DISCHARGE OF VOLATILE ORGANIC COMPOUNDS FROM A CONTAMINATED AQUIFER AND THEIR FATE IN A STREAM

by

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ABSTRACT

The goal of the study was to estimate how rapidly volatile organic compounds (VOCs) are discharged from a contaminated aquifer to a stream, to identify where the VOCs are discharged in the stream, to determine their fate in the stream, and to predict the biodegradation rate of a VOC in the stream. The upper reaches of the Aberjona watershed in Massachusetts, where groundwater was contaminated with VOCs, were studied.

First, the reaches of streams, where VOCs are naturally discharged, were identified and the natural flushing rates of VOCs from an aquifer to streams were estimated, employing an in-stream tracer technique. The results showed that the concentration of VOCs in the discharging groundwater as low as 0.05 μg/L of benzene was detected and the largest inflow observed was 2200 μg/L of trichloroethylene. The discharging rate of VOCs under natural conditions ranged from 5 g/yr of benzene to 43 kg/yr of trichloroethylene and to 84 kg/yr of toluene. This amount was comparable to the mass removed by on-going remedial action in the watershed.

Second, the study quantified *in-situ* volatilization and biodegradation rates of a VOC (toluene) in a stream with the use of the in-stream tracer technique. At this site, the result showed that, on the average over 14 field experiments in 2 years, dilution, volatilization and biodegradation accounted for 25%, 34% and 41%, respectively, of the decrease in toluene concentration in spring, respectively, and 8%, 26% and 66%, respectively, in summer. Volatilization rate constants of toluene were estimated as 0.62 hr^{-1} in summer and 0.20 hr^{-1} in winter, while biodegradation rate constants were 1.73 hr^{-1} in summer and 0.20 hr^{-1} in winter.

Third, the study predicted the biodegradation rate of toluene in a natural stream by adapting a biofilm kinetic model and combining laboratory experiments with the model. The results showed that the biofilm kinetic model modified in order to be applied to a natural stream successfully predicted *in-situ* biodegradation rates. The result also showed that mass transfer across the interface between bulk water and biofilm was not rate limiting and microbial kinetics appeared to be the rate limiting factor in the biodegradation of toluene at the studied site.

Thesis Supervisor: Dr. Harold F. Hemond
Title: Professor of Civil and Environmental Engineering

To my mother

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It was probably my junior year in college when I thought I might want to become an environmental scientist although my major was chemistry. My involvement in student movement at that time led me to concern about the social use of science, and environmental science seemed to serve public more directly than chemistry. However, I did not have the slightest idea that I would receive Ph.D in environmental engineering from MIT after 13 years from then. I feel I am finishing one chapter of my life. Without other people's help, this chapter could never have even begun. I would like to thank them on this page, although it is not possible to list them all.

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The widespread contamination of groundwater by volatile organic compounds (VOCs) is an issue of major public concern, and the remediation of groundwater contaminated with VOCs is often mandated by public agencies. Because of the costs involved, it is important to make sound decisions regarding remediation efforts. One of the pieces of information that is needed to know, but often unavailable, are answers to the questions, *"How rapidly are VOCs discharged from a contaminated aquifer to a stream and what is their fate in the stream?"*. Given the difficulty of extracting VOCs from groundwater and the low rates of recovery often reported for conventional remediation efforts (e.g. pump and treat) (1), it is important to put the benefits of such efforts in perspective. The research reported in this thesis addresses the natural flushing rate of contaminants from groundwater to streams, and the fate of the contaminants in the receiving streams.

The followings are specific questions to which each chapter in this thesis is addressed:

Chapter 2. a) How rapidly are contaminants discharged from an aquifer to a stream?

Because the groundwater is often discharged to surface water, VOCs in the groundwater can be naturally flushed out from a contaminated aquifer. The natural flushing of VOCs can be potentially as effective as "pump-and-treat" systems, the prevailing artificial method used to clean contaminated groundwater. Moreover, the natural flushing from groundwater to streams can conceivably be slowed down with the pump-and-treat systems if the pumping reverses the natural head difference between the groundwater and streams. Therefore, estimating the natural flushing rate is very important in order to make sound decisions about remediation.

In Chapter 2, the natural flushing rate of VOCs from groundwater to streams in the Aberjona watershed is estimated, using an in-stream tracer technique. The Aberjona watershed has been contaminated with various contaminants, including VOCs, and there are two Superfund sites in the watershed. An expensive pump-and-treat system has been employed to clean groundwater contaminated with VOCs at one

Superfund site in the watershed. The study reported in Chapter 2 compares the measured natural flushing rate of VOCs at several locations with the mass of VOCs removed by remediation efforts at the Superfund site.

Chapter 2. b) Where are the groundwater contaminants discharged?

Knowing not only how rapidly VOCs are flushed out from an aquifer, but also where they discharge to a stream is very useful information. First, the information on the discharge zone can help estimate the areal extent of groundwater contamination. Second, this information can potentially be used to more effectively locate observation well sites and monitor remediation progress. Third, the information also can help in assessing human exposure to the contaminants.

The study reported in Chapter 2 also located the discharging zone of contaminated groundwater in streams, employing an in-stream tracer technique. No previous study has used this in-stream technique to investigate the discharge of VOCs to streams, yet the technique has some advantages over conventional techniques such as: 1) ability to incorporate the heterogeneity of the inflow with very simple instruments and 2) no need to install any meters in the bottom of stream bed.

Chapter 3. What is the fate of VOCs discharged to surface waters?

Once the VOCs are discharged to surfacewater, they are potentially affected by physical, chemical, and biological processes. The information on the fate of VOCs can be valuable to assess the ecological impact of the contaminants, as well as to assess human exposure. It can also help investigating the VOCs volatilized from streams as a source of VOCs in air. It has been indicated that, although many ambient VOC measurements had been made, little information was available to relate them to their sources (2).

Not many studies on the fate of VOCs in streams have been conducted, partly because volatilization is often assumed to be the dominant removal process in streams. However, biodegradation of a VOC (toluene in this study) can be as important as volatilization in favorable environmental conditions. Most of the previous studies (1, 3, 4) were performed in the way that water and soil samples were taken from a contaminated site and the disappearance of VOCs of interest was observed in the laboratory and the laboratory data were extrapolated to model the fate of VOCs in the field. A few studies of *in-situ* biodegradation (4, 5) have been done. Field measurements, as reported in Chapter 3, are essential to verify whether such laboratory studies are applicable to processes occurring in nature. It is very hard in laboratory studies to include all the complex interactions and represent *in-situ* environmental conditions. Extrapolating the laboratory studies to predict the fate of VOCs in field can easily fail without investigating them in the field.

The study reported in Chapter 3 investigated the fate of toluene in a stream and determined *in-situ* biodegradation and volatilization rate of toluene directly in the field site, using the in-stream tracer technique. This study also illustrated the suitability of microcosms in extrapolating the laboratory result to predict the fate of toluene in a field condition in conjunction with the study of Cohen et al.(6).

Chapter 4. How can we predict the biodegradation rate of a VOC in a natural stream?

In-situ biodegradation of contaminants by attached microorganisms can play a major role in alleviating contamination of shallow streams (7-10). In the study reported in Chapter 3, the biodegradation by attached microorganisms was also found to be the most significant degradation process of toluene. It is, therefore, essential to quantify *in-situ* biodegradation rates in order to understand the fate of a chemical in streams. Although it is more accurate to determine the biodegradation rate in the field directly as reported in Chapter 3, it is often difficult to separate the biodegradation process because a variety of transformation and transport processes typically contribute to a contaminant's disappearance. Also, it often takes much more resources to conduct field experiments than laboratory experiments. Because of these difficulties, *in-situ* biodegradation rates often have to be estimated by extrapolation from the results of laboratory microcosm studies.

Generally, two approaches have been taken to predict *in-situ* biodegradation rates of a contaminant on the basis of laboratory microcosm studies. One approach is to know the important environmental conditions such as temperature, nutrient and oxygen levels *a priori* and reproduce them in the laboratory microcosms (6, 9, 11-14); such a method, however, does not provide any basis for predicting biodegradation under altered conditions. A second method is to employ a kinetic model to quantify the environmental parameters and calculate the *in-situ* biodegradation rates with the parameters appropriate for the field conditions. Many researchers have applied biofilm kinetic models to natural biofilms in shallow streams in order to predict the biodegradation rates of organic carbon (8, 15-17) or nitrogen (18) or organic compound (19). However, no study that applied the biofilm kinetic model in predicting the removal rates of a volatile organic compound in a natural stream has been reported to this date.

The study reported in Chapter 4 developed a tool to estimate the *in-situ* biodegradation rates of toluene in a stream by adapting a biofilm kinetic model with parameters obtainable from batch culture experiments, field measurements and the use of existing equations. The study compared the estimated rates with the actual *in-situ* rates measured in the field as reported in Chapter 3. The study also determined the limiting process of the toluene biodegradation.

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Chapter 2. Natural Discharging of VOCs from a Contaminated Aquifer to Surface Waters on a Massachusetts Watershed

Abstract

The concentrations and total fluxes of volatile organic compounds (VOCs) in the groundwater discharging to streams were measured throughout 2 years, with spatial resolution ranging from tens to hundreds of meters in the headwaters of a heavily industrial watershed in Massachusetts. Concentrations and fluxes of VOCs discharged via groundwater to each stream reach were determined by measuring the concentrations of VOCs and two injected tracers (one conservative, the other volatile) and simultaneously solving the mass balance equations for the tracers and VOCs in the reach. Concentrations in the inflow as low as 0.05 μg/L of benzene could be reliably detected in East Drainage Ditch; the largest inflow observed was 2200 μg/L of trichloroethylene in Sweetwater Brook. The natural discharging rate of the identified VOCs from all the tested sites was estimated to be 140 kg/yr. This amount was comparable to the mass of VOCs removed by remediation efforts at two locations in a Superfund site in the watershed. The results are pertinent both for locating sources of groundwater contamination and for assessing discharging rates of contaminated aquifers under natural gradient conditions.

Introduction

Volatile organic compounds (VOCs) are among the most widely distributed and problematic categories of contaminants in groundwater. The remediation of groundwater contaminated with VOCs is often mandated by public agencies. However, it has been questioned if current technologies could ever restore groundwater to a state clean enough to justify the high cost, since the inherent complexities of the Earth's subsurface and the characteristics of the contaminants make remediation exceedingly difficult at many sites [1].

Because of the difficulties of remediation, natural discharging of contaminants from a contaminated aquifer could be potentially as effective as remediation in removing VOCs from a contaminated aquifer. Since the groundwater is often discharged to surfacewater, VOCs in the groundwater can be naturally flushed out from the contaminated aquifer. The natural discharging of VOCs may be significant under certain conditions. Pump-and-treat systems, the most prevailing method to clean contaminated groundwater in the United States, could even slow down the natural discharging of VOCs by altering the natural head difference between the groundwater and streams. Therefore, estimating natural discharging rate of VOCs from the contaminated aquifer can be important in making sound decisions regarding the remediation.

In this work, we investigate the natural discharging of VOCs in contaminated groundwater in the upper reaches of the Aberjona watershed, a heavily industrialized catchment 25 square miles in area, located 15 km north of Boston, and including parts of the towns of Woburn, Reading, Wilmington, Burlington, Lexington, Winchester, and Stoneham (Fig. 2.1). Chemical wastes of industrial origin have been discharged into the Aberjona watershed for over 150 years, chemical contamination is documented at over 50 sites, and two Superfund sites have been designated in the watershed. Specially, contamination of groundwater with VOCs has been a major public concern in this watershed and expensive pump-and-treat systems have been employed at two locations in one Superfund site (Well G & H area) since 1993 in order to remove the VOCs from contaminated groundwater.

The objectives of this work are: to assess discharging rates of contaminants under natural gradient conditions, to determine whether the natural discharging can be significant in comparison to the artificial remediation, and to identify locations on the watershed where the discharge of contaminated groundwater occurs.

Background

Commonly, the characteristics of discharging groundwater have been measured by analyzing water samples obtained from water sampling devices installed in the streambed. Lee et al. [2, 3] used seepage meters to measure seepage fluxes of groundwater to overlying surface water and to collect samples of the seeping water for water quality analyses. Fusillo et al. [4] used minipiezometers to collect samples of the ground water immediately beneath a streambed, and measured the VOCs in the about-to-be-discharged water. Avery et al. [5] used both well points driven into a river bottom, and seepage meters, to determine the concentration of VOCs in the groundwater discharged to the Rock River in Illinois. As an alternative to more conventional chemical analysis, Vroblesky et al. [6] used vapor samplers composed of activated carbon fused to a ferromagnetic wire in a test tube to collect VOCs in bottom sediment and thus infer the concentrations of specific contaminants in the discharging groundwater.

Such methods can provide high spatial resolution in the measurement of VOC concentrations in the streambed. However, they are best suited to the determination of patterns of concentration, and require (except in the case of seepage meters) separate discharge measurements if VOC fluxes are to be determined. Moreover, heterogeneity on scales of a few meters or less can be expected to be a major source of variability in making inferences about a whole reach of stream from a few point measurements. Thus, there is a need for a method that 1) determines both total flux and concentration, and 2) integrates over reaches of stream (with a spatial resolution of the order of perhaps tens of meters).

In-stream tracers provide a basis for integrated flux measurements, and have the additional benefit of not requiring disturbance of the stream bottom. This can be especially helpful if access to a stream is hindered, or if installing seepage meters and piezometers is difficult due to bottom conditions. The use of in-stream tracer techniques to measure inflows of naturally-occurring substances has been documented by Genereux and Hemond [7], who used introduced tracers to determine levels of ^{222}Rn, an indicator of hydrologic flow path, entering a stream under conditions of steady flow. In this method, the average concentration of a volatile chemical in water feeding a given stream reach is determined by measuring the concentrations of the chemical and two injected tracers (one conservative, the other volatile) in the stream water, and solving the coupled mass balance equations for all three in the reach of interest. Mass balance for each substance is expressed as follows [7]:

$$\frac{dC}{dx}=\frac{q}{Q}C_q-\left(\frac{q}{Q}+\frac{k_v}{U}\right)C \qquad (2.1)$$

where C is concentration of a VOC in the stream [μg/L], x is distance along the stream [m], q is lateral inflow rate [L/s/m], C_q is concentration of the VOC in lateral inflow [μg/L], Q is stream discharge rate [L/s], U is stream velocity [m/s], and k_v is gas exchange coefficient for the VOC [sec^{-1}].

In essence, evaluating all other terms of the mass balance of conservative tracer enables the determination of q. Incorporation of q into mass balance of the volatile tracer then permits the determination of k_v. It is convenient, but not essential, that the volatile tracer has a gas exchange coefficient identical to that of the substance of interest. Several researchers have shown that the ratio of the volatilization rate constant of high-volatility compounds to the oxygen reaeration rate constant measured in the laboratory is a constant for a range of turbulence levels readily achieved in the laboratory [8, 9]. Knowing the ratio of the volatilization rate of a volatile organic compound to that of a volatile tracer and measuring the volatilization rate of the tracer in a stream can thus give the estimation of the volatilization rate of the volatile organic compound of interest in the stream, and thereby permit calculation of C_q, the lateral inflow concentration of the compound.

Methods

Study Sites

The streams studied were in the upper portion of the Aberjona River watershed. Two reaches of Landfill Creek, three reaches of the East Drainage Ditch, one reach of the upper Aberjona River, and one reach of Sweetwater Brook were investigated (Fig. 2.1). The stream reaches were selected, after reconnaissance of streams in the watershed, for the presence of elevated concentrations of VOCs and the low stream flowrates (Fig. 2.2). A reach of the East Drainage Ditch (II) and the Sweetwater Brook were studied intensively at all seasons of the year. Other sites were studied less intensively. The characteristics of each site are summarized in Table 2.1.

Tracer Methodology

Genereux and Hemond [7] present a detailed derivation of expressions from which the flowrates, the lateral inflow rate, and the concentration of a chemical in water entering a reach of stream are determined from concentration measurements of stream water together with measurements of the two deliberately introduced tracers. The results are:

$$Q_i = \frac{Q_{inj} C_{inj}}{\alpha S_i} \tag{2.2}$$

$$q_{ij}=\frac{C_{inj}Q_{inj}}{\alpha\,\Delta x_{ij}}\left(\frac{1}{S_j}-\frac{1}{S_i}\right) \tag{2.3}$$

$$C_{ij}^{x}=\frac{S_iC_j^{x}-S_jC_i^{x}+\frac{1}{4}(S_j+S_i)(C^{x_j}+C^{x_i})\lambda^{x}\ln\left(\frac{G_iS_j}{G_jS_i}\right)}{S_i-S_j} \tag{2.4}$$

where Q_i is the flowrate at the ith station [L/s], Q_{inj} is injection rate of salt solution [L/s], C_{inj} is concentration of injected salt solution [M], α is the response factor of the conductivity reading to the concentration of salt solution [M/μS], S_i is the increase in specific conductivity at station i after the injection of salt solution [μS], q_{ij} is groundwater lateral inflow between station i and j [L/m/s], Δx_{ij} is distance between the ith and jth station [m], C_{ij}^{x} is concentration of a VOC, x, in the inflow between station i and j [μg/L], C_j^{x} is the concentration of a VOC, x, found at station j [μg/L], G_i is concentration of propane at station i [μg/L], and λ^{x} is the ratio of the volatilization rate constant of a VOC, x, to propane.

