

ANALYSIS OF WATER SAMPLES FOR TOXIC VOLATILE ORGANIC COMPOUNDS:  
STATE OF THE ART METHODS AND STRATEGIES FOR SAMPLING

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INTRODUCTION

Although rapid development of advanced analytical methods for determination of toxic volatile organic compounds (VOC) in water coincided with their discovery in river and drinking waters (1, 2), evidence of interest in this subject dates from rarely cited research reports in the early 1950s (3, 4). Methods of analysis of water for VOC were refined throughout the 1970s so that today rapid analysis of aqueous samples for complex mixtures of VOC at parts per billion (ppb) concentration ranges are relatively rapid and inexpensive. Few major changes have occurred in the basic approach or technology of these methods, except of course, in trends toward even more automated analyses and data management.

The major limitations today then, are found less in analytical instrumentation and more with sample collection, storage and transportation. Objectives of this talk include:

1. A brief overview of principles and practices of analyses of water for VOC at trace concentration levels
2. Presentation of new approaches to management of personnel and resources for monitoring VOC in rivers downstream from points of discharge

Research for this second section was a cooperative effort between civil engineers and analytical chemists at New Mexico State University

(NMSU) and was funded by the New Mexico Water Resources Research Institute (WRRRI) for two years. Results from this new approach show the importance of such management and provide practical tools for management of sampling operations in environmental monitoring of rivers.

#### GENERAL BACKGROUND

Before a detailed discussion of either section is started, an appraisal of the problems and the special nature of VOC may provide a basis of an understanding of the analytical approach and the need for river models in chemical analyses. Three general aspects of VOC in water were major technical limitations in the mid-1970s. They were:

1. The volatile and thus transient nature of VOC during sample handling
2. An aqueous matrix which may be considered deleterious to expensive analytical instrumentation
3. The presence of VOC at microgram per liter (ppb) concentration levels in sometimes complex mixtures

Nevertheless, detailed well-documented analytical methods were described as early as 1977 by the U.S. Environmental Protection Agency (EPA). Clearly, solutions to the above problems were found. Few major changes in analytical methods have occurred since the late 1970s and few major changes during the next five years may be expected. An appreciation of these procedures may be useful to those of you who depend on analytical chemists. However, only a brief review will be presented since a complete description is beyond the scope of this meeting. Technical solutions to each of the limitations cited above were based on

characteristics of volatility or vapor pressure of the toxic organic compounds.

### Vapor Pressure

In figure 1, plots of vapor pressure of pure substances are shown as a function of temperature for (a) ethyl ether ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ), (b) ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) and (c) water ( $\text{HOH}$ ). The molecules are relatively small in size or molecular weight. Two conclusions may be drawn from these curves:

1. Not all small molecules have identical vapor pressure (tendency to vaporize)
2. Small changes in molecular structure such as the presence of polar bonds (O-H in ethanol versus nonpolar O- $\text{CH}_2\text{CH}_3$  in ether) lead to startling differences in vapor pressure.

Polar groups may have favorable molecule-to-molecule specific interactions, such as hydrogen bonding, and these interactions lead to decreases in vapor pressure. Thus, even though water has a molecular weight of only 18 amu (atomic mass units), hydrogen bonding leads to much lower vapor pressure than ethyl ether with a much greater molecular weight of 74 amu. As a general rule then, VOC are defined as small non-polar molecules. Polar groups such as OH, COOH or  $\text{NH}_2$  in compounds greatly reduce volatility. Compounds containing these polar groups are generally not included in the family of VOC.

