}'C_l)/(1/k_g + K_{H}'/k_l)$$

$$= (C_g/K_{H}' - C_l)/(1/k_l + 1/K_{H}'k_g)$$

(4)

which may be written as:

$$F = KL(C_g - K_{H}'C_l) = KL(C_g/K_{H}' - C_l)$$

(5)
where $K_G$ and $K_L$ are the overall mass transfer coefficients for the gas and liquid phases (cm/h), respectively, and may be considered as the overall resistance to volatilization flux. Mathematically, $K_G$ and $K_L$ are described as:

$$1/K_G = 1/k_g + K_H/k_l$$

(6)

$$1/K_L = 1/k_l + 1/K_H/k_g$$

(7)

As $C_g = P/RT$ and $K_H = K_{H_0} = K_H/RT$, Equation (5) can be rewritten as:

$$F = K_L(C_l - P/K_H)$$

(8)

where $P$ is the partial pressure of the compound in the atmosphere (atm); $K_H$ is the Henry’s law constant (atm m$^3$/mol).

Combining Equation (8) with a mass balance differential equation in an unsteady state model results in:

$$dC_l/dt = -K_L(C_l - P/K_H)/Z$$

(9)

General solution of Equation (9) is:

$$C_l = P/K_H + (C_{l0} - P/K_H)e^{-K_Lt/Z}$$

(10)

where $Z$ is the mean depth of the water body (cm), and $C_{l0}$ is the initial chemical concentration in the water body. If $P$ is negligible, Equation (10) simplifies to

$$C_l = C_{l0}e^{-K_Lt/Z}$$

(11)

Equation (11) indicates that $C_l$ can be described as a simple first-order exponential decay with a rate constant of $K_L/Z$.

### Calculation procedure of Henry’s law constant

Based on the experiment, the $K_{H_i}$ may be calculated simply with the data on concentration changes of NDMA in the aqueous phase, $C_i$, and the corresponding depth of the water body, $Z$; both are function of time, $t$. First, the NDMA concentration data are fit by a least-square fitting technique to Equation (11) through which $K_L/Z$ may be obtained. In turn, $K_L$ is obtained from $K_L/Z$ with known $Z$. Finally, $K_{H_i}$ is obtained through Equation (12) that is equivalent to Equation (7).

$$K_{H_i} = \frac{1}{k_g(1/K_L - 1/k_l)}$$

(12)

where $k_l$ and $k_g$ depend on the water turbulence and wind speed, respectively.

### RESULTS AND DISCUSSION

#### Calculation of Henry’s law constant of NDMA

The changes of NDMA concentration in the water reservoir during the course of the volatilization experiment are illustrated in Figure 1(a). Measurements of replicates were highly reproducible, as evident from the very narrow data dispersions. The NDMA concentrations of the aqueous phase were fitted by the non-linear regression model according to Equation (11), which yielded a relationship of $y = 69.269e^{-0.0274x}$ with $R^2 = 0.99$. Therefore, $K_L/Z = 0.0274$ h$^{-1}$.

During the experiment, the water containing NDMA was continuously vaporized. Figure 1(b) shows that the water depth in the experimental containers changed linearly with time as $y$ (cm) = $-0.0113x$ (h) + 1.6259 with $R^2 = 0.99$. From

![Figure 1](https://iwaponline.com/wst/article-pdf/64/8/1636/444683/1636.pdf)
the regression equation, the mean water depth was estimated at 1.35 cm. As $K_l/Z = 0.0274 \text{ h}^{-1}$ and $Z = 1.35 \text{ cm}$, $K_L$ was calculated to be 0.0370 cm/h. The exchange coefficients $k_i$ and $k_f$ are primarily functions of wind and water turbulence, respectively (Southworth 1979). Typically, 20 cm/h for $k_i$ and 3,000 cm/h for $k_f$ are used under the natural and experimental conditions (Liss 1973). Let $k_i = 20 \text{ cm/h}$ and $k_f = 3,000 \text{ cm/h}$, $K_{H'}$ of NDMA is $1.24 \times 10^{-5}$, according to Equation (12).

