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TRANSFER OF VOLATILE CHEMICALS ACROSS THE AIR-WATER INTERFACE UNDER DIFFERENT WIND CONDITIONS

presented by

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Master of Science degree in Civil Engineering

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TRANSFER OF VOLATILE CHEMICALS ACROSS THE AIR-WATER INTERFACE UNDER DIFFERENT WIND CONDITIONS

by

Sinisa Sirovica

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

TRANSFER OF VOLATILE CHEMICALS ACROSS THE AIR-WATER INTERFACE UNDER DIFFERENT WIND CONDITIONS

By

Sinisa Sirovica

Mass transfer across the air-water interface was studied for a wide range of wind conditions. The study was aimed at the evaluation of the liquid and gas phase mass transfer coefficients, k_{ℓ} and k_{σ} respectively, as defined by Whitman's two film theory. Wind-tunnel experiments were performed to simulate field conditions. Values of k, were determined using toluene as a volatile agent and values of $\boldsymbol{k}_{_{\boldsymbol{\alpha}}}$ were determined from water evaporation measurements. Two independant methods were applied for the evaluation of the coefficients and yielded consistent results. The effect of temperature was considered. A linear relation was obtained between k, and the shear velocity u^* for $u^* > 0.10$ m/s. A linear relationship was also found between $k_{\underline{\sigma}}$ and u^{\star} for the $\underline{\sigma}$ experimental range considered. A comparison of k_{σ} values obtained in the laboratory with field data showed an underprediction in k_{α} by approximately 25%.

To My Parents

Ankica and Borivoje

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LIST OF SYMBOLS

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Symbol	Description
A	Surface area of water (m ²)
Cl	Concentration of toluene in water $(mol/m^3, mg/m^3)$
С _д	Concentration of toluene in air $(mol/m^3, mg/m^3)$
C _{li}	Concentration of toluene at the interface (mol/m ³ , mg/m ³)
C _{lo}	<pre>Initial toluene concentration in water (mol/m³, mg/m³)</pre>
c ₁₀	Water vapor concentration at height of 10 cm $(mol/m^3, mg/m^3)$
C _s	Saturated water vapor concentration (mg/m^3)
Е	Water evaporation rate (g/m ² .hr, cm/3hrs)
Fg	Chemical potential in gas phase (atm)
FL	Chemical potential in liquid phase (atm)
н	Henry's constant (atm.m³/mol)
к	Mass transfer coefficient (m²/s)
k _l	Liquid phase mass transfer coefficient (m/hr)
k q	Gas phase mass transfer coefficient (m/hr)
к ₁₀	Mass transfer coefficient at $z = 10$ cm
L	Water depth (m)
N	Toluene mass flux (mol/m².s)
P	Partial pressure (atm)
P. i	Partial pressure at interface (atm)
r ·	Film resistance

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Symbol	Description
R	Universal gas constant (atm.m³/molºK)
Т	Absolute temperature (^O K)
u*	Shear velocity (m/s)
U	Wind velocity (m/s)
U ₁₀	Wind velocity at 10 cm (m/s)
^U 8	Wind velocity at 8 m (m/s)
X _i	Concentration of toluene at the interface (mole fraction)
x	Distance to the upwind edge (m)
z	Distance above the water surface (cm)
^z 0	Surface roughness length (cm)
α	Power-law exponent
Г	Gamma function

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1.0 INTRODUCTION

The transfer of volatile chemicals across the air-water interface occurs by molecular and turbulent diffusion. The development of a full understanding of this process and hence the prediction of transfer rates for any chemical under different environmental conditions presents a problem that has not yet been fully elucidated. When a natural water body is in contact with the atmosphere, the following questions are important. In which direction does the transfer take place? How fast is it occurring? What factors enhance it or reduce it? The answer to these questions requires an understanding of wind-wave interaction, chemistry and the transfer process itself.

One aspect of the transfer process is the volatilization of aqueous pollutants from natural waters into the atmosphere. This process affects pollution levels in the aqueous environment. For example, it was found that some hydrocarbons and chlorinated hydrocarbons in natural water are predominantly eliminated by volatilization to the atmosphere (Dilling et al, 1975; Mackay and Leinonen, 1975; Schwarzenbach et al., 1979)

The transfer of a chemical from one phase to the other has been investigated by studying the turbulent flow behavior in the region close to the water surface and

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several mass transfer models have been proposed. Because of the complex and not fully understood nature of the volatilization process, these proposed models embody many simplifying assumptions. The simplest is the two-film theory model. Although the model is a gross simplification of the actual diffusion process that takes place, it nevertheless has been found useful in predicting transfer rates on either side of the interface. (Liss and Slater, 1974;Liss, 1975; Mackay and Leinonen, 1975).

It is reasonable to make a distinction between two hydrodynamic regimes of the air-water interface: one regime for turbulence generated by flow in open channels and the other regime for water turbulence produced by the wind. The former is typical for rivers and streams, the latter is typical for lakes and ponds. Present understanding of the mass transfer process across the surface of natural waters, although not complete, has reached a stage where the effects of rivers and streams are fairly well understood (e.g. Dobbins, 1962; Fortescue and Pearson, 1967; Ueda et al., 1977), but the effects of wind are less understood. In order to determine the transfer rate it is essential to obtain values of the mass transfer coefficient for a wide range of wind conditions.

The general objective of this research is to develop expressions describing quantitativily the effects of wind on the mass transfer of aqueous pollutants across

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the air-water interface of stagnant natural waters (e.g. lakes and ponds). The specific objectives of this study are :

- To quantify the wind-wave interaction for a wide range of wind conditions in terms of wind velocity, surface shear stress;
- 2. To develop a method of measuring concentrations of chemicals in air and water that will permit evaluation of transfer rates;
- 3. To develop relations between the mass transfer coefficient and parameters obtained from the first objective;
- 4. To compare our laboratory results to existing experimental results obtained in the field.

2.0 THEORY

The two-film model originally developed by Whitman and Lewis (1924) assumes that there exists a thin film of stagnant fluid on either side of the gas-liquid interface. The transfer process in these films occurs by molecular diffusion. Outside the films turbulent motion is present in the form of eddies and transfer then occurs by turbulent diffusion. The turbulent mixing in the gas and liquid region outside the films is assumed to maintain the concentrations of the bulk at a constant value. It is further assumed that the concentrations on either side of the interface are in equilibrium and that Henry's law is applicable. Under these steady-state conditions the transfer rate depends on the molecular diffusivity, film thickness of each phase and on Henry's constant. The model does not incorporate any relationship between the fluid dynamics at the interface and the transfer process. Nevertheless, the two-film model is useful in describing processes at the interface and for calculations of mass transfer rates.

Figure 1 shows a typical plot of partial pressure versus mole fraction for an environmental pollutant. Most pollutants in natural waters are present in very small concentrations. Hence Henry's law should be applicable; i.e. the chemical at the interface exerts a partial

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Figure 1. Relation between partial pressure and mole fraction of a solute in solution.

pressure P_i (atm) which is proportional to the concentration X_i (mole fraction) at the interface. Mathematically,

$$P_{i} = HX_{i}, \qquad (1)$$

where H is Henry's constant for a given chemical

The two-film model is shown schematically in Figure 2. The model assumes no resistance to transfer across the interface and as a result the concentrations at the interface are in equilibrium. The driving force of mass transfer is the difference in chemical potential of each phase. Chemical potential of each phase is expressed as follows:

$$F_{g} = C_{g}RT$$
(2)

for the gas phase and,

$$F_{\varrho} = C_{\varrho} H \tag{3}$$

for the liquid phase,

where F is chemical potential (atm),

C is concentration of chemical (mol/m^3) ,

T is absolute temperature (^OK),

H is Henry's constant (atm.m³/mol),

R is the gas constant $(atm.m^3/mol.^{\circ}K)$.

