

**MODELLING OF TOXIC CONTAMINANTS
IN THE NIAGARA RIVER PLUME
IN LAKE ONTARIO**

by

I. Stepien, D.C.L. Lam. C.R. Murthy,
M.E. Fox and J. Carey

National Water Research Institute
Burlington, Ontario, Canada
January 1986
NWRI Contribution #86-3

ABSTRACT

The transport and compartmental distribution of chlorinated benzenes in the Niagara Bar area were simulated using a two-dimensional model and the results were compared with observational data collected during 1982 and 1983 experiments. The interaction between suspended sediment and compartmental concentrations of pollutants has been described by a partitioning submodel and physical parameters of the model (partition coefficient, settling velocity) were calibrated with field data. It was found that the dynamics of the Niagara plume are strongly controlled by the wind driven field of currents and the time-dependent loading of contaminants. The model may be used for the purposes of nearshore and short-time prediction of fate and transport of toxic chemicals in the coastal zone.

RÉSUMÉ

Le transport et la distribution par tranche des benzènes chlorés dans la région de la barre de la rivière Niagara ont été simulés au moyen d'un modèle à deux dimensions et les résultats ont été comparés aux données d'observation recueillies au cours des expériences de 1982 et de 1983. L'interaction entre les sédiments en suspension et la concentration des tranches de polluants a été décrite par un sous-modèle de distribution et les paramètres physiques du modèle (coefficient de distribution, vitesse de sédimentation) ont été étalonnés au moyen des données recueillies sur les lieux. On a découvert que la dynamique du panache de la rivière Niagara est largement dominée par le champ des courants dus au vent et la charge de contaminants qui varie en fonction du temps. Le modèle peut être utilisé pour prévoir à court terme le destin et le transport des substances chimiques toxiques dans la zone littorale.

INTRODUCTION

The coastal zone of Lake Ontario in the vicinity of the Niagara River mouth is one of the International Joint Commission's high priority research areas. The main reason for this interest is the well-documented contamination of the Niagara River (Allan et al., 1983; Vincent et al., 1982), the main contributor of the water (and pollutants) to Lake Ontario. Coastal zone physical processes are generally difficult to model (Lam et al., 1984), primarily because of the irregular variations and complex interrelationships of the small- and medium-sized scale components of these processes. In addition, the information essential for the construction of toxic fate models is usually incomplete or sometimes does not exist (Halfon, 1984). Under these conditions, a combined experimental and modelling research program seems to be a logical approach towards the analysis of the coastal processes.

In this paper, dynamics of the Niagara River Plume was simulated and the results of computations were compared with data collected during 1982 and 1983 field experiments. The purpose of the paper is twofold: 1) to examine the predictive ability of a two-dimensional advection-diffusion model (Simons and Lam, 1982), especially in the context of interactions of the Niagara River with the open waters of Lake Ontario; 2) to examine the limnological and ecotoxicological experimental data base as a combined data set. This

effort is extended towards the accurate estimation and prediction of the transport and compartmental distribution of the contaminants in the Niagara Bar area.

FIELD STUDY DATA BASE

Combined field surveys of the physical characteristics of the Niagara River plume in Lake Ontario and surveys of the selected toxic contaminants were conducted in 1982 and 1983. Detailed descriptions of these experiments are given in Murthy et al. (1984) and Fox (1985).

For the purposes of this paper, only part of the data collected during 1982-83 field studies was utilized. The chemicals chosen as tracers were 1,2,4-TeCB, 1,2,3,4-TeCB and 1,2,4 TCB. Analyses of the spatial distribution of concentration of these compounds indicated that the major source of these compounds to Lake Ontario is the Niagara River.

MODEL FORMULATION

Because of the strong river flow and lake circulation, the Niagara River water remains in the Niagara River Bar area (Fig. 1) for only several hours. Over such a short time frame, long-term processes

are relatively insignificant. Therefore, in the model formulation, it is more pertinent to consider the advection-diffusion, settling-resuspension and adsorption-desorption processes, as well as their interactions. Slower processes, such as biodegradation, bioaccumulation and volatilization (Halfon, 1984), that may be significant for long-term changes can be neglected in the present case.

Central to the model formulation is the concept that the chemicals are present both in the aqueous phase (i.e. dissolved in the lake water), as well as in the solid phase (i.e. associated with the suspended sediment particles). We assume that the system is at or near equilibrium. This assumption is probably valid for compounds which enter the river dissolved, but may not be valid for those which enter already adsorbed because desorption rates are slow (Oliver, 1985). The exact proportion of dissolved to adsorbed form at equilibrium, is dependent on the properties of the individual chemicals and the characteristics of the suspended particles.

Thus,

$$C_P = \frac{\Pi \cdot C_{ss}}{1 + \Pi \cdot C_{ss}} C_T \quad (1)$$

$$C_d = \frac{1}{1 + \Pi \cdot C_{SS}} C_T \quad (2)$$

where: C_T - total concentration (ng/L)
 C_p - particulate concentration (ng/L)
 C_d - dissolved concentration (ng/L)
 C_{SS} - suspended sediment concentration (mg/L)
 Π - partition coefficient (L/mg)

Note that C_d refers to the dissolved form of the chemical in the lake water, C_p refers to the solid form of the chemical adsorbed in the suspended sediment but calculated on the same per-unit-volume-of-water basis as C_d so that the total concentration is $C_T = C_d + C_p$. On the other hand, the partition coefficient Π is defined in L/mg which is reciprocal to the unit of the concentration of the suspended sediment C_{SS} , so that their product, ΠC_{SS} , is a dimensionless quantity in Eqs. (1) and (2). These definitions are necessary because the toxicant concentrations are many orders of magnitude less than the suspended sediment concentration.

In some cases, the suspended sediment concentration can be assumed as constant (e.g. Schnoor, 1982) and, if so, only one more equation is required, in addition to Eqs. (1) and (2), for the three unknowns C_d , C_p and C_T . However, in the case of the Niagara River area, C_{SS} varies substantially from the river mouth to the offshore zone, with a decrease of over 60%, because the heavy load of

suspended sediment contained in the river discharge settles rapidly by the time it reaches the offshore area. Thus, in our model, C_{SS} is allowed to vary in both space and time and constitutes one more unknown, making a total of four. As a result, two additional equations are required for describing the temporal and spatial changes of C_{SS} and C_T :

$$\frac{\partial C_{SS}}{\partial t} + \nabla \cdot \vec{U} C_{SS} = K \nabla^2 C_{SS} - W \cdot C_{SS} \quad (3)$$

$$\frac{\partial C_T}{\partial t} + \nabla \cdot \vec{U} C_T = K \nabla^2 C_T - W \frac{\Pi C_{SS}}{1 + \Pi C_{SS}} C_T \quad (4)$$

where \vec{U} is the two-dimensional velocity vector, ∇ is the two-dimensional spatial gradient operator, K is the turbulent eddy diffusivity and W is the net settling velocity.