### Analytical Techniques

Because VOC are often found in mixtures rather than as isolated species, and because molecule-specific detectors do not exist, gas chromatographic (GC) methods are ideal to physically separate individual com-

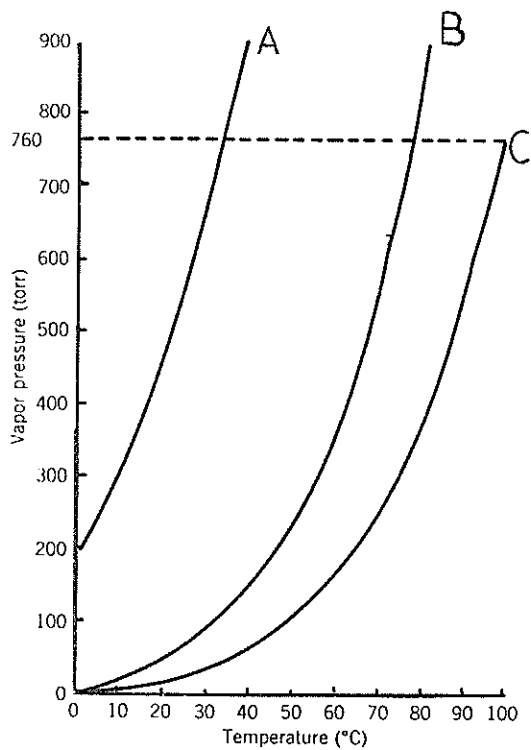


Fig. 1. Plot of Vapor Pressure Versus Temperature for (a) Ethyl Ether, (b) Ethanol, and (c) Water. Taken from Brady and Humeston; General Chemistry; Wiley, 1978, p. 232.

ponents in a sample before measurement using a detector. Unfortunately, direct injection of aqueous samples suffers from artifacts caused by chemical reactions in heated injection ports. Moreover, sensitivity is limited, using direct injection methods for water, to milligram-per-liter (ppm) levels and above because sample sizes are limited to approximately 10 to 20 microliters. In addition, certain detectors are degraded in performance from water introduced into the GC by direct aqueous injection.

Vapor pressure can be used to advantage in two ways: To remove VOC from water and concentrate VOC from up to one liter of solution for GC analysis. The approach used involves dynamic headspace enrichment or purge and trap procedures. These procedures are shown in-series with a GC in figure 2. The heart of this approach is the purging device and sorbent trap. Inert gas is forced into the purging device where 10 to 100 mL of aqueous sample have been placed. The gas is used to force VOC from solution to the vapor phase while gas is flowing through the sample. Thus, extraction efficiencies during 5 to 10 minute extractions may exceed 95 percent for most VOC. However, traces of VOC are diluted into as many as 500 mL of inert gas during extraction of VOC from water. The sorbent trap is used to collect virtually all of the VOC from the inert gas stream which is then released from the system. In the next analytical step, not shown in figure 2, purging is stopped and the trap is placed directly in-series with the GC. When the trap is heated rapidly, VOC are vaporized and carried into the GC for subsequent separation, detection and quantification. An example of results from such analyses is shown in figure 3 and is typical of results found in numerous articles on VOC in water samples. Detection limits of 0.1 ppb are no longer uncommon and the advent of fused silica capillary GC columns portends improved selectivity but not major changes in basic principles. Purging systems are commercially available for connection to GC and may be used to automatically analyze up to 10 samples. As a result of these advances, in 1981 our group at NMSU concluded that a major remaining limitation was that of sample collection and treatment.

