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MATHEMATICAL SIMULATION OF POLLUTANT  
TRANSPORT IN BOSTON HARBOR

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## Introduction

The disposal of municipal and industrial wastes into coastal waters such as Boston Harbor is widespread. Sewage, industrial, and stormwater releases can introduce a large variety of hazardous compounds, infectious microorganisms, suspended solids, and oxygen-consuming organic matter into the surrounding waters. The resulting contamination not only diminishes the ability of the area to support recreational activities, but may also seriously restrict commercial fishing and have adverse ecological effects.

Fortunately, programs are beginning to be implemented to cleanup these coastal waters and better manage and utilize their resources in the future. Such programs involve engineering and management decisions which must ultimately be based on a good understanding of the complex physical, chemical, and biological processes occurring in the region. The application of an accurate mathematical simulation model, coupled with complementary physical and chemical measurements, can be used to gain this understanding.

The present work is multidisciplinary in nature and represents the initial steps of a model calibration and verification study. The immediate goals of this work were to use a combined measurement/modeling approach in Boston Harbor to: 1) validate newly developed mathematical simulation models, 2) begin to quantitatively evaluate large-scale pollutant transport in the region, and 3) specifically investigate the process of volatilization in the harbor. The ultimate goal of this study is to combine hydrodynamic circulation and transport modeling with complementary current velocity measurements and large-scale tracer experiments in order to develop a flexible modeling framework which can be used as an efficient predictive tool for coastal zone management.

The first phase of this study has recently been completed<sup>1</sup>. Two previously developed circulation and transport models were modified and applied with high spatial resolution to Massachusetts Bay and Boston Harbor in order to simulate two-dimensional contaminant concentrations. In addition, a number of halogenated hydrocarbons present in municipal sewage effluent were identified and employed as large-scale tracers of sewage related contamination. The concentrations of a number of these compounds were measured at their source (sewage outfalls) and throughout Boston Harbor during different seasons. The mathematical models were then calibrated by comparing simulated concentrations to observed concentrations in order to evaluate the predictive capabilities of the models and quantitatively investigate pollutant transport in the region.

#### Chemical Aspects of the Tracers

Chemical tracer experiments can be used to gain a great deal of knowledge regarding the advective and dispersive processes acting in a system. Such experiments consist essentially of determining the concentration of a tracer at its source(s), subsequently observing the tracer at a number of locations throughout the water body, and finally deducing the flow field and dispersion characteristics necessary to explain the spatial and temporal tracer distribution patterns. Tracer experiments can utilize either continuous or instantaneous sources and can be based on natural (e.g.,  $\text{CO}_2$ ), artificially introduced (e.g., dye), or ongoing continuous anthropogenic (e.g., industrial and municipal discharges) inputs. Continuous input experiments are better suited to study long term, large-scale phenomena. Moreover, effective natural tracers are constrained by cost and practicality (especially for large-scale continuous experiments), as well as environmental acceptability (e.g., radioactive tracers). In light of these considerations, we chose to utilize existing anthropogenic inputs for our tracer experiments.

A good chemical tracer must satisfy three criteria: 1) it should have an understandable source function; 2) it should be readily measurable without background interferences after dilution to levels several orders of magnitude below its source concentration; and 3) it should be physically,

chemically, and biologically conservative or at worst transform or react in an easily predictable manner. Based on a consideration of these criteria, a suite of low-molecular-weight halogenated hydrocarbons appeared well suited to serve as our tracers.

The compounds that we chose belong to a group of chemicals known as the volatile halogenated organic compounds (VHOC). These compounds, along with some of their physiochemical properties, are listed in Table 1. The sources of these compounds will be discussed below. Primarily due to the recent interest in a subclass of these compounds (the trihalomethanes), the available analytical methods have become highly developed, and part-per-trillion detection limits can be achieved with a relatively quick and simple analytical technique<sup>2</sup>.

The VHOCs are not conservative tracers. Nevertheless, they do not exhibit a strong tendency to sorb to particular matter<sup>3</sup>, and are essentially chemically and biologically inert overtime scales of interest<sup>4</sup>. The mechanism primarily responsible for their removal from natural waters is volatilization. The process of volatilization is well studied and a good deal of literature exists on the subject<sup>5</sup>. Therefore, the nonconservative behavior of these compounds does not pose any serious difficulties.

It is convenient to divide the compounds in Table 1 into two groups based on their major sources. These two groups are the "solvents" and the "trihalomethanes" (THM). The solvents include tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, and carbon tetrachloride. The trihalomethanes include chlorodibromomethane, bromodichloromethane, and bromoform. Chloroform is a member of both groups.

The solvents are compounds used in such activities as degreasing, dry cleaning, stain removal, and as media for chemical processes. These compounds are released into the environment in large quantities primarily through municipal sewage discharges and local industrial outfalls. Estimated U.S. release rates of these compounds is on the order at  $10^8$  lbs/yr<sup>6</sup>.

Table 1  
 Physiochemical Properties of Selected Tracers <sup>a</sup>

Compound	Formula	MW	BP (°C)	solu- bility <sup>b</sup> (mol/L)	vapor press. <sup>b</sup> (atm)
1,1,1-trichloroethane	CH <sub>3</sub> OCL <sub>3</sub>	133.41	74.1	10 <sup>-2.07</sup>	10 <sup>-0.78</sup>
tetrachloroethylene	OCL <sub>2</sub> =OCL <sub>2</sub>	165.83	121.0	10 <sup>-3.04</sup>	10 <sup>-1.60</sup>
trichloroethylene	CHCl=OCL <sub>2</sub>	131.39	87	10 <sup>-2.04</sup>	10 <sup>-1.01</sup>
carbon tetrachloride	OCL <sub>4</sub>	153.82	76.54	10 <sup>-2.20</sup>	10 <sup>-0.82</sup>
chloroform	CHCl <sub>3</sub>	119.38	61.7	10 <sup>-1.19</sup>	10 <sup>-0.59</sup>
bromodichloromethane	CHBrCL <sub>2</sub>	163.83	90	10 <sup>-1.62</sup>	10 <sup>-1.20</sup>
chlorodibromomethane	CHBr <sub>2</sub> Cl	208.29	120	10 <sup>-1.65</sup>	10 <sup>-1.59</sup>
bromoform	CHBr <sub>3</sub>	252.75	149.5	10 <sup>-1.91</sup>	10 <sup>-2.13</sup>

<sup>a</sup> from Kossik et al. <sup>1</sup>

<sup>b</sup> at 25°C

The trihalomethanes have a quite different source history. These compounds are primarily the products of reactions between chlorine and naturally occurring organic material. That is, they result from the chlorination of discharge water. Rook<sup>7-8</sup> first reported on the occurrence of these compounds in chlorinated water supplies. Since then there has been a plethora of literature on the subject.<sup>9-12</sup> Various formation mechanisms have been suggested<sup>13-15</sup>. However, due to the complexity of the organic precursors and the variety of reaction pathways, the chemistry of the trihalomethane reaction is not completely understood. Considerations regarding the kinetics of these reactions are addressed in some detail in Kossik et al.<sup>1</sup>

In contrast to the solvents, the THMs are introduced into a discharge system just prior to release. (A small amount of these compounds would also be expected to be present in a sewage system prior to chlorination as a result of the chlorination of drinking water. This, however, is small compared to the quantities created upon chlorination at the sewage treatment plant). As a result, the primary sources of THMs to surface waters are: a) chlorinated sewage discharges, and b) waste heat discharges in which cooling water is chlorinated to control biofouling.

Hence, we have reason to believe that both the solvents and the trihalomethanes should be quite common in coastal regions near population centers. However, as pointed out by Helz<sup>16</sup>, the sources of these compounds to a system such as Boston Harbor may not be sufficiently characterizable in terms of both location and strength to facilitate the use of these VHOCS as chemical tracers. The present work helps to address this question.