The subscripts g and L stand for gas and liquid phase respectively. At equilibrium,

$$C_{g}RT = C_{l}H.$$
 (4)

Apart from difference in chemical potential between gas and liquid phase the rate of transfer is also



Concentration or Partial Pressure

Figure 2. Schematic of the two-film model of volatilization from the surface of water bodies.

affected by the resistance to transfer within each film. Knowing how the chemical partitions gives an idea as to which film governs the transfer process. If a chemical partitions mostly into the gas phase then it is the liquid film which governs the transfer process and vice versa if the chemical partitions mostly in the liquid phase, the gas film governs the transfer process. Chemicals with high H values ($>10^{-3}$ tm.m³/mol) tend to partition into the gas phase while those with low H values ($<10^{-5}$ tm.m³/mol) tend to partition into the liquid phase (Mackay, 1979). For intermediate values of H chemicals tend to partition more equally between the two phases so that both films play a significant role in the transfer process. A plot of vapor pressures versus solubility for various compounds is shown in Figure 3. The diagonal lines have constant H values and the more departure from the central diagonal line ($H = 10^{-4} \text{ atm.m}^3/\text{mol}$) the more the transfer is governed by one film only.

The air-water exchange kinetics can be treated as two resistances in series, in which each film has its own resistance to transfer. The flux through each film must be the same as there can be no accumulation or depletion of the chemical at the interface. This mass flux N $(mol/m^2.hr)$ can be expressed in terms of a resistance r with a chemical potential F as the driving force. For transfer from the liquid phase to the gas phase,

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$$N = (F_{\ell} - F_{i}) / r_{\ell}, \qquad (5)$$

and

$$N = (F_i - F_q) / r_q.$$
 (6)

The subscripts 2, i, g stand for liquid phase, interface and gas phase. Eliminating F yields

$$N = (F_{\ell} - F_g) / r_{t'}$$
(7)

where r_{+} is the total resistance,

$$r_t = r_l + r_q. \tag{8}$$

N can also be expressed in terms of mass transfer coefficients k_{l} and k_{g} (m/hr). These coefficients are defined by

$$k_{g} = N/(C_{i}-C_{g}), \qquad (9)$$

and

$$k_{l} = N/(C_{l} - C_{i}).$$
 (10)

Using equations (2), (3), (5), (6), (9) and (10), the relations between the mass transfer coefficient and the resistance are

$$r_{g} = RT/k_{g}, \qquad (11)$$

and

$$\mathbf{r}_{\ell} = \mathbf{H}/\mathbf{k}_{\ell} \,. \tag{12}$$

Substitution of equations (11) and (12) into equation (7) yields

$$N = \frac{C_{\ell} - C_{g} RT/H}{1/k_{\ell} + RT/Hk_{g}}$$
(13)

or

$$N = \frac{C_{\ell} H/RT - C_{g}}{1/k_{g} + H/RTk_{\ell}}$$
(14)

Hence prediction of transfer rates across a gas-liquid interface requires the knowledge of three parameters if the film model is to be used. These are H, k_g and k_l . H can be estimated from chemistry handbooks giving the chemical vapor pressure and solubility at a given temperature or can be obtained experimentally. Values for k_g can be obtained experimentally by considering water as the transferring agent. In that case the liquid phase resistance is nil and k_g can be evaluated from

$$x_{q} = N/(C_{\ell}H/RT-C_{q}).$$
(15)

Values of k_{ℓ} can be obtained experimentally by selecting a "liquid phase controlled compound" (e.g. toluene, H = 6.7 x $1G^{-3}$ atm.m³/mol). The expression for k_{ℓ} then becomes

$$k_{l} = N/(C_{l} - C_{q}RT/H).$$
(16)

Once mass transfer coefficients have been obtained experimentally in the laboratory for specific compounds, they can be used to predict those of other compounds by the following relations:

$$k_{\ell}^{*} = k_{\ell} \sqrt{M/M'}$$
 (17)

and

$$k''_{g} = k_{g} \sqrt{M/M'},$$
 (18)

where M' is the molecular weight of the compound of interest and M is the molecular weight of the compound used in the experiments. The laboratory results can be applied to field conditions using the shear stress exerted by the wind as a criterion for similarity. This concept is illustrated in Section 5.5.

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3.0 EXPERIMENTAL PROCEDURES

A series of wind tunnel experiments were performed to determine the liquid phase and gas phase mass transfer coefficients. Toluene was chosen as the volatile chemical to determine the k_2 coefficients. This compound with its high Henry's law constant, has a high chemical stability, has relatively non-toxic properties and is detectable at low concentrations in water as well as in air. The k_g coefficients were determined using the water vapor flux from the water surface.

This chapter describes the wind tunnel facility, the experimental setup and the measuring procedures. All specific information concerning instrumentation used is in Appendix B.

3.1 Wind Tunnel Facility

The experiments were performed in the Environmental Wind Tunnel at the Fluid Mechanics Laboratory of Michigan State University. The wind tunnel is shown schematically in Figure 4. It is of the opencircuit type with a 12 m test section. An axial fan is employed to draw ambient air through the tunnel. The mean velocity can be adjusted continuously from 1 m/s to 12 m/s using a variable speed control system. The revolutions of

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Environmental Wind Tunnel, Fluid Mechanics Laboratory, Michigan State University. Fig. 4.

the fan are monitored by a digital frequency counter so that velocities can be reproduced precisely. The entrance conditions consist of flow straighteners made from cardboard. The straighteners dimensions are 60 cm in length with an outside diameter of 5 cm and an inside diameter of 4.7 cm. The straighteners are mounted on an adjustable plastic frame installed in the tunnel such that the bottom row of straighteners is positioned just above the water surface. A plastic sheet covers the bottom straighteners preventing them from getting wet. The tunnel has a constant width of 1 m and a maximum height of 1.25 m. The ceiling is adjustable so that longitudinal pressure gradients can be adjusted. The bottom of the tunnel and the lower part of the side walls are sealed and water resistant permitting a maximum depth of 25 cm. The wind tunnel is equipped with a probe support carriage. The vertical position can be set remotely by a stepping motor control system. Vertical positions of probes can be read with an accuracy of 10^{-4} m.

3.2 Experimental setup

The experimental arrangement is shown in Figure 5. Prior to all experiments the tunnel was cleaned with soap and water. It was then filled with 2.5 m^3 of tap water which gave a water depth of 22 cm. The two experimental

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stations were positioned at 6.75 m and 9.25 m, sufficiently far downwind to yield approximately uniform wind and wave conditions. Wind velocities, toluene concentrations in air and water and humidities were monitored at these two different fetches. A venting system was installed to maintain the background toluene levels and humidity low.

The temperature of air was monitored in the free stream and that of water at 10 cm below the surface, both at a fetch of 9.25 m.