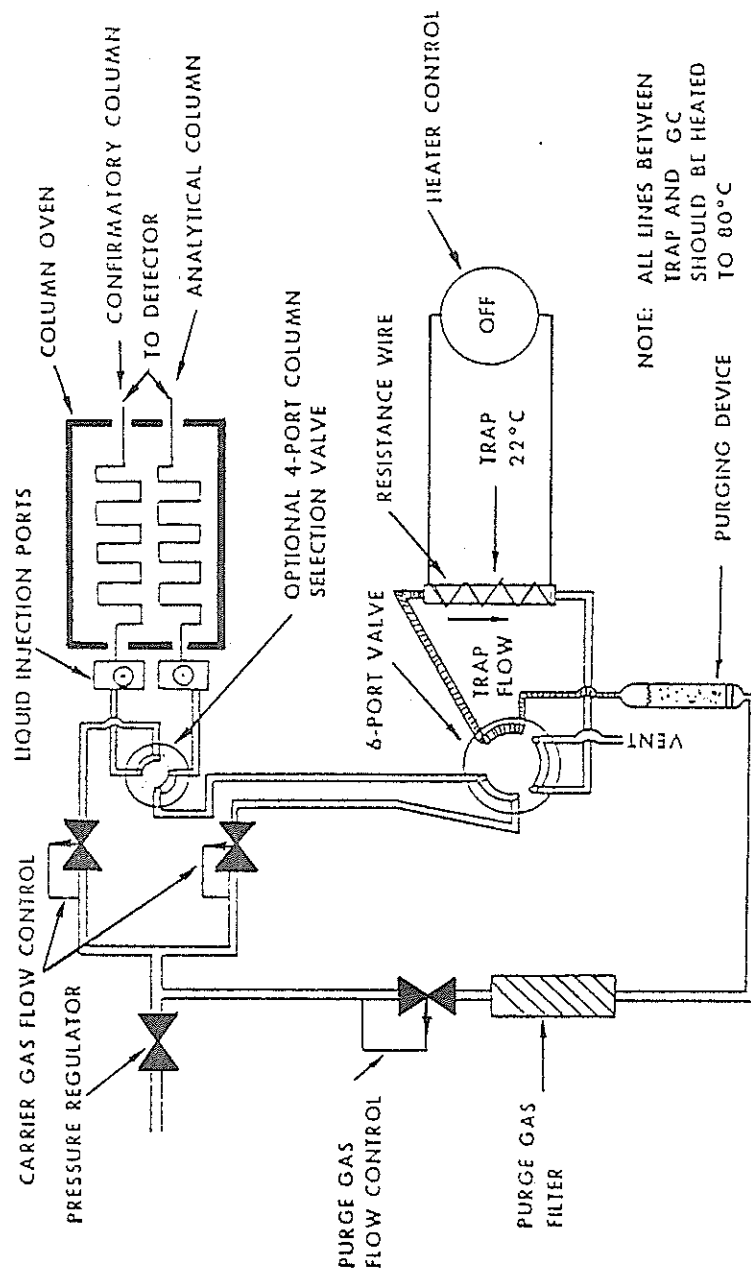


Fig. 2. Purge and Trap Instrumentation Combined In-series with Gas Chromatograph (upper right portion)