Field Methodology

One or more continuous stream reaches, from several tens to a few hundreds of meters in length and relatively homogeneous in appearance, were chosen for study at each site. Measurements were made at the upstream and downstream end of each reach. An effort was made to avoid placing measuring stations where large groundwater discharge occurred, in order to minimize any error due to incomplete transverse mixing (locations of large groundwater inflow generally became evident after one or two field experiments). The total length of stream studied was restricted to lengths that would attain steady state with respect to the introduced tracers within 6 to 7 hours. The first measuring station was located sufficiently far downstream of the tracer injection point to allow an adequate mixing zone.

The conservative tracer (NaCl) solution was 3 M to 5 M food grade salt injected from a 50-L Mariotte bottle. The injection rate was adjusted by choice of orifice (orifices are made of disposable pipette tips by cutting off the ends in various lengths). Tracer injection rates varied from 200 ml/min to 600 ml/min, depending on streamflow.

Propane gas, the volatile tracer, was bubbled into the stream through a glass frit (pore size 5-15 μm, 1.3 cm diameter) at a constant pressure between 3-80 kPa, depending on stream flow rate. About 0.5 kg/hr of propane was typically used. The biodegradability of propane was tested and found to be negligible and thus the propane gas could serve as a volatile tracer [10]. It was also shown in the same study [10] that the attenuation of trichloroethylene concentration due to volatilization was well predicted in a stream with using the propane gas as a volatile tracer.

The background value of conductivity was measured at all stations for about 10 minutes before the injection of tracers begins, using a portable conductivity meter (Amber Science Digital Conductivity Meter, model 604). After the injection of tracers began, the conductivities at each station were measured every 30 seconds until the conductivity values reach a steady state.

After steady state was reached, water samples were taken at each station in 300-mL BOD bottles, preserved with 2.4 ml of 3.5 % mercuric chloride solution, for the analysis of VOC in the laboratory.

In general, the ratio of the volatilization rate constant of a VOC of interest to that of propane (the deliberately introduced volatile tracer), λ, is not unity. To estimate the ratio of the volatilization rate constant of a VOC of interest to that of propane, we used ratios from the study of Smith et al. [9] where possible, and calculated the ratio for other VOCs on the basis of their diffusion coefficients in water. The calculation was done in two different ways: (1) k_v proportional to the molecular diffusion coefficients, consistent with thin film theory, and (2) k_v proportional to the square root of the ratio of molecular diffusion coefficients, following surface-renewal theory. The two values were taken as the maximum and the minimum values of the ratio of volatilization rate constants. The ratios are listed in Table 2.2.

Finally, the concentration of VOCs in the lateral inflow was calculated by Eqn (2.3). The errors associated with flow rates were calculated conservatively, as presented in [11].

VOC analysis

80 ml water samples were purged by helium for 30 minutes and trapped in a Supelco Volatile Purge Trap packed with 60/80 Chromosorb (US EPA Method 601), and VOCs are thermally desorbed at 180 °C for 4 minutes and transferred to the analytical column by carrier gas flow. Analysis was done using a Perkin-Elmer 3920B Gas Chromatograph [flame ionization detector, Helium carrier, 8'x1/8" OD stainless steel packed column (Supelco 60/80 Carbopack B/1% SP-1000)] with a temperature program [30 °C start, ramp to 210 °C at 8 °C per minute]. The GC was calibrated with standard solutions containing methylene chloride, 1,1-dichloroethane, chloroform, 1,1-dichloroethene, 1,2-dichloroethene, 1,1,1-trichloroethane, carbon tetrachloride, 1,2-dichloropropane, 1,3-dichloropropene, trichloroethylene, benzene, toluene, chlorobenzene, and ethyl benzene. The detection limits are approximately 0.1 μg/L, depending on compounds. Samples were analyzed at most within 2 days of collection. The reproducibility was examined by analyzing triplicate standards and shown to be less than $\pm$ 5%.

Results

Sweetwater Brook

Hydraulics. The Sweetwater Brook site was divided into from 3 to 5 reaches and studied over a 2-year interval. Typical flowrates between 66 m and 550 m downstream from SWBK 2950 were approximately 60 L/s in spring, about half this value in summer and fall. Only one datum, 46 L/s, was available in winter.

Sweetwater Brook showed persistent lateral inflow in the second and third upstream subreach (between 33 m and 116 m from SWBK 2950) on most of experiment dates (Fig. 2.3). There was much less lateral inflow in the fourth and fifth downstream subreaches (between 116 m and 550 m from SWBK 2950) than in the upstream reaches. When the fifth subreach was subdivided for measurement purposes, it was found that most of the lateral inflow occurred in the upper portion of the downstream reaches, between 217 m and 283 m from SWBK 2950 (data not shown).

VOCs. Trichloroethylene (TCE) was the VOC of highest concentration in surfacewater at the Sweetwater Brook site, ranging from 10 to 40 μg/L. This finding suggested that a source of contamination might be located within the immediate vicinity of the brook. TCE and 1,2-DCE (1,2-dichloroethene) showed their highest concentrations at 66 m or 116 m downstream from SWBK 2950 on all experiments. Over the course of the study, the concentration of TCE at 66 m increased steadily from 0.1 μg/L on 6/3/91 to 33 μg/L on 11/14/92. It became evident that there was not only inflow of TCE between 66 m and 116 m, but there was an increasing inflow between 33 m and 66 m throughout the period of the study.

The concentrations of VOCs in the inflow between 33 m and 66 m were not measured until April, 1992, after which they reached values as high as 2200 μg/L for TCE (Fig. 2.4a) and 200 μg/L for 1,2-DCE (Fig. 2.4b). The concentrations of TCE and 1,2-DCE in the inflow of the reach between 66 m and 116 m ranged up to 460 μg/L (Fig. 2.4a) and 49 μg/L (Fig. 2.4b), respectively. This finding is consistent with earlier observations of TCE in this stream in the range of concentration of 10 to 150 μg/L, and 2290 μg/L reported in groundwater in an adjacent well [12]. There were no detectable inflows of VOCs in other reaches (downstream from 116 m), despite the presence of groundwater inflows in the reach between 217 m and 550 m.

East Drainage Ditch I

This reach is the furthest upstream among the studied reaches in the East Drainage Ditch. The lateral inflow was very low, only 0.011 L/s/m; VOC concentrations were 23 μg/L of 1,1,1-trichloroethane and 12 μg/L of trichloroethylene (Fig. 2.7b). While the next downstream study site (East Drainage Ditch II) showed very high concentrations of toluene which were evidently originating upstream, toluene was not found in East Drainage Ditch I, suggesting that the source of toluene is between this reach and East Drainage Ditch II.

East Drainage Ditch II

Hydraulics. This site was divided into three reaches of equal length except on 9/28/91 and 10/27/91, when the first upstream reach was further divided into three subreaches. The flowrates at this site varied from 5 L/s to 42 L/s; average flowrates over spring, summer, fall and winter months were 23, 9, 15 and 15 L/s, respectively.

The first reach between 0 to 134 m typically showed the highest lateral inflow rates among the three reaches (Fig. 2.5). In the first upstream reach between 0 and 134 m, the inflows ranged from undetectable (5/30/92) to 0.053 L/s/m (5/3/92). When this first reach was treated as 3 subreaches on 9/28/91, most of the inflow (0.025 L/s/m) occurred in the second subreach (between 44 and 88 m); inflow in the first subreach (between 0 m and 44 m) was 0.014 L/s/m and inflow in the third reach (between 88 m and 133 m) was 0.0023 L/s/m. On 10/27/91, none of the three subreaches between 0 and 133 m showed measurable inflows.

In the second reach, the inflows varied from undetectable (1/29/92 and 5/3/92) to 0.017 L/s/m (11/25/90) (Fig. 2.5). In the last downstream reach between 266 m and 400 m downstream from EDDW 4800, the inflows range from undetectable (11/25/90, 9/28/91 and 5/3/92) to 0.010 L/s/m (7/19/92).

VOCs. A high diversity of VOCs was found in this site. VOCs in the stream in this study area were 1,1-dichloroethane (DCA), 1,2-dichloroethene (DCE), 1,1,1-trichloroethane (TCA), carbon tetrachloride (CCl_4), trichloroethylene (TCE), benzene, and toluene. Toluene was the VOC of highest concentration in streamwater, ranging from 59 μg/L to 380 μg/L at EDDW 4800 [10(Ch.3 in this thesis)]. Carbon tetrachloride, 1,2-DCE and TCE occurred in the range between 10 and 100 μg/L. The concentrations of 1,1-dichloroethane and benzene in this stream were lower, ranging from 0.5 to 13 μg/L and from less than 0.05 to 3.1 μg/L, respectively.

In all experiments, the inflow in the first upstream subreach (between 0 and

133 m downstream from EDDW 4800) contained the highest levels of chlorinated VOCs, including DCA, DCE, TCA, CCl_4 and TCE (Fig.2.6). The most abundant were TCE and 1,2-DCE. Significantly, despite the high levels of toluene at this site, inflow of toluene could not be demonstrated; in this subreach, the major source appears to lie upstream.

Only two experiments, on 7/3/90 and 7/19/92, showed VOCs in the inflow of the second subreach in addition to the first reach (Fig. 2.6). One experiment, on 3/1/92, showed the inflow of VOCs in the last downstream reach, and TCA was the only VOC in the inflow.

East Drainage Ditch III

East Drainage Ditch III showed the highest hydraulic inflow, 0.27 L/s/m, measured anywhere in the stream (Fig. 2.7a). This portion of the East Drainage Ditch also showed low concentrations of VOCs in the inflow, 2.2 μg/L of trichloroethylene and 0.05 μg/L of benzene (Fig. 2.7a).

Aberjona River

The Aberjona River site is directly downstream of the Industriplex Superfund site. This site showed a small groundwater inflow (0.009 L/s/m), containing only 2.3 μg/L of 1,1,1-trichloroethane (Fig. 2.7c), even though some of the groundwater in the nearby Industriplex site is highly contaminated with VOCs [13].

Landfill Creek I

The Landfill Creek site, as its name suggests, drains a now-closed landfill site. This site showed less inflow (0.02 L/s/m) than the downstream reach (Landfill Creek II); however, the inflow contained 1,1,1-TCA and 1,1-DCA (Fig. 2.7e).

Landfill Creek II

This site is downstream of Landfill Creek I. Landfill Creek II was studied as two reaches on 10/16/90 and as one reach on 9/25/90. The result shown in Fig. 2.7d was obtained from the experiment on 10/16/90. The upstream and downstream reaches showed 0.09 L/s/m and 0.02 L/s/m of inflow, respectively (Fig. 2.7d). Benzene and chlorobenzene were found in the inflow in the upstream subreach but no inflow of VOCs was found in the downstream subreach (Fig. 2.7d). There was no noticeable inflow in the whole reach on 9/25/90.

Discussion

Relation of VOC discharge to adjacent groundwater contamination

The discharge of VOCs indicated the contamination of nearby groundwater and the flow of groundwater. Groundwater near the reach of East Drainage Ditch I (Olin Chemical site in Fig. 2.8) was shown to be contaminated with various VOCs including TCA (6 μg/L on average from over 70 monitoring wells, 22 μg/L of maximum), TCE (20 μg/L on average, 460 μg/L maximum), benzene (11 μg/L on average, 120 μg/L maximum) and toluene (300 μg/L on average, 12000 μg/L maximum) [14]. For comparison, our study showed the discharge of TCA and TCE at East Drainage Ditch I (Fig. 2.8). This is consistent with the finding of Altevogt [15] which detected 1,1,1-TCA in soil gas alongside this stream.

It was shown that toluene was discharged to the reach between East Drainage Ditch I and II (Fig. 2.8). Although the groundwater in the southern part of Industriplex Superfund site (Fig. 2.8) has been found to be contaminated with benzene (48 mg/L) and toluene (29 mg/L) [13], the source of toluene in this stream may not be related to the Industriplex site. That is because 1) the hydraulic gradient in this area indicates that the groundwater flows from northeast to southwest; thus the source of toluene discharged into this stream is suggested to lie north of the Industriplex site, and 2) benzene was found at a much lower level (in the range of 1 μg/L) in this stream while toluene was at a very high level (>100 μg/L), unlike groundwater in the Industriplex site. However, groundwater in a nearby state-identified hazardous waste site (Ritter Trucking Company site in Fig. 2.8) was shown to be more contaminated with toluene (1300 μg/L, [16]) and much less with benzene (200 μg/L,

[16]). Although a conclusive connection can not be made, the contamination of groundwater with toluene at this site is consistent with our finding of the continuous discharge of toluene from groundwater to this stream reach.

TCA was a common VOC discharged from groundwater in the upper section of the watershed, including East Drainage Ditch I and II, Aberjona River, and Landfill Creek I. This is consistent with results of investigations at many chemical disposal sites in this area, which have documented contamination of groundwater with TCA and DCA [16-19].

At Sweetwater Brook, our finding of the discharge of DCE and TCE to the reach of Sweetwater Brook was consistent with contamination reported in nearby groundwater [20]. It has been reported that TCE can be biodegraded to DCE under methanogenic conditions [21], and some researchers have reported that the ratio of the concentration of DCE to the concentration of TCE was higher in the streambed-water sample than in the ground water samples, as a result of the dechlorination of TCE [4]. We do not have a strong evidence for this at this site, although we have found that the ratio of the concentration of DCE to TCE in the inflow (approximately 0.1) was higher than the ratio of the concentration of DCE to TCE in a nearby monitoring well (0.04 from 90 μg/L of DCE and 2300 μg/L of TCE, [22]). The difference was small and it could be due to different retardation factors for TCE and DCE, not the dechlorination of TCE.

A new source of TCE and DCE contamination in the Sweetwater Brook (the reach between 33 and 66 m) was found during the course of this study. Concentrations of TCE and DCE discharged to this reach were found to be higher than those discharged to a downstream reach between 66 m and 116 m (Fig. 2.4)

At Sweetwater Brook, the concentration of TCE in the inflow has changed along with that of DCE over the course of the experiments (Fig. 2.4). This suggests that the source of TCE is likely to be related to the source of DCE. However, at East Drainage Ditch II, the increase in concentrations of some VOCs in the inflow did not necessarily accompany the increase in concentrations of other VOCs in the inflow. While the concentration of TCE in the inflow in the first subreach (0-134 m) change with the concentration of DCE, the concentrations of carbon tetrachloride, DCA and TCA in the inflow do not change along with the concentration of TCE and DCE (Fig. 2.6). This suggests that the source of TCE may be related to the source of DCE but not related to the source of carbon tetrachloride, TCA or DCA.

Spatial variability of groundwater inflow

Groundwater inflow rates in the upper Aberjona Watershed were found to vary greatly, not only from stream to stream but from reach to reach within streams. Such high spatial variability was not expected, since the sites studied appear relatively homogeneous in their geological characteristics [23]. Although there have not been much data to compare the spatial variability of our findings with that of elsewhere, a high degree of heterogeneity in lateral inflow has been also found at Walker Branch [3, 24-26]; however, the geological setting at Walker Branch appears to be much more heterogeneous than the Aberjona Valley.

Comparison of natural discharge from the aquifer and remedial efforts

From the concentrations of VOCs in groundwater discharged to surface water and the corresponding lateral inflow rates, it was estimated that the natural discharging rate of VOCs in the studied sites ranged from 5 g/yr of benzene to 43 kg/yr of trichloroethylene to 84 kg/yr of toluene (Fig. 2.8). Although toluene concentration in the inflow at East Drainage Ditch was not estimated, the mass of toluene discharged to the stream per year was obtained by multiplying the concentration of toluene by the corresponding flow rate of the reach (EDDW 4800) reported in a previous study (200 μg/L and 15 L/s on average, [10]) since most of toluene present at EDDW 4800 was discharged from groundwater to within 100 m upstream from EDDW 4800. The natural discharging rate of the VOCs identified by this study in all of the experiment sites was estimated to be 140 kg/yr.

The authors are not aware of on-going remediation to remove VOCs from groundwater near the studied sites. However, there has been remedial action to clean groundwater at other locations within the watershed (e.g. Well G & H Superfund site,

Fig. 2.8). At the Well G & H Superfund site, the remedial action removed 16 kg of total VOCs from groundwater over two years at one location (W.R.Grace site, [27, 28]) and 16 kg of TCE and 300 kg of tetrachloroethene from groundwater for two years at another location [Unifirst site, 29, 30]. For comparison, TCE removal by natural discharging at the Sweetwater Brook site was shown to approximate 90 kg over 2 years in our study.

These results show that natural discharging is significant in removing VOCs from the aquifer. However, the pump and treat system, which is commonly employed to clean up contaminated groundwater, can potentially slow down the natural discharging rate since it can reverse the head difference between streams and groundwater. It is recommended to consider natural discharging in making decisions regarding remediation by estimating the natural discharging rates under natural conditions, determining the significance of the natural discharging in cleaning the contaminated groundwater, and investigating if employing the pump and treatment system would delay the natural discharging at a contaminated site. In certain cases, it may be best to leave the contaminated aquifer to flush out by itself, considering the cost of remediation and the difficulties of restoring contaminated groundwater.

Conclusion

Our study has shown that the discharge of VOCs from groundwater to streams indicated contamination of groundwater at nearby sites. This study found a new source of VOCs at one site over the course of experiments. Our study also showed that the discharge of VOCs from groundwater to streams under natural conditions could be as effective as remediation in removing VOCs from a contaminated aquifer. Therefore, it would be worth considering the natural discharging of contaminants in planning remedial action.