The velocity vector \vec{U} over the numerical grid shown in Fig. 1 is obtained from a hydrodynamical model (Simons and Lam, 1982) and the diffusivity K and settling velocity are determined from calibration with suspended sediment data. Note that while net settling is applied to C_{SS} in Eq. (3), it is applied to the particulate portion of C_T in Eq. (4), i.e. $C_p = \Pi C_{SS} \cdot C_T / (1 + \Pi C_{SS})$. To solve for the four unknowns C_p , C_d , C_{SS} , C_T

from the equations (1) - (4), C_{SS} can be conveniently obtained first from Eq. (3) by finite difference methods (e.g. Simons and Lam, 1982), as this equation is not dependent on the other variables. Then, C_T can be solved from Eq. (4), using the same numerical methods and the values of C_{SS} just computed. Finally, C_p and C_d can be determined directly from Eq. (1) and (2), respectively, using the computed values of C_{SS} and C_T . The boundary conditions for Eqs. (3) and (4) are such that C_{SS} and C_T are specified at the inflow with no total flux at solid boundaries and no diffusive flux at open boundaries (Lam et al., 1984).

RESULTS

The model has been applied to four episodes observed under various influences of river flow and wind conditions. In one of the episodes (October 4, 1983), all four variables were measured and thus provided the necessary information for model calibration. The calibrated coefficients were then held fixed in the other three episodes, except for the partition coefficient which was allowed to change for different chemicals.

Effects of River Flow

The spatial distribution of concentration of toxic chemicals in the Niagara plume is not only controlled by the current structure

in the coastal zone but also by the time-dependent loading of contaminants from the Niagara River. That second factor is partially connected with the fluctuations of discharge caused by water usage at the hydro power stations, located in the middle part of the Niagara River (Fig. 2). Figure 3 shows the discharges through Canadian and USA hydro power stations and the discharge of the Niagara River at the Ashland Avenue gauge for May 10-12, 1983 (Falkenirk and Yee, 1985; see also Fig. 2). The discharge of Ashland Avenue, upstream of the power stations, shows a strong diurnal fluctuation related to the nightly filling of the power stations storage reservoirs with Niagara River water diverted from sites further upstream. The discharge varies periodically over a range of from 5400 to 8200 m³/s. For contaminants introduced upstream from the power stations, these variations of discharge will certainly cause the variation of contaminant concentration in the river. In the simplest case, we can assume that the concentration at the river mouth is inversely proportional to the discharge as a result of dilution effect (Turk, 1980). Using this assumption, time-dependent concentrations at the river mouth were derived and used as the input concentration to Lake Ontario.

The computed two-dimensional distributions of total, dissolved and adsorbed 1,2,3,4-TeCB concentration are shown in Fig. 4. In general, the model reconstructed reasonably well the isolated patch of high concentration in the northeast part of the Niagara Bar shown in the observed data at 15 hours after entering the

lake (Carey and Fox, 1985; Fig. 5). This particular patch apparently results from the alternating low-flow and high-flow conditions in the river while the experiments were conducted. In other words, at low flow the river concentration is high and creates the patch which moves with the river plume in the lake: at high flow the river concentration is lower and the patch in the lake appears to be isolated.

Effects of Wind Condition

The direction and shape of the plume can also be modified by lake currents which are influenced by different wind conditions. On August 10, 1983, the plume was controlled by an easterly wind. Figure 5 shows distribution of the horizontal velocity field obtained from the Lagrangian transport model (Murthy et al., 1984). The computed and observed values of another chlorinated benzene, 1,2,4-TCB, are shown in Fig. 6. The decreasing gradient of the observed concentration in the westward direction is reflected in the computed values. The simulation also shows an eastward movement of the plume, but unfortunately there is no observation to verify it because the sample stations were chosen according to an anticipated plume direction determined during the experiment (Carey and Fox, 1985). The relatively higher C_p/C_d ratio is connected with the lower value (0.05) of the 1,2,4-TCB solid/water partition coefficient.

In the case of October 4, 1983, the current field was controlled by a strong westerly wind and the plume was developed distinctly along the eastern shoreline. The computed and observed values of total and compartmental 1,2,3,4-TeCB are shown in Fig. 8; spatial distribution of suspended sediment concentration (observed and computed) are also given. Since this episode has the complete set of observed concentrations, it was used for model calibration purposes. The calibrated values for the eddy diffusivity is $10^3 \text{ cm}^2/\text{s}$ and the net settling velocity is 200 cm/day.

On the other hand, the value of partition coefficient Π (Eqs. 3-4) may be determined from the literature, as well as from available field data base. Table I presents a set of the observed data from October 4, 1983, and also the values of partition coefficient for 1,2,3,4-TeCB computed directly from the observed concentrations. Note that the value of the partition coefficients depends on the units (L/mg) used in Eqs. (1) - (2).

Effects of Different Chemicals

A further test of the model is on its simulation capability for different chemicals. As shown in Fig. 9, the total concentration for 1,2,3,4 TeCB, 1,2,4,5-TeCB and 1,2,4-TCB were measured during the same experiment on November 8, 1982. As the effects of river discharge and lake circulation on the spatial distribution of these

chemicals are the same for this episode, the influence of the partition coefficient may be detected through a comparison of the computed and observed concentrations. It was found that, in order to obtain close agreement between the computed and observed concentrations, the partition coefficients for 1,2,3,4-TeCB, 1,2,4,5-TeCB and 1,2,4-TCB have to be set 0.1, 0.1, 0.05 respectively. These values are within reasonable range of those reported in the literature (Carey and Fox, 1985).

CONCLUSION

The two-dimensional advection-diffusion model satisfactorily simulates the spatial changes of concentration of toxic chemicals as observed in the Niagara Bar area. The comparison of computed and observed data, however, should be made with caution. Such a comparison is limited by the measurement error of contaminant concentration. A cursory analysis of the data indicates that a single sample might be determined within quite a wide error margin for as much as 50% of the observed value. Given such uncertainty of measurement, a more rigorous comparison of computed and observed concentration is not possible.

It was found during this study that additional information concerning discharge/time and concentration/time relationships are essential and have been incorporated in on-going experiments at the

site. For example, during the 1985 survey season, two automatic water samplers were installed in the survey area. The first sampler was located at the Niagara mouth and the second was installed at the mouth of the Welland Canal. Presently, these devices are able to provide 72 hourly samples during a typical three-day cruise. Such new data sets should provide useful information for improvement of the model.

It is also recommended that in future studies an effort should be made to provide a time series estimate of concentration at a few stations in the Niagara grid. The lack of this kind of data is felt very clearly in the interpretation of the survey data. The weekly data available at a station in the mouth of the Niagara River are not of sufficient temporal scale to be particularly useful in this type of analysis.

REFERENCES

- Allen, R.J., Murdoch, A. and Sudor, A. 1983. An introduction to the Niagara River/Lake Ontario pollution problem. *J. Great Lakes*, 9(2), 111-117.
- Carey, J. and Fox, M. 1985. Personal communication. Environmental Contaminants Division, National Water Research Institute, Burlington, Ontario.
- Falkenirk, L. and Yee, P. 1985. Personal communication. Water Planning and Management, Inland Waters Directorate, Burlington, Ontario.