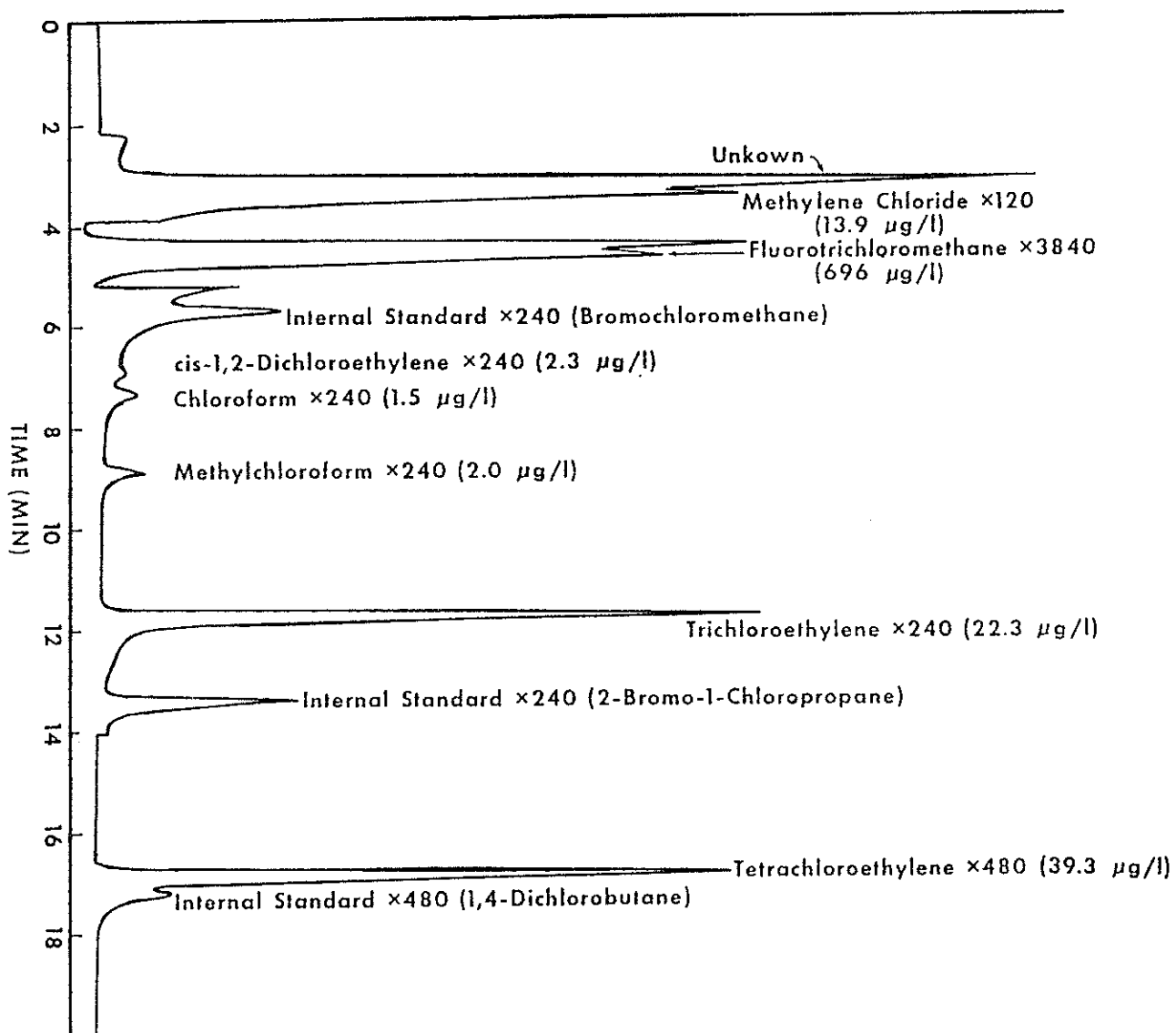


Fig. 3. Results from GC Analysis of Contaminated Well Water Using Purge and Trap Procedures (not original NMSU data)

### Sampling Rivers and Streams

Collecting water samples on rivers or streams downstream from a site of discharge includes at least two major factors. These are: number and locations for taking samples, and storage and transportation of samples to preserve sample integrity. Only the first factor is of concern here. The critical nature of choosing where to sample a river can be seen in figure 4 which shows general behavior of VOC in rivers. In the diagram in the river section shown, the concentration of benzene versus distance downstream from the point of discharge is plotted. Decrease in VOC concentration due to volatilization as a discharge moves downstream. This decrease in concentration is common for all VOC in all rivers. However, the rate of decrease for particular VOC on specific rivers will greatly influence a sampling program.

Development and testing of a model for loss of VOC from the river were the major results from our research. The major objective of this work was the presentation of this model in a form that chemists, engineers, laboratory managers, environmentalists, industrial personnel and others could conveniently use. With such a model, decisions on the best placement of sampling sites can be made. For example, in figure 4, collection of samples at points A, C and F would provide little detail on the decay process. However, collection of samples at A, between A and B; at B; and between B and C, would provide a more complete characterization of the environmental effect of the discharge on concentrations. The implications of our research are obvious for cities that are downstream from industrial or domestic discharges and in which the rivers are used as a source of raw water for human consumption. Although photolysis,