Acknowledgment

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Table 2.1. Characteristics of Study Sites

Studied Stream		Experiment Date	Length of Reach (m)	Sum of Concentration Ranges of Identifed VOCs (μg/L)	Characteristics
East Drainage Ditch	I	10/27/90	100	higher than 100	1. man-made ditch. 2. highly contaminated with VOCs at site II and III. 3. very high concentration of toluene at site II. 4. muddy sediment at site III. 5. stream bottom filled with gravel and sand at site II.
(EDDW 4800[a])	II	7/3/90-9/20/92	400	higher than 100	
	III	10/1/90	120	higher than 10 less than 100	
Landfill Creek	I	9/23/90	30	less than 10	1. An old landfill site is nearby. 2. Site II is not a confined stream but a type of wetland. 3. Site I is well-confined stream. 4. muddy sediment
	II	10/16/90, 9/25/90	120	less than 10	
Aberjona River		8/11/90	170	less than 10	1. included in "Industriplex" Superfund site 2. pebbly bottom 3. well-constrained stream
Sweetwater Brook (SWBK 2950[b])		6/13/90-11/14/92	550	less than 100 higher than 10	1. distinguished inflow of TCE 2. well-constrained stream with hard bottom 3. Several drainage pipes are connected to stream.

a. The most upstream measuring station was named as EDDW 4800, which was at 4800 ft upstream from the confluence between the East Drainage Ditch and the Halls Brook. The measuring stations were placed at 0 m, 134 m, 268 m and 402 m downstream from EDDW 4800 on most of experiments.

b. The most upstream measuring station in this site was named as SWBK 2950, which was at 2950 ft upstream from the confluence between the Sweetwater Brook and the

Aberjona River. The measuring stations were placed at 0 m, 33 m, 66 m, 116 m, 217 m and 550 m downstream from SWBK 2950 on most of experiments.

Table 2.2. Ratios of Volatilization Rate Constants of VOCs to Propane (λ)

Volatile Organic Compounds	k_v (chemical) / k_v (propane)
carbon tetrachloride	0.88 ± 0.10[a]
chloroform	0.79 ± 0.07[a]
1,1-dichloroethane	0.99 ± 0.15[a]
1,2-dichloroethene	0.92 ± 0.30[b,d]
tetrachloroethylene	0.72 ± 0.13[a]
trichloroethylene	0.79 ± 0.21[a]
1,1,1-trichloroethane	0.92 ± 0.14[b,d]
benzene	0.78 ± 0.04[a]
toluene	0.86 ± 0.05[c,d]
chlorobenzene	0.73 ± 0.04[b,d]
ethylbenzene	0.62 ± 0.05[b,d]

a. taken from [9].

b. calculated from molecular diffusion coefficients; molecular diffusion coefficients based on [31].

c. calculated from molecular diffusion coefficients; molecular diffusion coefficients based on [32].

d. The uncertainty range was obtained by employing the exponential factor of the ratio of molecular diffusion coefficients of two compounds to range from 1/2 to 1 (see text for details).

Fig. 2.1. Study Site Location Map
(source: [33]. The heavy bar indicates the boundary of the watershed.)

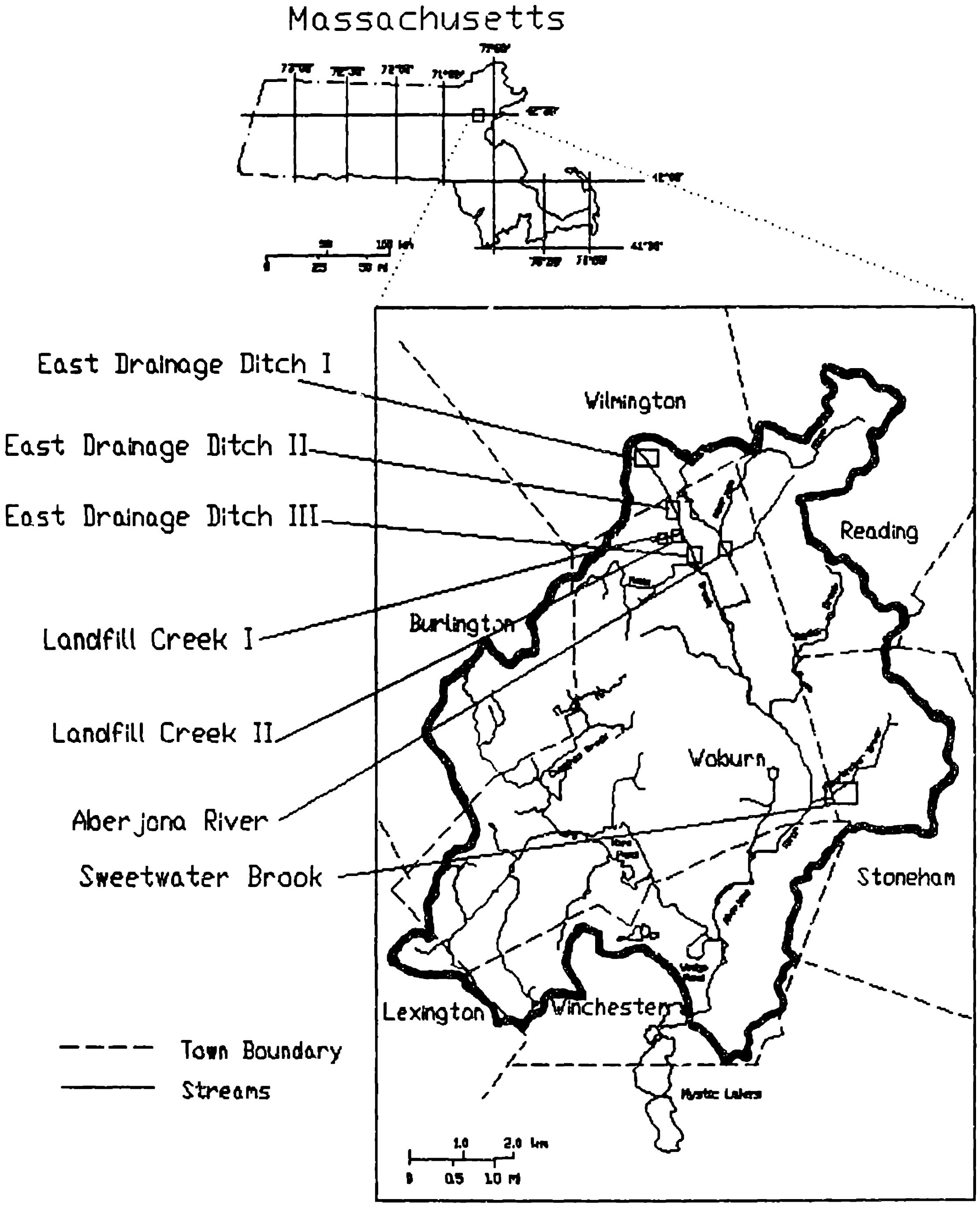


Fig. 2.2. Volatile Organic Compounds in Surfacewater and Groundwater[a]
(a: Groundwater data were obtained from [20]. The heavy bar indicates the boundary of the watershed.)

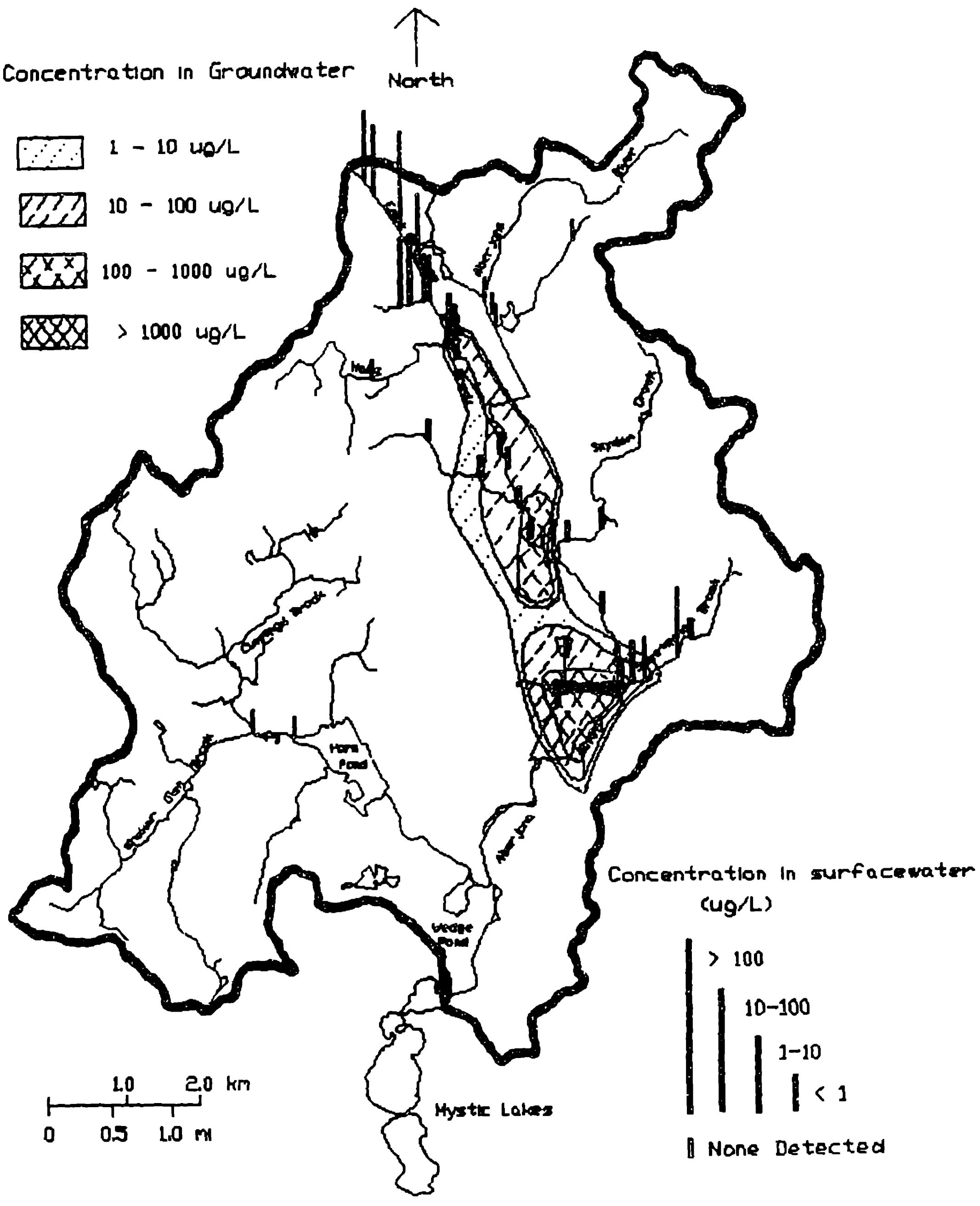


Fig. 2.3. Lateral Inflow at Sweetwater Brook

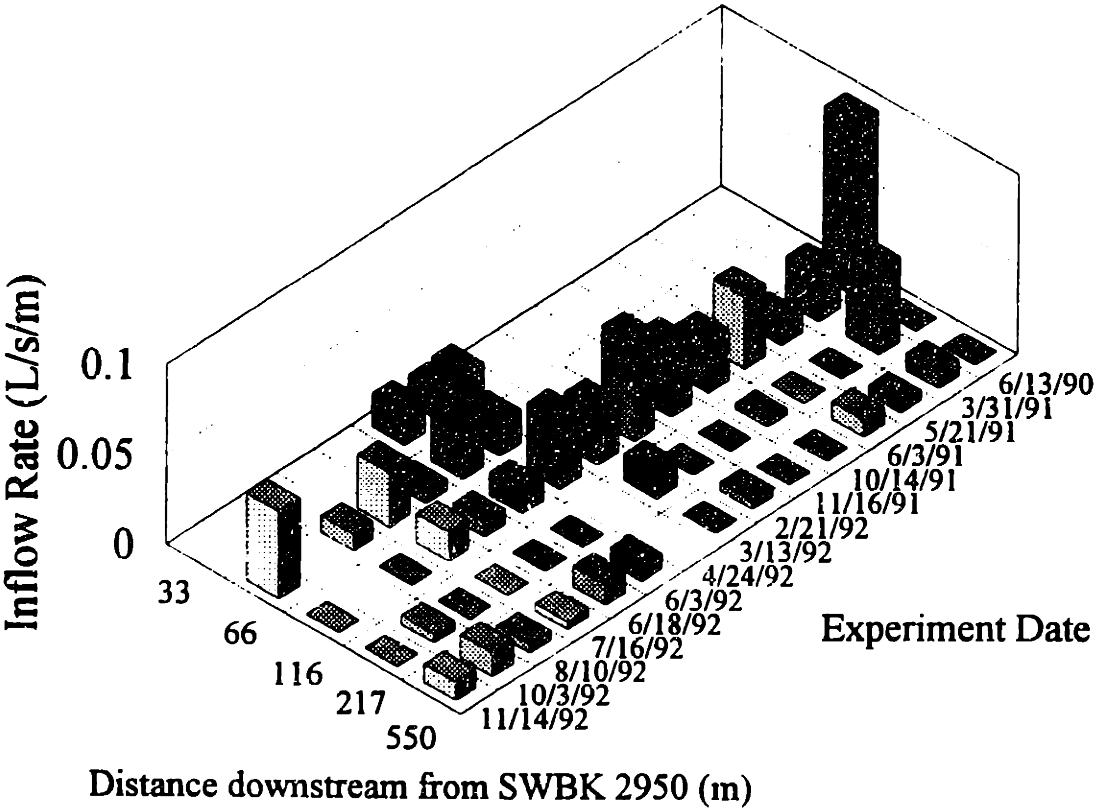


Fig. 2.4. VOCs in the Inflow at Sweetwater Brook

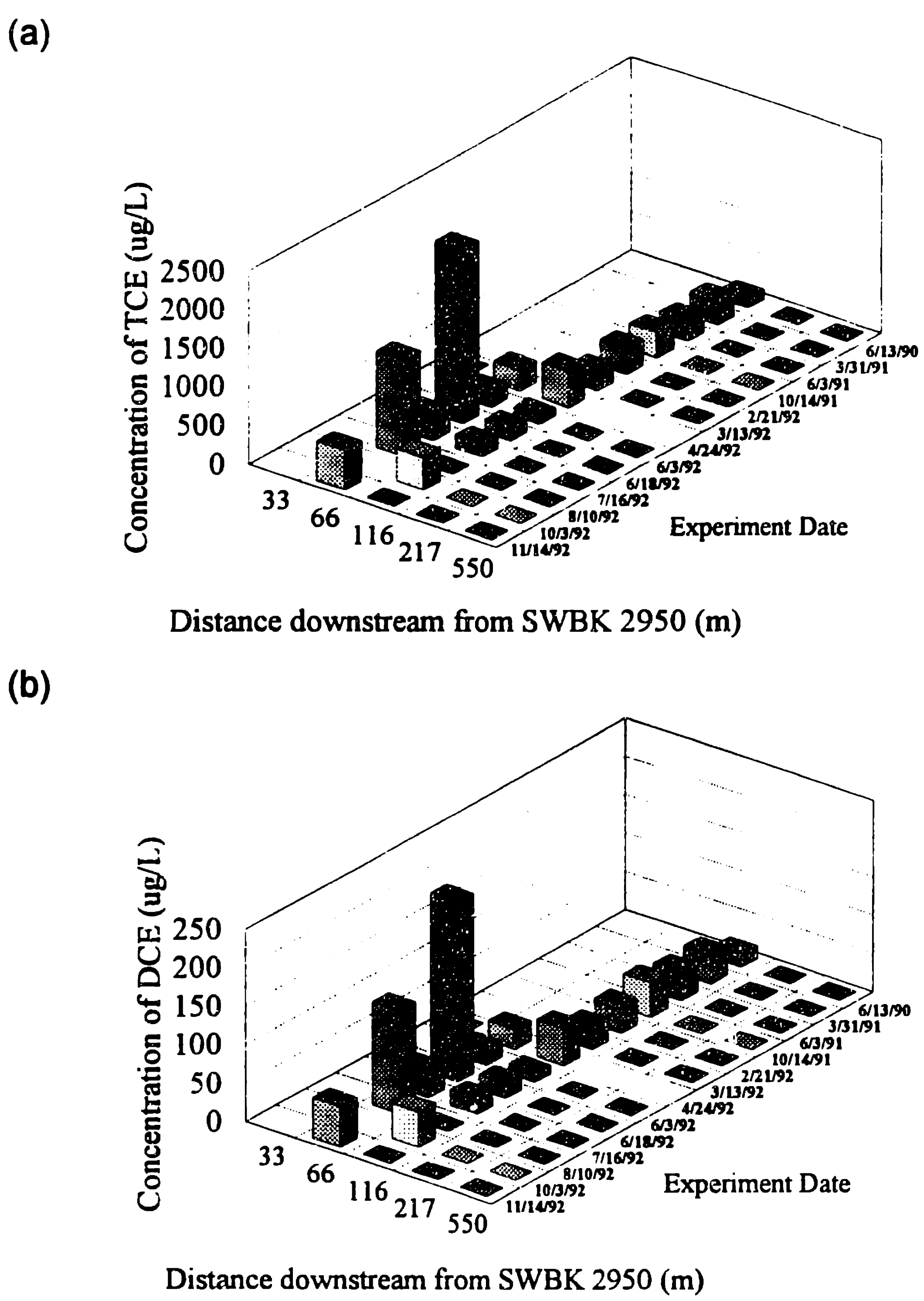
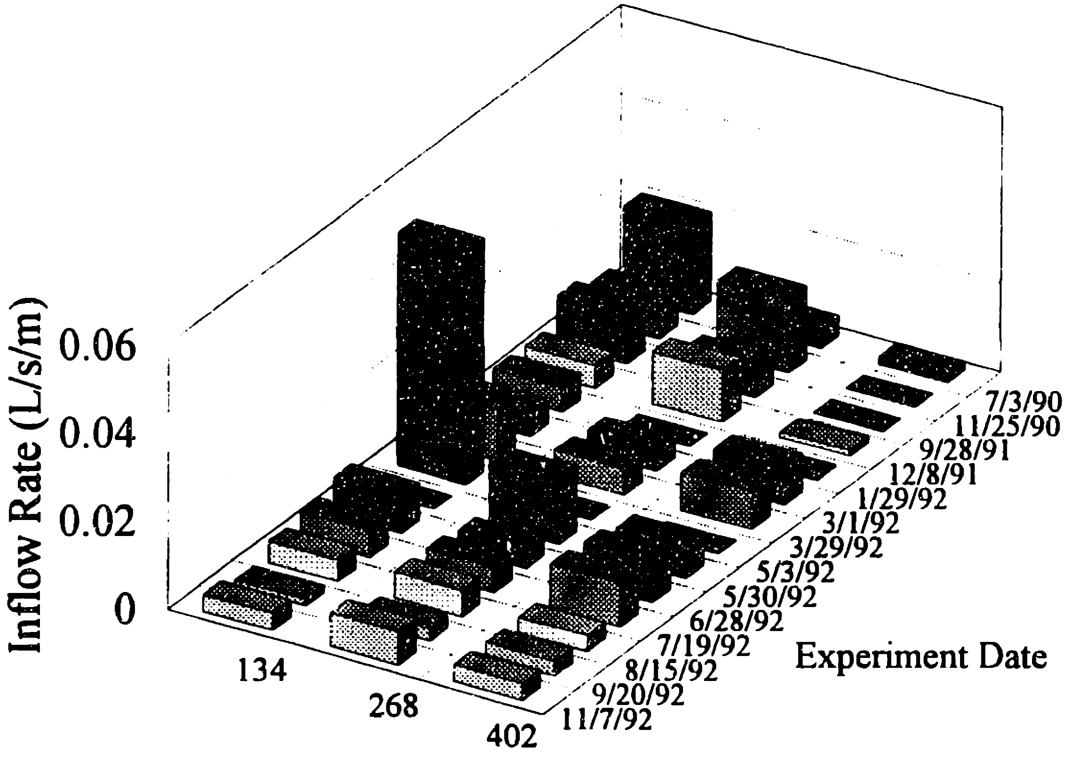


