

SIMULATING FATE PROCESSES OF A VOLATILE ORGANIC COMPOUND AT KWANGYANG BAY, KOREA : PRELIMINARY STUDY

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광양만에서 휘발성 유기화합물의 거동 모의실험 : 예비연구

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ABSTRACT

Kwangyang Bay is a semi-enclosed coastal basin and one of quickly developing areas in Korea. Many industrial complexes have been established along the bay, producing iron steel, fertilizer and particularly petroleum chemicals. In this study source and occurrence of volatile organic compounds(VOC) were studied at streams, wastewater treatment works and surface water of the bay during July 1996 and April 1997. The principal fate processes of VOC are advection-diffusion, volatilisation and adsorption onto sediments. A mathematical model is developed to investigate the fate of benzene as a target VOC. Simulation resulted in good agreement with measurements.

Key Words : VOC, fate process, mathematical model, semi-enclosed bay, water quality

INTRODUCTION

In the late 1970s Yochon Industrial Complex (IC) had been firstly established at the south of Kwangyang Bay, Korea, and then an iron steel company has been built on a river delta called

Seomjin River in the early 1980s(Fig. 1). In 1990s Yulchon IC and a container harbour have been built north. In addition, reclamation has been continuously progressed along the coastline. It is expected that 50% of the water basin will be changed to a land in 2002, where another indus

trial complexes will be built. Hence environmental pollution will be increased correspondingly and water quality management should be an important concern in this area.

Benzene and toluene were reported to be predominantly found compounds along the basin from petrochemical industrial complexes (NIER, 1997). To investigate occurrence and fate processes of various volatile organic compounds prevalent in the study region, benzene was focused as a target VOC for the first stage of the ongoing research project. Benzene sources were surveyed and simulated at stream mouths and wastewater treatment works (WTW). Totally 10 streams and 4 treatment works (P1-P4) were investigated four times in years of 1996 and 1997. Effluents were sampled at the surface layer of water column along the Bay at 3 points (Fig. 1). Discharged VOC experiences physical and bio-geochemical processes: 1) advected and diffused by tidal currents and turbulence; 2) volatilized in the interface of water and air due to partial pressure of gases and concentration gradients, which is the main process relating to fate process of VOC; and 3) adsorbed onto sediments.

A mathematical model is developed to investigate the fate processes and behaviour of VOC in water column. Prior to simulating fate processes, a 3-D hydrodynamic model has been setup to represent the flow fields in the bay. For treating non-linear advection terms in the governing equation a highly accurate finite difference explicit scheme has been used based on the ULTIMATE QUICKEST scheme.

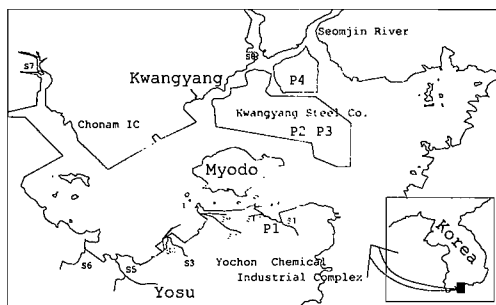


Figure 1. Map showing study area including industrial complexes, streams, wastewater treatment works and measurement points of VOC at surface water

MATERIAL

VOC sources

Chemical pollutants from industrial complexes are discharged into the receiving basin as a dumping site mainly through streams and coastal outfalls after treated. Locations of streams and industrial complexes are illustrated in Fig. 1. The concentration of VOC and flow rate at streams and WTWs were measured on a season basis (spring, summer, autumn and winter) throughout the years: 25 July 1996, 16 October 1996, 12 February 1997 and 11 April 1997. In stream, samplings were made taken at 10 and 30cm depths at each location. The measurements are presented in Table 1.

Table 1. Summary of VOC source through streams

	S1	S2	S3	S4	S5
Benzene.	0.98	0.35	ND	0.23	1.78
Flow rate	20,571	12,982	16,200	28,758	53,597
	S6	S7	S8	S9	S10
Benzene.	0.23	ND	15.10	ND	ND
Flow rate	9,636	243,456	213,580	6,514	367

(concentration- $\mu\text{g/l}$: flow rate- m^3/day :

ND : not detected)

Industrial complexes discharging effluents consist of Kwangyang IC, Yochon IC and Chonam IC (Fig. 1). Two WTWs have been established at Kwangyang Steel Industry(P2 and P3) and one at the related industrial complex(P4). The Chonam IC disposed relatively small amount of $85\text{m}^3/\text{day}$ into the water basin such that this value was neglected in this study. Measurements were conducted at 4 points(Fig. 1) for the same period as seen for streams and shown in Table 2.