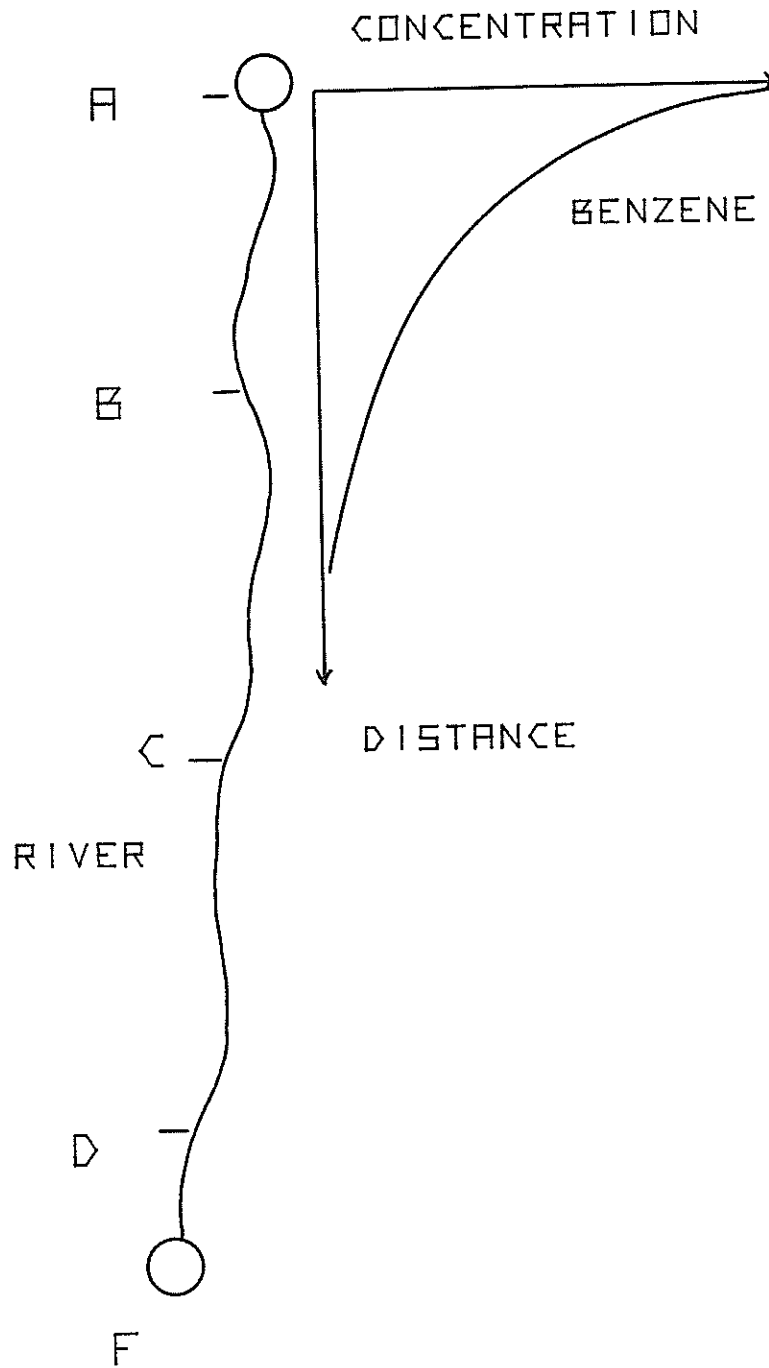


Fig. 4. Illustration of River Section with Behavior of Benzene  
River Water Concentration Plotted Relative to River Length

biodegradation and adsorption on sediment are other mechanisms for VOC loss, volatilization may be expected to be kinetically preferred for between one to seven days.