Fig. 2.5. Lateral Inflow at East Drainage Ditch II



Distance downstream from EDDW 4800 (m)

Fig. 2.6. VOCs in the Inflow at East Drainage Ditch II
(Note: The location of a bar on the graph indicates only the subreach where the VOC of interest is discharged not the exact location in the subreach. The VOCs are represented by letters as following: a=DCA, b=DCE, c=TCA, d=CCl_4, e=TCE.)

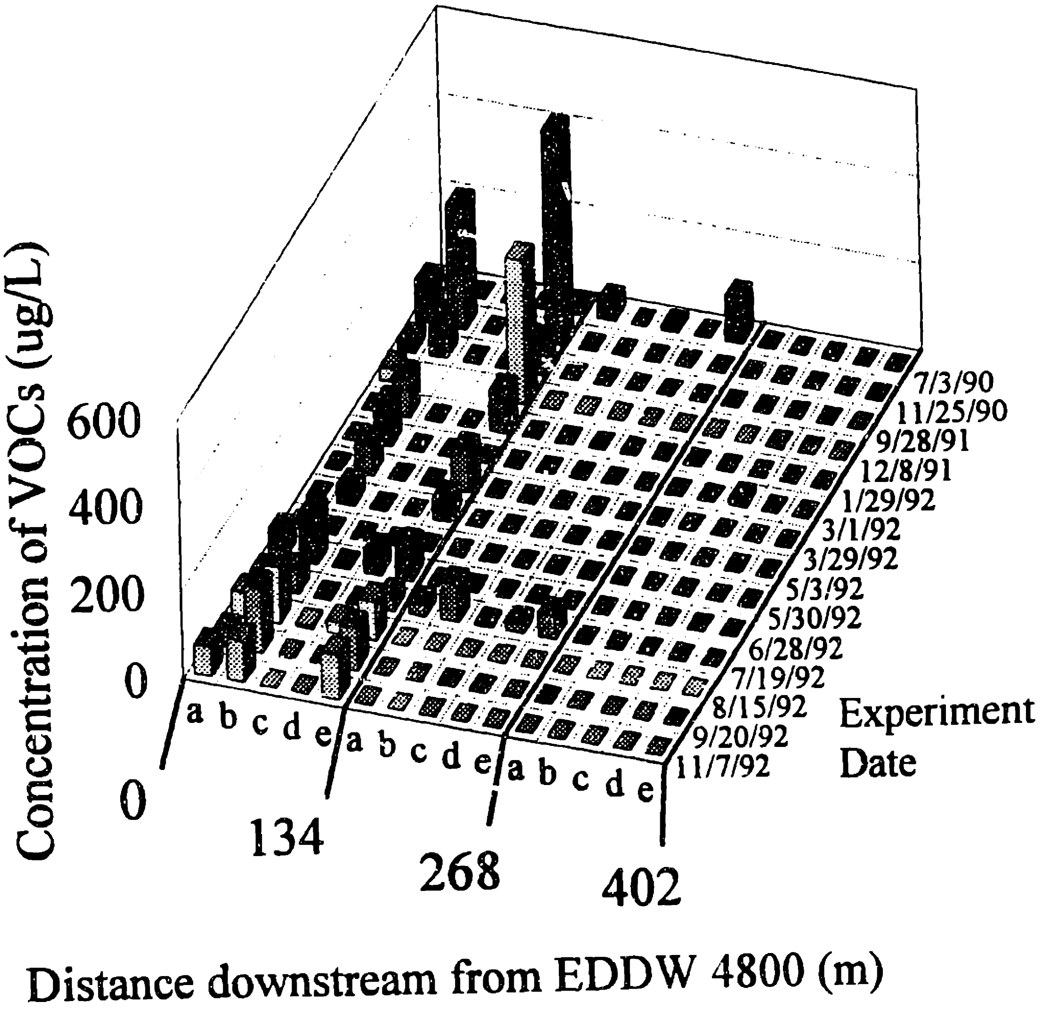


Fig. 2.7. Lateral Inflow and Discharge of VOCs at (a) East Drainage Ditch I, (b) East Drainage Ditch III, (c) Aberjona River, (d) Landfill Creek I, and (e) Landfill Creek II

(Note: The concentrations of VOCs in inflow are represented by the height of the corresponding box not the whole bar. For example, the concentration of benzene in the inflow at Landfill Creek II (d) is 2.4 μg/L not 13 μg/L.)

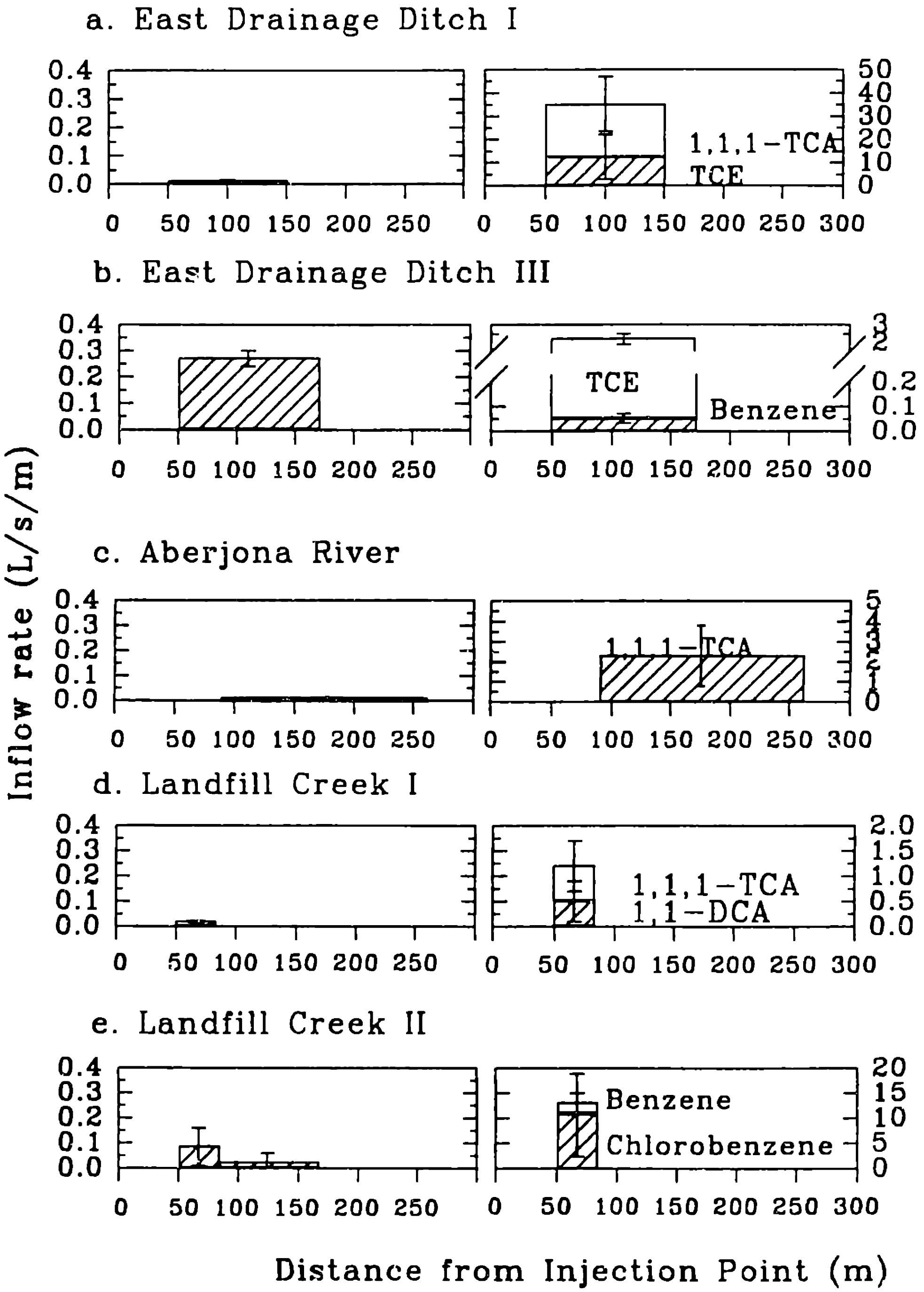
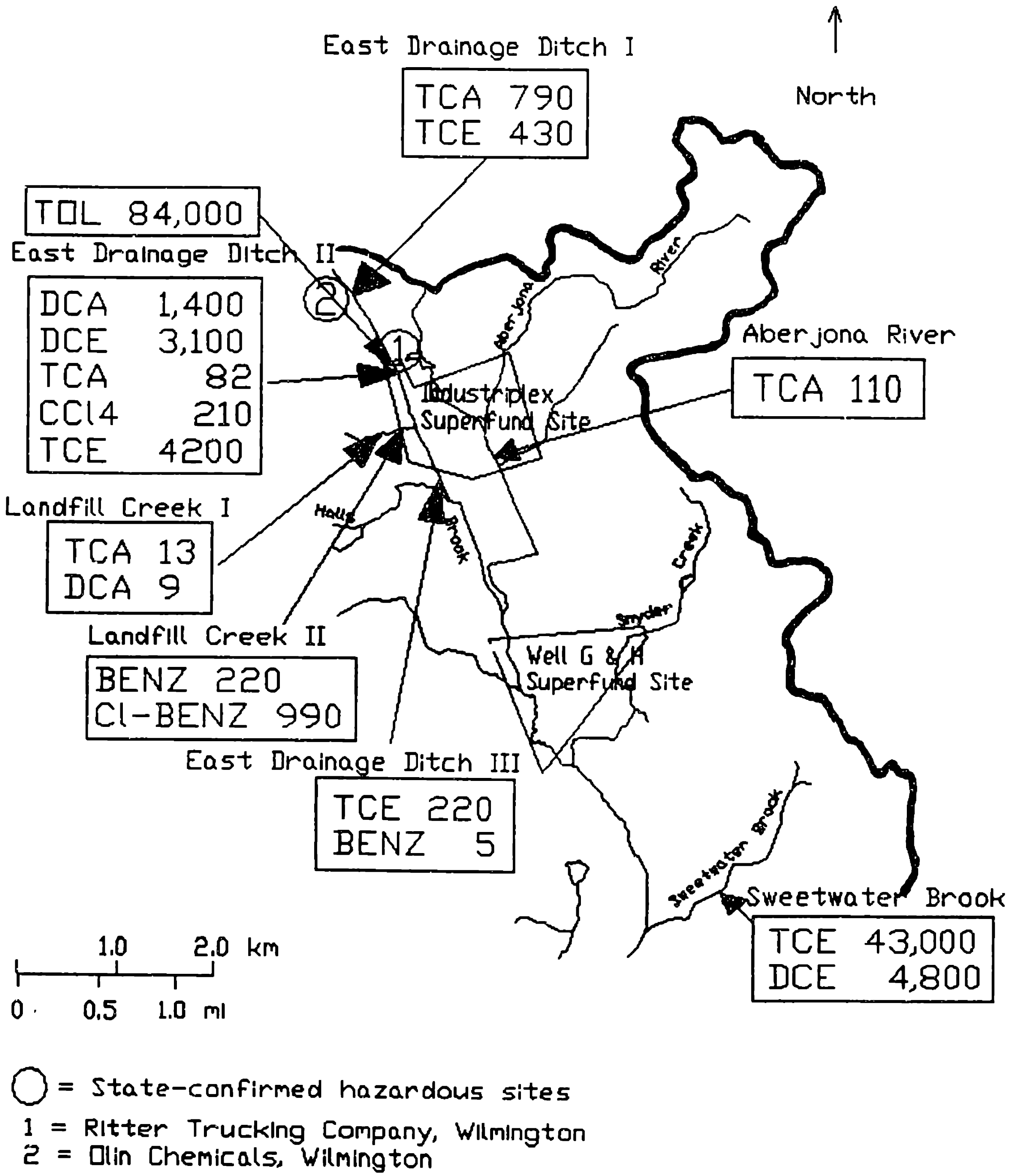


Fig. 2.8. Natural Discharging Rates of VOCs (g/yr)



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Chapter 3. *In-situ* Biodegradation of Toluene in a Contaminated Stream: Part 1. Field Studies

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[4] Environmental Working Group

Abstract

In-situ toluene biodegradation rates in a stream were determined throughout the year using a mass balance approach in which sodium chloride and propane tracers accounted for dilution and volatilization, respectively, and allowed biodegradation rates to be estimated. Dilution, volatilization and biodegradation accounted for 25%, 34% and 41% of the decrease in toluene concentration in the high flow season (spring), respectively, and 8%, 26% and 66% in the low flow season (summer). Volatilization rate constants of toluene were estimated as 0.62 hr^{-1} in summer and 0.20 hr^{-1} in winter, while biodegradation rate constants were 1.73 hr^{-1} in summer and 0.20 hr^{-1} in winter. Our results show that biodegradation was the most significant sink for toluene in the stream throughout the year. The benthic uptake rate constant of toluene ranged from 0.03 m/hr in winter to 0.21 m/hr in summer. Biodegradation rate constants were strongly dependent on stream temperature, but were uncorrelated or weakly correlated with stream velocity.

Introduction

In-situ biodegradation processes of xenobiotic chemicals in surface waters can play an important role in alleviating environmental pollution (1). However, it is difficult to quantify *in-situ* biodegradation rates because a variety of transformation and transport processes which include dilution, volatilization and sorption typically contribute to a contaminant's disappearance. Because of these difficulties, *in-situ* biodegradation rates are usually estimated by extrapolation from the results of laboratory microcosm studies. Laboratory microcosms make it much easier to control for abiotic processes of attenuation and to determine the degree to which rates are influenced by changes in individual parameters such as temperature. However, extrapolation of laboratory results to the field is uncertain because many environmental factors are not necessarily reproduced under laboratory conditions. Thus, in general, determinations of both *in-situ* biodegradation rates and lab microcosm studies are desirable in order to determine the nature of the biological transformations and the factors which control these transformations (1).

Several investigators have combined mass balance techniques and laboratory microcosm studies to estimate *in-situ* degradation rates of nonvolatile organic compounds in flowing streams and other ecosystems (2-7). To date, however, only one attempt to observe *in-situ* biodegradation for a volatile compound in a field site has been reported (8), and *in-situ* biodegradation could not be conclusively shown to occur in the study. Thus our understanding of biotic loss rates for volatile chemicals in streams is limited. Of particular interest is the significance of biodegradation compared to volatilization, and the degree to which seasonal and other environmental factors control biodegradation. In addition, little work has been done in relating laboratory results to field situations, making it difficult to evaluate the significance of these results for the natural environment.