#### The Boston Harbor System

Boston Harbor is located on the western edge of Massachusetts Bay, a semi-enclosed coastal embayment approximately 100km long and 40km wide in the western Gulf of Maine (Figure 1). A detail of Boston Harbor is presented in Figure 2. As can be seen, the system is geographically complex and a number of small islands are scattered throughout the harbor. The bathymetry of the harbor is further complicated by the presence of two

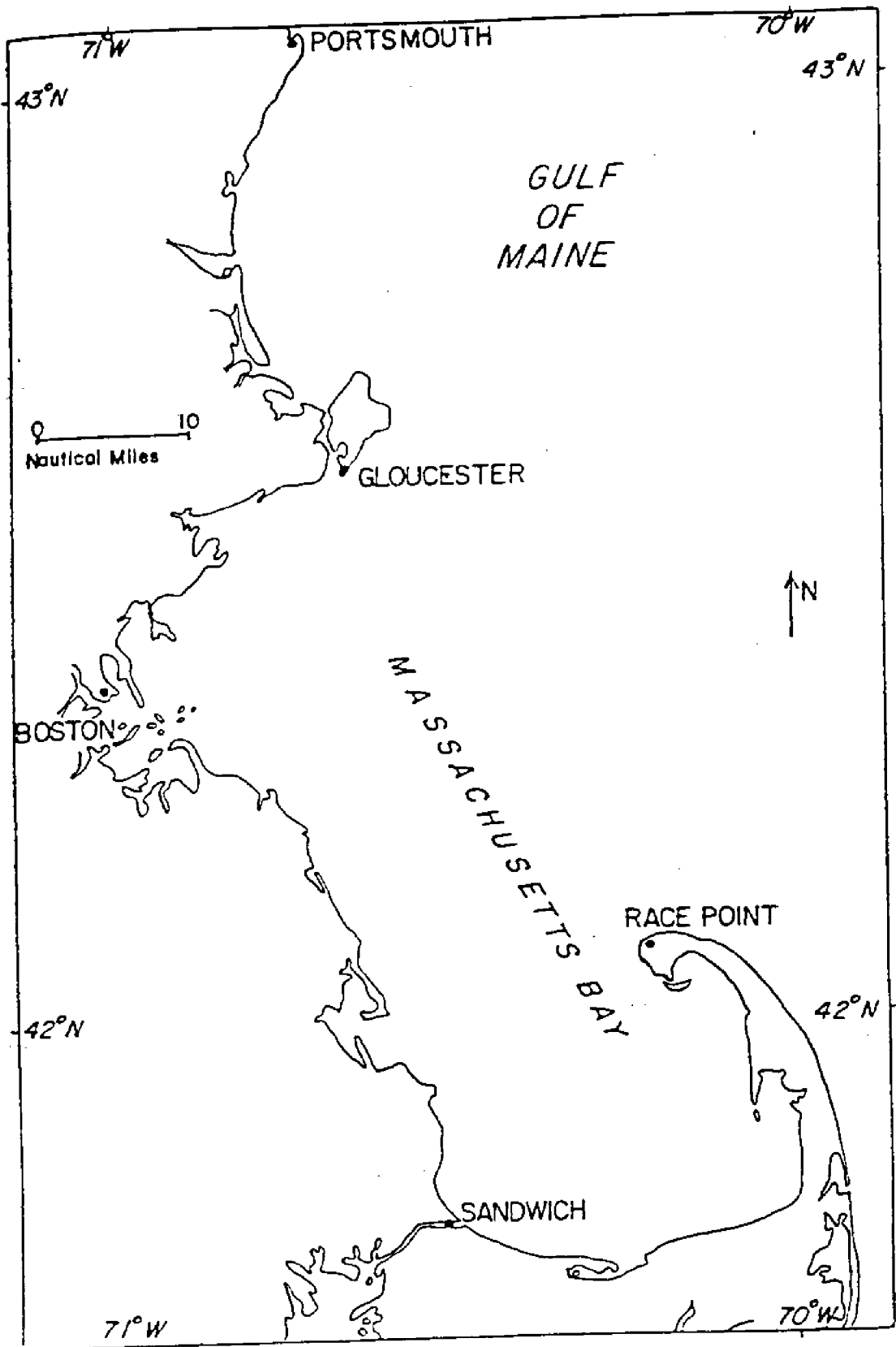


Figure 1 Map of Massachusetts Bay



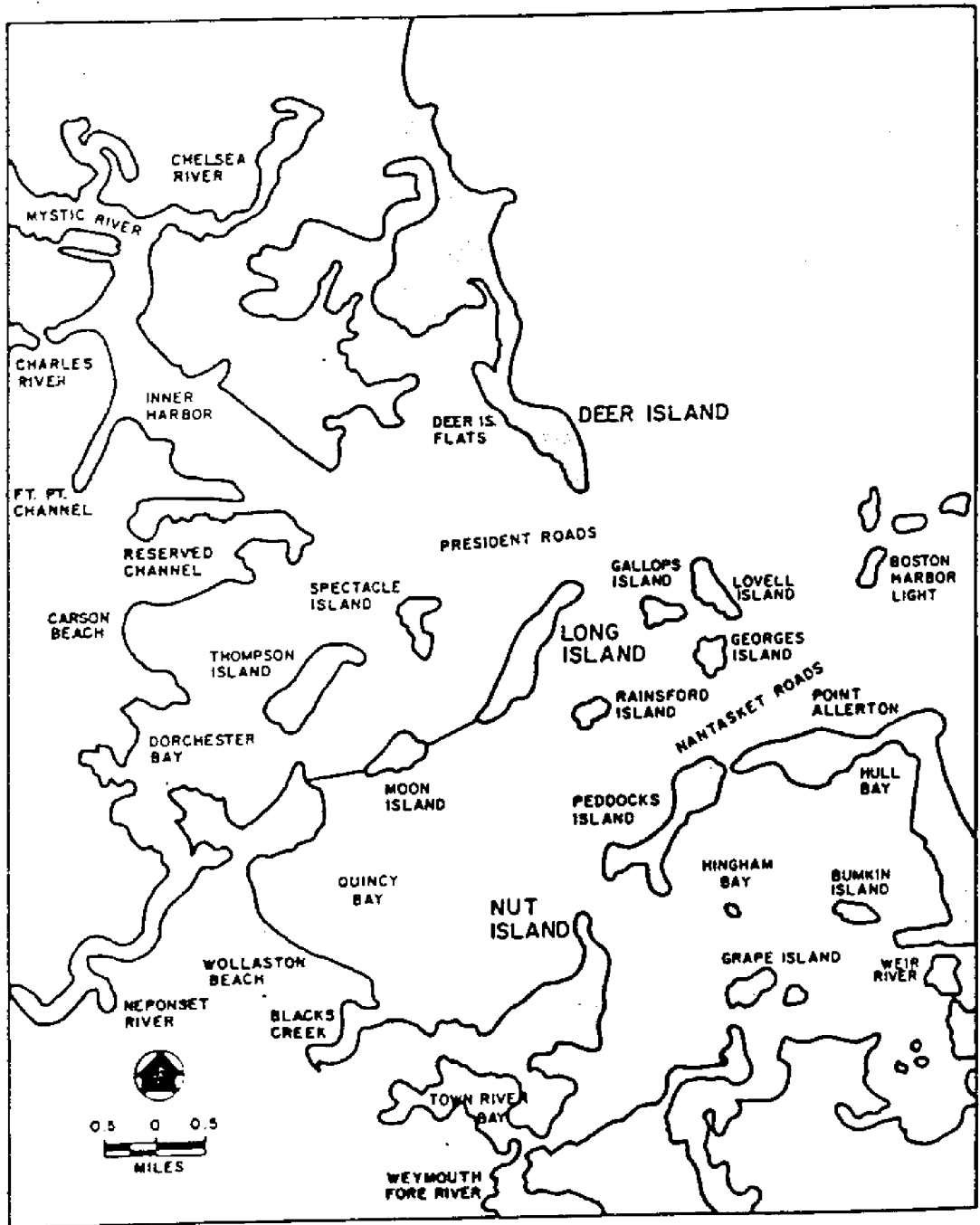


Figure 2 Map of Boston Harbor

shipping channels, President Roads and Nantasket Roads. Tidal flows dominate the water exchange, with nearly half of the volume of the harbor leaving on the outgoing tide. Riverine inputs and effluent flows (approximately  $10^6$  m<sup>3</sup>/day) are negligible in comparison.

The primary sources of contaminants to the harbor are the wastewater treatment facilities at Deer Island and Nut Island, where effluent currently receives primary treatment and chlorination before discharge. The combined outfall discharges from these two plants varies from approximately 10 to 20 m<sup>3</sup>/sec. In addition, there are over 100 combined stormwater and sewer overflows (CSOs), some of which discharge to the harbor under both wet and dry conditions. The CSO input is quite variable, with average daily flow being approximately  $0.7\text{m}^3\text{sec}^{-1}$ . This figure may increase by an order of magnitude during severe rain events. There also exist numerous industrial shoreline discharges particularly in the Inner Harbor Region. The larger industrial outfalls discharge up to  $0.2\text{m}^3/\text{sec}$  of effluent into the harbor<sup>17</sup>.