- Fox, M.E. 1985. A practical sampling and extraction system for the quantitative analysis of sub ng/l organochlorine contaminants in filtered water and suspended solids. Environmental Contaminants Division, National Water Research Institute, Burlington, Ontario.
- Halfon, E. 1984. Predicting the environmental fate of toxic contaminants in large lakes: data requirements for mathematical models. In QSAR in Environmental Toxicology, Kaiser, K.L.E., (Ed.), D. Reidel Publishing Company, Dordrecht, Holland, 137-152.
- Lam, D.C.L., Murthy, C.R. and Simpson, R.B. 1984. Effluent transport and diffusion models for the coastal zone. Lecture Notes on Coastal and Estuarine Studies, Series No. 5, Springer-Verlag, N.Y., 168 pp.
- Murthy, C.R., Lam, D.C.L., Simons, T.J., Miners, K.J., Bull, J.A., Schertzer, W.M. 1984. Dynamics of the Niagara River plume in Lake Ontario. Aquatic Physics and Systems Division, National Water Research Institute, Burlington, Ontario.
- Oliver, B.G. and Nicol, K.D. 1983. Chlorinated contaminants in the Niagara River, 1981 to 1983. Environmental Contaminants Division, National Water Research Institute, Burlington, Ontario.
- Oliver, B.G. and Charlton, M.N. 1983. Chlorinate organic contaminants on settling particulates in the Niagara River vicinity of Lake Ontario. Environmental Contaminants Division, National Water Research Institute, Burlington, Ontario.
- Schnoor, J.L. 1982. Fate and transport modelling for toxic substances. In Modelling the Fate Chemicals in the Aquatic Environment. Ann Arbor Science, 745-163.

Simons, T.J. and Lam, D.C.L. 1982. Documentation of two-dimensional x-y model package for computing lake circulations and pollutant transports. Aquatic Physics and Systems Division, National Water Research Institute, Burlington, Ontario.

Turk, J.T. 1980. Applications of Hudson River basin PCB-transport studies. In Contaminants and Sediments. Baker, R., (Ed.), 1:171-183.

Vincent, J. and Fronzen, A. 1982. An overview of environmental pollution in the Niagara Frontier. New York, US EPA, National Enforcement Investigation Center, Denver, Colorado.

FIGURES

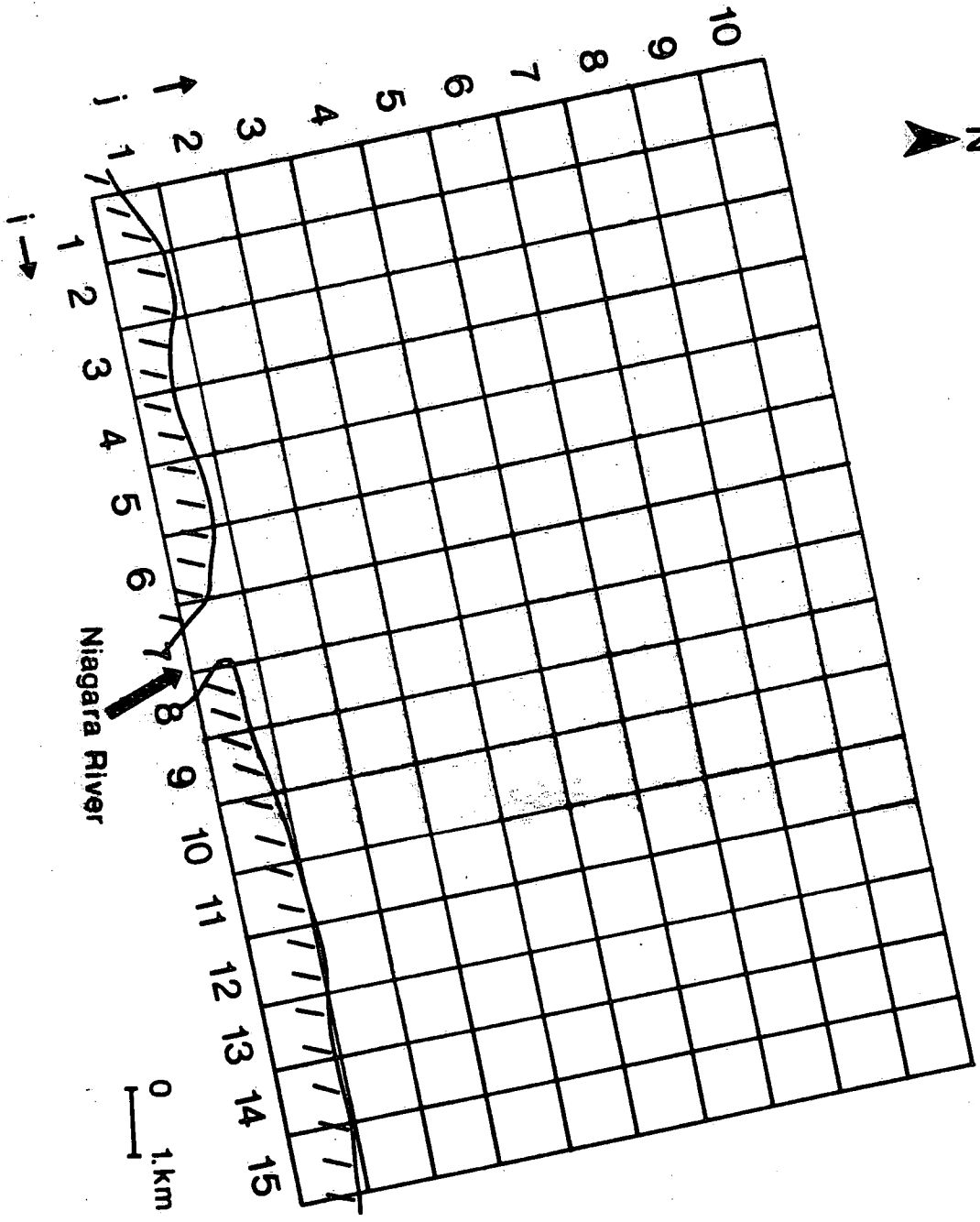
- Fig. 1 Niagara study area in the western basin of Lake Ontario.
- Fig. 2 Diagram of Niagara River and localization of the discharge gauges.
- Fig. 3 Discharge through hydropower stations: Canada (o), USA (Δ) and Niagara River discharge, Ashland Av. gauge (+). Upper diagram - total discharge below the reservoirs.
- Fig. 4 Computed and observed distributions of total, dissolved and particulate 1,2,3,4-TeCB concentration, May 11, 1983.
- Fig. 5 Horizontal velocity field, Lagrangian transport model, August 10, 1983.
- Fig. 6 Computed and observed distributions of total, dissolved and particulate 1,2,4-TCB concentration, August 10, 1983.
- Fig. 7 Horizontal velocity field, Lagrangian transport model, October 4, 1983.
- Fig. 8 Total and fractional 1,2,3,4-TeCB concentration and suspended sediment concentration (observed and computed), 4 October 1983.
- Fig. 9 Computed and observed total concentrations: 1,2,3,4-TeCB-top, 1,2,4,5-TeCB-middle, 1,2,4-TCB-bottom, November 8, 1982.

on coefficient: original concentration of 1,2,3,4-TeCB; concentration of suspended sediment:
 Cruise 4 October 1983.