This paper presents *in-situ* biodegradation rates of toluene by naturally occurring attached microorganisms in a contaminated stream; a companion paper in this volume reports on studies in the laboratory. Our objectives were to determine *in-situ* biodegradation rates at a field site, to understand the relative importance of biotic to abiotic processes in a stream with at least 3 years of history of contamination, and to understand the effect of environmental factors on the biotic reactions of toluene in a stream.

Background

Previous studies on degradation of xenobiotic chemicals in streams have determined potential degradation processes in laboratory microcosms (5,9), in the field (8,10), or both (3,4). Wanner et al. (5) estimated biodegradation of insecticides in laboratory microcosms and concluded that the biodegradation was the most significant sink for the chemicals. This approach predicted the actual concentrations of the chemicals in the river reasonably well, but indicated the limits of predictive modeling based on laboratory data only. Kolpin and Kalkhoff (7) used a mass balance technique in the field to conclude that photolysis was a more significant sink for atrazine[2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] than biodegradation, based on their findings of no change in the concentration of biotic degradation products downstream. This approach, however, couldn't and didn't intend to quantify degradation rates by each process. Pignatello et al. (4) estimated photolysis loss rates of pentachlorophenol (PCP) in an artificial stream (where there was no groundwater inflow) by measuring PCP concentration decrease during the day. They simultaneously estimated volatilization rates by measuring PCP concentration in air, and sorption rates by observing PCP initial loss rates upon the injection of PCP before microbial adaptation began. Using this technique, they estimated that biological processes accounted for 26-46% of PCP loss. This technique cannot be directly applied to a stream where dilution by groundwater inflow is a significant attenuation process. Other researchers have used tracers to account for abiotic processes in real streams. Rhodamine dye has been used to account for dispersion of a non-volatile organic contaminant (2,4-dichlorophenoxyacetic acid methyl ester) in a stream (2).

Rathbun et al.(8) attempted to determine an *in-situ* biodegradation rate of acetone in a stream using rhodamine-WT dye to account for dispersion and t-butyl alcohol to account for volatilization, but could not observe the biodegradation of acetone. In this study, we successfully determined *in-situ* biodegradation rates of a volatile organic compound (toluene) by the use of tracers in a stream. We used sodium chloride and propane as tracers for dilution and volatilization, respectively, thus permitting estimation of biodegradation of toluene in a stream. In addition to the intentionally injected tracers, trichloroethylene which was fortuitously present in the site served as an abiotic tracer for sorption.

It is shown in the companion study (11) that attached, rather than suspended, bacteria are mainly responsible for the biodegradation of toluene in the subject stream. Thus, the mass balance expression for toluene in a reach of the stream at steady-state (assuming no toluene in groundwater inflow in the reach) can be expressed, following Genereux and Hemond (12) with addition of a biodegradation term (J_oA_s/V) (2) as:

$$U\frac{dC}{dx} = -\frac{q}{A}C - k_v C - J_o\frac{A_s}{V} \tag{3.1}$$

where U is stream velocity (m/hr), C is concentration of toluene in the stream (mg/m^3 or μg/L), x is the coordinate direction along the stream (m), q is the lateral inflow to stream per unit stream length (m^2/hr), A is the cross-sectional area of the stream (m^2), k_v is the first-order volatilization rate constant (hr^{-1}), J_o is the uptake rate of toluene by benthic microbes (mg-Toluene/(m^2-hr)), and A_s/V is the ratio of surface area of stream bottom (m^2) to volume of stream water (m^3).

The uptake rate of toluene by benthic microbes (J_o) is assumed to be first-order with respect to toluene concentration in this stream; thus, the benthic uptake rate constant or a biodegradation rate constant (k_b) (m/hr) is defined in this paper as:

$$k_b = \frac{J_o}{C}. \qquad (3.2)$$

For the benthic uptake rate to be first-order with respect to toluene concentration, toluene concentration must be low enough not to saturate the microbial activity. Cohen et al. (11) in the companion paper show that toluene biodegradation rates in a shake-flask system containing sediment and water samples from this site were first-order with respect to toluene concentration up to approximately 200 μg/L and approached zero-order above 400 μg/L. Toluene concentration at one upstream location at our site was close enough to or below 200 μg/L except 4 dates (Table 3.1). Thus, it is reasonable at our site to consider the benthic uptake rate to be first-order with respect to toluene concentration.

Since the volume of overlying water (V) is equal to A_sZ where Z is the mean depth of the stream (m), the ratio (A_s/V) is equal to 1/Z. Stream flow rate, Q (m^3/hr), equals cross-sectional area (A) times stream velocity (U). Therefore, combining equations (3.1) and (3.2) yields:

$$\frac{dC}{dx} = -\left(\frac{q}{Q} + \frac{k_v}{U} + \frac{k_b}{UZ}\right)C \qquad (3.3)$$

On the right-hand side of equation (3.3), processes of decreasing toluene concentration in the stream include dilution upon groundwater inflow (q/Q), volatilization (k_v/U) and biodegradation by benthic microbes (k_b/UZ).

Use of introduced tracers allows parameters involved in dilution and volatilization (q, Q, k_v and U) to be determined. For a conservative nonvolatile tracer, k_v and k_b are zero; this can be exploited to estimate the dilution term (q/Q). Additional use of a tracer that is volatilized, but not biotransformed, permits k_v for the tracer to be estimated. The k_v of toluene can be estimated from the k_v of the volatile tracer (13), permitting determination of k_b.

In this work, it is assumed that abiotic processes other than dilution and volatilization are not important. Photolysis of toluene was assumed to be insignificant in this stream environment (14). After steady state is reached, longitudinal dispersion can generally be neglected in stream mass balance studies. Sorption to streambed sediments, although not a likely sink at steady state because of the fact that the sediments must eventually equilibrate with a constant level of toluene in the water, needed to be considered; we did not control the source of toluene in the site and could not, therefore, assure constant concentration of toluene throughout the study. Results indicated that sorption was not a significant sink, as will be discussed later. Sorption of toluene to organic matter in suspended particles was not a significant sink under typical suspended sediment concentrations (0-50 mg/L), due to the relatively low the organic carbon-water partition coefficient (K_{oc}) of toluene. Therefore, the significant abiotic processes in attenuating toluene concentrations in the studied stream were considered to be dilution and volatilization.

Experimental Section and Data Analysis

Study Site

A reach of the East Drainage Ditch, a small stream in an industrialized area of Wilmington and Woburn, Mass, was studied (Fig. 3.1). The stream is a part of the Aberjona Watershed, a ninety square kilometer area approximately twenty kilometers north of Boston (15,16). The East Drainage Ditch is a tributary of the Aberjona River, which flows into the Mystic Lakes in the southern part of the watershed. The watershed has historically been the site of tanning and chemical manufacture, and the East Drainage Ditch is contaminated with metals (As, Cr) and a variety of volatile organic compounds including toluene and trichloroethylene. Toluene in the stream arises from a source of subsurface contamination approximately 50 m upstream of the study site. This location was determined by sampling over a number of locations at different times (unpublished data).

The study reach lies besides a railroad track between 1600 m and 1200 m upstream from the confluence of the East Drainage Ditch and the Aberjona River (Fig. 3.1). The average width of the study reach was obtained by measuring the stream width every 30 m along the whole reach, and is estimated to be 1.2 m. The mean depth is usually less than 30 cm and the length of the reach is 400 m. There is often groundwater inflow in the upstream section of the study reach during high flow season (spring). At the upstream end of the reach, toluene concentration usually exceeds 100 μg/L. Measurements of conductivity and solvent concentrations were made at four equally spaced sampling stations.

Field Methodology

Toluene was already present in the stream prior to our study and no additional toluene was injected to the stream. During the experiments, tracers were injected for 3-5 hours at a point 30 m upstream from the studied reach. The 30 m length of the reach allowed an adequate mixing zone. The conservative tracer (3 M to 5 M food grade salt solution) was injected at a constant flow rate of approximately 200 ml/min from a 50-L Mariotte bottle. The injection rate was adjusted by choice of orifice (orifices were made of disposable 1-ml pipette tips cut off at various lengths). Propane gas, the volatile tracer, was bubbled into the stream through a glass frit (pore size 5-15 μm, 1.3 cm diameter) at a constant pressure of 3 kPa, resulting in a concentration range of 1-90 μg/L.

The background value of conductivity was measured at all stations for 10 minutes before the injection of tracers began, using a portable conductivity meter (Amber Science Digital Conductivity Meter, model 604). After the tracer injection began, the conductivities at each station were measured every 30 seconds until the values reached steady state.

After the steady state had been reached (typically 2-4 hours), water samples were taken at each station in 300-mL BOD bottles, preserved with 2.4 ml of mercuric chloride solution (3.5%) and stored at 0-4 °C, for the analysis of propane, toluene and trichloroethylene in the laboratory. Samples were analyzed no more than 2 days after collection.

Analysis of volatile organic compounds

Unfiltered water samples (80 ml) were purged by helium for 30 minutes through a Supelco Volatile Purge Trap packed with 60/80 Chromosorb (US EPA Method 601), and volatile organic compounds were thermally desorbed and transferred to the analytical column by carrier gas flow. Analysis was done using a Perkin-Elmer 3920B Gas Chromatograph [flame ionization detector, Helium carrier, 8'x1/8" OD stainless steel packed column (Supelco 60/80 Carbopack B/1% SP-1000)] with a temperature program [30 °C start, ramp to 210 °C at 8 °C per minute]. The detection limit was 0.1 μg/L for toluene and propane and 1 μg/L for trichloroethylene.

Sediment characteristics

To determine the sediment characteristics (bulk density, porosity and organic carbon content), two sediment cores were taken using a freezing core technique (17). Each core was cut at 1-cm intervals. After drying the sediment in a 80 °C oven, the bulk density was calculated by dividing the weight of dry sediment by the volume of fresh sediment and determined as 0.03 kg/L. The porosity was calculated by dividing the volume of water lost by drying by the volume of the fresh sediment and determined to be 0.7. After igniting the dry sediment in a 450 °C furnace overnight, the fraction of organic matter was calculated by dividing the weight of the organic matter by the weight of dry sediment and was determined to be 0.4.

Biodegradability of propane

About 80 ml of stream water (containing an ambient level of toluene) and 5 g of stream bottom sediment were put in 120 ml serum bottle with a teflon-coated serum stopper, yielding 30 ml of headspace in the bottle. Propane was added to attain an initial aqueous concentration of 1.3 μg/L. After 5.5 hr, the serum bottles were opened and additional toluene was added to yield concentration of approximately 600 μg/L. Control samples were prepared by adding 1 ml of saturated HgCl solution. The bottles were constantly shaken with a wrist-action shaker. It was assumed that the vapor phase and aqueous phase of the chemicals were at equilibrium during the experiment. Toluene and propane in the gas phase were measured periodically by analyzing 1 ml of the headspace of the serum bottles via gas chromatography.

Calculation of stream dilution factor (lateral inflow rate)

The final equation used to calculate the dilution factor is:

$$Q_j = Q_1 \frac{\Delta\gamma_1}{\Delta\gamma_j} \tag{4.4}$$

where Q_j is flow rate at station j and $\Delta\gamma_j$, the increase of specific conductance due to the injection of salt solution at station j, which is calculated by determining the steady-state specific conductance(γ_{ss}) minus the background specific conductance(γ_{bb}). The flow rate at the first station (j=1) is estimated by equating Q_1 as the injection rate of the salt solution to the stream, and taking $\Delta\gamma_1$ to be the specific conductance of the salt solution in equation (3.4). The lateral inflow, q, is obtained as the difference of two flowrates at two stations divided by the lateral distance between the two stations. Detailed derivation of equation (3.4) can be found in (12).

Calculation of volatilization rate constant

The volatilization rate constant of propane between two stations, i and j, ($k_{v,ij}^{P}$) was calculated from:

$$k_{v,ij}^{P} = \left(\frac{1}{\tau_{ij}}\right) \ln\left(\frac{G_i \Delta\gamma_j}{G_j \Delta\gamma_i}\right) \tag{4.5}$$

where G is the concentration of propane, and τ_{ij} is the travel time of a solute over the distance from the i^{th} station to the j^{th} station. Genereux and Hemond (12) provide a detailed derivation of equation (3.5).

Since the ratio of volatilization rate constants of two volatile compounds depend on the diffusivities of the compounds (13) and varies little under different stream conditions (18), the volatilization rate constant of a volatile organic compound, $k_v(voc)$ can be related to that of propane, $k_v(propane)$ as following:

$$k_v(voc)=\lambda\ k_v(propane)=\left[\frac{D_w(voc)}{D_w(propane)}\right]^{\alpha} k_v(propane) \qquad (4.6)$$

where λ is a constant, D_w is the diffusivity of the compound in water, and α ranges from 0.5 to 1 (18). The exponent α can be determined only by experiments (19); we took the whole range of α as an uncertainty level. The diffusivities of toluene and propane in water are taken as 0.95×10^{-5} and 1.16×10^{-5} cm^2/sec (20). λ for toluene was calculated as 0.86 ± 0.05 from equation (3.6). λ for trichloroethylene was taken as 0.79 ± 0.21 (13).

Calculation of the biodegradation rate constant

In solving equation (3.3) for C from the 1^{st} to the 4^{th} station, U, k_v, Z and k_b are defined as average values for the studied reach and treated as constants. A term (Q_4/Q_1) was obtained from the equation (3.4) and the volatilization rate constant of toluene in the reach from the 1^{st} station to the 4^{th} station ($k_{v,14}$) was obtained from equations (3.5) and (3.6). The resulting equation is:

$$k_b=Z\ \frac{\ln\left(\frac{C_1}{C_4}\right)+(\lambda-1)\ln\left(\frac{\Delta\gamma_1}{\Delta\gamma_4}\right)+\lambda\ln\left(\frac{G_4}{G_1}\right)}{\tau_{14}}\ . \qquad (4.7)$$

The mean depth of stream (Z) was calculated by dividing the average flow rate by the stream velocity and the average width of the stream on each experiment.

Calculation of predicted concentrations in the absence of biodegradation

Concentrations of toluene and trichloroethylene that would occur at each downstream station in the absence of biodegradation were predicted from observed concentrations at the previous station, accounting for dilution and volatilization. Excluding the biodegradation term (k_b/UZ) in equation (3.3) and combining with equations (3.4), (3.5) and (3.6), solving for C yields:

$$C_j^{pred} = C_{j-1}\left(\frac{G_j}{G_{j-1}}\right)^{\lambda}\left(\frac{\Delta\gamma_{j-1}}{\Delta\gamma_j}\right)^{\lambda-1} \qquad (4.8)$$

where C_j^{pred} is the predicted concentration of either toluene or trichloroethylene at the j^{th} station and C_{j-1} is the observed concentration of either toluene or trichloroethylene at a previous $(j-1)^{th}$ station.

Calculation of amount of toluene sorbed into sediment

Although the assumption of steady-state toluene concentration was tested during two 24-hour periods, the possibility of temporal variability was considered. Accordingly, a worst-case scenario was examined; namely, that a pulse of toluene was released from an upstream location and its concentration downstream was modified by transient diffusion (including instantaneous sorption equilibrium) into the sediment. The profile of toluene concentration which results from the vertical diffusion of toluene from overlying water into sediment during a time interval, τ can be expressed as following:

$$C_p(z,\tau)=C_w\, erfc(\frac{z}{2\sqrt{D^{*}\tau}})$$

$$C_s(z,\tau)=C_p(z,\tau)\ K_d \qquad (3.9)$$

$$where \quad D^{*}=\frac{D_w n}{1+\frac{\rho_b}{n}K_d}$$

where C_p is the concentration of toluene in porewater of the sediment, z is depth in the sediment, τ is time, C_w is the concentration of toluene in the overlying water, K_d is the distribution coefficient of toluene between water and sediment, n is porosity of the sediment, ρ_b is the bulk density of sediment, and C_s is the concentration of toluene sorbed into sediment. The K_d was estimated as $f_{om}K_{om}$, where f_{om} was the fraction of organic matter and K_{om} was the distribution coefficient between organic matter and water (100 L/kg) estimated by the equations given by Schwarzenbach et al. (18).

The sediment bed of each subreach was assumed to be exposed to toluene in the overlying water at a concentration equal to that in water leaving the previous subreach for a period of time equal to the travel time over the subreach. The diffused mass of toluene into the porewater over a maximum penetrating depth (1.5 cm) of the sediment during this travel time, and the mass of toluene sorbed into the sediment, were estimated from the concentration of toluene in porewater and sediment calculated by equation (3.9), using porosity, bulk density, and fraction of organic matter of the sediments taken from this site.

Results and Discussion

Experiments were conducted on 14 days during a 28- month period. The results of average flowrate, the concentration of toluene at the first station, temperature, velocity, depth (Z), the biodegradation rate constant (k_b), the biodegradation rate constant in units of time^{-1} (k_b/Z), and the volatilization rate constant on each experiment date were summarized in Table 3.1.

Biodegradability of propane.

In the batch experiment, propane biodegradation was not discernable over a 10 hour period, while toluene biodegradation was rapid (Fig. 3.2). The decrease of propane at 6 hr is due to loss when the bottles were opened. This provides evidence that propane, during a short period of injection (several hours) in this study, was not significantly biodegraded relative to toluene and could serve as an index of volatilization.