The VHOC loading of CSOs and direct industrial discharges is difficult to quantify. This is because these smaller sources are both numerous and quite variable. On the other hand, the wastewater treatment facilities, which account for over 90% of the effluent flow into the system<sup>17</sup>, and whose discharges should contain both the solvents (from industrial inputs) and the haloforms (resulting from chlorination prior to discharge) in high concentrations, can be more readily characterized in terms of VHOC loading by making measurements at only two locations.

In light of this, we chose to model only the VHOCs discharged through the wastewater treatment plants. The validity of this approximation can be tested by making measurements in the harbor and/or using modeling techniques to predict pollutant distributions. If these methods suggest that a particular VHOC had additional sources that are significant (other than the treatment plants), we can conclude that it may be impractical to use that compound as a tracer (at least in Boston Harbor). This, in itself, would be useful information.

Hence, the characterization of the VHOC source function to Boston Harbor centered entirely around measurements at the wastewater treatment plants. Complementary measurements of VHOC concentration in receiving waters were focused in the northern portion of the harbor. Since this region is primarily affected by the Deer Island outfall, effluent measurements were concentrated at the Deer Island treatment plant. Due to the geometry of the harbor and the resulting circulation pattern, as well as the fact the Deer Island discharges approximately two to three times more effluent than Nut Island, the relative influence of the Nut Island outfall on the northern harbor is small. Hence, its exact characterization was not critical.

#### Tracer Experiments in Boston Harbor

Measurements were made at Deer Island on seventeen different dates from August 1984 to September 1985. Sampling was concentrated around the spring, summer and fall months to coincide with and complement the sampling of the harbor waters. An effort was made to characterize the source on timescales of hours, days, weeks, and months. Chemical analyses were performed with a gas chromatograph using electron capture detection. The sampling and analytical procedures are described in detail by Kossik et al<sup>1</sup>.

Since we were interested in the mass input rate at the Deer Island source rather than simply the effluent concentration, the variability of both the effluent flow rate and the concentration had to be considered. Over the dates that samples were collected, the flow rate ranged from 7.0 m<sup>3</sup>/sec to over 15.4 m<sup>3</sup>/sec with a mean of 11.3 m<sup>3</sup>/sec and standard deviation of 2.5 m<sup>3</sup>/sec.

Table 2 summarizes the results of the effluent measurements both in terms of concentration and mass input. It is evident that the source is widely variable with respect to all of the VHOCs. Furthermore, the fact that variability in C<sub>o</sub> (concentration) is the same as that of C<sub>o</sub>Q<sub>o</sub> (mass input) indicates that C<sub>o</sub> and Q<sub>o</sub> are not significantly correlated. The various mass loadings varied on an hourly basis by 10% to 20%, while the variation on a daily basis was substantially greater (approximately 50%), and

Table 2

Effluent Concentrations and Mass Input Rates  
at Deer Island for Selected Tracers\*

<u>compound</u>	<u>C<sub>o</sub> concentration† (ppb)</u>	<u>C<sub>o</sub>Q<sub>o</sub> mass input† (kg/day)</u>
CH <sub>3</sub> OCL <sub>3</sub>	9.98 ± 5.01	9.55 ± 5.06
CHCl=OCl <sub>2</sub>	7.24 ± 1.11	7.52 ± 4.08
CHCl <sub>2</sub> Br	4.49 ± 2.29	4.11 ± 1.75
CHClBr <sub>2</sub>	3.34 ± 2.34	2.98 ± 1.80
OCl <sub>2</sub> =OCl <sub>2</sub>	14.50 ± 6.86	14.81 ± 7.94
CHBr <sub>3</sub>	1.65 ± 1.40	1.39 ± 1.01

\*Chloroform is excluded due to solvent contamination. Carbon tetrachloride was present only at very low levels in the effluent and at essentially background levels in the harbor, and is also excluded.

†Mean ± standard deviation; n = 54 with the exception of bromoform, where n = 40.

essentially the same as weekly and monthly fluctuations. This is not surprising in that the major factors affecting the source strength (i.e., effluent flow rate and municipal and industrial loading) would be expected to vary, for the most part, on the timescale of a day or so (e.g., day/night cycle, weekday/weekend variations, tidal cycle) rather than on an hourly or weekly basis. Seasonal (monthly) variations are apparently no greater than these daily fluctuations.

It is evident from these measurements that the mass loadings of VHOCs in the Deer Island effluent vary by up to 50% on a daily basis. This makes source characterization more difficult. However, dispersion processes within the harbor will damp out some of this variation, perhaps allowing these loadings to be treated approximately as constants for modeling purposes. The magnitude of the error incurred by making this assumption will be discussed subsequently.

The complementary measurements of VHOC concentration in receiving waters was focused in the northwest portion of the harbor. Seawater samples were collected in this region on three separate occasions (October 30, 1984; April 25, 1985; and July 2, 1985). Surface water samples were collected by hand, while deep samples were collected with 5L Niskin bottles. In an attempt to make sample collection as synoptic as possible, sampling was carried out within the 2 hours surrounding high water slack.

Figure 3 presents results for one of the VHOCs on the October sampling date. Results are presented as means and standard deviations of duplicate surface and deep-water samples. Similar results were produced for the other selected VHOCs. Two important conclusions could be drawn from these field results. First, for most locations away from the buoyant plume, the surface and deep water concentrations were similar (within 15%), implying that the water column was relatively well mixed. This was also supported by temperature data. This was the case even in July, when we expect the water column to be the most stratified (with respect to the other dates). This supports the validity of the two-dimensional modeling approach which was employed. In addition, it was found that throughout the sampling domain, the VHOC concentrations were, at most, only a few times lower than

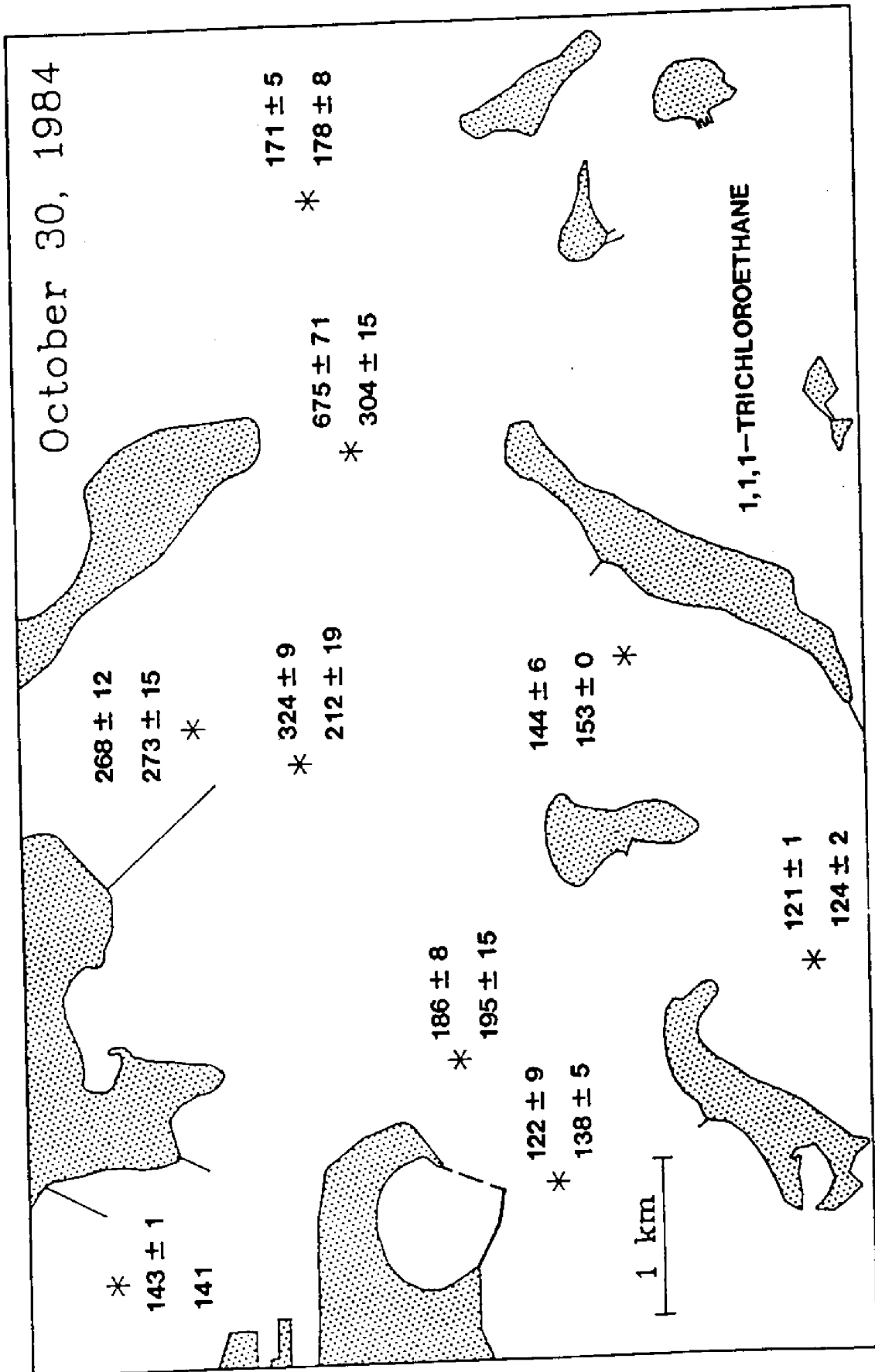


Figure 3 Tracer Concentrations in Boston Harbor (parts-per-trillion) at High Water Slack (surface and deep water measurements; mean of duplicates)

the concentration in the immediate vicinity of the outfall. This suggests that the harbor flushing efficiency is rather low and water essentially moves in and out without significantly exchanging with "clean" bay water.

