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Estimate of ammonia transfer from Lake Dianchi water to the air

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Abstract—The factors affecting ammonia transfer from water to the air were studied in Tianjin and Kunming City of China. The mass transfer coefficient (*Ke*) was found to be a linear function of temperature, and increased with increasing wind speed. *Ke* was independent of pH and concentration of ammonia nitrogen in water. The *Ke* obtained in Kunming is greater than those in Tianjin under similar test conditions. The *Ke* has been shown to range from 1.03 to 1.52 cm/h in distilled water system. The estimated rates of ammonia transferred from the surface 0.2m section of Lake Dianchi Caohai water to the air were 36 to 242 μg-N/(L.h) at different pH and ammonia nitrogen concentrations.

Keywords: ammonia; transfer; Lake Dianchi.

1 Introduction

Information about disappearance of ammonia from water has been reported (Stratton, 1969; Weiler, 1979; Murphy, 1981). During two periods of high pH and high ammonia concentration, disappearance rates of ammonia of 20—30 μg-N/(L.h) were observed in a hypertrophic prairie lake at which rates of ammonia uptake by phytoplankton were 2.6—4.3 μg-N/(L.h).

This disappearance of ammonia was explained by mass transfer of ammonia from water surface to the air (Murphy, 1981). The rate of transfer has been shown to obey a first order reaction (Stratton, 1969), and the mass-transfer coefficient was found to be a linear function of wind speed and temperature (Weiler, 1979).

Though much is known of the biological transformations of nitrogen compounds the over-all nitrogen cycle in a natural system is extremely complex. To investigate the eutrophication of Lake Dianchi, a nitrogen cycle model has been developed. Ten processes were considered, and

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the rate of ammonia transferred from water to the air as an essential parameter has been involved in the model. The purpose of the present study is to obtain a typical transfer rate of ammonia for the calculation of nitrogen cycle model of Lake Dianchi.

2 Material and methods

A simulated test device was designed and it is alike to a laboratory wind wave tank that has been used for determination of the liquid - phase mass transfer coefficient of hydrocarbons from aqueous solution (Cohen, 1978) and to a wind tunnel that has been used for study of ammonia loss from water (Weiler, 1979).

The device consists of a power supply, an air blower, an air flow buffer room, a wind tunnel and a volatilize tank, as shown in Fig. 1. The tank was constructed in such a way that the air flow joined the water surface tangentially. The air flow generated by the air pump entered the tunnel inlet and passed through the buffer room which ensured an uniform distribution of velocity, and then was in contact with the water surface. The device was made of non - transparent material in order to inhibit the growth of algae during the test.

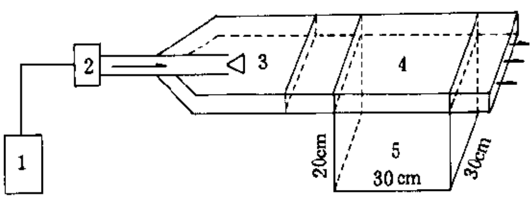

Fig. 1 Schematic diagram of experimental device
1: power supply; 2: air blower;
3: air flow buffer room;
4: wind tunnel; 5: volatilized tank

The test was run in two kinds of medium, one was distilled water containing ammonium chloride, another was lake water. The concentration of ammonia in water can be regulated by adding ammonium chloride aqueous solution into the water samples. The pH values of the test solution can be adjusted with diluted acid or alkali liquor without using buffer solution because the pH values varied in the range of ± 0.1 pH during the period of test.

Poured water slowly into the tank and then marked the water level in order to calibrate the ammonia concentration in the tank due to volume change caused by water evaporation. During the test, parameters such as temperature, evaporation of water were monitored. The wind speed was controlled via regulating the flow of the air pump and measured by an anemometer.

At various time intervals 25 ml aliquot of water sample was taken from the tank through a sampling - hole. For each sampling, two samples were taken from two different depths, one was 10 cm, another, 15 cm under the water surface. The concentration of ammonium ion plus ammonia in the sample was analyzed by the Nessler standard method (American, 1975).

3 Results and discussion

3.1 Equations related to the ammonia transfer

For the sake of convenience, the abbreviations UAN, IAN, TAN, H, U, TEM, t were used in this paper to denote the un - ionized ammonia, ionized ammonia, un - ionized ammonia plus ionized ammonia, hydrogen ion, wind speed, temperature and reaction time, respectively.