Table 2. Summary of VOC source from various Industrial Complex Wastewater Treatment Works

	P1	P2	P3	P4
Benzene	32.5	ND	0.6	ND
Flow rate	67,107	10,557	13,770	323

(concentration- $\mu\text{g}/\text{l}$: flow rate- m^3/day :
ND : not detected)

Field Measurements

Surface water measurements were made to investigate occurrence and distribution of VOC in the receiving basin. Three points were surveyed around Myodo(Fig. 1). The mean concentration of VOC is shown in Table 3.

Table 3. Summary of benzene concentration measured at surface water

	1	2	3
Mean	ND	0.10	ND
SD	ND	0.20	ND

(SD : standard deviation, unit : $\mu\text{g}/\text{l}$: ND : not detected)

Sampling from the vessels was carried out with the engine switched off and the vessel orientated towards the oncoming current direction so as to eliminate the risk of contamination from exhaust frames or fuel residues. Water samples

were taken at the surface layers of the water column with a submersible pumping system. The Purge-and-trap technique was used for the all samples collected. These sorbents can be thermally desorbed and allow the transfer of the whole preconcentrated mass of VOC towards the gas chromatographs(GC). The GC was a Hewlett Packard 5890 series II, fitted with data handling facilities. Thermally desorbed components were chromatographed on a HP-PONA column(50m length $\times$ 0.2mm ID $10 \times 0.5\mu\text{m}$ film thickness). Detection and quantification of VOC were carried out by mass spectroscopy(HP 5971 series, Hewlett Packard). Mass spectral analysis was carried out using a library search(Wiley 138K database). The basic operating conditions were as follows: Mass range: 15-650 atomic mass units: Scan threshold: 250: Solvent Delay: 6.5min: Nominal Electron Energy: 1812 EM Volts: Mass Spectroscopy Detection Temp.: 230°C : Mass Spectroscopy Detection Option : EI.

METHODS

Governing Equation

The principal processes responsible for removing VOC from the water column include advection-diffusion, volatilization and adsorption onto sediments (Bianchi and Varney, 1998). Volatilization changes in aqueous concentration and by the proximity of sources. Adsorption process varies widely in their efficiency, and are dependent upon the availability of adsorbing solid surfaces within the water column and VOC affinity for adsorption processes. The three dimensional equation for the fate processes of VOC can be written as:-

$$\frac{\partial S}{\partial t} + \frac{\partial}{\partial x}(uS) + \frac{\partial}{\partial y}(vS) + \frac{\partial}{\partial z}(wS) = \frac{\partial}{\partial x}(v_x \frac{\partial S}{\partial x}) + \frac{\partial}{\partial y}(v_y \frac{\partial S}{\partial y}) + \frac{\partial}{\partial z}(v_z \frac{\partial S}{\partial z}) + S_v + S_A \quad (1)$$

where t =time, x, y, z =Cartesian co-ordinates in the horizontal(x, y) and vertical plane(z), u, v, w = components of velocity in x -, y -, z - directions respectively, S = concentration of VOC, v_x, v_y and v_z =turbulent diffusion coefficients in x -, y - and z - directions respectively, and S_v and S_A are fluxes due to volatilization and adsorption.

Firstly volatilization term can be written as:-

$$S_v = -\frac{1}{H_w} K_{(T)W} \left(\frac{S_a}{H} - S_w \right) \quad (2)$$

where H_w is water depth, $K_{(T)W}$ is the total transfer velocity, *i.e.* referred to as the gas exchange constant, S_a and S_w are the gas concentrations in air and water respectively, and H is the dimensionless Henry's Law constant. This constant is one of the most important parameters in modelling environmental systems. This parameter is an expression of phase equilibrium, and considering the theoretical backgrounds the dependency of H upon temperature and salinity can be represented using double linear regression:-

$$\ln H = a\left(\frac{1}{T}\right) + bZ + c \quad (3)$$

where T is temperature in Kelvin; Z the salinity; a, b and c are constants and given in Dewulf *et al.* (1995).

The gas exchange constant is strongly and non linearly dependent on the wind speed, and

the three relationships derived by Liss and Merlivat (1986) using carbon dioxide as a model gas describing such variation can be given as follows:-

$$K_{(T)W} = 0.17U \quad (\text{where } U < 3.6 \text{ m/s}) \quad (4)$$

$$K_{(T)W} = 2.85U - 9.65 \quad (\text{where } 3.6 < U < 13 \text{ m/s}) \quad (5)$$

$$K_{(T)W} = 5.9U - 49.3 \quad (\text{where } U > 13 \text{ m/s}) \quad (6)$$

where $K_{(T)W}$ is in cm/hr, and U is wind speed at a height of 10 metres above the sea surface in m/s. However, a correction must be applied for volatile organic compounds other than carbon dioxide to allow for different molecular diffusivities using the ratio of the square roots of the molecular weights of CO_2 and organic compounds (Liss and Slater, 1974).