#### Description of Mathematical Models

The tracer studies which have been described above were carried out to augment a concurrent modeling study. The tools utilized to simulate pollutant transport in Boston Harbor consisted essentially of two separate mathematical models which were run in series. The first predicts fluid flow or circulation. That is, if one wants to predict where a contaminant will move when input into a water body, one must first know where the water itself moves. Once information regarding the advective velocity field has been obtained, one can attempt to simulate the second process, contaminant advection and dispersion. This process represents the transport and mixing of a contaminant within a water body.

The two models used in this study numerically solve equations that mathematically represent the governing conservation laws. These models are known by the acronyms of TEA and ELA. TEA (Tidal Embayment Analysis) simulates water circulation in embayments in which the circulation pattern is predominantly tidally driven. ELA (Eulerian-Lagrangian Analysis) uses the results of TEA as input in order to simulate the transport of a contaminant released into the embayment. A simplified computational structure for the TEA/ELA modeling system is shown in Figure 4. Both models were developed at the Ralph Parsons Laboratory for Water Resources and Hydrodynamics at MIT. Detailed descriptions of the models are presented elsewhere<sup>1, 18-22</sup>. For the present purposes, a brief description of each model follows.

TEA is a two-dimensional harmonic finite element circulation model. The finite element method (FEM) facilitates the use of an irregular grid to better represent the complex geometry of many tidal embayments. TEA solves the linearized depth-averaged forms of the Navier-Stokes and continuity equations.

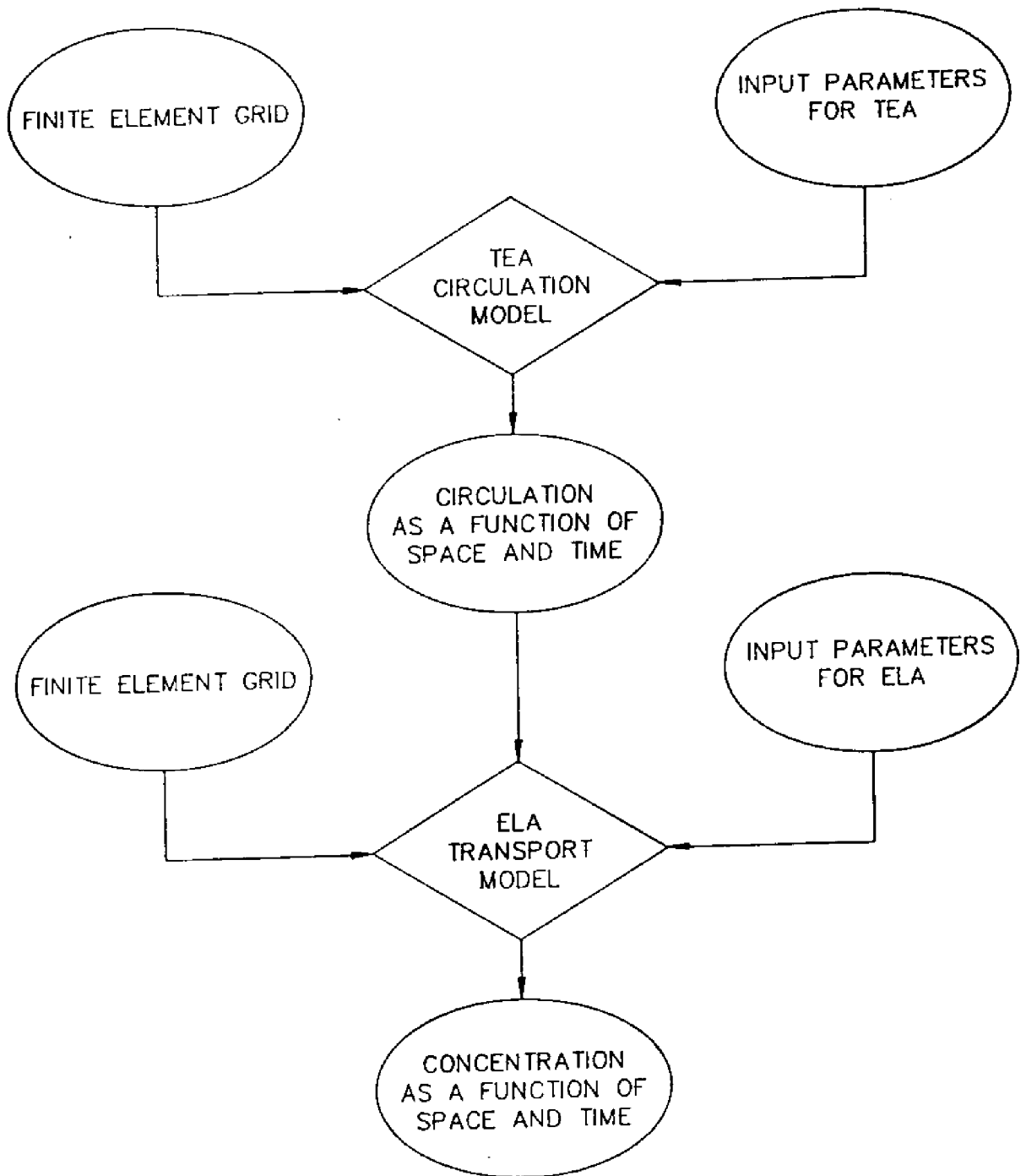


Figure 4 Computational structure for TEA/ELA modeling system (diamonds represent computer programs, ovals represent input/output files)



Linearizing the governing equations can introduce significant error, depending on the magnitude of the nonlinear terms. Open ocean tides can be accurately described by the simple superpositioning of a series of harmonic components. In shallow water, however, nonlinear effects can become significant. TEA does not include these nonlinear terms. Although a nonlinear version of TEA has been developed which accounts for nonlinear effects, the linear version was used for this work. This choice was primarily based on a lack of validation data available to justify the expense of using the nonlinear version. In any case, linear TEA provided a reasonable representation of the general tidal circulation pattern in Boston Harbor and was quite useful for our application.

TEA takes advantage of the periodic nature of the tidal phenomenon and operates in the frequency domain rather than the time domain. This so-called harmonic method offers a number of advantages over traditional time-stepping techniques, perhaps the most important being the ability to apply much finer spatial resolution without the expense of small timesteps. As a result, TEA is much cheaper than time-stepping models for predominantly tidal flow. The model solves for the spatial variation of elevation and velocity using a Galerkin FEM with piecewise-linear polynomial basis functions.

The solution procedure generates the entire time history of velocity and elevation at each corner node of a triangular finite element grid. Furthermore, any number of solutions can be linearly superimposed to simulate simultaneous forcing functions.

For example, a steady current can be generated by applying a steady wind field or by using the boundary conditions to define a mean slope. This solution can then be superimposed on a semidiurnal tide generated by forcing the system at a frequency of  $2\pi/T$  (where  $T = 12.4$  hrs).

ELA is a two-dimensional Eulerian-Lagrangian finite element transport model. By applying the principle of mass conservation to a passive pollutant dissolved in a turbulent flow, one can mathematically describe the physics of transport in the advection-diffusion equation. ELA numerically solves the depth-averaged form of the equation.

An Eulerian-Lagrangian method is employed to solve this transport equation. Essentially, this consists of decoupling the equation into a pure-advection component and a pure-diffusion component. The advection component is solved with a backwards method of characteristics, while the diffusion component is solved using finite elements. A fourth order Runge-Kutta method with constant time-stepping is used to solve the set of ordinary differential equations associated with the backward tracking of fluid parcels. Having solved the advection component of the equation, the diffusion component is then solved using Galerkin FEM with quadratic Lagrange polynomial basis functions. An implicit time-stepping scheme is used to solve for the temporal variation in the diffusion equations.