The equilibrium of UAN and IAN in solution can be expressed as follows:

$$IAN(aq) \stackrel{K}{=\!=} UAN(aq) + H(aq) \quad , \tag{1}$$

$$UAN(aq) = UAN(g) \quad . \tag{2}$$

Where K is the equilibrium constant which is defined as

$$K = \frac{[UAN(aq)] - [H(aq)]}{[IAN(aq)]} \quad . \tag{3}$$

Equation (2) is a slow step. It represents the transfer of un - ionized ammonia from water into the atmosphere. From Equation (2), the transfer rate can be obtained:

$$\frac{d[UAN(aq)]}{dt} = - K[UAN(aq)] \quad . \tag{4}$$

In the solution, the concentration determined should be the sum of UAN plus IAN, equal to TAN:

$$[TAN(aq)] = [IAN(aq)] + [UAN(aq)] \quad . \tag{5}$$

Combining Equation (5) and (3) gives

$$[UAN(aq)] = \frac{K}{K + [H]}[TAN(aq)] \quad . \tag{6}$$

Substitute Equation (6) into (4), and ignore the change of pH value of the solution during a 6h test, thus

$$\frac{d[TAN(aq)]}{dt} = - k[TAN(aq)] \quad , \tag{7}$$

where k is the reaction rate constant.

Equation (7) expresses the relationship between TAN and time in the loss process of ammonia. Apparently, Equation (7) shows a first order reaction kinetic. In fact, when ln (TAN) was plotted against t, a least means square line was fitted, and the correlation coefficient was $\gg$ 0. 992 for all runs done.

An equation to describe the mass transfer process of ammonia through the liquid - air interface has been reported (Weiler, 1979).

$$\frac{d[N]}{dt} = - Ke \frac{A}{V}[UAN] \quad . \tag{8}$$

Where, $d[N]/dt$ is the variation of TAN, A/V the area/volume ratio of the vessel, $[UAN]$ the concentration of un-ionized ammonia at a given pH, temperature and TAN concentration. Ke is the exchange rate coefficient or mass transfer coefficient and has the units length/time. Combine with Equation (6), yield

$$\frac{d[N]}{dt} = - Ke \frac{K}{K + [H]} \frac{A}{V}[TAN(aq)] \quad . \tag{9}$$

To compare the Equation (9), with (7) we obtained

$$Ke = \frac{k(K + [H])}{K} \frac{V}{A} \quad . \tag{10}$$

In practice, ln *TAN* was plotted against *t*, from the slope of the least means square line, *k* was calculated. The *A*/*V* ratio was 0.05 in our test. It is similar to that of 0.046 in a raft container test (Weiler, 1979).

The equilibrium constant in Equation (1), *K* takes certain value corresponding to the measured temperature. When the pH value of the test solution are given, the *Ke* value can be calculated based on Equation (10).

3.2 Factors affecting the ammonia transfer

Factors which influence the transfer rate of ammonia are more complicated in a water body. As shown in Equation (1), the equilibrium of *IAN* and *UAN* is controlled by the pH. There are more *UAN* in water of higher pH value than those of lower pH. The percentage of *UAN* in water at pH = 8.0, at 20°C, is 3.83 (Trussell, 1972; Zhao, 1991), large portion of *TAN* exists in *IAN* form. When pH = 10.0, at same temperature, the percentage is 79.8 (Zhao, 1991), *TAN* turns to *UAN* form. Therefore the rate is higher in high pH than the case of low pH. It is evident that pH value of water will influence the transfer rate of ammonia. However, *Ke* is independent of pH (Weiler, 1979). The reason is that the *Ke* depends only on the mass transfer friction of the liquid - air interface but not on the concentration of *TAN* in aqueous phase. Table 1 shows the relationships between *Ke* and concentration of *TAN*, *Ke* and pH, in distilled water system. The *Ke* values in Table 1 compared well with those found in the literature (Weiler, 1979).

Table 1 The *Ke* values obtained in distilled water system, the abbreviation *TANI* denotes theinitial concentrations of *TAN* in water

Items		Tianjin			Kunming				Tianjin		
pH	8.9	9.0	8.9	8.9	8.9	9.0	8.5	8.9	9.0	9.3	10.0
TEM, °C	15.9	16.0	16.0	20.0	20.0	19.5	16.0	16.1	16.3	15.8	16.1
U, m/s	3.0	3.1	3.1	3.1	3.0	3.1	3.1	3.1	3.1	3.1	3.0
TANI, mg/L	4.91	11.02	22.28	11.08	11.21	11.10	11.02	11.01	11.02	11.03	11.10
Ke, cm/h	1.05	1.03	1.07	1.51	1.49	1.52	1.02	1.07	1.01	1.03	1.09

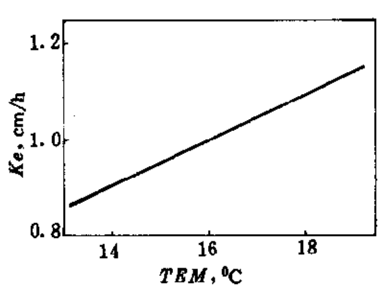

Fig. 2 Variation of *Ke* with temperature performed in Tianjin with a wind speed of 3.0 m/s

A study on the rate of transfer of ammonia from water to the atmosphere presented a linear regression equation to describe the variation of mass transfer coefficient with temperature, in which *Ke* increased with increasing temperature (Weiler, 1979). A similar result for the variation of *Ke* with temperature has also been found in our test as illustrated in Fig. 2.

