

## AIR-WATER EXCHANGE MODEL FOR ORGANIC COMPOUNDS

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### ABSTRACT

Air-water exchange models are useful for estimating rates of chemical transfer and loss from natural water bodies and effluent treatment lagoons. They are also used for estimating deposition rates of atmospheric contaminants, and for interpreting observed air and water concentrations to establish the direction and rate of transfer. This work presents a model to describe the dominant air-water exchange processes comprising the rates of volatilization, absorption at the water surface, dissolution in rainfall, and wet and dry particle deposition for a organic chemical. The model provides a rational method of estimating air-water exchange characteristics. The results show that a chemical with a relatively high Henry's law constant, being subject to volatilization, but with a low vapor pressure, being therefore subject to sorption to atmospheric particles, may cycle between air and water. A steady state but non-equilibrium condition may be reached in which the water is supersaturated with respect to air.

### INTRODUCTION

Air-water exchange models are useful for estimating the rates of deposition of potential atmospheric contaminants to natural water bodies. Through the concentration of the chemicals in the air and water media, they provide the directions of the transfer rates and the losses from the water body. The complexity of the various processes and the widely varying physical chemical properties of chemicals bring about situations where chemical behavior in the environment is far from obvious.

There have been several treatments of air-water exchange in the literature (Lyman et al., 1982; Brutsaert and Jirka, 1984; Pruppacher et al., 1983). This work presents a model to describe the dominant air-water exchange processes comprising the rates of

volatilization, absorption at the water surface, dissolution in rainfall, and wet and dry particle deposition for a organic chemical.

### AIR-WATER EXCHANGE MODEL

The model is based on a study of air-water exchange processes (Mackay et al., 1986) and is schematically represented in Figure 1.

#### Data input

The chemical studied in this work was the naphthalene. This chemical has a relatively high Henry's law constant and a relatively low vapor pressure.

The input data for the model are the physical chemical properties of the chemical, dimensions of the air and water compartments, total concentrations of the chemicals in the air and water, constituent fractions in the media and media densities. In addition, the advective and diffusive transport data as rain rate, wet and dry deposition velocities and scavenging ratio for the air must be entered. As the chemical properties are temperature dependents, the model assumes the standard temperature of 25°C. The properties of the chemical used in the model are shown below (Mackay, 1991; Thibodeaux, 1996). The model does not consider the degradation of the chemical in the media.

Chemical: Naphthalene

Temperature (°C): 25

Molecular mass (g/mol): 128.2

Melting point (°C): 80.2

Water solubility (g/m<sup>3</sup>): 31.7

**Vapor pressure (Pa): 10.4**

Log octanol - water partition coefficient: 3.35

**Total chemical concentration in air (ng/m<sup>3</sup>): 10**

**Total chemical concentration in water (ng/l): 700**

## Media

The water medium area and depth (and hence volume) are defined, it being assumed well mixed. It contains besides water itself suspended particles consisting of mineral and organic matter. The air phase is treated similarly, having the same area and a defined mixing layer height.

Water bulk density (kg/m<sup>3</sup>): 1000

Air particles density (kg/m<sup>3</sup>): 2000

Water particles density (kg/m<sup>3</sup>): 1500

## Model Calculations

The model specifically calculates partition coefficients, fugacity capacities (Z parameter), fugacities, chemical concentrations in the media constituents, masses, fractions, mass transfer resistances, transport D parameters and advective and diffusive rates. A fugacity calculation is then completed of the partitioning status of the chemical, assuming that the particles are in equilibrium with the medium.

The transport processes considered are the diffusive exchange by volatilization and the reverse absorption, the net dissolution of the chemical and the dry and wet deposition of aerosol particles. The model calculates the vapor pressure of the subcooled liquid. This parameter is obtained through the equilibrium between the solid and the subcooled liquid. This pressure is inversely related to the fugacity capacity of the aerosols. Hence, the lower this pressure the higher the capacity of chemical absorption by the aerosol particles.

A key parameter in the water box is the octanol-water partition coefficient, since it determines the chemical partition between the suspended particles containing organic carbon and the water. The mineral matter contained in the particles is neglected since its content is much lower than the organic matter content. Thus, the fugacity capacity of the particles in the water medium is a function of the fugacity capacity of the bulk water phase, the organic carbon fraction in the particles, the organic carbon-water partition coefficient and the particle density.