ELA offers a number of advantages over other available transport models (e.g., DISPER<sup>23</sup>). Most significantly, numerical diffusion is greatly reduced. Furthermore, ELA offers considerable computational savings for both periodic and aperiodic flow. Not unlike TEA, ELA has some inherent limitations imposed by both the assumptions made in deriving the governing equations, and the particular numerical solution technique used. While it is important to keep these in mind, it is very likely that the inaccuracies in the circulation model when applied to a complex system such as Boston Harbor will overshadow the inaccuracies in the transport model (i.e., circulation is more difficult to simulate than transport).

ELA outputs concentrations at each node of a triangular quadratic finite element grid (3 corner nodes and 3 side nodes per element). Concentrations can be saved and output every timestep.

#### Application of Numerical Models to Boston Harbor

Due to the great complexity of the Boston Harbor system, it has been recognized for some time that a thorough analysis of water quality problems in the harbor would require the use of mathematical models. Previous modeling efforts in the harbor are summarized by Kossik et al<sup>1</sup>.

In order to apply the models to Massachusetts Bay and Boston Harbor, it was necessary to define and discretize the domain. Due to uncertainty in the

boundary condition, we chose to model the entire Massachusetts Bay with a relatively coarse grid while applying high resolution to the harbor itself. Figure 5 illustrates the finite element grid. The majority of this grid has land boundaries. The open-ocean boundary extends linearly from Cape Ann to Cape Cod. This boundary has been studied to some extent<sup>24</sup> and Tide Table information is available at the edges.

A detail of Boston Harbor is shown in Figure 6, illustrating the level of grid resolution. High resolution is applied in areas of high concentration gradient (e.g., near outfalls) and between islands. The grid consists of 888 elements having 552 corner nodes. The circulation model is applied to this entire grid. The domain of the transport model, on the other hand, consists only of the elements shown in Figure 6. This detailed grid of Boston Harbor contains 694 of the original 888 elements. Since ELA utilizes quadratic rather than linear basis functions, there are six nodes associated with each element (three corner nodes and three nodes bisecting the sides). The quadratic grid has a total of 1575 nodes.

As has been pointed out above, nonlinear interactions undoubtedly play an important role in producing the residual circulation in Boston Harbor and such effects cannot be adequately modeled by linear TEA. However, it was felt that linear TEA could accurately represent the major features of the circulation pattern, and since the field data necessary to validate and calibrate the residual circulation do not presently exist, such an attempt was beyond the scope of the present work.

In addition, since harmonic analyses of tidal records<sup>25</sup> indicate that the semidiurnal ( $M_2$ ) constituent accounts for 60 to 70% of the observed variation in tidal velocity, we chose to simulate circulation using the  $M_2$  constituent as the only forcing function. In making this approximation, we were, in effect, choosing to model only the major features of the advective velocity field with TEA. The additional mixing, not explicitly accounted for by the circulation model, is then represented through the use of an elevated dispersion coefficient within the transport model. Details of boundary conditions and specific model parameters are given by Kossik et al<sup>1</sup>.