The wind speed will control the loss rate of ammonia when other conditions are kept constant. Mass transfer coefficient as an exponential function with wind speed for the volatilization of hydrocarbons from water into air have been reported (Cohen, 1978). For ammonia, transferred from water to air in a wind tunnel, the relation between *Ke* and wind speed has been expressed as a linear regression equation, and the transfer process was considered to be controlled by gas phase resistance (Weiler, 1979). Wind-water interaction is complex and is far from being fully understood. The most important contribution from wind is in causing waves and modifies the surface hydrodynamics. When wind speed is greater than 10 m/s, the relations will be much complicated due to the water wave. The wind speed above Lake Dianchi water ranged from 2.5 m/s to 3.1 m/s. The wind speeds used in our tests were 2 m/s and 3 m/s respectively. The results indicated that the *Ke* is smaller in lower wind speed than that in higher wind speed as shown in Table 2.

Table 2 The results for variation of *Ke* with wind speed in distilled water and lake water system, the abbreviation *TANI* represents the initial concentration of *TAN* in water

	Distilled water system				Lake water system	
	Tianjin		Kunming		Kunming	
U, m/s	3	2	3	2	3	2
pH	8.86	9.00	8.80	8.87	7.50	7.50
TANI, mg/L	11.12	6.25	11.44	10.53	11.44	10.95
TEM,℃	15.8	16.1	20.5	20.2	20.0	19.7
Ke, cm/h	1.04	0.81	1.50	1.23	1.03	0.84

The effect of atmosphere pressure on the transfer of ammonia from water has not yet reported. The *Ke* obtained in Tianjin and Kunming at the same test conditions (except the atmosphere) are also listed in Table 1 and Table 2. In Tianjin City, one meter above sea level, the atmosphere pressure is 1.0 atm. Kunming City, with an elevation of 1890 meters, the atmosphere is 0.78 atm. As a result of the effect of atmosphere pressure on the ammonia transfer, the *Ke* obtained in Kunming are greater than those obtained in Tianjin. Also, the atmosphere pressure effect not only on the *Ke* value but also on the transfer rate and rate constant of ammonia from water to the air.

3.3 Ammonia transfer from Lake Dianchi water to the air

The wind speed above Lake Dianci water ranged from 2.5 m/s to 3.1 m/s. The average value of water temperature is 20℃ during the testing period. Therefore, the test run in 3.0 m/s of wind speed and at 20℃ of water temperature. For Lake Dianchi Caohai water samples containing 14.81 mg/L of *TAN*, at pH = 8.10, the measured average value of *Ke* was 1.01 cm/h ($n=5$, $CV=4.6\%$). As compared to the *Ke* with an average value of 1.51 cm/h obtained from the test run in distilled water system at the same wind speed and water temperature, the former is small. It is obviously that the water quality affected the *Ke* and is a yet to be further studied problem. Adjusted the pH of lake water to 9.10 a measured-average *Ke* of 0.98 cm/h was obtained ($n=5$, $CV=4.4\%$). The average value of above two *Ke* was 1.00. Put this value into the following equation we can estimate the transfer rate of ammonia from water surface 0.2m section of Lake Dianchi Caohai:

$$r = \frac{Ke \cdot K}{K + [H]} \frac{A}{V} [TAN] \quad , \tag{11}$$

where $A/V = 0.05\ cm^{-1}$. For lake water, ignore the effect of water quality on K, at temperature of 20°C $K = 3.98E-10$ (Guan, 1991), at pH $= 8.10$, $[H] = 7.95E-9$, ignored the unit of $[H]$, the calculated rate was 36 μg/(L. h) based on Equation (11). At the same temperature, when pH equal to 9.10, $[H] = 7.95E-10$, the calculated rate was 242 μg/(L. h). For the samples of pH=8.10 and of pH=9.10, the observed average rates were 35 μg/(L. h) and 217 μg/(L. h), respectively, under the same test conditions. Therefore, the relative errors between the calculated and observed rate were 1.4% and 5.4%, respectively. A maximum relative error of 10.6% has been found from the data obtained from eight real lake water with different pH, temperature and concentrations of TAN. The above results show that the measured Ke value can be used to estimate the ammonia transfer rate from water as long as the concentration of TAN, the pH, temperature and wind speed are known.

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