The following experiments were performed at both stations :

1. Velocity measurements to determine the surface shear stress and other parameters of the velocity profiles.

2. Toluene measurements to evaluate k_0 .

3. Humidity measurements to evaluate k_{q} .

3.3 Velocity measurements

Wind velocity profiles were measured at a fetch of 6.75 m and 9.25 m. The profiles were measured for wind speeds varying from 1 to 10 m/s.

The following procedure was used to obtain velocities at discrete points in a vertical profile. 1. A pitot tube was mounted on the probe support carriage and connected to a pressure transducer. 2. The recorded pressures were converted by the pressure transducer to an electrical signal and read as a voltage on a digital voltmeter.

3. The pitot tube was traversed first upwards and then downwards up to 40 cm above the water surface.

4. The pressure change with distance traversed was instantanuously recorded on an x-y plotter both for the upward and downward profiles.

5. The upward and downward profile were used to correct for a lag between the pressure readout and the actual pressure at the pitot tube. An algorithm was developed to obtain velocities from the pressure plots. Details of the calculation procedure are given in Bouwmeester(1982).

The pressure transducer was calibrated using a differential manometer equipped with a micrometer dial gage so that water height differences as small as 10⁻⁴ in. could be recorded.

3.4 Toluene measurements

A total of thirteen runs were performed with wind speeds varying from 1 to 10 m/s. Before a series of runs were started, toluene was applied to the water. An experimental run consisted of setting a wind velocity, taking a water sample, sampling the air at one station,

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taking a second water sample, sampling the air at the other station and finally, taking a third water sample. Water and air temperatures as well as the background toluene concentration were monitored continuously during the runs. Details of each experimental step are given below.

3.4.1 Toluene application

Dissolving toluene in water presented a problem due to its low dissolution rate. Therefore a special technique was developed for the toluene application. Namely a water jet was used to disperse the toluene into fine particles making it dissolve more readily. The complete application procedure was as follows: 1. 60 ml of toluene was mixed with 180 ml of ethanol. 2. The mixture was transferred to a separatory funnel. 3. A submersible pump installed in the tunnel provided a strong jet of water.

4. The neck of the separatory funnel was placed in the water such that the tip was just in front of the water jet. The tip was slanted slightly to prevent the water from "shooting up" the funnel.

5. A tenth of the mixture was then released very slowly, the water jet being rotated around the tip of the funnel. In this way the mixture was dispersed into fine particles

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providing for rapid dissolution of the toluene.

6. This application was carried out at ten equidistant points to distribute the toluene uniformely over the full lenght of the channel.

7. Prior to a series of experimental runs the wind-tunnel was operated for two hours to enhance uniformity of the toluene concentration in the water.

3.4.2 Toluene measurements in air

Air was sampled for 30 minutes at five vertical positions, one station at one time. Four positions were close to the water surface and one was higher in the free stream to monitor the background concentration of toluene (See Figure 5). The air was led through charcoal tubes installed vertically to compact the carbon granules and, hence, to prevent channeling. The tubes contained two compartments and checks were made to verify that all the toluene was collected in the first compartment (See Appendix A, Section 3.1). The flow rate was set at about 1 1/min and monitored with an orifice-manometer system. This flow rate was sufficiently low to capture all toluene in the first compartment. After sampling the tubes were capped, stored in the refrigerator and analyzed within 48 hours. The collected toluene in the charcoal tubes was analyzed using gas chromatography as described in Appendix A.

3.4.3 Toluene measurements in water

The water was sampled before and after each air sampling. One water sample consisted of several aliquots taken at various points between the two stations giving a total volume of 100 ml. When discharging the aliquots into the sample bottle, care was taken to submerge the tip of the pipet under the water. This was done to prevent any losses of toluene occurring during the discharge. Ten ml of CS₂ were immediately added to the water sample. The solution was shaken sufficiently long to complete the toluene extraction from the water. Subsequently the samples were analyzed using gas chromatography as described in Appendix A.

3.5 Humidity measurements

Humidity measurements were obtained using the dry and wet bulb technique. Two thermistors were mounted on the probe support carriage to measure the dry-bulb and wet-bulb air temperatures. Both thermistors were calibrated to measure temperature via a digital voltmeter. The thermistor recording the wet-bulb temperature was covered with a wick which was kept wet. Each measurement

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consisted of traversing the pair of thermistors along a vertical profile. Dry and wet bulb temperatures were recorded at ten points along the profile. A total of seven measurements were taken at each station with wind speeds varying from 2 to 10 m/s. The water temperature was monitored continuously during the experiment.

4.0 CALCULATION PROCEDURES

The liquid phase mass transfer coefficients, k_{l} , as defined by equation (15) were determined by two independent methods. One method is based on a mass balance of toluene in the air above the water surface and is called the horizontal flux method. The other method is based on the relation between the depletion rate of toluene in the water and the toluene emission across the air-water interface; the so called depletion method. The gas phase mass transfer coefficients, k_{g} , as defined by equation (16) were determined by the horizontal flux method only. A detailed description of both methods is given in the following two sections.

4.1 Horizontal flux method

The liquid and gas phase mass transfer coefficients k_{l} and k_{g} were determined using equations (15) and (16) given in Chapter 2. This required the measurement of the mass flux across the air-water interface. In the horizontal flux method this flux is determined by applying a mass balance i.e., the increase in horizontal mass flux between the upwind edge and a station is equal to the mass leaving the air-water interface between the upwind edge and that station. By

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measuring concentration profiles at the upwind edge and at the station the increase in horizontal flux enables the determination of the average mass flux across the air-water interface.

The calculation of this mass flux involved the use of a simplified form of the convection-diffusion equation,

$$U \frac{\partial C}{\partial x} = \frac{\partial}{\partial z} \left(K \frac{\partial C}{\partial z} \right)$$
(19)

where x is distance to the upwind edge,

z is height above the water surface,

- U is local wind velocity; U = U(z),
- C is local concentration; C = C(x,z),
- K is mass transfer coefficient; K = K(z).

The boundary conditions are :

$$C \neq 0 \text{ for } z \neq \infty, N = 0 \text{ for } x < 0, \text{ and}$$
$$N = \left[K \frac{\partial C}{\partial z} \right]_{z=0} \text{ for } x \ge 0 \qquad (20)$$

where N = average mass flux across the air-water interface.

The solution for the concentrations is obtained following a procedure given by Pasquill (1974). The area source [represented by equation (20)] is considered as the superposition of an infinite series of line sources. The first step is then to determine the analytical solution for a line source. This is done as follows: 1) The velocity profile is appoximated by the power-law formula,

$$U = U_{10} (z/0.1)^{\alpha}$$
(21)

where U_{10} is the velocity at a height of 0.1 m above the water and α is the power-law exponent.

2) The profile of the mass transfer coefficient above the water is approximated by

$$X = K_{10} (z/0.1)^{1-\alpha}$$
 (22)

where K_{10} is the mass transfer coefficient at a height of 0.1 m. K_{10} is evaluated using the Reynolds analogy assumption of equating the mass transfer coefficient to the momentum transfer coefficient.

Thus

$$K_{10} = ku^*z,$$
 (23)

where k is von Karman's constant (= 0.4),

u* is shear velocity

Equations (19),(20) and the above expressions for K_{10} and U_{10} , yield the following closed form solution $C(\mathbf{x}, \mathbf{z}) = Nr/U_{10}\Gamma(\mathbf{s}) [U_{10}/r^2K_{10}\mathbf{x}] \exp [-U_{10}\mathbf{z}^r/r^2K_{10}\mathbf{x}]$ (24) where $r = 1+2\alpha$

 $s = (\alpha+1)/r$

 Γ is the gamma function.