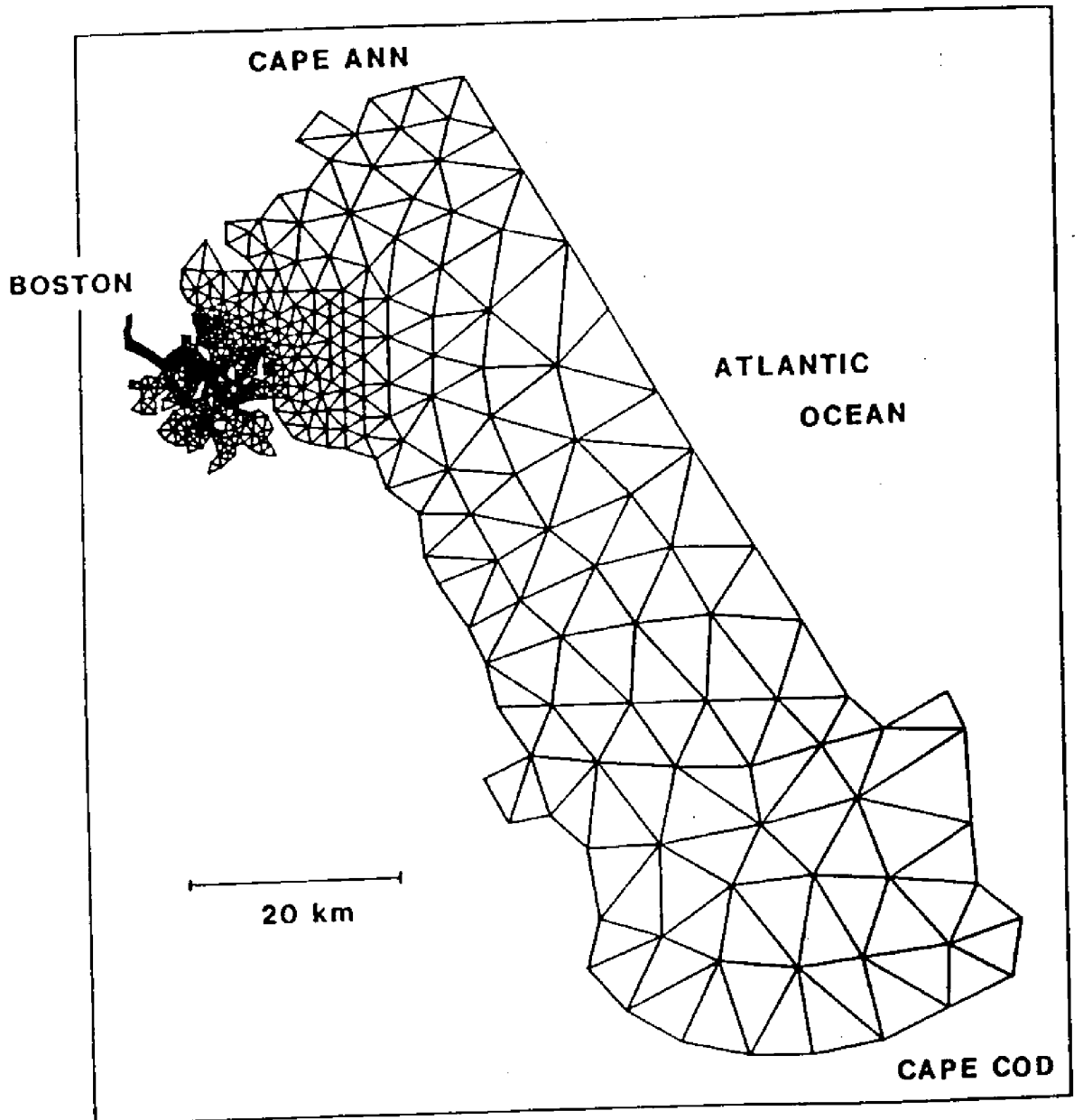


Figure 5 Finite element grid of Massachusetts Bay

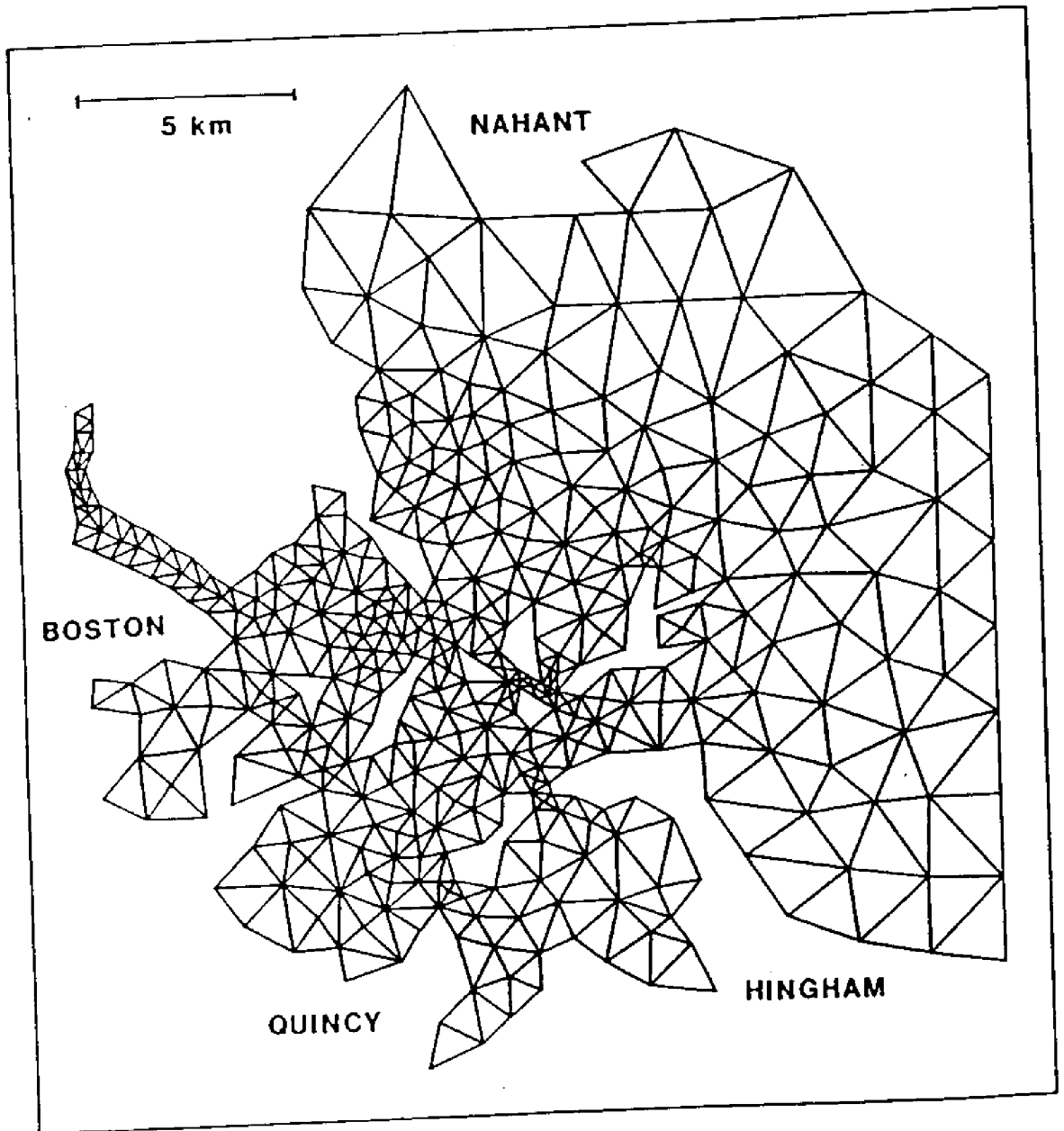


Figure 6 Finite element grid - detail of Boston Harbor

In light of the fact that calibration of a dispersion coefficient within the transport model would, to some extent, account for inadequacies in the simulation of the advective velocity field, and that hydrodynamic field data in the harbor are sparse, no attempt was made to specifically fit modeled circulation results to field measurements. Nevertheless, in order to assure ourselves that we were representing the major features of the circulation pattern, qualitative comparisons were made against measured currents reported in Tidal Current Charts and records of mean tide level at a number of stations. Simulated results compared favorably<sup>1</sup>, and linear TEA seemed to accurately represent the major features of the mean circulation pattern, thereby providing a reliable basis for the application of the transport model ELA to the harbor.

The transport model ELA requires as input a description of the velocity field (output from TEA), boundary conditions, source strength and location, a dispersion coefficient, and a decay rate (volatilization piston velocity). Since the volatilization rates of our tracers are fairly high, a zero concentration open ocean boundary condition was reasonable. The two wastewater treatment plants discharging effluent into the harbor at Deer and Nut Islands were the only sources modeled.

Three independent variables were varied in order to fit model simulations to measured concentration data. These were: 1)  $C_0 Q_0$ , the mass input rate (kg/sec); 2)  $D$ , a homogeneous, isotropic, temporally constant dispersion coefficient ( $m^2/sec$ ); and 3)  $k$ , a spatially and temporally constant volatilization piston velocity (m/sec).

As was pointed out previously,  $C_0 Q_0$  is temporally variable. However, we chose to input  $C_0 Q_0$  as a constant, but use it as one of the fitting parameters. Sensitivity analysis indicated that 50 to 100% of the variability introduced at the source would be damped by the dispersive processes simulated in the model. Hence, given the other approximations of the model, it was concluded that treating the input as constant was not unreasonable.

Due to the highly periodic nature of the tidal phenomenon, the dispersion coefficient should be time dependent. However, use of a temporally constant dispersion coefficient facilitates matrix manipulation within the numerical model (the diffusion matrix only needs to be inverted once) and is justified by the large ratio of total simulation time to tidal period (approximately 30 to 60). The dispersion coefficient should also be spatially variable and anisotropic, but this variability is extremely difficult to quantify. Hence, the dispersion coefficient was modeled as homogeneous, isotropic, and temporally constant. Because D accounted for additional mixing not explicitly represented by TEA, calibrated values were expected to be large. To some extent, these artificially high dispersion coefficients reflect the magnitude of the residual circulation and thus the efficiency of flushing. In fact, calibrated values of D will be used subsequently to estimate a harbor flushing rate. Note that the maximum physical value of D possible is approximately  $L^2/T$  where L is the tidal excursion (3-4km) and T is the tidal period (12.4 hrs). Hence,  $D_{max}$  200-350  $m^2/sec$ . Values of D ranging from 30  $m^2/sec$  to 150  $m^2/sec$  were used for our calibrations.

The piston velocity, k, was used as a third independent variable to fit model predictions to observations. Values of k ranging from 1 cm/hr to 11 cm/hr (reflecting the anticipated range of values) were used. Like dispersion coefficients, piston velocities are temporally and spatially dependent. These variations, however, are difficult to quantify and model. Hence, our piston velocities represent an effective mean value over the length of the simulation and the region examined.

The timestep used for our simulations was T/4 (where T=12.4 hrs). Simulations were run until concentration distributions reached a pseudo-steady state. That is, the simulations were started with an empty harbor (the initial condition being C=0 everywhere) and it took a finite amount of time for losses (decay and flushing) to balance the continuous input. Depending on the value of k used, this could take anywhere from several days to a month of simulated time. Figure 7 presents the results of a model simulation in the form of a contour map of predicted concentration for one particular set of model parameters.