The fugacities in each medium are calculated by the ratio between the total concentration of the chemical in each medium (data input) and the total fugacity of the medium. The total fugacity of the medium is the product of the fugacity capacities of the constituents of the medium by their volumetric fraction.

The advective rates depend significantly on the input data that control the flow rates of rain dissolution, dry and wet deposition. These rates also depend on the fugacity capacity of the water, specifically for the rain, and the aerosols. After calculating the flow rates and the fugacity capacities, the transport D parameters are determined. The advective rates are then obtained by multiplying the D parameters with the fugacity in the air. The fugacity in the air has an essential role in the dissolution and deposition of the chemicals. This is so as the increase of the total

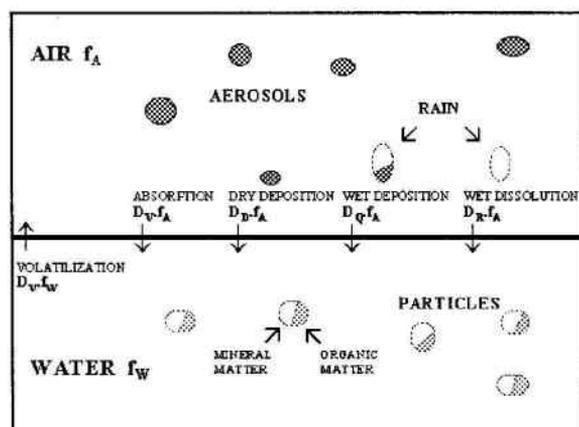


Figure 1 - Air-water exchange processes.

The air compartment is comprised of air itself, and a specified concentration of aerosols as atmospheric particles.

The properties of the environment used in the model are given below (Mackay, 1991; Hamacher, 1986; Lima, 1996; Thibodeaux, 1996):

Area (m<sup>2</sup>): 3.52E+08

Water depth (m): 7.7

Atmosphere height (m): 900

Particulate matter in water (g/m<sup>3</sup>): 75

Organic carbon content of particulate matter in water: 0.2

Aerosol or total suspended particles conc. in air (µg/m<sup>3</sup>): 50

Water-side mass transfer coefficient (m/h): 0.057

Air-side mass transfer coefficient (m/h): 5.34

Dry deposition velocity (cm/s): 0.20

Rain rate (m/year): 1.18

Scavenging coefficient: 200000

concentration of the chemical in the air box causes an increase in the fugacity and then in the advective rates.

The air-water exchange calculations are summarized below.

