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 1.0×10^{-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

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INTRODUCTION

N-Nitrosodimethylamine (NDMA) is a member of the carcinogen family, the *N*-nitrosamines, and is a disinfection by-product of great concerns (Mitch & Sedlak 2002a, b). The treated wastewater usually contains relatively high concentrations 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 300 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 irrigation, 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 volatilization 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 1.1×10^{-5} while the International Programme on Chemical Safety (IPCS 2002) cited 1.4×10^{-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- ^{14}C labeled NDMA (specific activity 57 mCi/mmol; radioactive purity >99%) was acquired from Moravek Biochemicals, USA. Stock solutions were prepared by dissolving ^{14}C -NDMA in 0.01M CaCl_2 solution. 200 ml of the 70 $\mu\text{g/L}$ 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 ($20 \pm 1^\circ\text{C}$). At 0, 0.5, 1, 2, 4, 8, 24 and 48 h following the treatment, 1.0 mL aliquots were withdrawn using a microsyringe 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 , $\text{g/cm}^2/\text{h}$) may be described as

$$F = k_g(C_g - C_{sg}) = k_l(C_{sl} - C_l) \quad (1)$$

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:

$$K_H' = C_{sg}/C_{sl} \quad (2)$$

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

$$C_{sg} = \frac{[C_g + (k_l/k_g)C_l] * k_g K_H'}{k_l + k_g K_H'} \quad (3a)$$

$$C_{sl} = [C_l + (k_g/k_l)C_g]/(1 + K_H') \quad (3b)$$

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

$$\begin{aligned} F &= (C_g - K_H' C_l)/(1/k_g + K_H'/k_l) \\ &= (C_g/K_H' - C_l)/(1/k_l + 1/K_H' k_g) \end{aligned} \quad (4)$$

which may be written as:

$$F = K_G(C_g - K_H' C_l) = K_L(C_g/K_H' - C_l) \quad (5)$$

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:

$$1/K_G = 1/k_g + K_H'/k_l \quad (6)$$

$$1/K_L = 1/k_l + 1/K_H'k_g \quad (7)$$

As $C_g = P/RT$ and $K_H' = K_H/RT$, Equation (5) can be rewritten as:

$$F = K_L(C_l - P/K_H)/Z \quad (8)$$

where P is the partial pressure of the compound in the atmosphere (atm); K_H is the Henry's law constant (atm m³/mol).

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

$$dC_l/dt = -K_L(C_l - P/K_H)/Z \quad (9)$$

General solution of Equation (9) is:

$$C_l = P/K_H + (C_{l0} - P/K_H)e^{-K_L t/Z} \quad (10)$$

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

$$C_l = C_{l0}e^{-K_L t/Z} \quad (11)$$

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' may be calculated simply with the data on concentration changes of NDMA in the aqueous phase, C_l , 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' is obtained through Equation (12) that is equivalent to Equation (7).

$$K_H' = \frac{1}{k_g(1/K_L - 1/k_l)} \quad (12)$$

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, $K_L/Z = 0.0274 \text{ h}^{-1}$.

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 $y (\text{cm}) = -0.0113x (\text{h}) + 1.6259$ with $R^2 = 0.99$. From

Figure 1 | Change of NDMA concentrations in the liquid phase (a) and water depth (b) with respect to time under experimental conditions.

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_g and k_l are primarily functions of wind and water turbulences, respectively (Southworth 1979). Typically, 20 cm/h for k_l and $3,000 \text{ cm/h}$ for k_g are used under the natural and experimental conditions (Liss 1973). Let $k_l = 20 \text{ cm/h}$ and $k_g = 3,000 \text{ cm/h}$, K_H' of NDMA is 1.24×10^{-5} , according to Equation (12).

Sensitivity of K_H' to k_l and k_g

The experimentally determined K_H' of NDMA may be affected by k_l and k_g that are not directly measured. Figure 2(a) shows the sensitivity of K_H' to the value of k_l 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_l representing the normal range of turbulence conditions in water. The resulting K_H' does not significantly change when k_l varies from 0.6 to 100 cm/h . k_l 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_l 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 300 r/min . Therefore, $k_l = 2 \text{ cm/h}$, 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 $k_l = 2 \text{ cm/h}$ instead of 20 cm/h , K_H' is 1.26×10^{-5} . The difference between this estimated value and initial estimate of 1.24×10^{-5} (when $k_l = 20 \text{ cm/h}$) is negligible.

The value of k_g has a significant effect on the K_H' of NDMA (Figure 2(b)). The k_g 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 $3,000 \text{ cm/h}$ (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 1983). Therefore, the k_g for our experiment would be considerably smaller than the assumed value of $3,000 \text{ cm/h}$. 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 1.26×10^{-4} instead of 1.26×10^{-5} for $k_g = 3,000 \text{ cm/h}$. As a result, the K_H' of NDMA is most likely around 1.0×10^{-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

Figure 2 | Effects of aqueous phase coefficient, k_l (a) and for gas phase coefficient, k_g (b) on K_H' of NDMA.

employed in the above K_H' 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_H' and the vertical axis represents the K_H' based on the average water depth of 1.35 cm for all of the NDMA concentrations. The corrected K_H' corresponding to various water depths were obtained by the explicit difference method, based on

Figure 3 | Experimentally determined K_H' of NDMA, water depth corrected vs. water depth averaged. The dash line in the graph represents the 1:1 line.

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_H' 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_H' based on the average water depth and the corrected K_H' is generally small. But the difference increase with K_H' . At K_H' of 10^{-4} and 10^{-2} , the underestimations are 1 and 25%, respectively. As the estimated K_H' of NDMA is 1.0×10^{-4} , the expected underestimation will be approximately 10%. 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_H' characterize the volatilization process of a chemical. Through which, the overall mass transfer coefficient, K_L corresponding to hypothetical k_g , k_l , and K_H' may be computed according to Equation (7). Applying the K_L obtained and substituting $k_g = 300 \text{ cm h}^{-1}$ and $k_l = 2 \text{ cm h}^{-1}$ for their respective values to Equation (11), the estimated K_H' by the method demonstrated may be obtained according to Equation (11).

Figure 4 | Hypothetical K_H' of varying k_g and k_l vs. K_H' estimated by assuming $k_g = 300 \text{ cm h}^{-1}$ and $k_l = 2 \text{ cm h}^{-1}$.

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 1×10^{-3} , the estimated K_H' are comparable to those of the hypothetical values for k_g 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 1.0×10^{-3} . Based on the method, the K_H' of NDMA is around 1.0×10^{-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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