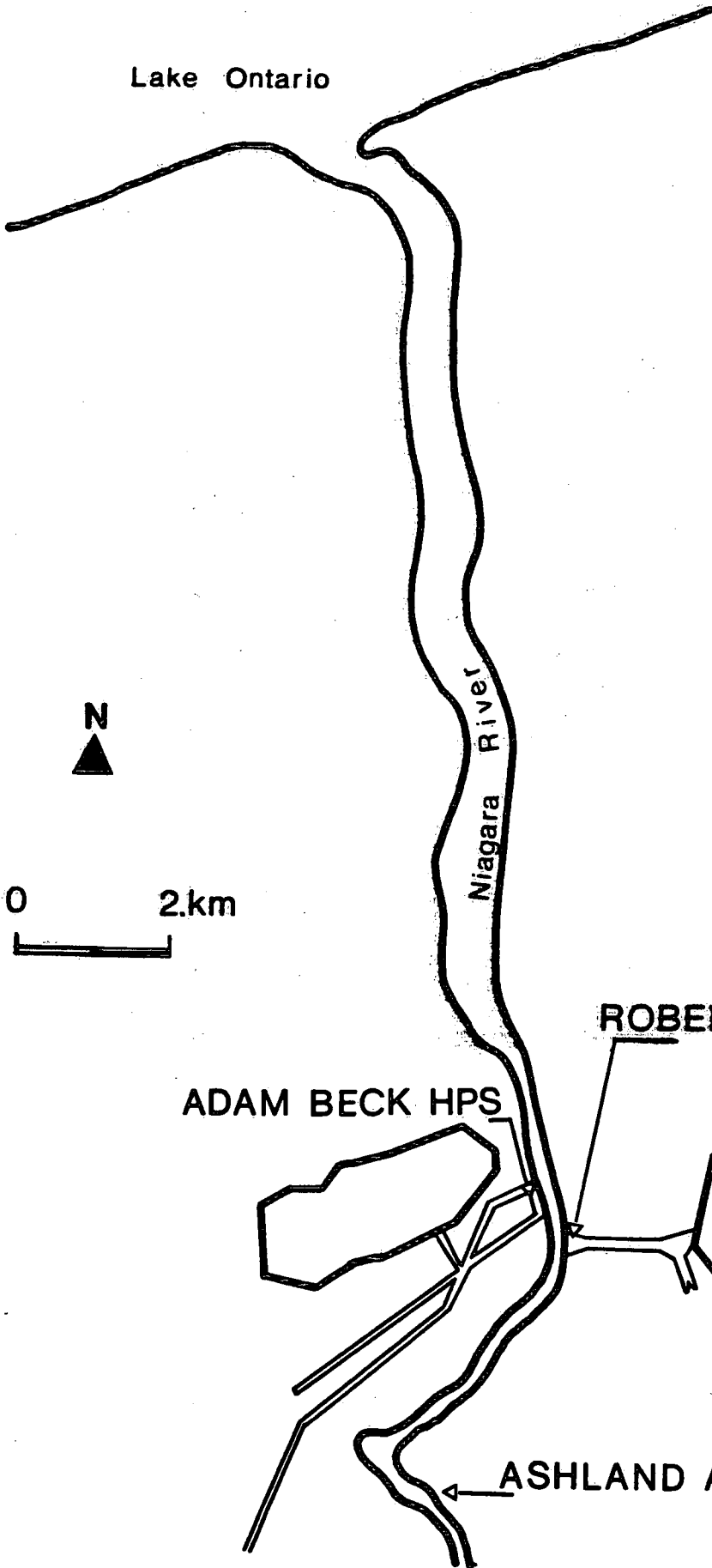
NR	Suspended Sediment		Partition Coefficient (Π)	
	Dissolved [ng/L]	Adsorbed [ng/L]	[L/mg]	[log Π]
1				
2	5.4	0.7	0.0309	3.09*10 ⁴
3	6.4	0.9	0.0350	3.35*10 ⁴
4	0.5	NS	ND	ND
5	NS	NS	ND	ND
6	3.6	2.1	0.1768	1.768*10 ⁵
7	0.9	0.2	0.0654	6.54 *10 ⁴
8	4.7	0.8	0.0370	3.7 *10 ⁴
9	3.2	1.6	0.1389	1.389*10 ⁵
10	2.1	1.6	0.1905	1.905*10 ⁵
	3.5	1.3	0.1600	1.06 *10 ⁵
			avg. →	7.59 *10 ⁴