Dilution and volatilization

There was noticeable groundwater inflow within the first subreach during the most of experiments. In spring when stream flow was usually high (Table 3.1), dilution was important in attenuating toluene concentrations (25±13% of total decrease, Table 3.2); in other seasons, when stream flow was usually lower, dilution was only responsible for approximately 10% of the total decrease of toluene concentration. The first-order volatilization rate constant of toluene ranged from 0.10 to 0.79 hr^{-1}, being the highest in summer (mean of 0.62 hr^{-1}) and the lowest in winter (mean of 0.20 hr^{-1}) (Table 3.1).

Biodegradation

When only dilution and volatilization were considered to predict the decrease of toluene concentration between stations, actual concentrations of toluene were always significantly lower than the predicted concentrations in warm seasons and this was not the case for trichloroethylene (Fig. 3.3). Having examined other potential sinks such as diffusion and sorption into sediments for their role in the observed decrease in toluene concentration, we attribute this difference to biodegradation.

The second subreach (from the second measuring station to the third) seemed the most active in biodegrading toluene among the three subreaches (Fig. 3.3). It is possible that there was groundwater inflow of toluene, along with trichloroethylene as discussed later, in the first subreach. If this were the case, the true biodegradation rate constants would be even higher than those calculated here.

Diffusion and Sorption

The possibility of sorption to sediments as a toluene sink was tested in two ways. One was to calculate a non-steady-state sorption rate of toluene into sediment on a supposed scenario (see above); the other was to examine the disappearance of the other contaminant (trichloroethylene, log $K_{ow} \simeq 2.42$), which has sorption characteristics similar to toluene(log $K_{ow} \simeq 2.69$).

The result of calculations of transient sorption rate showed that the amount of toluene that could be sorbed into sediment under the assumed worst-case scenario (see above) during travel along the reach was less than 3 to 21% (average 11%) of the mass of toluene lost in the reach via sinks other than volatilization during all 14 experiments. This result is consistent with reports that sediment sorption was responsible for only 3-8% of the total decrease of the insecticides disulfoton and thiometon at 8 days after a pulse injection in the Rhine river, while primary biodegradation accounted for 80-96% of the attenuation (5). Pignatello et. al (3) reported that 9-18% of the decrease in pentachlorophenol concentration was caused by an initial rapid (< 1 day) uptake of sediments and other matrices in a model stream; 80% of the loss was by biodegradation after an adaptation period. The actual sorption uptake at East Drainage Ditch is certainly much less, inasmuch as all indications are that the concentrations are relatively steady at this site. Moreover, upstream concentrations of toluene were monitored independently, using a gas-tight automatic sampler (unpublished data), and were shown to be steady over 24 hours.

Additional evidence for the minimal role of sorption is seen by comparison with the attenuation of trichloroethylene (TCE). During the companion laboratory study (11), rock and sediment samples were unable to biodegrade significant amounts of TCE relative to toluene. TCE served, therefore, as an additional tracer for abiotic processes, including sorption. Using equations given by Schwarzenbach et al. (18), the ratio of the first-order sorption rate constant of TCE to that of toluene was estimated as 1.1. The longitudinal profile of TCE in the stream (Fig. 3.3), obtained in the same way as that of toluene, showed that actual concentrations of TCE at the second station on most of experiments and the third station on two experiments (7/3/90 and 7/19/92) were higher than predicted, suggesting the possibility of groundwater inflow of TCE in the first (in most cases) and second (on two dates only) study subreach. From the second station to the fourth station, the predicted concentrations of TCE fall within the error range of the actual concentrations, suggesting that volatilization and dilution were the dominant concentration-attenuating processes for TCE. Diffusion and sorption, therefore, do not likely play important roles in attenuating toluene either.

Our result that TCE was not biodegraded while toluene was biodegraded in the studied stream is consistent with a previous study (21), which reported no detectable biodegradation of TCE by indigenous bacteria in soil-slurry samples during which more than 97% of the initial toluene was biodegraded. There are also reports that the fortuitous degradation of TCE could be inhibited by the presence of toluene, cresol and phenol (22), even though TCE degradation requires catabolic enzymes involved in the degradation of those compounds (23). In contrast to these results, Fan and Scow (24) reported the biodegradation of TCE by indigenous microbial populations in soil in the presence of toluene. Concentration levels of toluene (20 mg/L soil solution) and TCE (1 mg/L soil solution) in the system of Fan and Scow (24) were, however, much higher than those in our system (200 μg/L for toluene and 20 μg/L for TCE), and in the system of Wilson et al.(21) (85-666 μg/L).

Comparison of Biodegradation Rate Constants of Toluene in Different Systems

There are no reported *in-situ* biodegradation rate constants of toluene by attached bacteria in streams, and a direct comparison of our *in-situ* rate constants (where attached bacteria were dominant) with the rate constants of toluene in other laboratory systems (where suspended bacteria were dominant) is problematic. From the equation (3.3), the first order biodegradation rate constant comparable to the first order volatilization rate constant can be expressed as our reported biodegradation rate (benthic uptake rate) constant divided by the stream depth, that is, k_b/Z, giving units of hr^{-1}. This term can be compared with the first-order biodegradation rate constant in units of $time^{-1}$ that most previous studies on the fate of toluene reported . The value of k_b/Z during warm seasons (5/30/92-9/20/92 in Table 3.1, Fig. 3.4) ranged from 0.9 to 2.9 hr^{-1}, averaging 1.9 hr^{-1}, while it averaged 0.2 hr^{-1} during cold seasons (3/1/92- 5/3/92 and 9/28/91-1/29/92 in Table 3.1, Fig. 3.4). These constants were much higher than values reported from previous studies of biodegradation of toluene by indigenous bacteria (21,25-27). These previous studies reported values of 0.05 hr^{-1} under summer condition in a tank of seawater (without sediments) (25), 0.01 hr^{-1} at 6 °C in seawater samples (26), and 0.003 hr^{-1} for unamended strip-pit pond water with sediments and 0.24 hr^{-1} for one amended with nutrients at 20 °C (27). Wilson et al.(21) reported that over 90% of initial concentration of toluene was biodegraded in a soil-slurry samples at 20 °C in a week. This can be converted to a first-order rate constant of 0.01 hr^{-1}, with the assumption that the biodegradation rate is first-order with respect to toluene concentration. The higher rates in the stream system relative to the other systems is likely due to a combination of higher nutrient availability, larger toluene degrading biomass, and, in the case of samples containing sediments (27) or soils (21), a mass transport limitation due to very low turbulence in the microcosms.

Significance of Biodegradation Relative to Volatilization

From late spring through summer, biodegradation was much more significant sink than volatilization (Table 3.2). In summer, biodegradation was responsible for 66±7% of the decrease in toluene concentration at downstream sites while volatilization was responsible for 26±6% of the decrease (Table 3.2). A previous study of the fate of toluene in coastal seawater conditions (very low turbulence and no sediment in a batch experiment;25) also found a similar significance of biodegradation as a sink relative to volatilization in the summer. In winter, biodegradation was comparable to volatilization as a sink in our study (Table 3.2). This result is in contrast to the result of Wakeham et al.(25), which found volatilization to be much more significant than biodegradation in winter. It is likely that the bacteria in the system of Wakeham et al.(25) were not fully adapted to toluene. It could also be that the bacterial density in seawater under natural condition is much less than the ratio of attached bacteria to the volume of overlying water in our stream system. Bouwer (27) reported biodegradation (93%) was much more significant than volatilization (7%) for strip-pit pond water amended with nutrients (acetate, N and P) at 20 °C, but, for unamended water, volatilization (81%) was much more significant than biodegradation (19%). The natural conditions of our site, including high stream velocity, high ratio of the surface area of stream bottom to the volume of overlying water, and long microbial adaptation period likely combined to allow biodegradation to be the most significant sink for toluene throughout the year.

Effect of Environmental Factors on Biodegradation

Higher velocity could conceivably increase the biodegradation rate constant, since faster stream velocities could increase the mass transport of contaminants to attached bacteria (28). However, excessive velocity scours off attached bacteria and can thus decrease biodegradation rates (28,29). Some previous studies (2,30) reported that higher stream velocity increased the biodegradation rate constant, while authors in another study (31) reported that microbial transformation rate constants of an herbicide increased with decreasing water velocity in a stream. Authors of the latter study (31) explained their results based on the accumulation of leaf-litter in the bottom of stream at low water velocities; the surface area of the litter provided a larger colonized area for the herbicide-transforming organisms, resulting in higher biotransformation rate constants in the fall season despite low temperature. The condition of slow stream velocity coincides with the condition of high temperature in our system (Table 3.1), which makes the separation of the two environmental factors less certain. However, our results shows that the biodegradation rate constants generally increased with higher temperature, while it was not the case with stream velocities. It can be concluded that temperature exerts a greater influence on the biodegradation rate constants than stream velocity at our site. Cohen et al. (11)

concluded that decreases in the biodegradation rate constants in winter are mainly due to the influence of temperature on microbial activity, rather than a decrease in numbers of bacteria.

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Symbols

A	cross-sectional area of stream (m^2)
A_s	surface area of the stream bottom (m^2)
C	concentration of toluene or trichloroethylene ($\mu g/L$ or mg/m^3)
D_w	diffusivity of a compound in water (cm^2/s)
f_{om}	fraction of organic matter in the sediment
G	concentration of propane (mg/m^3)
k_b	biodegradation rate constant (m/hr)
k_v	volatilization rate constant (hr^{-1})
K_d	distribution coefficient between sediment and water (L/kg-sediment)
K_{om}	distribution coefficient of a chemical between organic matter and water (L/kg-om)
J_o	benthic uptake rate of toluene (mg-Toluene m^{-2} hr^{-1})
n	porosity of the sediment
q	lateral inflow to stream per unit lateral stream length (m^2/hr)
Q	flowrate of the stream (m^3/hr)
t	time
U	stream velocity (m/hr)
V	volume of the overlying stream water (m^3)
x	coordinate direction along the stream
z	vertical direction along the sediment
Z	stream depth (m)
α	exponential factor of ratio of diffusivities of two volatile compounds to determine λ
γ	specific conductance ($\mu S/cm$)
$\Delta\gamma$	increase of specific conductance ($=\gamma_{ss}-\gamma_b$) ($\mu S/cm$)
λ	ratio of volatilization rate constant of a volatile to a tracer (propane)
ρ_b	bulk density of the sediment (kg/L)
τ	travel time (hr)

Subscripts

bb	background
i (or j)	the ith (or jth) sampling station in the studied reach
ij	from the ith to the jth sampling station
ss	steady-state
p	pore water in the sediment
s	sediment
w	overlying water over the sediment

Superscripts

p	propane
pred	predicted accounting for volatilization and dilution

Table 3.1. Summary of *In-situ* Toluene Mass Balance Data: Biodegradation rate constants, Volatilization rate constants and Stream parameters

Season	Date	Average Flowrate, Q (m^3/hr)[a]	Ground Water Inflow, Q_4-Q_1 (m^3/hr)	Toluene Concentration at the first station, C_1 (mg/m^3)	Water Temperature (°C)[b]	Water Velocity, U (m/hr)[c]	Stream Depth, Z (m)[d]	Biodegradation rate constant, k_b (m/hr)	k_b/Z (hr^{-1})	Volatilization rate constant, k_v (hr^{-1})
Spring	3/1/92	46	2.5	214	1.0	313	0.12	0	0	0.27
	3/29/92	80	3.5	117	10.5	473	0.14	0.02	0.15	0.29
	5/3/92	146	7.1	88	15.3	473	0.26	0.10	0.39	0.10
	5/30/92	52	2.8	59	18.0	213	0.20	0.59	2.87	0.42
Summer	7/3/90	39	3.5	149	14.5	262	0.15	0.40	2.68	0.69
	6/28/92	37	2.9	325	20.0	251	0.12	0.21	1.67	0.53
	7/19/92	25	2.9	209	22.5	221	0.09	0.16	1.67	0.74
	8/15/92	27	1.9	244	18.0	241	0.09	0.08	0.87	0.52
Fall	11/25/90	71	3.3	172	8.0	482	0.15	0.06	0.38	0.44
	9/28/91	94	2.4	381	14.5	635	0.15	0	0	0.79
	9/20/92	17	1.0	185	--	195	0.07	0.10	1.42	0.41
	11/7/92	30	2.1	202	7.0	171	0.15	0.07	0.49	0.22
Winter	12/8/91	65	2.4	332	7.3	350	0.15	0.02	0.13	0.16
	1/29/92	45	0.8	127	3.8	389	0.10	0.03	0.26	0.24
Spring Avg.		81±40[a]	3.5±2.4	120± 58	11±6	368±111	0.18±0.05	0.18±0.24	0.81±1.20	0.27±0.11
Summer Avg.		32±6	2.1±1.0	232± 63	19±3	244± 15	0.11±0.02	0.21±0.12	1.73±0.64	0.62±0.10
Fall Avg.		53±31	2.2±0.8	232± 85	11±4	371±195	0.13±0.03	0.06±0.04	0.57±0.52	0.46±0.21
Winter Avg.		47±14	1.6±0.8	229±1033	6±2	369± 20	0.13±0.03	0.03±0.01	0.20±0.06	0.20±0.04
Yearly Avg.		55±33	2.8±1.4	200±91	13±6	334±133	0.14±0.05	0.13±0.16	0.92±0.95	0.42±0.21

a. Average flow rate is the average over the four sampling stations.
b. Temperature is the average at the four sampling stations over the period of experiment (several hours).
c. Water velocity is the bulk velocity over the whole studied reach, obtained by dividing the length of the reach by the travel time of sodium chloride solution on each experiment.
d. The depth was obtained by dividing average flow rate by water velocity and stream width (1.2 m).
e. Errors represent one standard deviation from the mean.

Table 3.2. Relative Importance of Various Processes for Decrease in Toluene Concentration at Downstream

Season	Date	Contribution of each process[*], %		
		Dilution	Volatilization	Biotransformation
Spring	3/1/92	36	64	0
	3/29/92	30	47	24
	5/3/92	30	14	55
	5/30/92	3	12	85
Summer	6/23/92	7	22	70
	7/3/90	6	19	75
	7/19/92	9	28	63
	8/15/92	10	34	56
Fall	9/20/92	5	21	74
	9/28/91	16	84	0
	11/7/92	13	27	60
	11/25/90	20	43	37
Winter	12/8/91	29	39	32
	1/29/92	12	42	46
Spring Avg.		25±13	34±22	41±32
Summer Avg.		8±1	26±6	66±7
Fall Avg.		14±5	44±25	43±28
Winter Avg.		15±9	37±8	37±7
Yearly Avg.		16±11	35±19	48±26

a. Contribution of each process was estimated by using equation (3). For example, dilution (%)= $100 \times (q/Q) / [q/Q + k_v/U + k_b/(UZ)]$.

Fig. 3.1. Map of Study Site. The East Drainage Ditch site. part of the Aberjona watershed. The boundary of the watershed is indicated by heavy dark bar. The flow direction is marked by arrow.

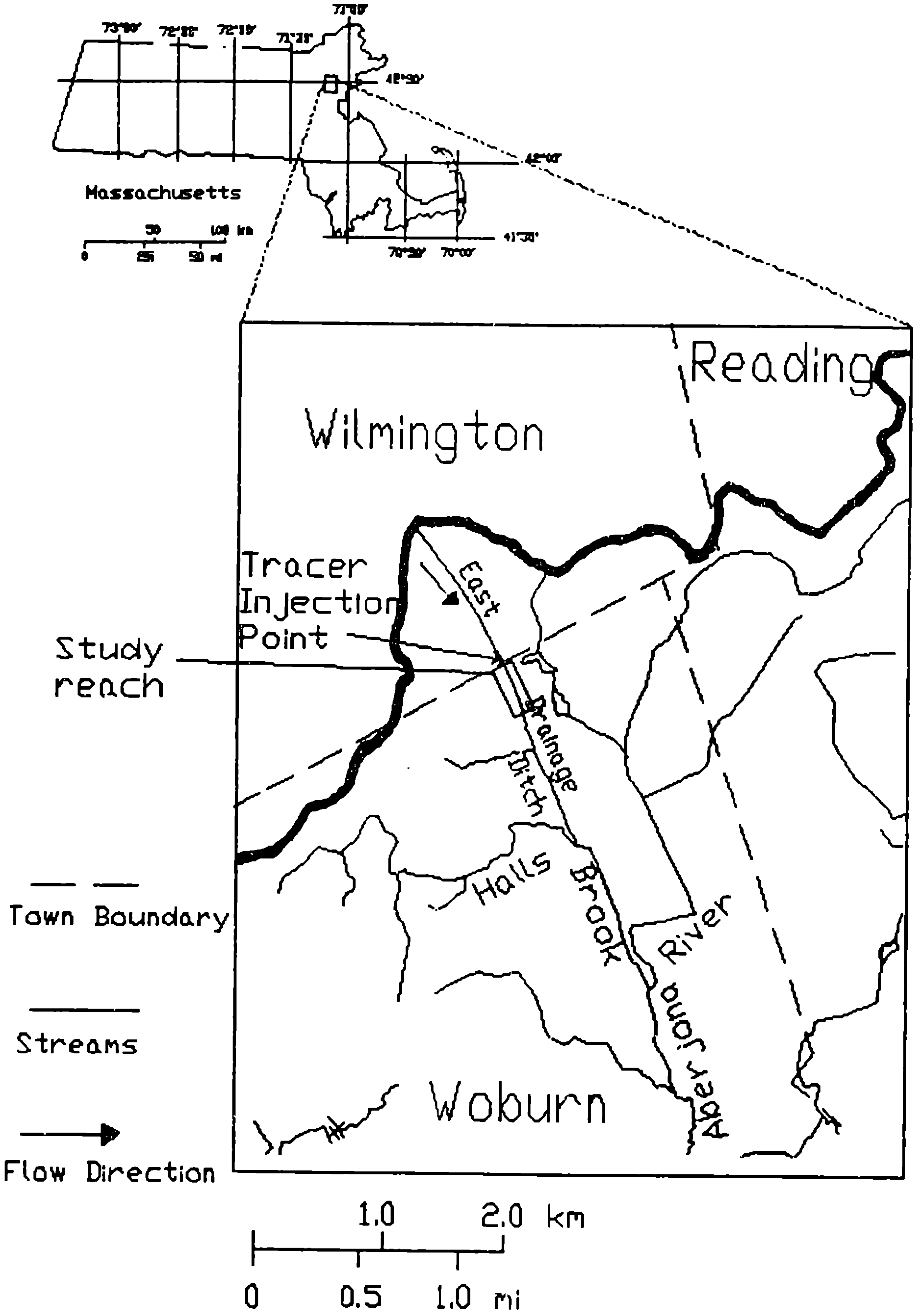


Fig. 3.2. Biodegradability of Propane. The arrow indicates the time when bottles were opened and toluene was added. Decrease in propane concentration after the arrow was due to loss when the bottles were opened. Empty and filled symbols represent control and live samples. respectively.