**Sensitivity of $K_{H'}$ to $k_i$ and $k_f$**

The experimentally determined $K_{H'}$ of NDMA may be affected by $k_i$ and $k_f$ that are not directly measured. Figure 2(a) shows the sensitivity of $K_{H'}$ to the value of $k_i$ whose value decreases with the increase of turbulence and it is difficult to be estimated accurately. $K_{H'}$ of NDMA is not sensitive to $k_i$ representing the normal range of turbulence conditions in water. The resulting $K_{H'}$ does not significantly change when $k_i$ varies from 0.6 to 100 cm/h. $k_i$ values are typically 1 to 3 cm/h corresponding to a wind speed less than 3 m/s in a natural water body (Cohen et al. 1978). Southworth (1979) obtained 0.6 cm/h of $k_i$ in quiescent laboratory condition. During the experiment, the airflow velocity (i.e., wind speed) in the fume hood was approximately 0.5 m/s, which is less than 3 m/s and the solution was continuously stirred at 500 r/min. Therefore, $k_i = 2 \text{ cm/h}$, the average of 1 to 3 cm/h, is a realistic value for the experiment instead of the initial estimate of 20 cm/h and is used, hereafter, in calculations of $K_{H'}$ of NDMA. When $k_i = 2 \text{ cm/h}$ instead of 20 cm/h, $K_{H'}$ is $1.26 \times 10^{-5}$. The difference between this estimated value and initial estimate of $1.24 \times 10^{-5}$ (when $k_i = 20 \text{ cm/h}$) is negligible.

The value of $k_f$ has a significant effect on the $K_{H'}$ of NDMA (Figure 2(b)). The $k_f$ is influenced primarily by gaseous phase and, to a lesser extent, aqueous phase mixing (Liss 1973). Its value decreases with the decrease of wind velocity (Southworth 1979). During the course of the experiment, the airflow velocity (i.e., wind speed) in the fume hood was maintained at approximately 0.5 m/s. However, the water surface was protected from the wind by 4 cm of freeboard above the glass dish. The actual wind velocity on the water surface would be much lower than 0.5 m/s and might be negligible for the experiment.

Southworth (1979) obtained the $k_g$ of 3,000 cm/h (the assumed value in the initial calculation) under the wind speed of 4 m/s at a river and 3 to 4 m/s in subsequent laboratory experiments. Southworth (1979) also showed that $k_g$ varied from 118 to 539 cm/h under windless conditions when the contents were propeller mixed at speeds ranging from 0 to 200 r/min and $k_g$ was 964 cm/h on the river with wind speed reached 1 m/s. These values were obtained at 25°C for a hypothetical compound with a molecular weight of 100. The temperature effect on $k_g$ may be negligible (Southworth 1979). The $k_g$ of two compounds is inversely proportional to the square roots of their molecular weights (Liss & Slater 1974). Accordingly, $k_g$ of NDMA is expected to be approximately 14.6% higher than the hypothetical compound as the molecular weight of NDMA is 76.08 (Weast 1985). Therefore, the $k_g$ for our experiment would be considerably smaller than the assumed value of 3,000 cm/h. Under the circumstances, it would be reasonable to assume that $k_g$ is one order of magnitude smaller than the initially assumed value. When 300 cm/h was used as the $k_g$, $K_{H'}$ of NDMA would be $1.26 \times 10^{-4}$ instead of $1.26 \times 10^{-5}$ for $k_g = 3,000 \text{ cm/h}$. As a result, the $K_{H'}$ of NDMA is most likely around $1.0 \times 10^{-4}$.