#### Volatilization from Water

In the last two years, NMSU has prepared a detailed description of volatilization of VOC from rivers. Only a summary will be presented here to emphasize major concepts and key ideas for practical use of the equations. Total movement of mass of a VOC from water to air (i.e., volatilization) is given in equation 1, where  $F$  is mass flux,  $K_L$  is liquid film diffusion coefficient,  $C_L$  is concentration of VOC in liquid,  $C_g$  is concentration of VOC in gas (atmosphere),  $T$  is temperature in °K,  $R$  is the universal gas constant, and  $H$  is Henry's Law constant.

$$F = K_L(C_L - C_g RT/H) \quad (1)$$

The diffusion coefficient for a VOC across a film is related to both the diffusion coefficient of the respective VOC in solution ( $D_L$ ) and the thickness of the film ( $\delta$ ), as opposed to the bulk of the phase as in equation 2.

$$K_L = D_L / \delta \quad (2)$$

The problem with direct application of this model to environmental systems is the tremendous uncertainty in knowing the film thickness. Film thickness is a function of river conditions. However prediction of  $D_L$  for a wide range of VOC is possible using the Wilke-Chang relationship. Almost all research on river and lake modeling has been directed toward evaluation of the film thickness. Moreover, by determining a tra-

cer compound-to-VOC ratio, the effect of film thickness can be removed as in equation 3, where  $\eta$  represents a measure of river turbulence.

$$\frac{K_L}{K_L^\circ} = \frac{D_L}{D_L^\circ} \times \frac{\delta_L^\circ}{\delta_L} = \left( \frac{D_L}{D_L^\circ} \right)^\eta \quad (3)$$

Choice of a tracer to use in a stream has been a difficult issue. Contaminants actually have been added to rivers as tracers. This was the only acceptable approach until the completion of our work. Oxygen might be expected to be a poor choice for a tracer because of its high biological and chemical reactivity. However, reaeration models based on hydrologic data can be used for any river for which such information is available. In contrast, characterization of the film thickness through addition of impurities to rivers is an untenable approach for wide-scale, practical application of models. The decrease of concentration of VOC in a river, if longitudinal diffusion is not important, is shown in equation 4.

$$C_L/C_L^i = \exp(-K_2 t (K_L/K_L^\circ)) \quad (4)$$

Where  $C_L$  is concentration of VOC in river as the discharge moves downstream,  $C_L^i$  is initial river concentration of specific VOC,  $t$  is time,  $K_2 = K_L^\circ / L$  (average depth)  $K_L$  and  $K_L^\circ$  are shown in equations 5 and 6.

$$K_L = K_L^\circ (V_b^\circ / V_b)^{0.06 \eta} \quad (5)$$

$$K_L^\circ = 5.015 v^{0.969} / L^{0.673} \quad (6)$$

Equation 5 is derived from equation 3 and the Wilke-Chang relationship. Equation 6 comes from one of many laboratory studies of oxygen reaeration completed during the 1960s. Thus, by using hydrologic properties alone, a model for rivers with different properties can be calculated. If this model can be validated on large-scale systems, including rivers, a simple, practical model would then be available to help solve problems illustrated through figure 4.

#### APPLICATION

The application and results of our model, which has been shown to be valid within 10 percent on very large-scale studies at NMSU, can be seen in figures 5 and 6. The figures clearly show the need and usefulness of these studies. They show the decay in concentration of VOC in two rivers of widely different character. The Rio Grande (figure 5) is a shallow, broad river that drops rapidly in elevation while the Tennessee River is a deep, slow-moving river which drops slightly in elevation. In addition, decay curves are shown for VOC of two extremes, methylene chloride (very volatile) and dichlorobenzene (less volatile). The behavior of all other VOC falls between these two extremes. Comparison of plots in these two figures shows two major trends:

1. Although large variations in molecular structure exist between methylene chloride and dichlorobenzene, the significance of these differences is not large in the river.
2. Differences in stream or river characteristics lead to major differences in rates of removal through volatilization. For example, in the Tennessee River, 90 percent removal occurs only after 20 to 30 days and 30 to 430 km, while similar removal in the Rio Grande occurs within 1 to 1.4 days and in only 37 to 50 km.