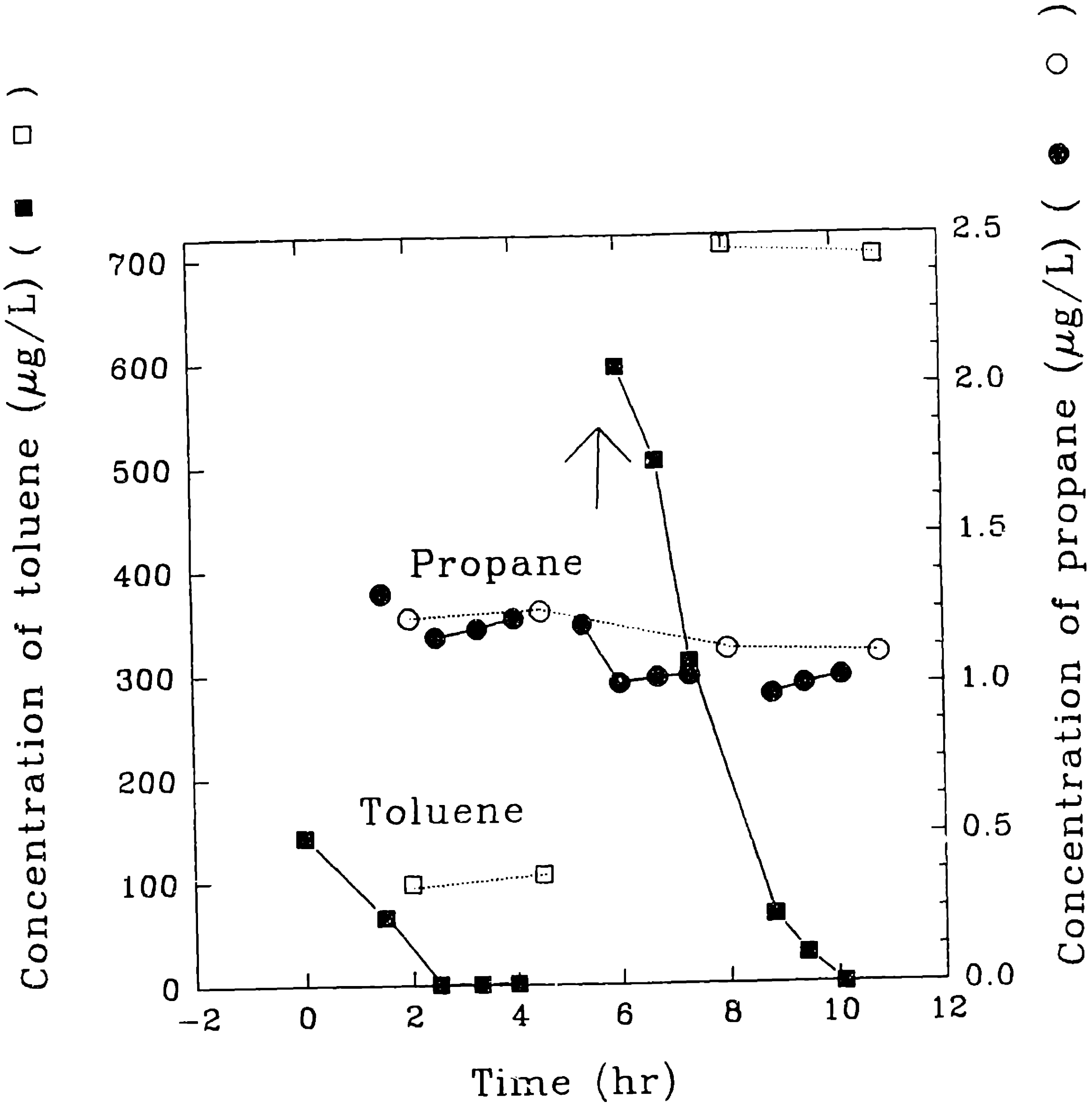


Fig. 3.3. Predicted and Actual Concentrations of Toluene and Trichloroethylene at Downstream. The predicted concentrations at a downstream sampling station (indicated as closed circles for toluene and closed triangles for TCE) were calculated by accounting for only dilution and volatilization, using Eqn.(3.8), from its previous sampling station. The actual concentrations (indicated as open circles for toluene and open triangles for TCE) were the concentrations measured from water samples taken at sampling stations. Error analysis was based on Kline (32). Error range was ±11%.

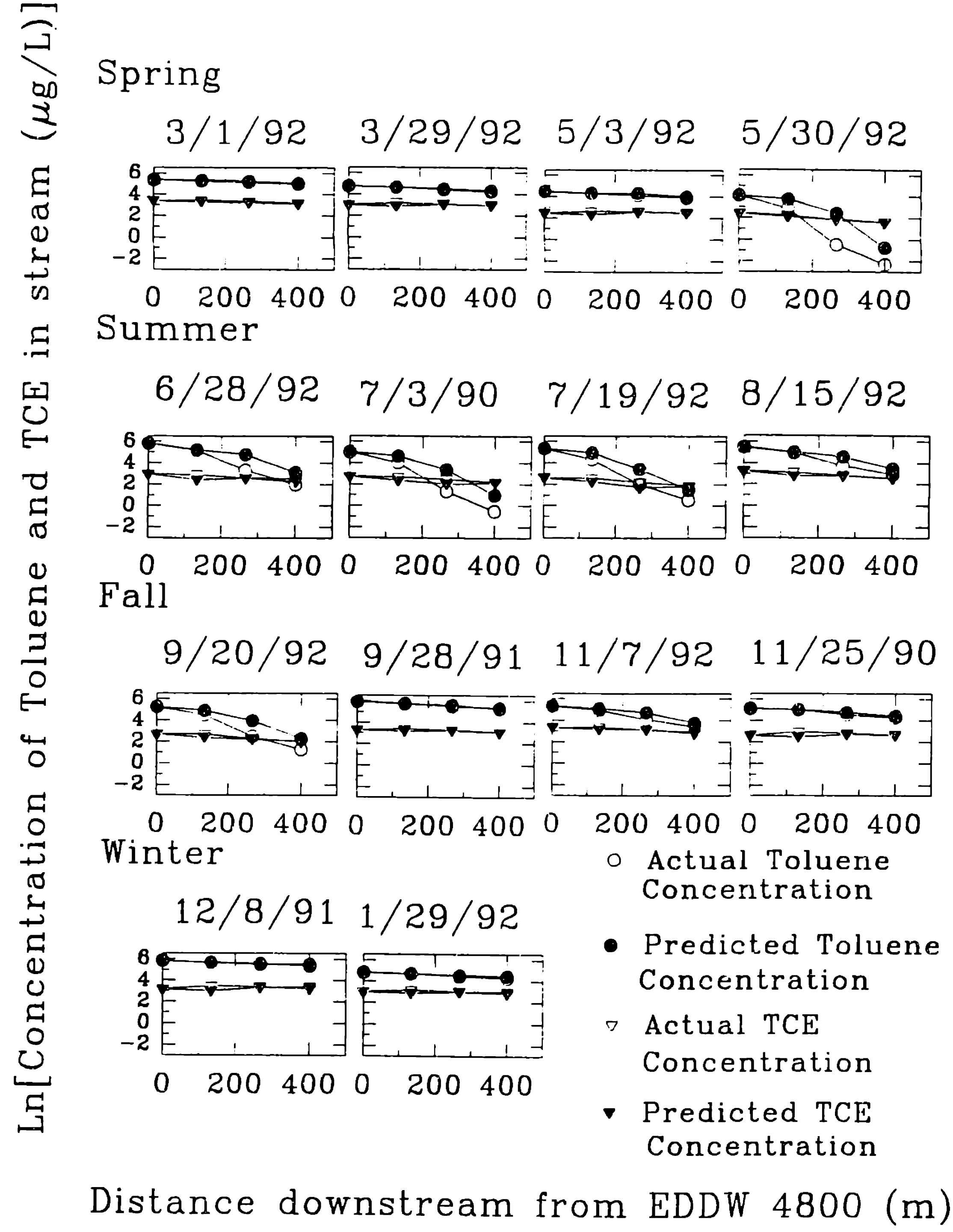
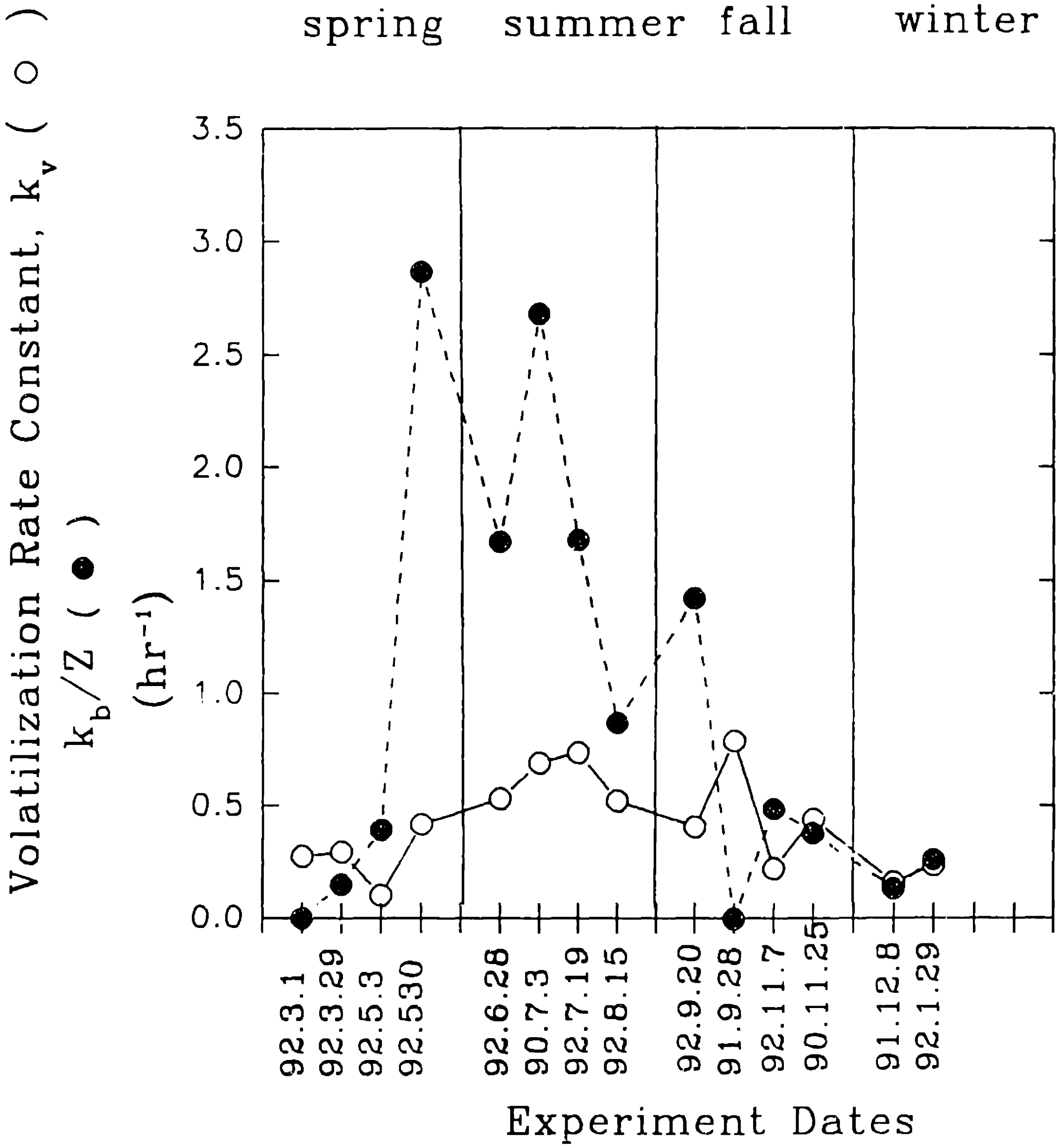


Fig. 3.4. Volatilization Rate Constants and Depth-normalized Biodegradation Rate Constants. Volatilization rate constants (indicated as open circles) were determined from propane volatilization data, using Eqn.(3.5) and (3.6). Depth-normalized biodegradation rate constants (indicated as closed circles) were estimated by dividing the biodegradation rate constants estimated from Eqn.(3.7) by the mean stream depth.



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Chapter 4. Predicting the Biodegradation Rate of Toluene in a Natural Stream

Abstract

Biodegradation rates of toluene in a natural stream, where attached microorganisms were primarily responsible for biodegradation, were estimated by adapting a biofilm kinetic model, and compared with measured *in-situ* rates. The biodegradation rate constants estimated by the model were 0.2 m/hr for summer and 0.06 m/hr for fall, which were reasonably close to *in-situ* biodegradation rates. By using the model, the limiting process in the biodegradation of toluene was also investigated. Mass transfer across the interface between bulk stream water and biofilm was not rate limiting; microbial kinetics appeared to be the rate limiting factor in the biodegradation of toluene at this site. Diffusion within the biofilm did not limit biodegradation rates in the spring, when the biofilms were very thin; however, diffusion within the biofilms became a limiting factor in the summer and fall.

Introduction

In-situ biodegradation of xenobiotic chemicals by attached microorganisms can play a major role in alleviating contamination of shallow streams [1-4]. It is, therefore, essential to quantify *in-situ* biodegradation rates in order to understand the fate of a chemical in streams. However, it is difficult to estimate *in-situ* biodegradation rates because a variety of transformation and transport processes typically contribute to a contaminant's disappearance. Moreover, it often takes much more resources to conduct field experiments than laboratory experiments. Because of these difficulties, *in-situ* biodegradation rates are usually estimated by extrapolation from the results of laboratory microcosm studies.

Two approaches have been generally taken to predict *in-situ* biodegradation rates of a contaminant on the basis of laboratory microcosm studies. One approach is to know the important environmental conditions such as temperature, nutrient and oxygen levels *a priori* and reproduce them in the laboratory microcosms; such a method does not necessarily elucidate the mechanisms of influencing the rates. A second method is to employ a kinetic model to quantify the environmental parameters and calculate the *in-situ* biodegradation rates with the parameters appropriate for the field conditions.

The first method has been more commonly employed for the prediction of the biodegradation rates of xenobiotic chemicals by attached microorganisms in streams [3, 5-9]. However, this method may neglect or fail to reproduce an important environmental condition, and thus result in inaccurate predictions of rates [3, 5, 6]. Moreover, this method is very limited when applying laboratory results to changing field conditions. For example, Cohen et al. [6] reported the underestimation of the biodegradation rate of toluene in a flow-through column study due to turbulence level in their column being much lower than that in the field.

The second method attempts to represent the mechanisms involved in the biodegradation, and thus predict rates for different arbitrary field conditions. Many researchers have applied biofilm kinetic models, which have predicted the flux of substrate into many types of biofilm grown under laboratory conditions [10-15], to natural biofilms in shallow streams [4, 16-20].

For example, Gantzer et al. [19] predicted the removal rates of *p*-cresol and the butoxyethyl ester of 2,4-dichlorophenoxyacetic acid very closely by using the biofilm kinetic model. They determined parameters such as microbial kinetic rate constant, biofilm density, mass transfer coefficients and diffusion coefficient through the biofilm in order to estimate the biodegradation rates with the biofilm kinetic model, and compare the estimated rates with the observed rates. Their study, however, did not intend to predict the removal rates of chemicals in a real stream. Instead, it compared removal rates obtained from their model with the rates observed on a teflon strip colonized in a pond and a river. Our study determined the removal rates of a xenobiotic chemical by biofilms grown on naturally occurring objects such as gravel and plant litters in a real stream. This could help better understanding the fate of the chemical in real streams.