Fugacity Ratio: 2.84E-01

Subcooled liquid vapor pressure (Pa): 3.66E+01

**Henry's Law constant (Pa.m<sup>3</sup>/mol): 4.21E+01**

Octanol - water partition coefficient: 2.24E+03

Air-water partition coefficient: 1.70E-02

Organic carbon - water partition coefficient: 9.18E+02

Aerosol-air partition coefficient: 1.64E+05

Particle-water partition coefficient: 2.75E+02

#### Environment conditions

Dry deposition velocity (m/h): 7.20E+00

Dry deposition rate (m<sup>3</sup>/h): 6.34E-02

Rain rate (m/h): 1.35E-04

Dissolution rate by rain (m<sup>3</sup>/h): 4.74E+04

Wet deposition rate (m<sup>3</sup>/h): 2.37E-01

Air density (kg/m<sup>3</sup>): 1.19E+00

#### Volume fractions

##### Air compartment

Aerosol particles: 2.50E-11

Air: 1.00E+00

Total: 1.00E+00

##### Water compartment

Particles: 5.00E-05

Water: 1.00E+00

Total: 1.00E+00

#### Volumes (m<sup>3</sup>)

##### Air compartment

Total: 3.17E+11

##### Water compartment

Total: 2.71E+09

#### Fugacity capacities of the chemical (Z) (mol/m<sup>3</sup>.Pa)

In air: 4.03E-04

In water: 2.38E-02

In air particles: 6.62E+01

In water particles: 6.55E+00

In bulk air: 4.03E-04

In bulk water: 2.41E-02

#### Concentrations and fugacities of the chemical

##### Air compartment

Molar concentration in bulk phase (mol/m<sup>3</sup>): 7.80E-11

**Mass concentration bulk phase (g/m<sup>3</sup>): 1.00E-08**

**Fugacity in bulk phase (Pa): 1.93E-07**

Molar concentration in the gas phase (mol/m<sup>3</sup>): 7.80E-11

Mass concentration in the gas phase (g/m<sup>3</sup>): 1.00E-08

Molar concentration in the air particles (mol/m<sup>3</sup>): 1.28E-05

Mass concentration in the air particles (g/m<sup>3</sup>): 1.64E-03

Molar conc. in part.in relat'n to medium (mol/m<sup>3</sup>): 3.20E-16

Mass conc. in part.in relat'n to medium (g/m<sup>3</sup>): 4.10E-14

##### Water compartment

Molar concentration in bulk phase (mol/m<sup>3</sup>): 5.46E-06

**Mass concentration in bulk phase (g/m<sup>3</sup>): 7.00E-04**

**Fugacity in bulk phase (Pa): 2.27E-04**

Molar conc. in the dissolved phase (mol/m<sup>3</sup>): 5.39E-06

Mass concentration in the dissolved phase (g/m<sup>3</sup>): 6.91E-04

Molar conc. in the water particles (mol/m<sup>3</sup>): 1.48E-03

Mass concentration in the water particles (g/m<sup>3</sup>): 1.90E-01

Molar conc. in part.in relat'n to medium (mol/m<sup>3</sup>): 7.42E-08

Mass conc. in part. in relat'n to medium (g/m<sup>3</sup>): 9.51E-06

Water-air fugacity ratio: 1.17E+03

#### Parameters D (mol/Pa.h) and resistances (mol/Pa.h)<sup>-1</sup> for transport processes

Parameter D for water: 4.77E+05

Resistance in water: 2.10E-06

Parameter D for air: 7.58E+05

Resistance in air: 1.32E-06

Total resistance: 3.41E-06

**Resistance in air (%): 38.6**

**Resistance in water (%): 61.4**

Parameter D for volatilization: 2.93E+05

Parameter D for absorption: 2.93E+05

Parameter D for dissolution in the rain: 1.13E+03

Parameter D for dry deposition: 4.19E+00

Parameter D for wet deposition: 1.57E+01

Total parameter D for air-water transfer: 2.94E+05

Overall air phase mass transfer coefficient (m/h):  
2.06E+00

Overall water phase mass transfer coeff. (m/h):  
3.50E-02

Air-water transport processes rates

**Absorption rate (mol/h): 5.66E-02**

**Volatilization rate (mol/h): 6.63E+01**

**Rain dissolution rate (mol/h): 2.18E-04**

**Dry deposition rate (mol/h): 8.11E-07**

**Wet deposition rate (mol/h): 3.03E-06**

Total transfer air-water (mol/h): 5.68E-02

**Net transfer air-water (mol/h): - 6.63E+01**

**Air to water mass transfer rate of the chemical (kg/h): 7.29E-03**

**Water to air mass transfer rate of the chemical (kg/h): 8.51E+00**

Steady State

Water-air fugacity ratio: 1.004E+00

Water fugacity prevailing over air: 1.94E-07

Air fugacity prevailing over water: 2.26E-04

Air compartment

Amount of chemical (mol): 2.47E+01

**Amount of chemical (kg): 3.17E+00**

**Residence time (h): 4.35E+02**

Water compartment

Amount of chemical (mol): 1.48E+04

**Amount of chemical (kg): 1.90E+03**

**Residence time (h): 2.23E+02**

Molar concentration of chemical in the rain drops (mol/m<sup>3</sup>): 4.66E-09

Mass concentration of chemical in the rain drops (g/m<sup>3</sup>): 5.97E-07

Washout ratio ( ng/L water / ng/L air): 5.97E+01

Washout ratio ( mass/mass): 7.08E-02

Total concentration of particles in suspension (ng/m<sup>3</sup>): 1.22E+10

## RESULTS AND DISCUSSION

The fugacities and the mass concentrations of the chemical in the bulk air and water compartments together with the overall air/water exchange rates are presented in Figure 2. The diagram indicates a propensity for a net volatilization of the chemical to the air because its fugacity in this medium is smaller. This result derives from the fact that the chemical moves from the higher to the lower fugacity medium.