The solution for an area source is now obtained by integrating along the x-direction from the upwind edge to the point of consideration; i.e., $C(x,z) = \int_{x}^{x} Nr/U_{10}\Gamma(s) [U_{10}/r^{2}K_{10}x] \exp \left[-U_{10}z^{r}/r^{2}K_{10}x\right] dx \quad (25)$

The calculation of the mass flux N was carried out as follows. First the solution for C(x,z) was obtained by setting N equal to unity. Denoting this solution by $C_1(x,z)$ and denoting the actual concentration measured experimentally by $C_2(x,z)$, the unknown flux N was determined by relating C_2 to C_1 .

The evaluation of C_1 required the following parameters : U_{10} , u*, x, and z. U_{10} and u* were obtained graphically by plotting the measured velocity profiles on semilog paper. The coordinates x and z were those of the various samplers. The calculation of C_1 using equation (25), was carried out on a computer. The calculation procedure included the numerical integretion of line source solutions. The line sources were equally distributed over the area, except for the section directly in front of the point of consideration which had a denser distribution of line sources. This was done to avoid numerical errors due to discretization.

With a known mass flux, N, and known concentrations in the water and air, k_{l} and k_{g} were determined using equations (15) and (16).

As the chemical potential of toluene in the air was several orders of magnitude smaller than that in the water ($C_q RT/H \ll C_g$) equation (16) in Chapter 2 could be simplified to

$$k_{\ell} = N/C_{\ell}.$$
 (26)

4.2 Depletion method

The mass flux N across the air-water interface can be expressed by equation (14) in Chapter 2.

$$N = k_0 (C_0 - P/H),$$
 (27)

where $P = C_g RT$, the terms having the usual meaning. A mass balance in an unsteady state model, assuming only volatilization losses, yields

$$VdC_o/dt = -NA, \qquad (28)$$

where V is the volume of water in the wind tunnel and A is the surface area exposed to volatilization. Eliminating N using equation (27) and using L = V/A, where L is the water depth in the wind-tunnel, we get

$$dC_{\ell}/dt = -k_{\ell}(C_{\ell}-P/H)/L.$$
(29)

Integrating equation (29) to express the toluene concentrations as a function of time t and denoting the initial concentration by C_{l_n} , gives

$$C_{\ell} = P/H + (C_{\ell_0} - P/H) \exp(-k_{\ell} t/L).$$
 (30)

For a low solubility compound, such as toluene (P/H << C_g), equation (30) simplifies to

$$C_{\ell} = C_{\ell_0} \exp(-k_{\ell} t/L), \qquad (31)$$

so that

$$k_{l} = (L/t) \ln(C_{l_{0}}/C_{l}).$$
 (32)

Equation (32) can be used to calculate $k_{\rm g}$ by measuring the change in toluene concentration with time.

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5.0 EXPERIMENTAL RESULTS AND DISCUSSION

The primary objective of this study was to develop relations between wind conditions and liquid phase and gas phase mass transfer coefficients. Relations were obtained between k_{l} and u* and between k_{g} and u*. Comparison is made between the two theoretical methods used and the effect of temperature is discussed. Comparison of experimental k_{g} results with existing field results is also made.

During the experiments the background toluene concentration was kept low by keeping an exhaust fan running. The maximum concentration ever recorded was 2 ppm well below the maximum permissible level of 200 ppm.

5.1 Velocity measurements

Figure 6 and 7 show plots of measured wind velocity profiles above the mean water level at stations 1 and 2, respectively. A straight line was drawn through the logarithmic portion of each profile. The velocity parameters U_{10} and u* were determined from these profiles. The power law exponent as defined in equation (21), and U_{10} and u* are listed in Table 1.



Figure 6. Vertical wind velocity distribution at station 1.

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Figure 7. Vertical wind velocity distribution at station 2.

	U ₁₀ (m/s)	U* (m/s)	α
STATION 1 X = 6.75 m	1.10 2.24 2.82* 3.40 4.59 5.61 6.68 7.75 8.90 10.03*	0.047 0.095 0.127 0.158 0.265 0.367 0.470 0.570 0.680 0.780	0.117 0.116 0.124 0.129 0.164 0.190 0.207 0.218 0.228 0.235
STATION 2 X = 9.25 m	1.09 2.27 2.80* 3.34 4.38 5.44 6.46 7.48 8.52 9.56*	0.055 0.110 0.163 0.215 0.315 0.410 0.505 0.595 0.695 0.790	0.141 0.135 0.166 0.186 0.212 0.225 0.235 0.240 0.247 0.251

Table 1. Velocity Parameters

* Velocities marked with an asterisk were obtained by interpolation.

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5.2 Determination of k_g values

Values for k_{ℓ} were determined using the two methods described in Sections 4.1 and 4.2. The two methods are independant of each other. Therefore a comparison of the k_{ℓ} values obtained with both methods provides a means to check the consistency and accuracy of the experiments.

The experimental data of toluene concentrations in the air and in the water is listed in table Cl of Appendix C.

These results together with the velocity data are used to obtain k_g values under different wind conditions.

5.2.1 Horizontal flux method

The evaluation of k_{g} values using the horizontal flux method consisted of two steps. First the convective-diffusion equation and measured toluene concentrations in the air were used to calculate the mass transfer rate across the air-water interface. Then k_{g} was obtained from the ratio of mass transfer rate to measured aqueous toluene concentration [equation (26)].

Figure 8 shows an example of a series of measured concentration profiles (Runs 7 and 8). A plot of these measured concentrations, C_2 , versus the corresponding calculated concentrations, C_1 , is presented in Figure 9.



Figure 8. Examples of measured concentration profiles.



Figure 9. Measured concentration, C_2 , vs. calculated concentration, C_1 .

A best fit straight line was drawn through each series of points. The slope of this line is equal to the mass flux across the interface. The toluene concentration in water used to calculate k_{ℓ} was the average of the concentrations prior to and after the air sampling. The k_{ℓ} results for all the runs are plotted in Figure 10 versus U_{10} and in Figure 11 versus u*. It is noted that some of the k_{ℓ} values in these figures were adjusted to a temperature of $20^{\circ}C$; see Section 5.3.

Results from Figure 10 indicate that for $U_{10} < 2$ m/s k_l is relatively small and that wind has little effect. In this range the water surface is calm and any transfer appears to be controlled by molecular diffusion and water currents with no or little turbulence. For this range of velocities values of k_l do not exceed 0.03 m/hr. For $U_{10} > 2$ m/s k_l increases substantially up to approximately 0.4 m/hr at $U_{10} = 10$ m/s. The increase is fairly linear. This behavior is consistent with the observation made by Wu (1975) that the wind induced drift current is turbulent for this velocity range.

Another interpretation of the sudden increase in k_{l} could be based on the following. It was observed during the experiments that the first ripples started occurring around 2 m/s coinciding with the increase in the transfer rate. A study by Banner et al.(1975) has shown that wave breaking may occur at the onset of ripples.

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This can explain the increase in transfer around a U_{10} value of 2 m/s.

A contributing factor to the increase in k_{g} is the enhancement of interfacial area due to wave growth. This is appreciable above a U_{10} value of 4 m/s. Approximate calculations indicated that the increase in area was at maximum 10 %.