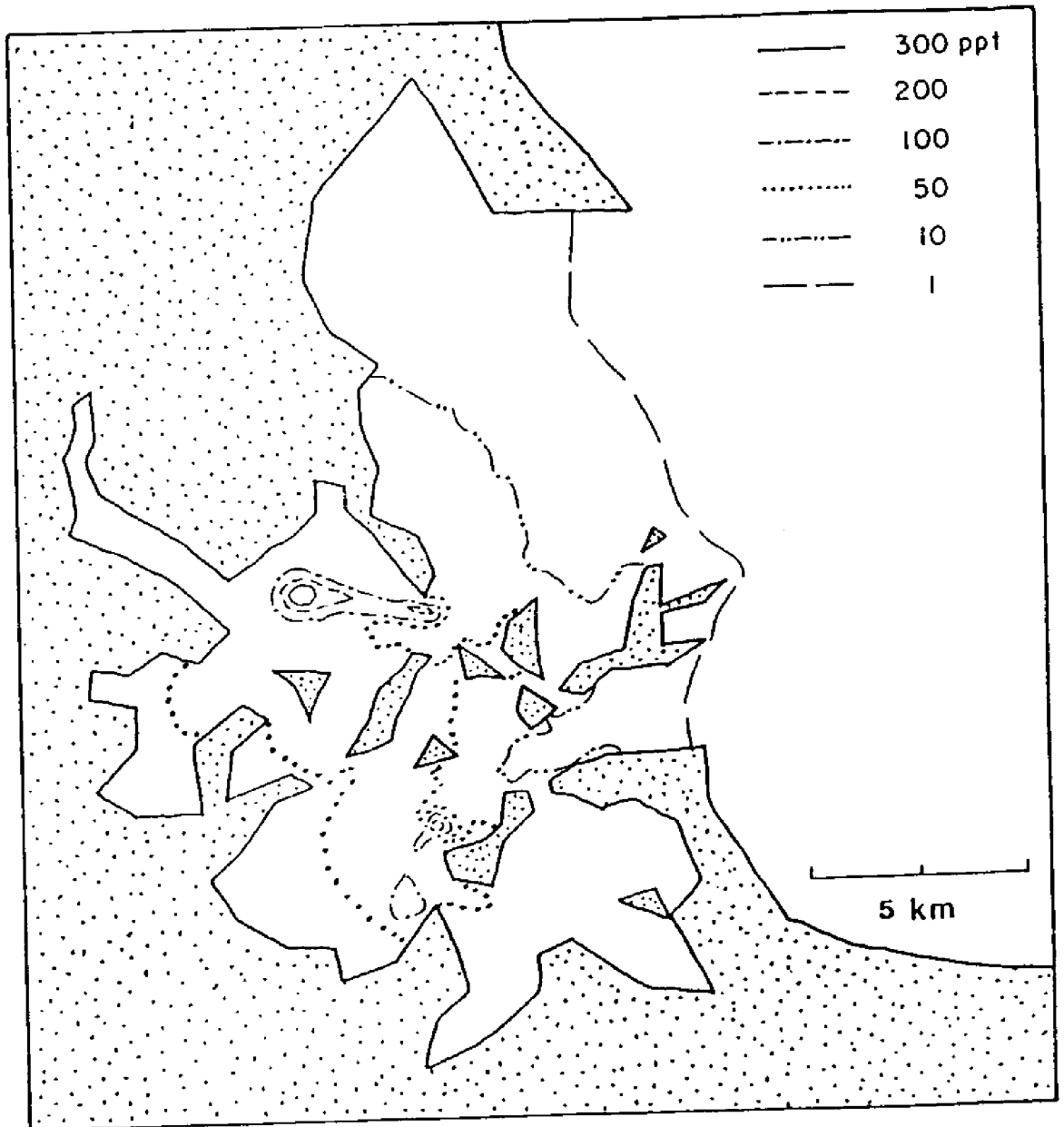


Figure 7 Simulated Concentrations (parts-per-trillion) in Boston Harbor at High Water Slack ( $D = 70 \text{ m}^2/\text{sec}$ ;  $k = 4 \text{ cm/hr}$ )



## Calibration of the Transport Model

Calibration of the transport model serves a dual purpose. First, by comparing model predictions to observations one can begin to evaluate the predictive capabilities of the model. In effect, it allows one to evaluate whether the pertinent physical and chemical processes are being included in, and adequately represented by, the model. Second, by adjusting model parameters to calibrate simulated concentrations to observed concentrations, one can obtain information regarding the processes represented by these parameters. This is the classic "inverse problem" of using experimental data on a dependent variable (e.g., concentration) to obtain values for the independent variables (e.g., dispersion coefficient and volatilization rate).

Model calibration and parameter estimation can become quite involved. Our limited data, however, did not warrant the use of a highly complex technique. A relatively simple calibration procedure was quite adequate for our purposes. As has been pointed out above, ELA was calibrated using the dispersion coefficient  $D$ , the piston velocity  $k$ , and the source strength  $C_0 Q_0$  as the independent variables. Calibrations were based on comparisons between measurements and corresponding simulated concentrations at high water slack. Although the measurements were not completely synoptic with high tide, simulations indicated that the temporal error incurred was no greater than the spatial uncertainty of the sampling location (approx. 100m).

In the first step of the calibration procedure, a large number of simulation runs were made in which the three independent variables ( $D, k$ , and  $C_0 Q_0$ ) were widely varied. Based on these results, an analytical interpolation function was developed that was used to describe simulated concentrations resulting from any combination of the model parameters  $D, k$ , and  $C_0 Q_0$ . Having done so, the error between the simulated concentration and the measured concentration at a given point was defined as:

$$E_i = \frac{C_j^m - C_j}{C_j^m} \quad (1)$$

where  $E_i$  is the relative fitting error at location  $i$ ,  $C_i^m$  is the measured concentration at location  $i$ , and  $C_i$  is the simulated concentration at location  $i$  (a function of  $D, k$ , and  $C_0 Q_0$ ). Based on this, the root mean square relative error for a given calibration becomes:

$$E_r = \left[ \frac{1}{n} \sum_{i=1}^n E_i^2 \right]^{1/2} \quad (2)$$

where  $E_r$  is the total relative fitting error,  $n$  is the number of calibration points, and  $E_i$  is as specified above. By minimizing  $E_r$  with respect to  $D, k$ , and  $C_0$ , best-fit values of these three parameters were obtained for each tracer compound on each sampling date.

### General Discussion of Calibration Results

The results of the calibrations are tabulated in Table 3. For each compound on each date, the values of  $D, k$ , and  $C_0 Q_0$  that resulted in the best fit to the measurements are given along with the corresponding minimum error. These results can be used quite effectively to: 1) elucidate information regarding the behavior of the tracers in the Boston Harbor system; and 2) reach some preliminary conclusions regarding model performance. This is done by considering the values of the best-fit parameters and evaluating the magnitude of the fitting error. The former consists of examining the best-fit parameters to determine whether or not they represent physically realistic values. Since we have actual measurements of  $C_0 Q_0$ , and have some knowledge of the factors governing  $k$ , these two parameters can be readily evaluated in this manner. This is more difficult to do for  $D$ , however, since this parameter is used to correct for inaccuracies in our representation of the mean velocity field. We do know, however, that on any given date the value of  $D$  must be the same for each tracer since the physical mixing processes act equally on all dissolved substances. Hence, we can draw conclusions based on the relative value of the calibrated dispersion coefficients from compound to compound.

Table 3

Calibration Results: Best Fit Values of D, k, and  $C_0Q_0$

Date	Compound	D (m <sup>2</sup> /sec)	k (cm/hr)	$C_0Q_0^a$ (kg/day)	Et (%)	n†
10-30-84	CH <sub>3</sub> CCl <sub>3</sub>	50	4.5	26.1	12.3	6
"	CCl <sub>2</sub> =CCl <sub>2</sub>	45	2.3	15.5	4.4	6
"	CHCl=CCl <sub>2</sub>	60	<1*	12.5	25.4	6
"	CHCl <sub>2</sub> Br	45	2.7	3.2	2.9	3
"	CHClBr <sub>2</sub>	50	1.1	1.4	2.6	3
"	CHBr <sub>3</sub>	45	1.3	3.0	0.6	3
4-25-85	CH <sub>3</sub> CCl <sub>3</sub>	80	6.5	83.8	16.6	6
"	CCl <sub>2</sub> =CCl <sub>2</sub>	70	6.1	103.4	20.4	6
"	CHCl=CCl <sub>2</sub>	95	4.3	48.8	12.9	6
"	CHCl <sub>2</sub> Br	75	4.8	7.9	14.1	6
"	CHClBr <sub>2</sub>	85	4.4	5.2	13.5	6
"	CHBr <sub>3</sub>	>150*	<1*	38.0	14.0	6
7-2-85	CH <sub>3</sub> CCl <sub>3</sub>	>150*	5.9	95.5	4.9	6
"	CCl <sub>2</sub> =CCl <sub>2</sub>	>150*	3.4	95.2	3.6	6
"	CHCl=CCl <sub>2</sub>	>150*	3.0	51.1	6.5	6
"	CHCl <sub>2</sub> Br	100	10.4	18.2	19.2	6
"	CHClBr <sub>2</sub>	105	9.0	10.0	21.2	6
"	CHBr <sub>3</sub>	>150*	<1*	21.9	19.9	6

a input at Deer Island based on a modeled  $Q_0$  of 18.4 m<sup>3</sup>/sec  
 † root mean square relative error  
 ‡ number of calibration points  
 \* outside range of calibration values (k = 1-11 cm/hr,  
 D = 30-150 m<sup>2</sup>/sec)

Having convinced ourselves that the model is adequately representing the pertinent chemical and physical processes, we can address the inverse problem. This involves using the values of the best-fit parameters to draw conclusions regarding the processes represented by these parameters. The following sections specifically discuss the calibration results with respect to the behavior of the tracer compounds, model performance, and the inverse problem.

### Behavior of the Tracer Compounds

In order to evaluate the behavior of the tracer compounds, it is easiest to begin by examining the various calibrated values of  $C_0Q_0$  in Table 3, since this is the parameter about which the most information is known (Table 2). A comparison of calibrated values of  $C_0Q_0$  to measured values of  $C_0Q_0$  separates the tracers into two groups: 1) the solvents and bromoform, whose calibrated values are up to 10 times greater than observed values, and 2) bromodichloromethane and chlorodibromomethane, whose calibrated values are within or slightly above observed ranges. It is also apparent that in July the values of  $D$  for the solvents and bromoform are at least 1 1/2 times higher and the values of  $k$  are at least two to three times lower than the corresponding values for  $CHCl_2Br$  and  $CHClBr_2$ . The bromoform calibration in April follows the same pattern.