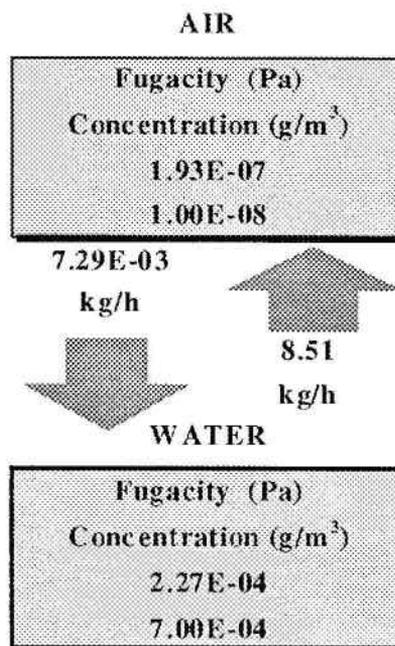


Figure 2 – Overall exchange rates between compartments, fugacities and concentration values.

The fugacities and the mass concentrations of the chemical in the bulk air ( $f_A$ ,  $\rho_A$ ) and bulk water ( $f_W$ ,  $\rho_W$ ) compartments were calculated by the expression:

$$f_j = \frac{C_j}{Z_j} \quad \text{and} \quad \rho_j = C_j \cdot M \quad (1)$$

where:  $C_j$  is the molar concentration of naphthalene in the bulk  $j$  (air or water) compartment (mol/m<sup>3</sup>);  $Z_j$  is the

fugacity capacity of naphthalene in the bulk  $j$  (air or water) compartment ( $\text{mol}/\text{m}^3 \cdot \text{Pa}$ );

$M$  is the molecular mass of naphthalene ( $\text{g}/\text{mol}$ )

The overall air/water exchange rates

( $\dot{\rho}_{\text{air} \rightarrow \text{water}}$  and  $\dot{\rho}_{\text{water} \rightarrow \text{air}}$ ) are evaluated by the equations:

$$\dot{\rho}_{\text{air} \rightarrow \text{water}} = \frac{(\dot{N}_{V_a} + \dot{N}_D + \dot{N}_Q + \dot{N}_R \dot{N}_{V_a}) \cdot M}{1000}$$

and

$$\dot{\rho}_{\text{water} \rightarrow \text{air}} = \frac{\dot{N}_V \cdot M}{1000} \quad (2)$$

where:  $\dot{N}_{V_a} = D_V \cdot f_A$  is the absorption rate ( $\text{mol}/\text{h}$ ) and  $D_V$  is the corresponding parameter  $D$  ( $\text{mol}/\text{Pa} \cdot \text{h}$ );

$\dot{N}_D = D_D \cdot f_A$  is the dry deposition rate ( $\text{mol}/\text{h}$ ) and  $D_D$  is the corresponding parameter  $D$  ( $\text{mol}/\text{Pa} \cdot \text{h}$ );

$\dot{N}_Q = D_Q \cdot f_A$  is the wet deposition rate ( $\text{mol}/\text{h}$ ) and  $D_Q$  is the corresponding parameter  $D$  ( $\text{mol}/\text{Pa} \cdot \text{h}$ );

$\dot{N}_R = D_R \cdot f_A$  is the wet dissolution rate ( $\text{mol}/\text{h}$ ) and  $D_R$  is the corresponding parameter  $D$  ( $\text{mol}/\text{Pa} \cdot \text{h}$ );

$\dot{N}_V = D_V \cdot f_W$  is the volatilization rate ( $\text{mol}/\text{h}$ ) and  $D_V$  is the corresponding parameter  $D$  ( $\text{mol}/\text{Pa} \cdot \text{h}$ ).

The air-water exchange rates given in Figure 3 clearly indicate that the volatilization of the chemical is by far the most important process. The net air-water transfer rate is  $-66.3 \text{ mol}/\text{h}$ .

The resistances to the transport processes occurring in air and water compartments are presented in Figure 4, while the residence times of the chemical in these compartments are given in Figure 5. Since the fugacity of naphthalene in the air is smaller, there is a smaller tendency for the chemical to escape from this medium. Even though the resistance to transport in air is lower, naphthalene remains in this phase for a longer time.