ND - no data
 NS - no sample
 I° - loss on ignition

4.88



Lake Ontario



Niagara River

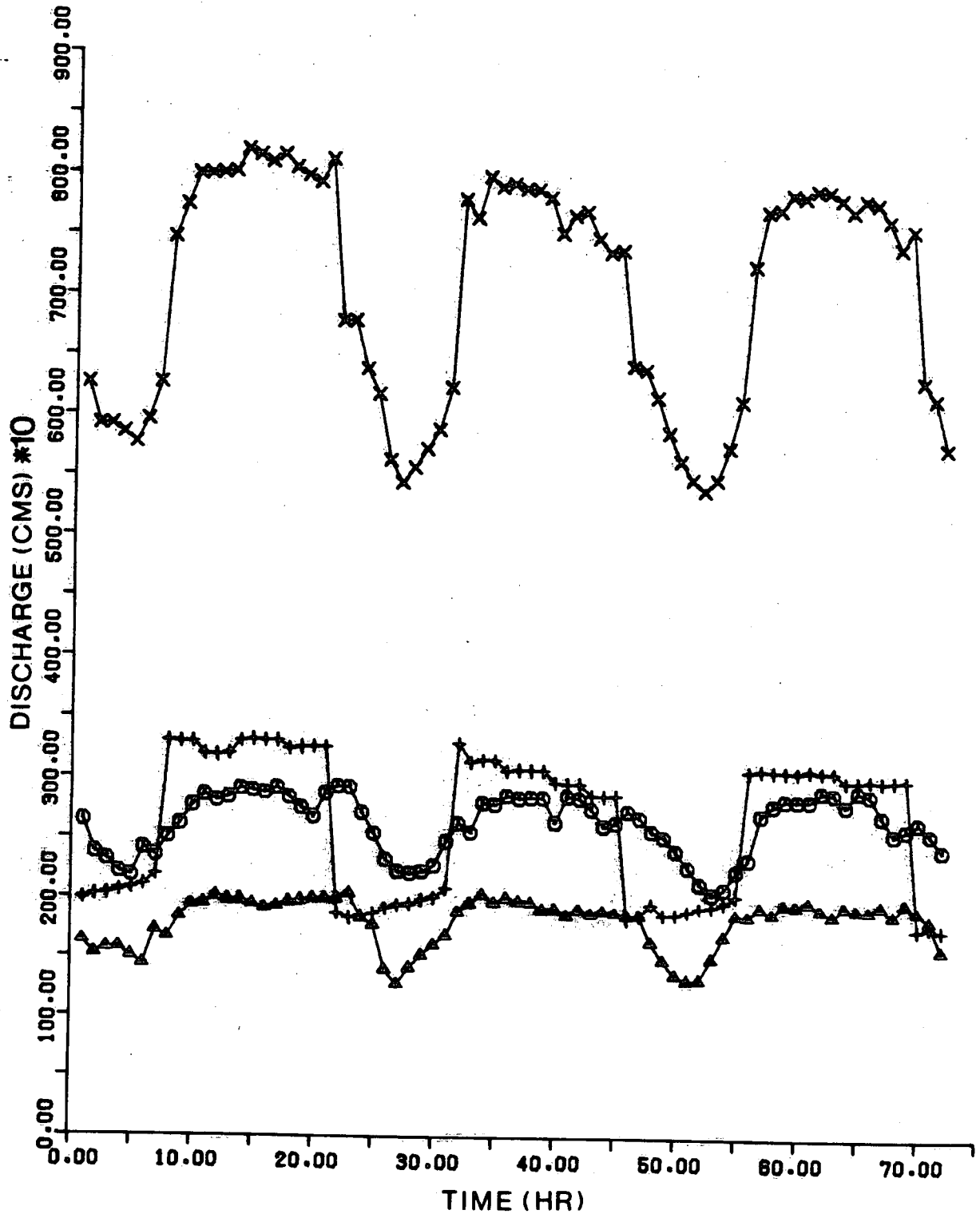


0 2.km

ROBERT MOSES HPS

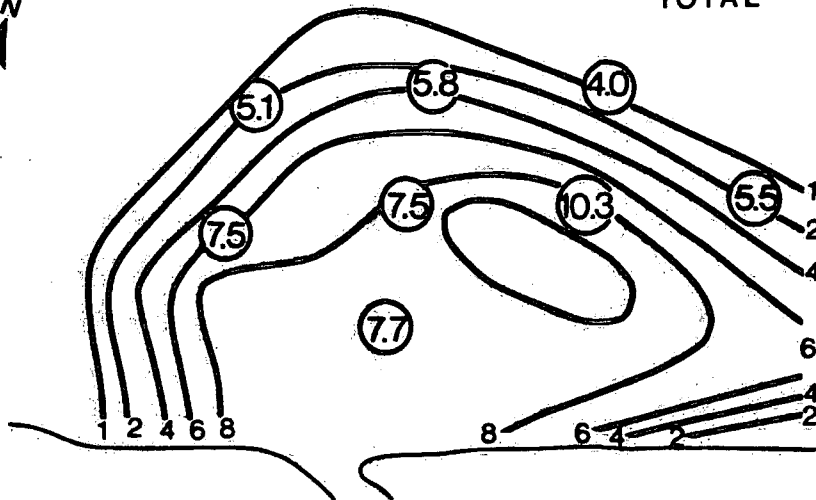
ADAM BECK HPS

ASHLAND AV.

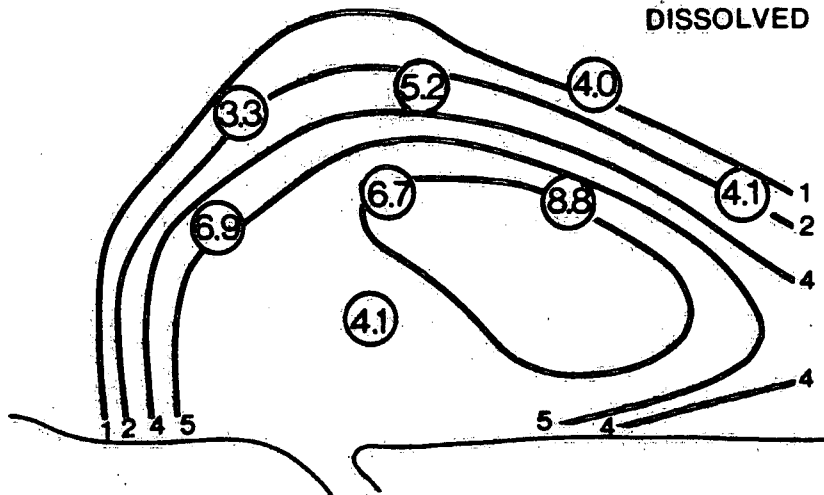




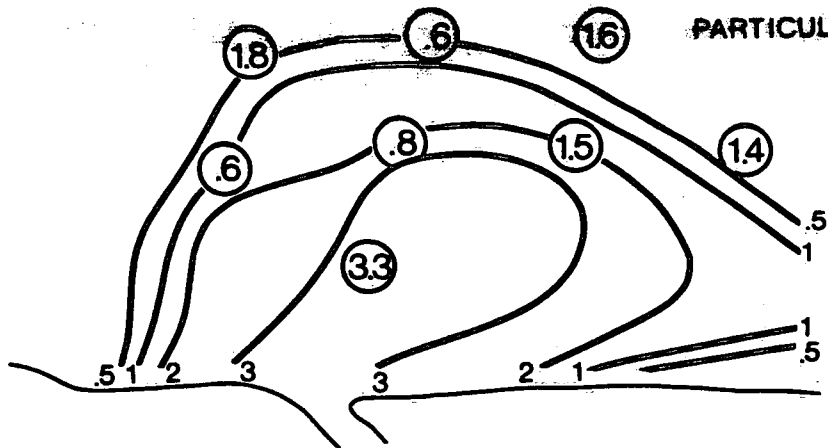
TOTAL



DISSOLVED



PARTICULATE

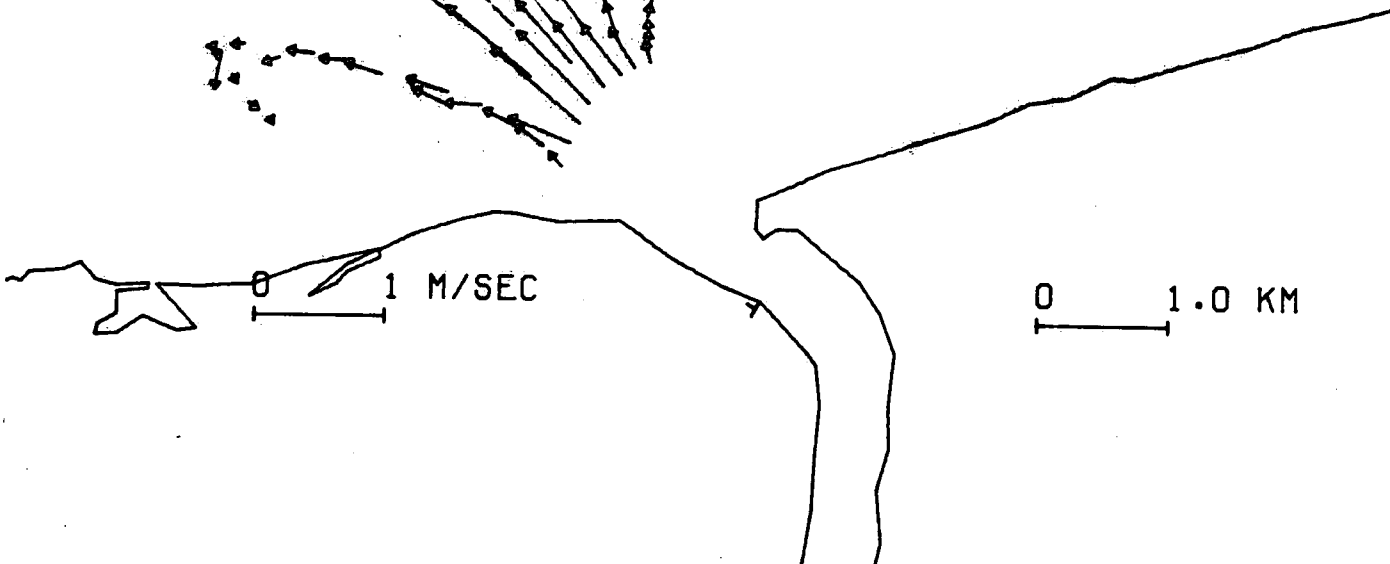
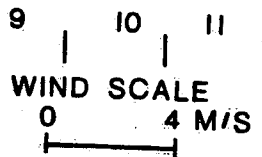
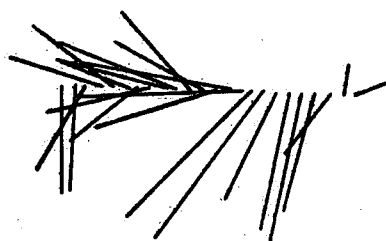