Whithin experimental error there is no difference between the k_{ℓ} values at the two stations. Apparently, the variation in mass transfer rate with fetch is not so significant. The original intention was to evaluate k_{ℓ} for the section between the two stations but due to relatively large experimental errors this proved to be unfeasible.

Results from Figure 11 indicate that k_{l} is also correlated to u*. For u* < 0.1 m/s little transfer is taking place. Above that value the transfer rate increases fairly linearly up to a k_{l} value of approximately 0.35 m/hr at u* = 0.75 m/s. Using linear regression analysis the following relation was determined for k_{l} as a function of u*:

 $k_{l} = 0.45u^{*} - 0.010,$ (33) where k_{o} is in m/hr and u* is in m/s.

-39-

5.2.2 Depletion method

Values for k_{ℓ} were also obtained using the procedure described in Section 4.2. The k_{ℓ} results for all the runs are plotted in Figure 12 versus U_{10} and in Figure 13 versus u*. Some of the k_{ℓ} values have again been adjusted to a temperature of 20°C; see Section 5.3.

Results indicate that whithin experimental error the k_{ℓ} values predicted by the depletion method do not differ from the ones predicted by the horizontal flux method. One would expect the depletion method to underpredict the horizontal flux method due to the effect of wind tunnel side walls. However the results seem to indicate that the side wall effect is negligible. The results support the conclusion that a linear relationship exists between k_{ℓ} and U_{10} for the U_{10} range of 2-10 m/s and between k_{ℓ} and u* for the u* range of 0.1-0.75 m/s.

5.3 Temperature correction

Due to the high evaporative cooling of the water during the runs with velocities between 6.5 m/s and 10 m/s, it was necessary to correct for the effect of temperature on the transfer process. The maximum change in temperature that occurred during a series of runs was from 20° C to 15° C.

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The experimental procedure was identical to the other experiments except that no air samples were taken. The wind speed was kept constant with $U_{10} = 7.62$ m/s and $u^* = 0.583$ m/s. This speed was representative for the range mentioned above. The temperatures were monitored with time. The range covered was from 28° C to 15° C and, during that time water samples were taken periodically. The k_l values were obtained using the depletion method and the results are shown in Figure 14. A best fit straight line gave the following equation :

$$k_{l} = k_{lu} + 0.010(T2-T1),$$
 (34)

where $\mathbf{k}_{\mbox{lu}}$ is the uncorrected mass transfer coefficient

Equation (34) was used to adjust the measured k_{ℓ} values to those for a temperature of 20°C. The results show that k_{ℓ} increases by 1 cm/hr for each °C rise in temperature. As equation (34) was obtained for $U_{10} = 7.62$ m/s, some error is introduced by applying it to the U_{10} range from 6.5 m/s to 10 m/s. The author believes these errors are small and not significant to alter the general trend of the k_{ℓ} plots. Additional experiments would have to be conducted to more completely investigate the effect of temperature.



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Figure 14. k_g vs. temperature for $U_{10} = 7.62$ m/s.

5.4 Determination of k_{q} values

Values for k_g were determined using the horizontal flux method described in Section 4.1. Instead of toluene concentrations in air, water vapor concentrations in conjuction with the velocity data were used to obtain the water evaporation rate. Table C2 in Appendix C summarizes the results of seven experimental runs.

Values of k_g , as defined by equation (15), were determined by taking for C_g the water vapor concentration at a height of 10 cm. Denoting this water vapor concentration by C_{10} and $C_{\ell}H/RT$ by C_s (the saturated water vapor concentration), equation (15) becomes

$$k = E/(C_{2}-C_{10}), \qquad (35)$$

where E is the water evaporation rate $(g/m^2.hr)$.

The k_g results for all the runs are plotted in Figure 15 versus U_{10} and in Figure 16 versus u*. The experimental method was not used for wind velocities < 3m/s because of inadequate evaporative cooling of the wet bulb. Results indicate that for the experimental range covered k_g is a fairly linear function of U_{10} and u*. Again no difference is observed between station 1 and station 2. The relation between k_g and u* using linear regression analysis was

 $k_{g} = 131.3u^{*} + 16.3$ (36) where k_{g} is in m/hr and u* is in m/s.



 k_g vs. U_{10} for station 1 and 2.



5.5 Comparison of k_{q} with field data

The evaporation equation developed by Marciano et al.(1954) was used to compare our laboratory data to field data. This equation is

$$E = 6.25 \times 10^{-4} U_8 (P_s - P_8), \qquad (37)$$

where E is evaporation in cm/3hrs,

U_R is wind speed in knots at 8 m,

 $\mathbf{P}_{\mathbf{c}}$ is the saturated water vapor pressure in mb, and

 P_8 is the water vapor pressure at 8 m in mb. Equation (37) was used to obtain an expression for k_g which could be compared to equation (36).

The following assumptions were made: 1. the surface shear stress u* is used to relate the wind conditions in the wind tunnel to those in the field; 2. the humidity and velocity profiles are logarithmic; 3. the relation between u* and surface roughness length, z_0 , is given by (Charnock; 1955)

$$z_0/(u^{*2}/g) = 0.0156.$$
 (38)

Using these assumptions, equation (37) yields the following expression for k_{σ}

 $k_{g} = 5.207 U_{8} \ln(8/z_{0})/\ln(1/z_{0})$ (39) where z_{0} is related to u* by equation (38) and U_{8} is related to u* by

$$U_8 = 2.5 u^* \ln (5031/u^{*2})$$
 (40)

Equations (36) and (39) are given in Figure 17. The laboratory data underpredicts the field data. A similar result was observed by Easterbrook (1968). From our results it appears that in the field situation the water evaporation is approximately 25% greater than in the laboratory wind tunnel. This may be explained by the limited fetch of the laboratory experiments.



Figure 17. k vs. u^* for field and laboratory data.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The experimental results presented and discussed support the following conclusions:

1. Both k_{l} and k_{g} increase linearly in the U₁₀ range of 2-10 m/s and in the u* range of 0.1-0.75 m/s;

2. At a U_{10} of 2 m/s the sudden increase in toluene mass transfer rate may be attributable to wave breaking occuring at the onset of ripples;

 The variation in mass transfer rate with fetch was not observed;

4. No difference in predicting mass transfer rates exists between the two theoretical methods used;

5. Temperature affects the transfer process considerably;

6. Water evaporation in the field is approximately 25% higher than in the wind tunnel for the same wind conditions.

No attention was paid to the effects of surface active agents. These are known to play an important role and are permanently present in most natural waters. Only a two component system, toluene and water, was considered for this study. In natural waters more than one pollutant is usually present so it would be of interest to test a system containing several components. In this way the effect of chemical reactivity on the transfer process can

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be investigated. It would also be of interest to have a wind tunnel with a larger fetch so that the horizontal flux method could be applied to a section in which the surface conditions are more uniform.

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APPENDIX A

APPENDIX A

MEASUREMENT OF TOLUENE CONCENTRATIONS IN AIR AND WATER

1. Introduction

A method has been developed to measure toluene concentrations in air and water. For water concentrations a sample of water is mixed with carbon disulphide (CS_2) ; the toluene present in the water partitions to the CS_2 and the resulting solution is analysed with a gas chromatograph. For air concentrations the air is passed through a charcoal tube where the toluene adsorbs onto the charcoal. The charcoal is mixed with CS_2 , the toluene again partitioning to the CS_2 which is then analyzed in the same way.