These results suggest that there may be other sources of both solvents and bromoform in the harbor that have not been accounted for, and that the calibration procedure is attempting to account for these sources by adjusting the values of  $D$ ,  $k$ , and  $C_0Q_0$ . The extra mass could be accounted for by increasing  $C_0Q_0$  and/or decreasing  $k$  and could then be mixed in the direction of the unmodeled sources by elevating the dispersion coefficient. These conclusions are supported by available data which, while qualitative, suggest that a number of additional solvent sources may indeed be present<sup>17</sup>. Although these sources are small and difficult to quantify, they are quite numerous and the solvents may be highly concentrated in their discharges. For the case of bromoform, the only significant sources are chlorinated discharges. In addition to the chlorinated treatment plant discharges, two power plants discharge cooling water to the harbor that is

periodically chlorinated to control biofouling. (Note that the power plants do not introduce significant amounts of  $\text{CHCl}_2\text{Br}$  or  $\text{CHClBr}_2$  since chlorination of salt water results almost exclusively in the production of bromoform<sup>16</sup>.)

Hence, it appears that only  $\text{CHCl}_2\text{Br}$  and  $\text{CHClBr}_2$  can be used effectively as tracers in Boston Harbor. The solvents simply have too many uncharacterizable sources. Given the widespread use and disposal of the chlorinated solvents, this is likely to be the case in other coastal regions as well. On the other hand, it should be relatively easy to characterize cooling water discharges with respect to bromoform, and since these sources are small in number and easy to identify, bromoform may still prove to be an effective tracer.

#### Model Performance

The complete evaluation of a complex numerical model requires a large amount of data. Few, if any, complex circulation and transport models are adequately validated. Nevertheless, limited data can often be used to draw some general conclusions regarding the behavior of a model. In our case, several general statements can be made.

The model simulations appear to agree well with observations. The relative fitting errors in Table 3 range from 1% to 20% and considering the uncertainties involved, this is a reasonable agreement. More importantly, for the case of the two haloforms (whose results are not biased by the presence of unmodeled sources), the best-fit parameters are physically realistic. The values of  $C_0$  are within (or slightly above) the observed ranges. In addition, they have the correct relative magnitude, with  $C_0$  for  $\text{CHCl}_2\text{Br}$  being somewhat greater than that of  $\text{CHClBr}_2$  (see Table 2). The values of  $k$  are also in expected ranges based on empirical equations<sup>26,27</sup> and previous studies<sup>28,29</sup>. (This will be discussed in more detail in the next section.) It is difficult to comment on the calibrated value of  $D$  since this parameter was used not only to represent dispersive processes, but also to account for advective processes not adequately modeled by TEA. Nevertheless, the values of  $D$  are less than the  $D_{\text{max}}$  defined previously.

The fact that the model calibrations were able to indicate the presence of other sources is another positive reflection on model behavior. In fact, this is the kind of problem that an effective harbor management tool would be called on to solve. More complete validation of TEA and ELA will require large-scale hydrodynamic and chemical measurements throughout the region. The results of this study indicate that the models seem to adequately represent the major processes involved and further modeling efforts are therefore justified.

#### The Inverse Problem - Volatilization in Boston Harbor

As pointed out by Broecker and Peng<sup>30</sup>, existing methods for studying volatilization processes in natural waters are difficult or impossible to apply to coastal regions and are typically used only in simple lake, stream, or open-ocean systems<sup>28,31,32</sup>. Hence, one of the objectives of this work was to investigate the use of nonconservative tracers in conjunction with modeling efforts as a tool for studying volatilization processes in natural waters. Such a method, if proved to be feasible in Boston Harbor, could then be applied to other regions where traditional methods are not applicable.

In order to evaluate the magnitude of the volatilization piston velocity, it was necessary to constrain the value of  $C_0Q_0$ . Due to the variability of the source strength, however, it was not possible to constrain  $C_0Q_0$  to a specific value and obtain a precise estimate for  $k$ . Table 4 presents calibration results for  $\text{CHCl}_2\text{Br}$  and  $\text{CHClBr}_2$ . These results were obtained by forcing  $C_0Q_0$  to a given value and then minimizing the error with respect to  $D$  and  $k$ . Values of  $C_0Q_0$  were chosen to represent the ranges (one standard deviation from the mean) observed in Deer Island sewage effluent (Table 2).

Based on these results, it is difficult to distinguish different piston velocities from date to date or compound to compound. Nevertheless, it can be stated that the piston velocity for these compounds on all three dates appears to fall within the range from 1 to 8 cm/hr, with the most likely value (based on effluent observations and calibration fitting errors) being

Table 4

Calibrated Piston Velocities for  $\text{CHCl}_2\text{Br}$  and  $\text{CHClBr}_2$ 

Date	$\text{CHCl}_2\text{BR}$			$\text{CHClBr}_2$		
	$C_0Q_0^{a,b}$ (kg/day)	k (cm/hr)	$E^d$ (%)	$C_0Q_0^{a,c}$ (kg/day)	k (cm/hr)	$E^d$ (%)
10-30-84	2.36	1.4	5.5	1.18	1.3	11.6
"	3.24	2.8	2.9	2.08	2.5	6.5
"	4.11	3.7	3.5	2.98	4.3	9.6
"	4.99	4.4	4.5	3.88	6.1	11.1
"	5.86	5.4	5.4	4.78	7.5	12.2
4-25-85	2.36	<1*	--	1.18	<1*	--
"	3.24	1.9	15.5	2.08	1.6	15.3
"	4.11	2.5	14.7	2.98	2.8	14.0
"	4.99	3.2	14.6	3.88	3.5	13.7
"	5.86	3.6	14.4	4.78	4.0	13.5
7-2-85	2.36	<1*	--	1.18	<1*	--
"	3.24	1.1	32.9	2.08	1.1	28.6
"	4.11	1.9	23.5	2.98	2.6	23.0
"	4.99	2.8	21.9	3.88	3.7	22.6
"	5.86	3.3	21.5	4.78	4.4	22.1

\* outside range of calibration values  
a based on modeled  $Q_0$  of  $18.4 \text{ m}^3/\text{sec}$  at Deer Island  
b  $C_0Q_0 = 4.11 \pm 1.75$ ;  $n = 54$  (Table 4.2)  
c  $C_0Q_0 = 2.98 \pm 1.80$ ;  $n = 54$  (Table 4.2)  
d root mean square relative error

2 to 5 cm/hr. This falls somewhere between the values reported for small lakes<sup>28</sup> and open ocean sites<sup>29,31</sup>. Since a coastal embayment can be considered to be intermediate between these two regimes (with respect to fetch, windspeed, waves, etc.), this is an intuitively pleasing result. In addition, these values agree well with empirical relationships relating windspeed to piston velocity. The empirical equations of Wolff and van der Heijde<sup>26</sup> require a wind speed of 8 to 13 knots to produce piston velocities of 2 to 5 cm/hr for these compounds. This corresponds well to the actual wind speeds observed<sup>1</sup>.

#### The Inverse Problem - Flushing Time for Boston Harbor

The flushing efficiency of a tidal embayment such as Boston Harbor depends not on the mean tidal circulation, but on the residual **circulation**, since most of the "contaminated" water that leaves on the ebb returns on the flood. In this study, residual circulation was represented by a calibrated dispersion coefficient. Hence, the magnitude of D should be related to the flushing time of the harbor: large values of D should correspond to small flushing times.

Using dimensional analysis, a flushing time for the harbor,  $t_f$ , can be defined as

$$t_f = \frac{(L)^2}{D} \quad (3)$$

where L is the characteristic length scale of the harbor, and D is the calibrated dispersion coefficient. Taking the value of L to be 8km and a typical calibrated D ranging from 50m<sup>2</sup>/sec to 100 m<sup>2</sup>/sec, the flushing time for the harbor is from one to two weeks. This value is consistent with estimates made by different methods (e.g., Ketchum<sup>33</sup>).

#### Summary and Direction of Future Work

The physical mixing of natural waters and the concurrent volatilization mechanisms affecting the fate of many chemicals discharged into these



waters can be extremely complex. The present work utilized a chemical tracer study to gain valuable insights into both of these processes. This was accomplished by calibrating a mathematical model to tracer measurements made in the region.

After using the model calibration to evaluate the behavior of the tracer compounds and investigate model performance, the physical mixing and volatilization processes acting in the region were evaluated based on calibrated values of the model parameters representing these processes.

Having demonstrated the basic ability of the model to simulate pollutant transport, future work needs to be focused on two extremes of the space/time spectrum: 1) modeling pollutant transport over short time scales (with respect to the tidal period), corresponding to distances within one tidal excursion from the source; and 2) modeling residual circulation occurring over several days to weeks. In addition, further efforts will focus on not only determining the rate of chemical volatilization, but on evaluating the volatilization mechanism by more precisely quantifying the ratios of volatilization rates of two or more compounds. These efforts will require much more exhaustive tracer experiments, consisting of perhaps 50 to 100 observations made synoptically near the source, in the backwater regions of the harbor, and well offshore into Massachusetts Bay, as well as complementary hydrodynamic measurements against which the circulation model can be validated.

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