**Effects of water depths on Henry’s law constant of NDMA**

Over the course of the experiment, the water depth of the reservoir changed from 1.65 to 1.10 cm as the water evaporated (Figure 1(b)). The mean water depth of 1.35 cm was

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**Figure 2** | Effects of aqueous phase coefficient, $k_i$ (a) and for gas phase coefficient, $k_g$ (b) on $K_{H'}$ of NDMA.
employed in the above $K_{H0}'$ calculations. The water depths may affect the NDMA concentration in the remaining water.

**Figure 3** graphically illustrates the potential impacts of the unsteady water depths. In the figure, the horizontal axis represents the water depth corrected $K_{H0}'$ and the vertical axis represents the $K_{H0}$ based on the average water depth of 1.35 cm for all of the NDMA concentrations. The corrected $K_{H0}'$ corresponding to various water depths were obtained by the explicit difference method, based on Equation (9). The calculated NDMA concentrations at 0.5, 1, 2, 4, 8, 24 and 48 h after starting the experiments were then employed to obtain the $K_{H0}'$ based on the mean water depth of 1.35 cm by the procedure described previously with $k_l$ of 2 cm/h and $k_g$ of 300 cm/h. The difference between the $K_{H0}$ based on the average water depth and the corrected $K_{H0}'$ is generally small. But the difference increase with $K_{H0}'$. At $K_{H0}'$ of $10^{-4}$ and $10^{-2}$, the underestimations are 1 and 25%, respectively. As the estimated $K_{H0}'$ of NDMA is $1.0 \times 10^{-4}$, the expected underestimation will be approximately 1%. The effects of the unsteady state water depths during the experiment on the outcomes are minor.

**Extension of the method**

The gas and liquid phase exchange coefficients, $k_g$ and $k_l$, and the $K_{H0}$ characterize the volatilization process of a chemical. Through which, the overall mass transfer coefficient, $K_L$ corresponding to hypothetical $k_{g0}$, $k_l$ and $K_{H0}'$ may be computed according to Equation (7). Applying the $K_L$ obtained and substituting $k_g = 300$ cm h$^{-1}$ and $k_l = 2$ cm h$^{-1}$ for their respective values to Equation (11), the estimated $K_{H0}'$ by the method demonstrated may be obtained according to Equation (11).

![Figure 3](https://iwaponline.com/wst/article-pdf/64/8/1636/444683/1636.pdf) | Experimentally determined $K_{H0}'$ of NDMA, water depth corrected vs. water depth averaged. The dash line in the graph represents the 1:1 line.

![Figure 4](https://iwaponline.com/wst/article-pdf/64/8/1636/444683/1636.pdf) | Hypothetical $K_{H0}'$ of varying $k_g$ and $k_l$ vs. $K_{H0}'$ estimated by assuming $k_g = 300$ cm h$^{-1}$ and $k_l = 2$ cm h$^{-1}$. 

Figure 4 shows the comparisons of the hypothetically obtained $K_{H}$ and their respective estimates by the method we developed. For chemical compound with $K_{H}$ equal or less than $1 \times 10^{-3}$, the estimated $K_{H'}$ are comparable to those of the hypothetical values for $k_{r}$ ranging from 200 to 600 cm/h and $k_{l}$ ranging from less than 1 to over 100 cm/h. It is indicative that the method demonstrated is expedient to delineate the $K_{H'}$ for other volatile and semi-volatile compounds.

CONCLUSIONS

We developed a simple method to estimate the dimensionless Henry’s law constant, $K_{H'}$, for volatile and semi-volatile chemicals under non-steady conditions based on the double boundary layer mass transfer approach and tested the sensibilities of the outcomes to the mass transfer parameters. The method is applicable to compounds with $K_{H}$ less than $1 \times 10^{-3}$. Based on the method, the $K_{H'}$ of NDMA is around $1 \times 10^{-4}$. The estimated $K_{H'}$ is sensitive to the gas phase coefficient, $k_{g}$. The application of the developed model can be further tested and validated for other chemicals like pyrenes which are more recognizable compounds with similar $K_{H'}$.

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