0 1 km

AUGUST 10, 1983

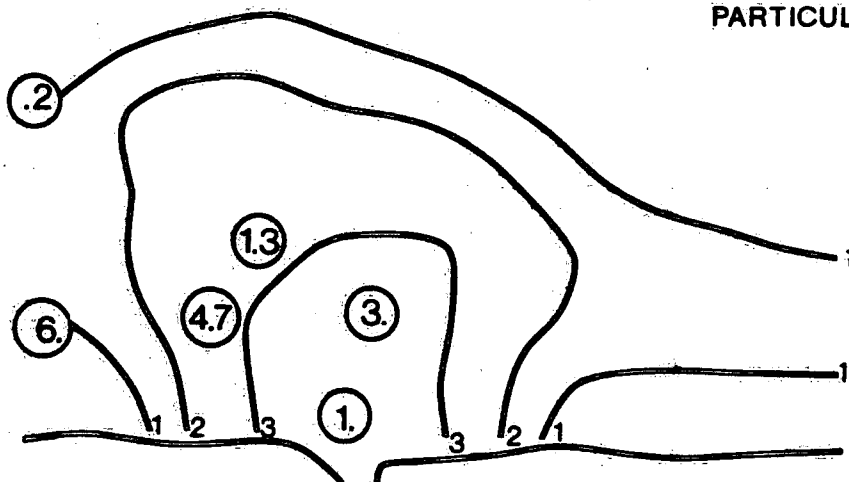


WIND HISTORY

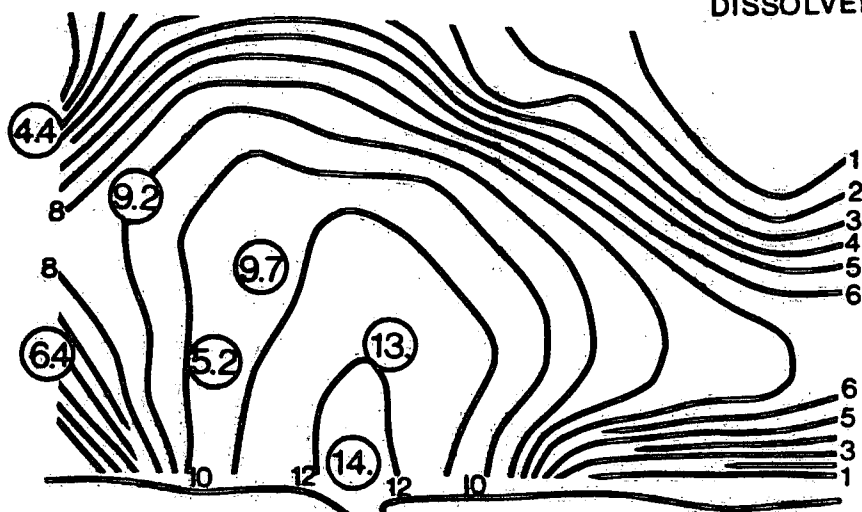




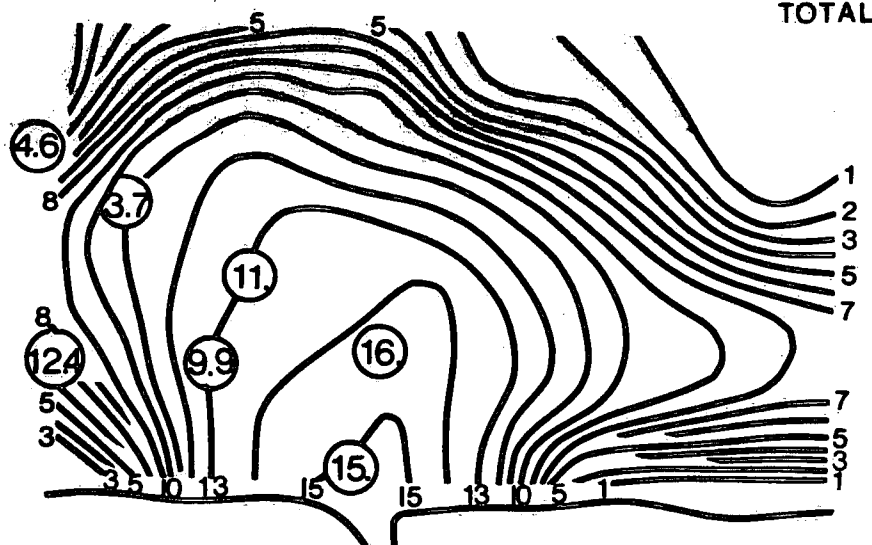
PARTICULATE



DISSOLVED



TOTAL

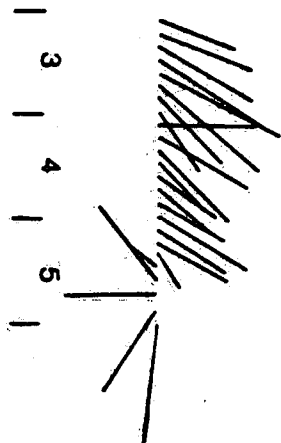