The transport resistances ( $R_j$ ) are calculated by the expressions:

$$R_j = \frac{1}{D_j} \quad \text{and} \quad R_j(\%) = \frac{R_j}{\sum R_j} \cdot 100 \quad (3)$$

where:  $D_j = k_j \cdot S \cdot Z_j$  is the parameter  $D$  for the  $j$  (air or water) compartment ( $\text{mol}/\text{Pa} \cdot \text{h}$ );

$k_j$  is the air side ( $j = A$ ) or water side ( $j = W$ ) mass transfer coefficient ( $\text{m}/\text{h}$ );

$S$  is the area of the air/water interface ( $\text{m}^2$ ) (the value used is for Guanabara Bay).

The residence times ( $t_j$ ) are given by the equations:

$$t_A = \frac{\rho_A \cdot V_A}{1000 \cdot \dot{\rho}_{\text{air} \rightarrow \text{water}}} \quad \text{and} \quad t_W = \frac{\rho_W \cdot V_W}{1000 \cdot \dot{\rho}_{\text{water} \rightarrow \text{air}}} \quad (4)$$

where:  $V_j$  is the volume of the  $j$  (air or water) compartment ( $\text{m}^3$ ) (the value used for water is for Guanabara Bay)..

The above results show that naphthalene, with a relatively high Henry's law constant, being subject to volatilization, but with a low vapor pressure, being therefore subject to sorption to atmospheric particles, may cycle between air and water. A steady state but non-equilibrium condition may be reached in which the water is supersaturated with respect to air.

## CONCLUSION

As a general conclusion of the work, it can be stated that naphthalene is predominantly transferred from the water to the air since it has a relatively high Henry's law constant and then a strong tendency to volatilization. However, the chemical has a relatively low vapor pressure, resides longer in the air and the resistance to transport in this medium is lower.

Naphthalene is thus subject to sorption to atmospheric aerosol particles and to re-deposition on the water phase. Therefore, the chemical may cycle between air and water and a steady state but non-equilibrium condition may be reached in which the water is supersaturated with respect to air.

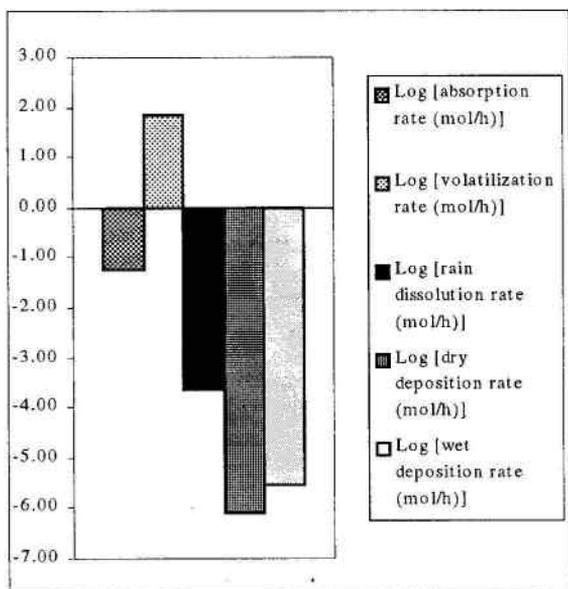


Figure 3 – Air –water exchange rates for naphthalene.



Figure 4 – Resistances to transport processes in air and water compartments.

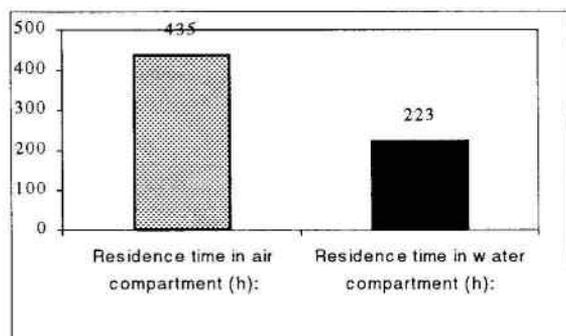


Figure 5 – Residence times for naphthalene in air and water compartments.

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