This report describes briefly the basic principles of gas chromatography and outlines procedures for the establishment of toluene concentration standards and calibration curves.

2. Theory of Gas Chromatography

A gas chromatograph (G.C.) separates volatile components present in a liquid or gas sample. It consists

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of three main parts, an injection port, a column and a detector. In conjuction with it a strip chart recorder and a chromatograph data system are commonly used as shown in Figure Al.



Figure Al. Schematic drawing of a gas chromatographic system.

2.1 Injection port

Liquid or gas samples are introduced with a syringe. This is done instanteneously so as to have a "plug" flow onto the column. The injection port is heated resulting in almost immediate vaporisation of liquids. These vapors are carried to the column by a non-reactive gas (e.g. nitrogen).

2.2 Column

The column tubing, normally in a coiled form, can be made from copper, stainless steel, aluminim and glass. The column contains a packing material which may be a dry solid coated with a liquid film. The packing material constitutes the stationary phase of the column whereas the gas transported through the column makes up the moving gas phase. When the carrier gas transports the injected sample through the column different components of the sample transfer in and out of the stationary phase. As the exchange rate depends on molecular weights, different components have different retention times and, therefore, separate out in the column making it possible to analyze them individually. The exchange rate between stationary and moving gas phase is also temperature and carrier gas flow rate dependent. This permits the adjustment of retention times. In general a higher temperature and a higher flow rate result in a shorter retention time and lower resolution.

2.3 Detector

The detector indicates the presence and measures the amount of components in the gas leaving the column. This is converted into an electrical signal by several possible methods. A suitable method for organic compounds is the use of a flame ionisation detector (FID). The FID operates on the principle that the conductivity of a gas is directly proportional to the concentration of charged particles within the gas. The effluent carrier gas is mixed with hydrogen and burned with air forming ions and electrons. These then pass through an electrode gap, decreasing the gap resistance thus varying the resistance across the gap. The particular usefulness of the FID is in its lack of response to the CS₂ used as a solvent, while its response to toluene is excellent.

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2.4 Strip chart recorder

These are nearly always used in conjuction with the G.C. to obtain permanent records of the results. The results come out as a chromatogram i.e. a series of peaks each peak identifying the resistance variation across the electrode gap caused by the ionisation of a particular compound. The area under the peak is an indication of the amount (i.e. mass) of the component present in the sample. A typical chromatogram resulting from one single injection is shown in Figure A2.

2.5 Chromatogram data system

This device is used to automatically quantify a chromatogram with preset parameter values. The most important are retention times and area counts under peaks. It can be used to perform other calculations such as internal standard calculations which will be discussed in Section 3.2.

3. Calibration

In order to obtain a calibration curve relating mass of toluene to area under a peak in a chromatogram it was necessary to prepare a series of standards. Two

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Peak	1:	cs ₂
Peak	2:	Benzene

Peak 3: Toluene

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Figure A2. Typical chromatogram

methods were applied; for the first one known amounts of toluene were dissolved in water and then extracted in CS₂: For the second one an additional step was introduced involving an adsorption-desorption process and employing a constant toluene emission device and a charcoal tube. This second method involved procedures similar to those used for the measurement of toluene in air. The first method, on the other hand, was similar to that for the evaluation of toluene concentrations in water.

3.1 Procedures and results for toluene in air

A toluene permeation tube was used as a source with a constant release rate being only dependent on temperature. The permeation rate was determined by measuring weight losses over different lenghts of time. For this purpose the tube was installed in a controlled temperature air bath at 50°C. Air was drawn past the tube to remove the toluene. A schematic of this system is shown in Figure A3.

The weight loss was recorded over a period of several weeks and the results are shown in Figure A4. From this graph a toluene permeation rate of 46 ug/hr was obtained.

The calibration permeation tube was now used to create calibration standards using the experimental setup

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Figure A3. Permeation tube calibration system.



Figure A4. Permeation tube weight loss vs. time.

shown in Figure A3. The procedure used to get a calibration standard is outlined below.

.The released toluene was adsorbed onto the charcoal tube for a selected lenght of time. The flow rate of approximately 1 liter/min was measured by a rotameter. This flow rate prevented any toluene from escaping capture in the charcoal tube.

.The charcoal tube was then removed and the charcoal was transferred into vials containing 2 ml CS₂ and a small amount of benzene. The benzene served as an interal standard.

.The toluene was then desorbed from the charcoal using a commercial shaker for a period of 30 minutes. The calibration standards, namely the CS₂ containing known amounts of toluene and benzene, were now obtained.

.One ul of the calibration standard was injected into the G.C. under the following conditions:

Injection port temp: 180°C FID detector temp: 250°C Column temp: 60°C Column pressure: 16 psi Sensitivity: 10⁻¹¹ Attenuation: 16 Nitrogen carrier flow rate: 2 ml/min Nitrogen make-up flow rate: 25 ml/min Hydrogen flow rate: 30 ml/min Air flow rate: 300 ml/min

Column manufacturer: Supelco

type: 2-3710, glass capillary, grade AA lenght: 30 meters coating: SP-2100 used in splitless mode

The peaks for toluene and benzene were recorded in the chromatogram and the evaluation of areas under peaks was carried out employing a data analyzer. The data analyzer was used to calculate the areas as shown by the stripped line in Figure A2.

A total of 6 calibration standards were obtained by installing charcoal tubes for different lenghts of time. The results are given in Table Al.

Figure A5 shows a plot of column 8 versus column 9. The slope of the calibration line obtained is called the relative response factor (RRF) and is defined as:

 $RRF = \frac{mass of toluene}{area under toluene peak} \times \frac{area under benzene peak}{mass of benzene}$

From Figure A5, RRF = 0.598

The mass of toluene in an unknown sample is then calculated from the formula:

Mass of toluene = RRF x (area under toluene peak) x Mass of benzene area under benzene peak)

Some additional notes on the calibration procedure are given below:

Area t/b	0.1384	0.5983	1.0547	1.8266	2.3694	3.0146
Conc. t/b	0.0717	0.3585	0.7170	1.0755	1.4340	1.7925
Area counts benzene (b)	103,226	97,292	102,213	100,845	97,852	95,971
Area counts toluene (t)	14,287	58,205	107,800	184,202	231,848	289, 311
Conc. Benz. mg/& CS ₂	53	53	53	53	53	53
Conc. tol. after desorbtion in 2 ml CS ₂ (mg/l)	3.8	19	38	57	76	95
Mass tol. adsorb. on charcoal (µg)	7.6	38	76	114	152	061
Adsorption time (min)	10	20	100	150	200	250
Sample No.	1	2	e	4	ы	9

Table Al. Calibration data for toluene in air.

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1. All glassware used was cleaned with acetone to remove any organic residue that might affect results.

- The charcoal tubes were positioned vertically to compact the granules and reduce the possibility of channelling.
- 3. The charcoal tube was installed such that the air entered directly without passing through any tubing or any other material that might adsorb some of the toluene.
- 4. The charcoal tubes contained two compartments. The first one containing 400 mg and the second 200 mg of granulated carbon. Both compartments were analyzed and it was found that 99% toluene adsorption occurs in the first compartment, i.e. no or minute traces of toluene are measured in the second compartment.
- 5. Thirty minutes shaking produced full extraction and no change in toluene concentration were observed for longer shaking periods.
- 6. Benzene was found to be appropriate as an internal standard for the G.C. analysis; it improved the accuracy of toluene concentration analysis significantly.
- 7. Two ml of CS₂ were used for desorption as that would maximize the toluene concentration and still keep all of the charcoal in the vial covered with CS₂.