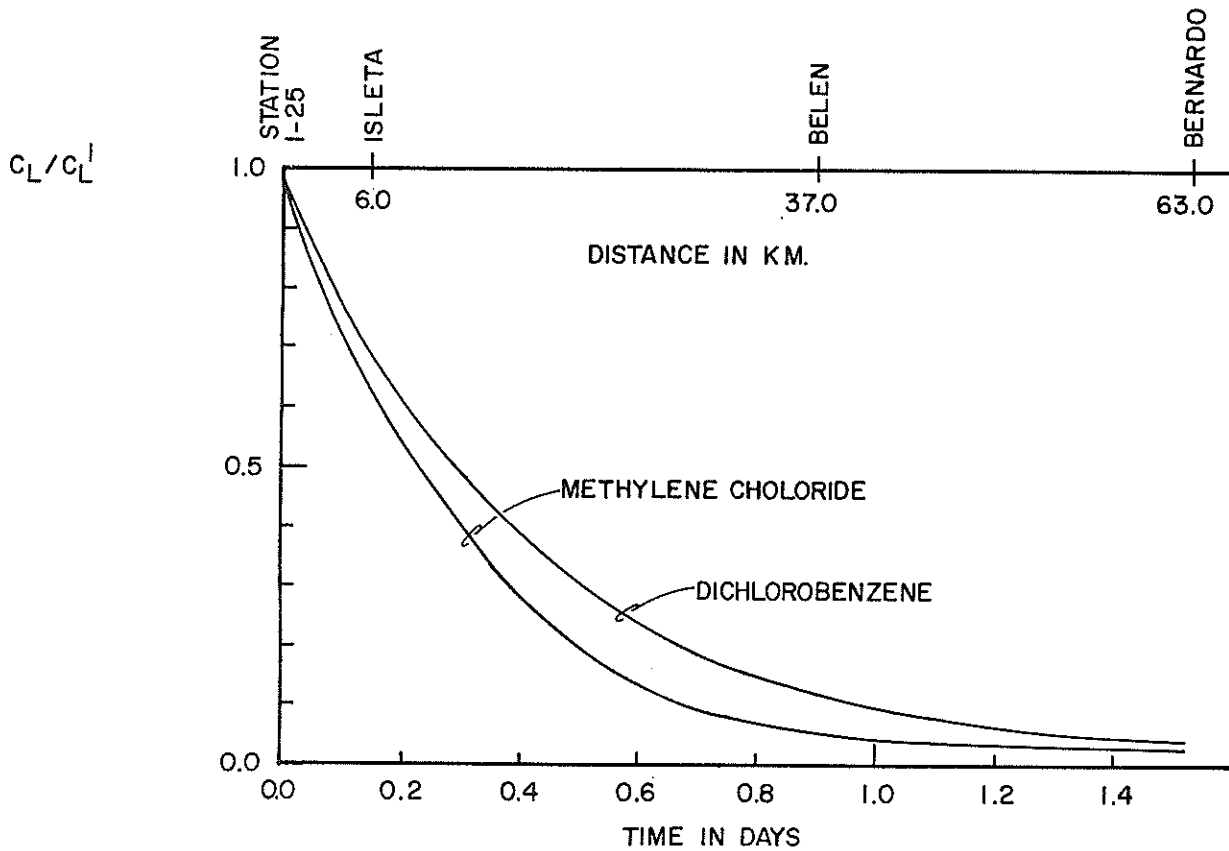


Fig. 5. Volatilization of VOC in the Rio Grande

Application of this model on the entire course of the Tennessee River would have substantial errors quantitatively because dispersion may be expected to become a major factor as the length of time a VOC is in the river is increased. Other mechanisms of removal previously mentioned (and ignored in our model) may become more significant with longer residence time of VOC in rivers.