0 1 km

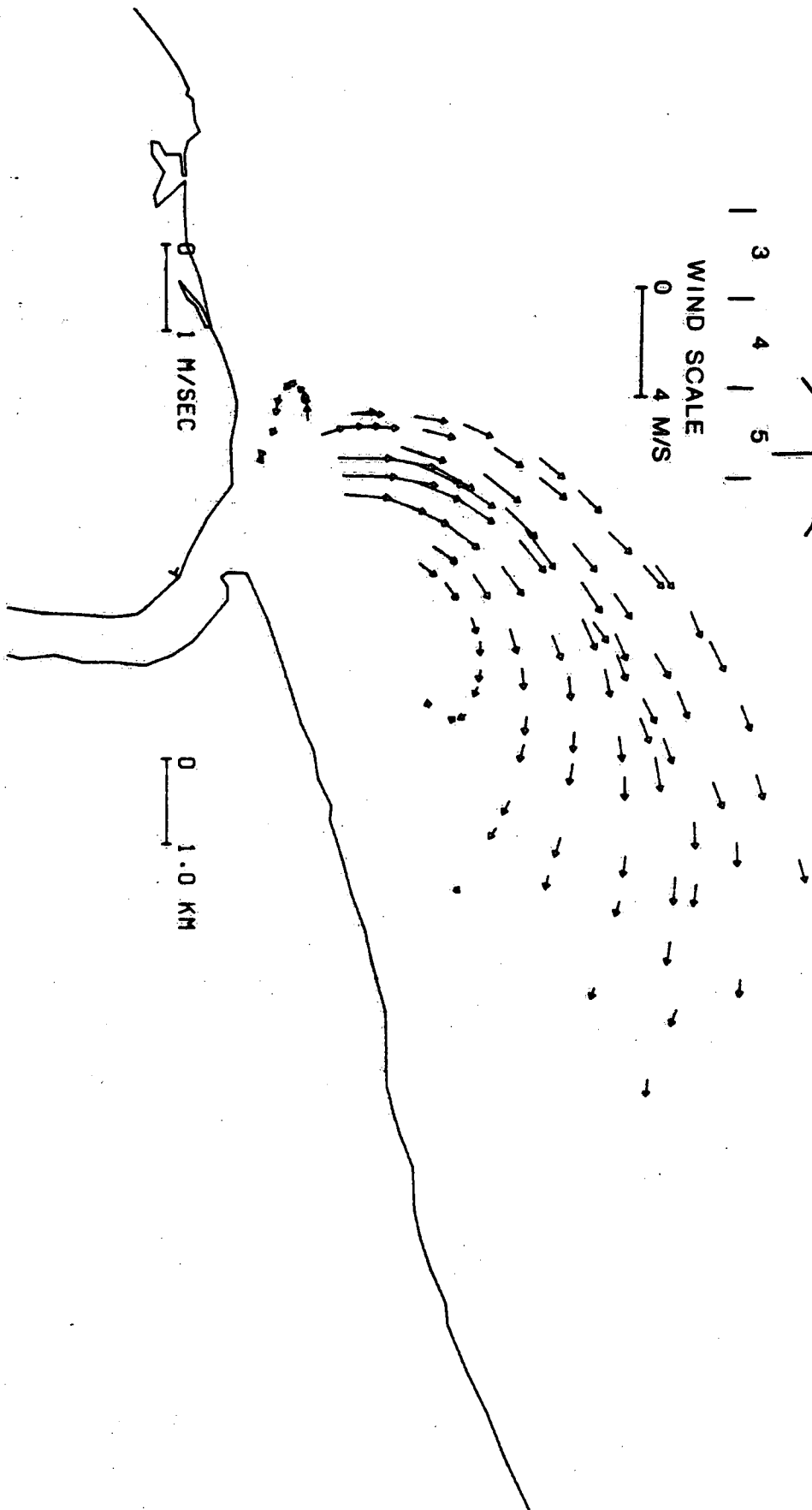
OCTOBER 4, 1983

WIND HISTORY

N



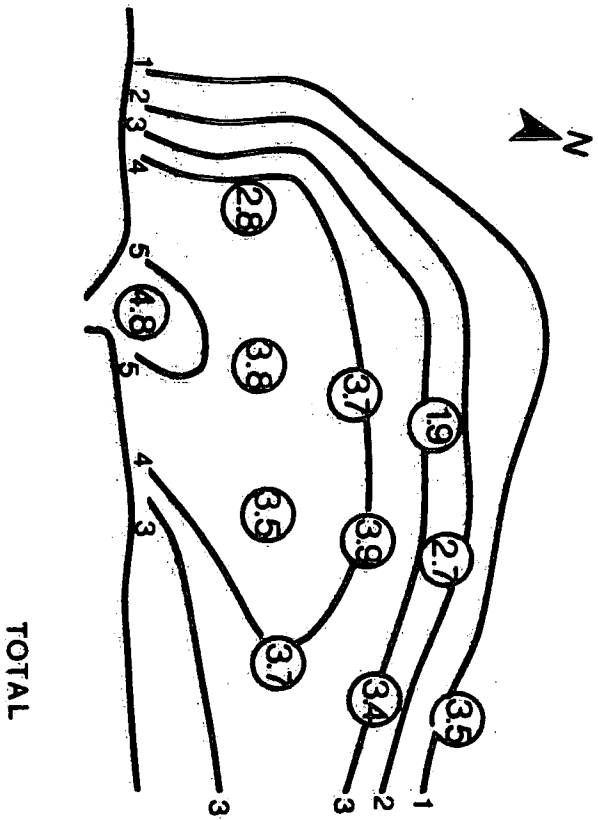
WIND SCALE
0 4 M/S



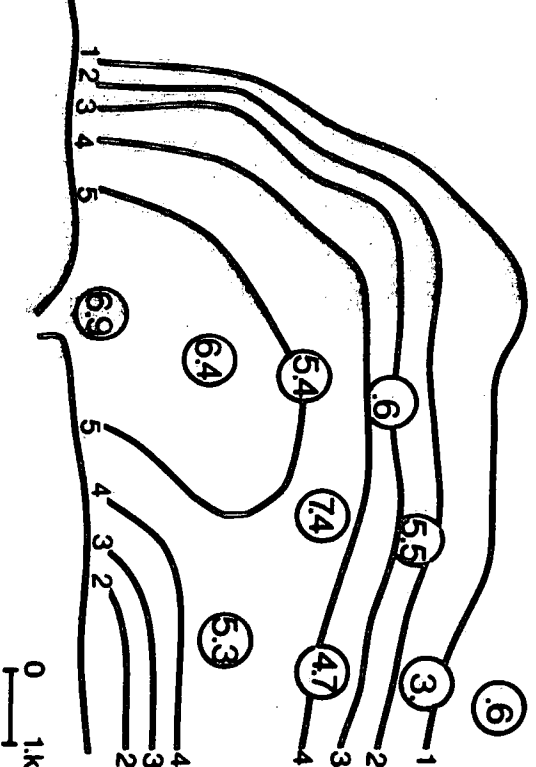
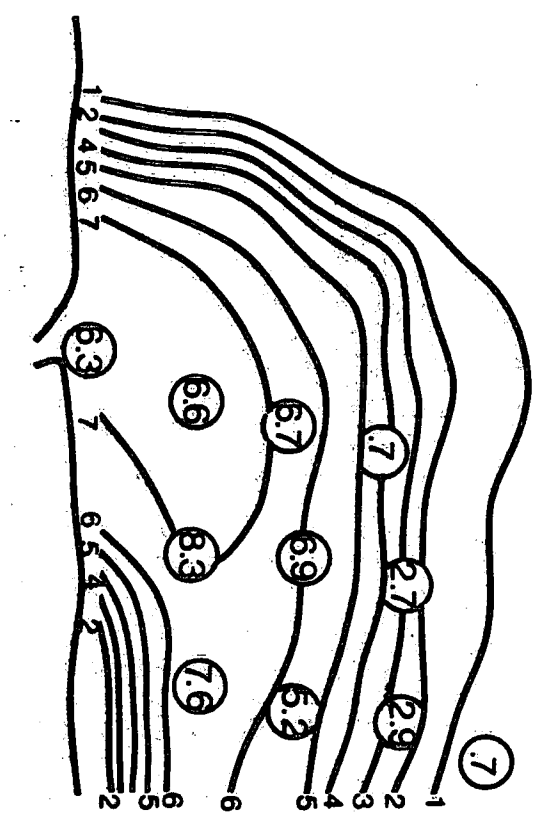