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3.2 Procedure and results for toluene in water

Water samples were taken in 100 ml aliquots. When discharging the aliquots into the sample bottle care was taken to submerge the tip of the pipet under the water. This was done to prevent any losses of toluene occuring during the discharge. Ten ml of CS_2 were added to each water sample. The mixture was then shaken manually for a period of about 30 seconds. This was repeated at least six times. The procedure resulted in complete extraction of toluene from the water. A check was made by performing a second extraction with CS_2 and no or minute traces of toluene were observed. Three toluene calibration standards were prepared by dissolving toluene in CS_2 containing the internal standard benzene. Upon analysis the results shown in table A2 were obtained.

These results are plotted also in Figure A5. We can infer from these results that within experimental error full extraction occurs from the charcoal. The Handbook of Chemistry and Physics indicates that some CS_2 dissolves in water thus making toluene concentrations higher than predicted. This was checked by adding water to a solution of CS_2 containing known concentrations of benzene and toluene. After a period of shaking no change in benzene and toluene concentrations were observed. Hence, either no measurable amount of CS_2 dissolves in

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Sample no.	Conc. tol. mg/l	Conc. benz. mg/l	Area counts toluene	Area counts benzene	Conc. t/b	Area t/b
FI	1.9	53	7452	98317	0.0358	0.0758
7	19.0	53	61056	9 7 5 9 9	0.3585	0.6256
e	190.0	53	595419	98532	3.5849	6.0429
					(1.1950)*	(2.0143)*

Table A2. Calibration data for toluene in CS2.

* Reduced 3 times to permit plotting.

water or the same portion of CS₂, benzene and toluene dissolve in water making no change in benzene and toluene concentrations. In either case the results are not affected by the partitioning.

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APPENDIX B

APPENDIX B

INSTRUMENTATION AND EQUIPMENT

Velocity measurements:

- United Sensor Pitot Static Tube

Datametrics Pressure transducer, Model 590D

Dwyer Differential micromanometer

Toluene measurements:

- Varian gas chromatograph, Model 3700
- Varian data analyser, Model CDS 111
- Varian recorder, Model 9176
- Supelco glass capillary column, 2-3170 (grade AA, SP2100, 30 meters long)
- Tractor permeation tube calibration system
- Supelco air pollution control charcoal tubes (NIOSH large size 200/400 mg)
- Sartorius top loading electronic balance, Model 1265 Mp
- Hamilton 10 ul syringe
- Supelco developing vibrator, Model 5KC
- Developing vials with teflon-lined septum caps (3.7 ml)
- Dynacol toluene permeation tube, lenght 18 cm, type ME

Humidity and temperature measurements:

- YSI thermister, Model 702A

- YSI thermivol signal conditioner, Model 740A Air Sampling System (non commercial):

Orifice, non commercial, diameter 1/64".

APPENDIX C

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	Height above water (cm)	Measured air conc. (mg/m ³)		Height above water (cm)	Measured air conc. (mg/m ³)
RUN 1 STATION 1 U = 1.10 m/s C10 = 10.67 mg/1 C1b = 10.50 mg/1 la	48.2 13.7 6.1 4.1 2.1	0.39 1.48 1.90 2.00 2.31	RUN 1 STATION 2 U = 1.09 m/s C10 = 10.50 mg/1 C1b = 10.35 mg/1 la	48.6 14.1 6.5 4.6 2.5	0.30 1.63 2.15 2.68 2.72
RUN 2	48.2	0.59	RUN 2	48.6	0.64
STATION 1	13.7	1.17	STATION 2	14.1	1.39
$U_1 = 2.24 \text{ m/s}$	6.1	2.01	U ₁₀ = 2.27 m/s	6.5	2.07
$C_{1b} = 9.61 \text{ mg/l}$	4.1	2.52	C _{1b} = 10.35 mg/1	4.6	2.26
$C_{1a} = 8.98 \text{ mg/l}$	2.1	3.39	C _{1a} = 9.61 mg/1	2.5	2.56
RUN 3	48.2	1.02	RUN 3	48.6	0.65
STATION 1	13.7	1.55	STATION 2	14.1	1.23
$U_1 = 2.82 \text{ m/s}$	6.1	2.28	$U_1 = 2.80 \text{ m/s}$	6.5	1.82
$C_{1b} = 8.98 \text{ mg/l}$	4.1	3.00	$C_{1b} = 8.05 \text{ mg/l}$	4.6	2.44
$C_{1a} = 8.05 \text{ mg/l}$	2.1	4.19	$C_{1a} = 7.19 \text{ mg/l}$	2.5	3.01
RUN 4	48.2	0.84	RUN 4	48.6	0.96
STATION 1	13.7	1.14	STATION 2	14.1	1.60
$U_1 = 3.40 \text{ m/s}$	6.1	1.90	$U_1 = 3.34 \text{ m/s}$	6.5	2.63
$C_{1b} = 6.10 \text{ mg/l}$	4.1	2.43	$C_{10} = 7.19 \text{ mg/l}$	4.6	3.22
$C_{1a} = 5.22 \text{ mg/l}$	2.1	3.24	$C_{1b} = 6.10 \text{ mg/l}$	2.5	4.12
RUN 5	48.2	1.35	RUN 5	48.6	0.98
STATION 1	13.7	1.79	STATION 2	14.1	1.36
$U_1 = 4.59 \text{ m/s}$	6.1	2.42	$U_1 = 4.38 \text{ m/s}$	6.5	2.14
$C_{10} = 5.22 \text{ mg/l}$	4.1	3.08	$C_{1b} = 3.90 \text{ mg/l}$	4.6	2.50
$C_{1a} = 3.90 \text{ mg/l}$	2.1	4.00	$C_{1a} = 2.88 \text{ mg/l}$	2.5	2.93
RUN 6	48.2	2.90	RUN 6	48.6	1.85
STATION 1	13.7	3.45	STATION 2	14.1	2.96
$U_{10} = 5.61 \text{ m/s}$	7.9	4.10	$U_{10} = 5.44 \text{ m/s}$	6.5	4.15
$C_{1b} = 9.64 \text{ mg/l}$	4.1	5.41	$C_{1b} = 6.23 \text{ mg/l}$	4.6	4.35
$C_{1a} = 6.23 \text{ mg/l}$	2.1	7.94	$C_{1a} = 4.53 \text{ mg/l}$	2.5	5.07
RUN 7	48.2	1.08	RUN 7	48.6	1.82
STATION 1	13.7	1.46	STATION 2	14.1	2.40
$U_{10} = 6.68 \text{ m/s}$	6.1	1.88	$U_1 = 6.46 \text{ m/s}$	6.5	3.06
$C_{1b}^{1b} = 2.63 \text{ mg/l}$	4.1	2.06	$C_{10}^{10} = 4.53 \text{ mg/l}$	4.6	3.33
$C_{1a}^{1b} = 1.77 \text{ mg/l}$	2.1	2.41	$C_{1a}^{10} = 2.63 \text{ mg/l}$	2.5	3.74

Table Cl. Toluene experimental data.