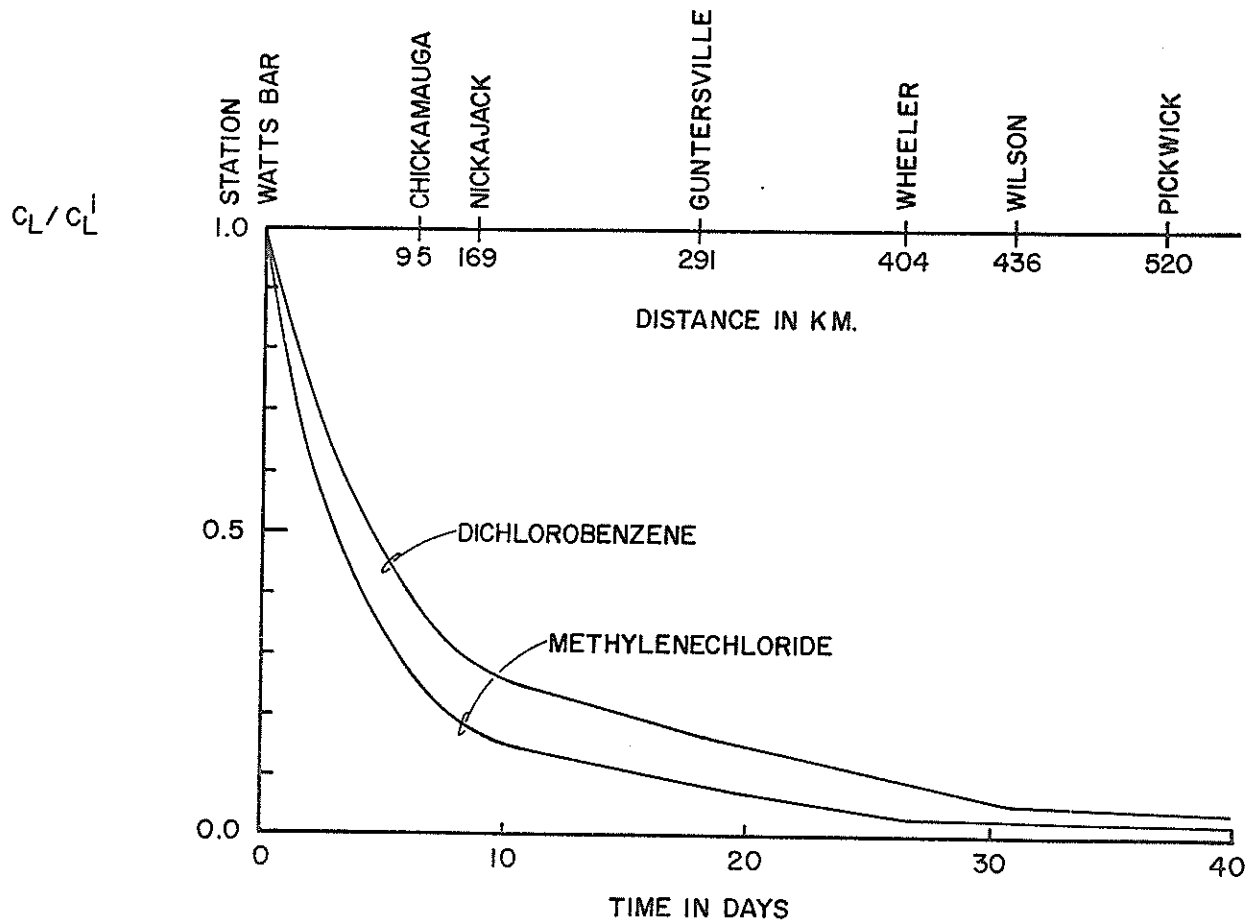


Fig. 6. Volatilization of VOC in the Tennessee River

Nevertheless, this model has been developed to aid decisions on where to sample a river. It may be used to provide a theoretical basis for choosing sites for sampling on various rivers. Field testing of the model is in progress to make fine adjustments, but our major problem here is that New Mexico rivers do not contain sufficient industrial VOC pollu-

tants for confident modeling. Use of other river systems is planned in states with more industry.

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NOTE: For reviews on analytical methods see:

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