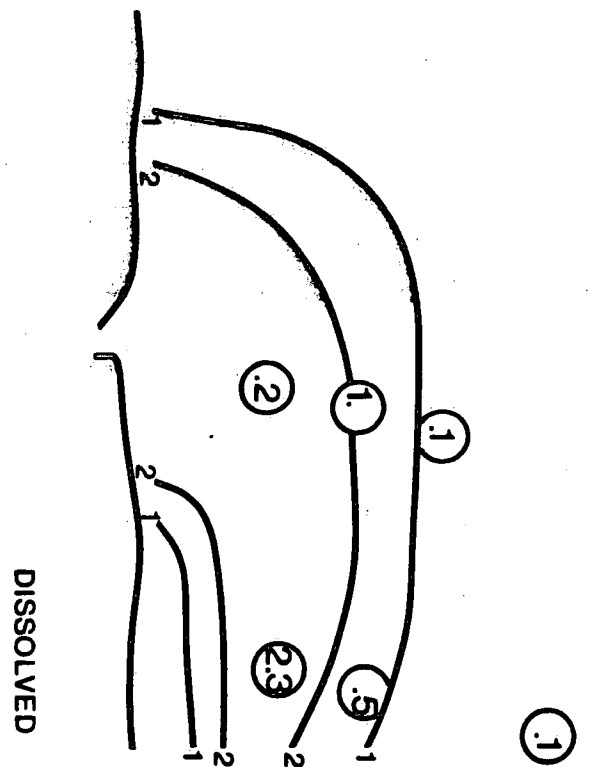
0 1 M/SEC

0 1.0 KM

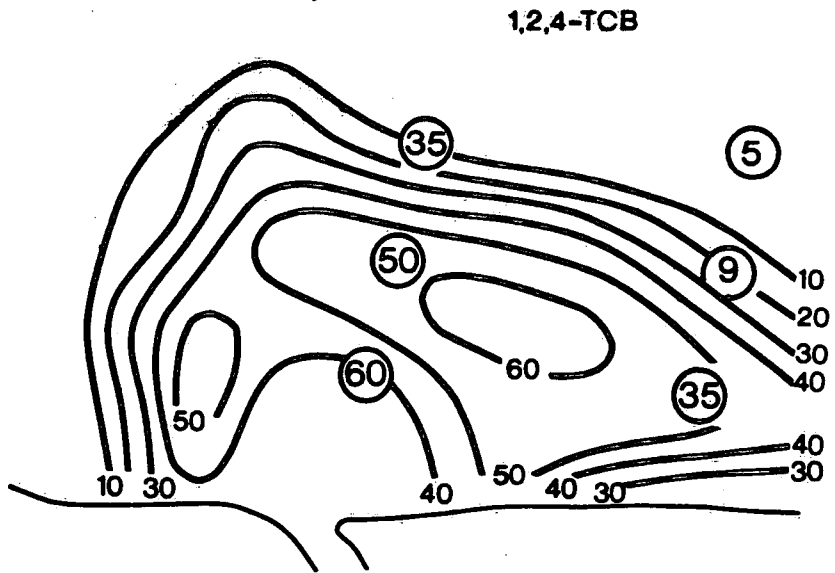
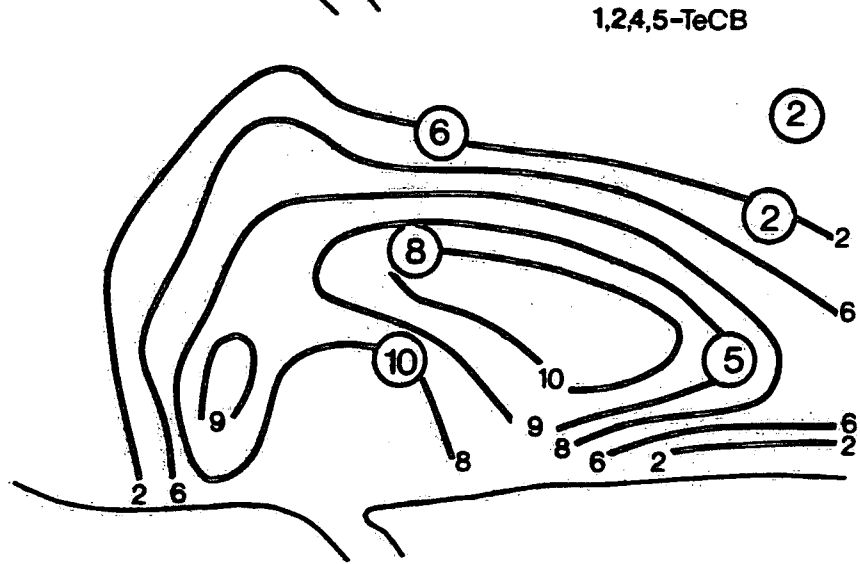
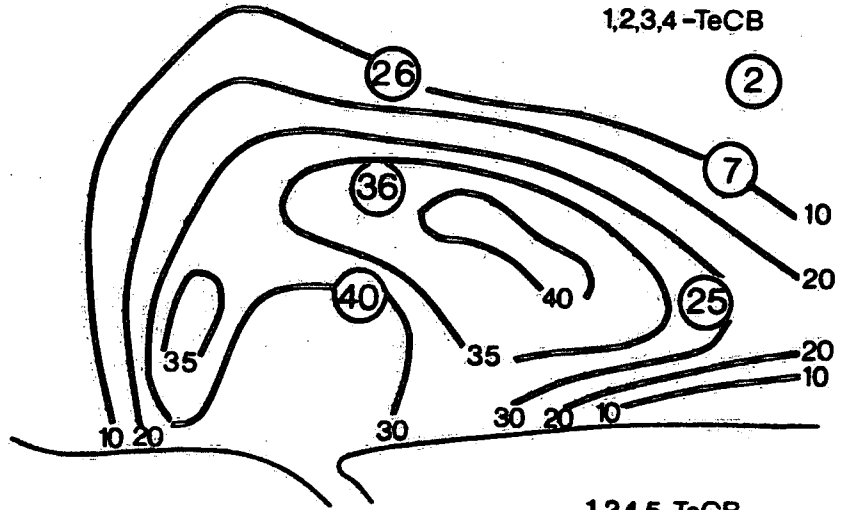
SUSP SEDIMENT



PARTICULATE



0 1 km



0 1 km