	Height above water (cm)	Measured air conc. (mg/m ³)		Height above water (cm)	Measured air conc. (mg/m ³)
RUN 8 STATION 1 U = 7.75 m/s Cl0 = 1.77 mg/l Clb = 0.98 mg/l	48.8 14.3 8.5 6.7 4.6	0.76 0.97 1.14 1.18 1.40	RUN 8 STATION 2 $U_1 = 7.48 \text{ m/s}$ $C_{1b} = 0.98 \text{ mg/l}$ $C_{1a} = 0.63 \text{ mg/l}$	49.4 15.1 7.4	0.49 0.62 0.76
RUN 9 STATION 1 U ₁ = 8.90 m/s C ₁₀ = 0.33 mg/1 C _{1b} = 0.21 mg/1 la	48.8 14.3 8.5 6.7 4.6	0.19 0.21 0.25 0.26 0.29	RUN 9 STATION 2 U ₁ = 8.52 m/s C ₁ b = 0.63 mg/1 C ₁ b = 0.33 mg/1 la	49.4 15.1 9.3 7.4 5.4	0.32 0.39 0.46 0.48 0.53
RUN 10 STATION 1 $U_{10} = 10.03 \text{ m/s}$ $C_{10} = 0.21 \text{ mg/l}$ $C_{1a} = 0.11 \text{ mg/l}$	48.8 14.3 8.5 6.7 4.6	0.136 0.149 0.166 0.178 0.187	RUN 10 STATION 2 $U_1 = 9.56 \text{ m/s}$ $C_{1b} = 0.11 \text{ mg/l}$ $C_{1a} = 0.07 \text{ mg/l}$	49.4 15.1 9.3 7.4	0.081 0.089 0.093 0.111
RUN 11 STATION 1 $U_{10} = 10.03 \text{ m/s}$ $C_{10} = 13.19 \text{ mg/l}$ $C_{1a} = 5.65 \text{ mg/l}$	48.9 14.3 6.7 2.6	8.49 9.30 11.94 12.04	RUN 11 STATION 2 $U_1 = 9.56 \text{ m/s}$ $C_{1b} = 5.65 \text{ mg/l}$ $C_{1a} = 2.53 \text{ mg/l}$	49.1 14.7 6.9 3.0	4.17 4.87 5.64 6.02
RUN 12 STATION 1 $U_{10} = 7.75 \text{ m/s}$ $C_{1b}^{10} = 1.67 \text{ mg/l}$ $C_{1a}^{10} = 1.17 \text{ mg/l}$	48.9 14.3 6.7 2.6	1.02 1.16 1.32 1.62	RUN 12 STATION 2 $U_1 = 7.48 \text{ m/s}$ $C_{10} = 2.53 \text{ mg/l}$ $C_{1a} = 1.67 \text{ mg/l}$	49.1 14.7 6.9 3.0	1.73 2.10 2.48 2.63
RUN 13 STATION 1 $U_{10} = 5.61 \text{ m/s}$ $C_{1b} = 1.17 \text{ mg/l}$ $C_{1a} = 0.96 \text{ mg/l}$	48.9 14.3 6.7 2.6	0.388 0.402 0.523 0.745	RUN 13 STATION 2 $U_{10} = 5.44 \text{ m/s}$ $C_{1b} = 0.96 \text{ mg/l}$ $C_{1a} = 0.66 \text{ mg/l}$	49.1 14.7 6.9 3.0	0.242 0.344 0.403 0.600

C_{lb}: Toluene concentration in water before air sampling.

C_{la}: Toluene concentration in water after air sampling.

	Height above water (cm)	Measured air conc. (gr/m ³)	E	leight above water (cm)	Measured air conc. (gr/m ³)
RUN 11 STATION 1	0.8 1.8	8.25 7.52	RUN 11 STATION 2	0.7 1.6	8.44 7.85
$U_{10} = 2.82 \text{ m/s}$	3 2.7	7.11	$U_{10} = 2.80 \text{ m/s}$	2.5	7.34
	4.6	6.62		4.5	6.88
	6.5	6.39		6.4	6.57
	10.4	6.15		10.2	6.23
	14.2	6.UI 5.05		14.0	6.12 5.07
	33.8	5.92		33.7	6.05
RUN 12	0.8	8.43	RUN 12	1.0	8.40
STATION 1	1.8	7.73	STATION 2	2.0	7.88
$U_{10} = 3.40 \text{ m/s}$	3 2.7	7.33	$U_{10} = 3.34 \text{ m/s}$	2.9	7.49
10	4.6	6.81	10	4.8	6.99
6 10	6.5	6.47		6.7	6.80
	10.4	6.17		10.5	6.38
	14.2	6.02		14.3	6.17
	27.5	5.97 5.84	-	18.1 33.7	6.08
RUN 13	1.1	8.17	RUN 13	1.3	8.03
STATION 1	2.1	7.71	STATION 2	2.3	7.85
$U_{10} = 4.59 \text{ m/s}$	3.0	7.41	U ₁₀ = 4.38 m/s	3.2	7.65
2.	4.9	7.04	20	5.1	7.24
	6.9	6.71		7.0	6.97
	14.5	6.27		10.8	6.57
	18.3 33.8	6.16		18.5 33.7	6.12 5.96
RUN 14	1.8	7.74	RUN 14	1.6	7.93
STATION 1	2.7	7.54	STATION 2	2.6	7.57
U ₁₀ = 5.61 m/s	3.7	7.37	$U_{10} = 5.44 \text{ m/s}$	3.5	7.39
	5.6	7.10	20	5.4	7.15
	7.5	6.84		7.4	6.98
	11.3	6.53		11.2	6.70
	15.1	6.43		10.0	6.55
	33.8	6.21		33.7	6.36
RUN 15	2.8	7.55	RUN 15	2.9	7.47
STATION 1	3.7	7.45	STATION 2	3.9	7.51
$U_{10} = 6.68 \text{ m/s}$	4.7	7.45	$U_{10} = 6.46 \text{ m/s}$	4.8	7.46
L V	6.6	7.27	TA	6.7	7.33
	8.5	7.05		8.6	7.14
	12.3	6.88		12.4	6.92
	16.1	6.80		16.2	6.68
	TA'A	6.75		20.1	6.57
	54.2	0.00		33.1	0.30

Table C2. Water vapor experimental data.

Table C2 (continued)

	Height above water (cm)	Measured air conc. (gr/m ³)	i z v	Height Above vater (cm)	Measured air conc. (gr/m ³)
RUN 16 STATION 1 U ₁₀ = 7.75 m/s	3.1 4.1 5.0 6.9 8.8 12.6 16.4 20.3 34.2	7.65 7.62 7.53 7.41 7.31 7.15 7.06 6.98 6.87	RUN 16 STATION 2 U ₁₀ = 7.48 m/s	3.2 4.2 5.1 7.0 8.9 12.8 16.6 20.4 33.7	7.72 7.55 7.54 7.34 7.21 7.04 6.85 6.73 6.49
RUN 17 STATION 1 U ₁₀ = 8.90 m/s	3.7 4.7 5.7 7.6 9.5 13.3 17.1 20.9 34.2	7.63 7.76 7.66 7.57 7.53 7.38 7.28 7.21 7.13	RUN 17 STATION 2 U ₁₀ = 8.52 m/s	3.9 4.8 5.8 7.7 9.6 13.4 17.2 21.0 33.7	7.39 7.39 7.45 7.31 7.22 7.04 6.93 6.80 6.69

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