The adsorption of non-polar compounds is related to the octanol-water partition coefficient of the sorbate and the organic carbon content of the sorbent. In most cases, adsorption to suspended matter has not been significantly considered for compounds with octanol-water partition coefficients below about 8.0 (Knap and Williams, 1981; Knap *et al.*, 1982). The adsorption process occurs quickly and the equilibrium is obtained in minutes or hours at the most, while desorption is assumed not to be processed once pollutants are adsorbed onto sediments. Hence, adsorption term can be written as:-

$$S_A = -K_p \cdot \frac{\partial S}{\partial t} \quad \text{if } \frac{\partial S}{\partial t} > 0 \quad \text{and} \quad (7)$$

$$S_A = 0 \quad \text{if } \frac{\partial S}{\partial t} \leq 0 \quad (8)$$

where S_A is concentration of VOC adsorbed onto sediments in solid phase ($\mu\text{g/g}$), S is

concentration of VOC in liquid phase ($\mu\text{g/ml}$), and K_p is the partition coefficient which can be estimated as:-

$$\log K_p = 0.72 \log K_{ow} + \log f_{oc} + 0.5 \quad (9)$$

where K_{ow} is the octanol water partition coefficient and f_{oc} is the fractional organic carbon content of the sorbent.

In this study the concentration of suspended sediment is calculated using the van Rijn's formulation(1984). Further details of sediment transport modelling is referred to Lin and Falconer(1996).

Model Setup

The model was set up with a computational domain of 132×136 grid squares. Each grid size was set 200m equally at the x- and y- directions and thereby giving a domain of $26.4\text{km} \times 27.2\text{km}$. Layer thickness was set using an irregular finite difference grid in the vertical to give finer vertical resolution. In this study 6 layers were given for water depth of 30m, and improved the representation of the free surface and bed shear stresses. A layer integrated 3-D hydrodynamic model was used to represent flow fields and provided the fate process model with hydrodynamic data. Details of the governing equations and numerical methods adopted for the model are referred to Lin and Falconer¹(1997). Simulation started from low tide for 4 spring and neap tidal cycles to yield stable predictions. For the fate process equation(1), an operator splitting algorithm has been used to split the

equation into two parts. One part involves solving the vertical differential terms and the other involves solving the horizontal differential terms. A highly accurate finite difference explicit scheme, based on the ULTIMATE QUICKEST scheme originally developed by Leonard and Niknafs(1991), has been used to solve the horizontal part of the equation(Lin and Falconer²(1997)). In order to overcome the small time-step limitation of using the scheme for relatively small vertical grid steps, an implicit finite volume scheme has been used to solve the vertical part of the equation. Pollutants from streams and outfalls were represented as continuous point source with discharge rate and concentration given at Tables 1 and 2.

RESULTS

For both spring and neap tides benzene discharged from 10 streams and 4 WTWs were simulated.

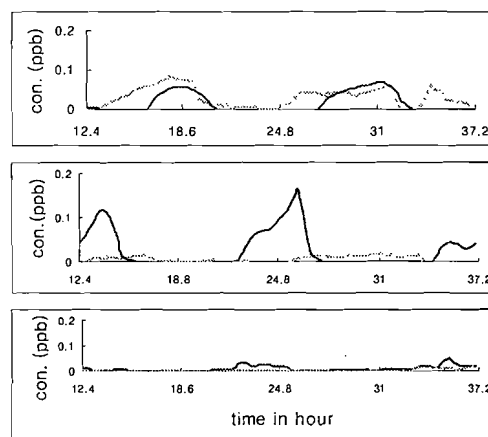


Fig. 2 Predicted values of benzene concentration at 3 points(from top to bottom- points 1,2 and 3; solid and dotted lines- neap and spring tides)

Sensitivity analysis has been made to show effectiveness of diffusion and volatilization processes in the governing equation(1). The ratios of concentration due to each process to total concentration were 7% and 11.7% respectively, which meant volatilization process played an important role in mass transfer, although advection term determined the distribution of concentration in the surface water. At point 2 concentration was predicted up to 0.17 ppb at neap tide. This value was in good agreement with measurement. At points 1 and 3 simulation resulted in very low peak values of 0.08 and 0.02 respectively. The reason for the discrepancy between prediction and measurements at points 1 and 3 is thought to be due to the fact that measurements were made, irrespective of tidal phase, during which concentration varied highly with time due to tidal dispersion.

CONCLUSION

Major findings from this study are summarized as follows:

- Concentration of VOC was measured at streams, WTWs and surface seawater.
- A 3-D VOC fate process model was developed and applied to Kwangyang Bay. Simulation was made for spring and neap tides, with continuous point sources given during ebb tide at 10 streams and 4 WTWs.
- From the model results it was shown that the predicted benzene concentration was in a range of measurements.

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