Srinanthakumar and Amirtharajah [17] predicted organic carbon decay in a stream with biofilm kinetics. They built an artificial channel alongside the stream in question in order to estimate parameters such as the biofilm production rate, area of biofilm, net detachment rate of biofilm, biofilm yield coefficient, and substrate uptake rate needed to apply the kinetic model to a natural stream. Although this work could estimate the parameters well, it is not always feasible to build such an artificial channel. Our study employed a simple batch experiment and field measurements in order to determine parameters needed to apply the biofilm model to a natural stream.

Williams and Lewis [18] modeled benthic nitrification-denitrification in a stream. The microbial kinetic parameters they used, however, were fitting parameters and were not determined independently. The use of fitting parameters can limit the applicability of the model to other environments. The present study did not use any fitting parameters, and all parameters were determined independently of the model.

Most of previous studies have assumed that oxygen was not limiting, and that the compound of interest was the only limiting substrate [17-19]. However, the importance of oxygen limitation in biofilms has been noted [21]. Our study examined the possibility of oxygen limitation in toluene biodegradation by calculating the thickness of aerobic layer in biofilms and comparing the aerobic thickness with the whole thickness measured independently.

Although the removal rates of naturally occurring organic compounds, dissolved oxygen, and some nonvolatile xenobiotic compounds in streams have been predicted by the application of biofilm kinetic models [4, 16-20], the authors are aware of no study to apply the biofilm model in predicting the removal rates of a volatile organic compound such as toluene in a natural stream. In this work, we adapted a biofilm kinetic model with parameters obtained from batch culture experiments, field measurements and the use of existing equations, in order to predict the removal rates of toluene in a shallow stream where a previous study [22] experimentally determined actual *in-situ* biodegradation rates using an in-stream tracer technique. Objectives of this work were to predict the biodegradation rates of toluene in a natural stream with the use of a biofilm kinetic model, to quantify each process involved in toluene biodegradation, and to determine which steps are limiting the biodegradation rate in a stream environment.

Background

Three major sequential steps describe the overall process of substrate uptake by attached microorganisms in the biofilm: (1) diffusion of substrate from bulk liquid to the interface between the liquid and the biofilm; (2) diffusion within the biofilm; and (3) biochemical reaction within the biofilm.

Fig. 4.1 illustrates the three characteristic substrate-concentration profiles in an idealized biofilm. Within a deep biofilm, the substrate concentration decreases asymptotically to zero. For a fully penetrated biofilm, C_s, the substrate concentration at the liquid/biofilm interface, does not change throughout the full thickness of the biofilm. Cases intermediate between fully penetrated and deep are called shallow biofilms. For all three cases, the substrate-concentration gradient becomes zero at or before the solid-surface boundary [23].

At steady-state, the flux from bulk water to a biofilm is balanced by microbial transformation within the biofilm, assuming that substrate is the only limiting substrate [23]:

$$D_f \frac{d^2 C_f}{dz^2} = \frac{V_m}{K_M + C_f} X_f C_f \tag{4.1}$$

where D_f is the diffusion coefficient of the substrate within the biofilm (m^2 h^{-1}), C_f is the concentration of a substrate (toluene in this study) in the biofilm (mg_s m^{-3} or $\mu g/L$), z is the distance in from the outer surface of the biofilm (m), V_m is the maximum specific rate of substrate transformation (mg_s mg_x^{-1} h^{-1}), K_M is the concentration of substrate at which removal is half the fastest possible (mg_s m^{-3} or $\mu g/L$), and X_f is the density of biomass in the biofilm (mg_x cm^{-3}).

It was shown in a previous study [6] that the microbial transformation rate of toluene in this site could be approximated as first-order with respect to toluene concentration, since the toluene concentration was below or close to 200 $\mu g/L$. Therefore, equation (4.1) can be expressed as:

$$D_f \frac{d^2 C_f}{dz^2} = K X_f C_f \tag{4.2}$$

where K is the mixed second-order rate constant (m^3 mg_x^{-1} h^{-1}).

Solving the equation (4.2), the flux of a substrate into a biofilm can be expressed as a function of the substrate concentration in bulk water as previously described [19, 24, 25]:

$$J_{biofilm} = \frac{k_m D_f \phi \tanh(\phi L_f)}{k_m + D_f \phi \tanh(\phi L_f)} C \equiv k_{biofilm} C \tag{4.3}$$

where k_m is a mass transfer coefficient (m h^{-1}) and defined as D/L, D is the molecular diffusion coefficient for the substrate in the bulk water (m^2 h^{-1}), L is the thickness of the effective diffusion layer (m), L_f is the thickness of the biofilm (m), C is the substrate concentration in the bulk water (mg_s m^{-3} or μg/L), $k_{biofilm}$ is the uptake rate constant of the substrate by the biofilm (m h^{-1}), and ϕ is a characteristic biofilm kinetic parameter (m^{-1}) that is defined by

$$\phi = \sqrt{\frac{KX_f}{D_f}} \, . \tag{4.4}$$

To examine the possibility of oxygen limitation, two estimations were made; one is to estimate the toluene biodegradation rates on the assumption that toluene is biodegraded in the whole thickness of the biofilm however thick the biofilm may be and the other is to estimate the rates on the assumption that toluene is biodegraded only in the aerobic part of the biofilm when a part of the biofilm becomes anaerobic. These estimations under two extreme assumptions allowed us to show a possible range of the toluene biodegradation rates and the sensitivity of the rates to the oxygen limitation in our site. When it is assumed that toluene is degraded only in the aerobic part of the biofilm, the biofilm thickness in the equation (4.3) is equated to the thickness of the aerobic layer of biofilms when the total thickness of biofilm is greater than the calculated thickness of the aerobic layer. Therefore, the $k_{biofilm}$ becomes:

$$k_{biofilm} = \frac{k_m D_f \phi \tanh(\phi L_{ae})}{k_m + D_f \phi \tanh(\phi L_{ae})} \quad if \quad L_f > L_{ae} \tag{4.5}$$

where L_{ae} is the thickness of the aerobic layer of the biofilm (m).

The streambed is composed of gravel, plant litter, and sediment. These materials often provide more surface area to be colonized than streambed itself.

Therefore, we proposed that the uptake rate constant of toluene per vertically projected streambed area ($k_{streambed}$) could be equated to an uptake rate constant of toluene per colonized surface area ($k_{biofilm}$) multiplied by the ratio of the colonized surface area to the projected streambed surface area as following:

$$k_{streambed} = k_{biofilm} \left(\frac{A_c}{A_s}\right) \tag{4.6}$$

where A_c is the colonized surface area (m^2) and A_s is the vertically projected streambed surface area (m^2). The previous study [22] reported that $k_{streambed}$ in the studied stream ranged from 0.08 to 0.40 m hr^{-1} during summer. In this work, we estimated $k_{streambed}$ by determining $k_{biofilm}$ in the laboratory study and A_c/A_s in the field. We then compared the $k_{streambed}$ with the seasonal average value of the *in-situ* $k_{streambed}$ reported in the previous study [22].

Method

Study Site

The studied stream reach is 400 m long, 1 m wide, and approximately 30 cm deep. The studied reach was contaminated with toluene (> 100 μg/L) along with other volatile organic compounds, including chlorinated solvents (> 10 μg/L). The coverage of the stream bottom includes gravel, sand, silt, and some plant material. The dimensions of the largest stones were approximately 3 cm. The study site is described in more detail elsewhere [22].

Determination of KX_f and ϕ

Plant litter (leaves and plant stems) and gravel were collected from the stream. The samples were covered by a reddish slime layer (biofilm). Biofilms attached were removed by scraping with a spatula, and vigorously stirring the samples with stream water for several minutes, until the bare surface of the substratum appeared. The colonized area (A_c) was estimated using pieces of graph paper after the biofilm was removed. The stream water which was used to stir the samples (and thus contained biofilms) was diluted with biofilm-free stream water to make approximately 80 ml and put in a 120-ml serum bottle with a teflon-coated serum stopper, yielding 40 ml of headspace in the bottle. Approximately 200 μg/L of toluene was added from a saturated stock solution. Control samples were prepared as above with the addition of 1 ml of saturated HgCl solution. The bottles were constantly shaken with a wrist-action shaker. It was assumed that the vapor phase and aqueous phase of toluene were at equilibrium during the experiment. Toluene in the gas phase was measured periodically by analyzing 1 ml of the headspace of the serum bottles via gas chromatography as described elsewhere [6].

The rate of biodegradation can be expressed as:

$$\frac{dC}{dt} = K_1 C \qquad (4.7)$$

where K_1 is a pseudo first-order rate constant (h^{-1}) determined from the slope of the plot of (ln C) vs. time. Since the biofilms are diluted with stream water in the bottle, K_1 is related to KX_f in equation (4.2) by:

$$K_1 \left(\frac{V_{slurry}}{V_{biofilm}}\right) = KX_f \qquad (4.8)$$

where V_{slurry} and $V_{biofilm}$ are the volumes of slurry sample and biofilm in the bottle, respectively. The volume of biofilm used in the batch experiment was determined by weighing the biofilm in slurry samples after filtering and converting the weight into volume using 1 g/cm^3 as the density of the wet biofilm (a density confirmed by measuring the volume and weight of the biofilm on one experiment).

The molecular diffusivity of toluene within the biofilm was assumed to be 0.8 D, where D is the diffusivity of toluene in water [14]. ϕ was calculated from KX_f and D_f as defined in equation (4.4).

Determination of L_f

The thickness of the biofilm was determined by dividing the volume of biofilm removed from a leaf or a stone by the surface area of the leaf or stone, A_c, that the biofilm was taken from.

Determination of k_m

The mass transfer coefficient, k_m, is defined as D/L where D is the molecular diffusion coefficient of toluene in the bulk water ($m^2\ h^{-1}$) and L is the thickness of the effective diffusive layer (m). The mass transfer coefficient was estimated from equations of Gantzer et al. [25] and Kawashima and Suzuki [20].

Gantzer et al. [25] report the following expression for gravel-lined streambed:

$$k_m = [88 + \frac{1.11\times10^{-11}}{d} Re^{4.33} Sc^{1/3}] \frac{D}{d} \tag{4.9}$$

where d is the mean streambed particle size (m), Re is the Reynolds number, and Sc, the Schmidt number (dimensionless), is equal to the kinematic viscosity of the substrate (ν) divided by D. The Reynolds number was obtained as follows [25]:

$$Re = \frac{U_* d}{\nu} \tag{4.10}$$

where U_*, the friction velocity ($m\ h^{-1}$), was estimated from [26]:

$$U_* = \sqrt{gRS_0} \tag{4.11}$$

where S_0 is the slope of the streambed, g is the gravitational acceleration and R is the hydraulic radius. The slope, 0.0047, was determined from a topographic map of the site [27].

The thickness of the diffusive layer was also determined from [20]:

$$L=\left(\frac{\varepsilon}{\nu^3}\right)^{-\frac{1}{4}} \tag{4.12}$$

where ϵ is the energy dissipation rate. The energy dissipation rate can be estimated from the velocity of a stream (U) and the slope of the stream bed [20]:

$$\varepsilon = g\,U\cos\theta \tag{4.13}$$

where θ is the slope angle of the stream bottom and was close to 1 in this site.

Determination of A_c/A_s

Four representative-appearing plots of the streambed, each having an area of approximately 2000 cm^2, were arbitrarily selected in the fall season. Gravel, plant litter and any other objects that appeared to be covered by red-colored slime were lifted out of the selected stream bottom, and the surface area of the objects was measured by the use of a sheet of graph paper. The color of the surfaces of the biofilms was used as a criterion of being aerobic; the red color, suggesting the presence of iron oxides, was considered to be oxygenated, and the black color was assumed to be indicative of more reducing conditions and hence anaerobic. However, the whole depth of the biofilm, even if the surface is reddish, is not necessarily oxygenated when the biofilm is thick, as discussed below. When, during removal of material for measurement of surface area, the materials in the stream bottom started appearing to be covered by black-colored slime, the measurement of colonized area ended.

Determination of the thickness of aerobic layer of biofilm, L_{ae}

In order to examine the possible variability of the toluene biodegradation rate constants due to oxygen limitation, the thickness of aerobic layer in biofilm was theoretically calculated as proposed by Kawashima and Suzuki [20]:

$$L_{ae} = -\frac{D_{of}L}{D_o} + \sqrt{\left(\frac{D_{of}L}{D_o}\right)^2 + \frac{2D_{of}C_o}{k_{ae}}} \qquad (4.14)$$

where L_{ae} is the thickness of aerobic layer of biofilm, D_{of} is the diffusivity of oxygen in biofilm as determined in the same way of the diffusivity of toluene in biofilm ($0.8D_o = 1.6\times10^{-9}$ m^2/s), L is the thickness of diffusive layer, D_o is the diffusivity of oxygen in water (2×10^{-9} m^2/s at 20 °C), C_o is the concentration of dissolved oxygen in the bulk water and k_{ae} is the DO consumption rate of biofilm. Measuring the concentration of dissolved oxygen in the stream showed that stream water was often supersaturated with oxygen during the day (data not shown); thus, the solubility of oxygen at relevant temperature was used for C_o.

Since the estimation of L_{ae} given by equation (4.14) is sensitive to the DO consumption rate of biofilm, two values were taken for k_{ae}; 0.5 g/m^3-sec given by Kawashima and Suzuki [20] and 1.4 g/m^3-sec obtained by experiments that measured the level of dissolved oxygen in a slurry sample in a closed vessel under light conditions, prepared in the same way as to determine the KX_f of biofilm, but with the addition of an oxygen electrode.

In order to estimate L_{ae} under temperatures similar to field conditions in spring and fall (11 °C), parameters that were influenced by temperature change were corrected for lower temperature; D_{of} and D_o at 10 °C are taken as 74% of those at 20 °C by following the report of Hyduk and Laudie [28]. Although the DO consumption rate is also likely to decrease with temperature, the DO consumption rate was not corrected for temperature since the sensitivity of L_{ae} to the DO consumption rate was already being considered by taking two values of the DO consumption rate. However, the potential decrease in the DO consumption rate with temperature and thus the change in the biodegradation rate constant are discussed in more detail below.

Estimation of biodegradation rate constant, $k_{streambed}$

Parameters that were influenced by temperature (KX_f, D_f, ϕ, D, k_m) were corrected for temperature change in field. The KX_f obtained in laboratory, where experiments were conducted at 20 °C, to field conditions where water temperature in spring and fall was 11 °C [22], was multiplied by 1/2 for estimating the biodegradation rates in spring and fall, using the result in the previous study [22] and the rule of thumb that a 10 °C decrease in temperature approximately halves biodegradation rates for marine organisms [29]. The diffusion coefficients of toluene in water and biofilm for spring and fall temperature were taken as 74 % of those for summer temperature (20 °C) by following [28]. The mass transfer coefficient, k_m, for spring and fall temperature were, therefore, corrected for the decreased diffusion coefficient of toluene in water. With the parameters corrected for temperature, the $k_{biofilm}$ was calculated under two different assumptions. One was that the whole depth of the biofilm could degrade toluene however thick the biofilm might be (no oxygen limitation); in this case, equation (4.3) was used. The other case was that only the aerobic part of the biofilm could degrade toluene (oxygen limitation); in this case, equation (4.5) was used.

Results and Discussion

The thickness of biofilms ranged from 60 to 6100 μm, with an average of 1500 μm (Table 4.1). In spring, the biofilms were much thinner than in other seasons, suggesting that the biofilm may be scoured with the high flow condition of spring or that the biofilms may thin due to lower temperatures and/or lower levels of organic carbon in cold seasons. In other seasons, the biofilms in this site were generally thicker than those reported in other studies [17, 19]. Gantzer et al. [19] reported a thickness of 200 μm for biofilms grown on a teflon strip in a river; however, biofilm grown on natural substratum may differ from biofilms grown on Teflon [30]. Thus, difference in the characteristics of surfaces may have partly contributed to the difference in the thickness of biofilms in our study and the study of Gantzer et. al [19]. Srinanthakumar et al. [17] reported thicknesses of 300-400 μm for biofilms in a cobble-lined river, where the stream velocity was 10 times higher than the stream velocity in our study. Their higher velocity may have scoured the biofilm and resulted in biofilms thinner than those in our study.

The depth of aerobic layer of biofilms was calculated as 140 μm at the high DO consumption rate of 1.5 g/m^3-sec at 20 °C , but as deep as 200 μm after being corrected for temperature to 10 °C (Table 4.1). Thickness was calculated as 240 μm at the low DO consumption rate of 0.5 g/m^3-sec at 20 °C, and ranged from 240 to 280 μm after being corrected for temperature. Although the difference between the aerobic thicknesses with the high DO consumption rate and those with the low DO consumption rate was 100 μm, the difference did not contribute to proportionately large changes in the biodegradation rate constant as discussed below. These aerobic thicknesses are consistent with reports by other researchers that the active depth of microbial films is about 100 μm [31, 32], and that the dissolved oxygen in microbial films is depleted at a depth of approximately 100 μm into the films [33-36]. The aerobic thicknesses calculated with the high DO consumption rate were less than the measured whole thickness of biofilms taken in summer and fall (Table 4.1), suggesting that oxygen may have some role in limiting the toluene biodegradation in summer and fall.

To compare the uptake rate of oxygen with that of toluene, the DO consumption rate was converted into a benthic oxygen uptake rate by multiplying the DO consumption rate (1.4 g/m^3-sec) by the aerobic biofilm thickness in summer (140 μm) and the surface area ratio, A_c/A_s (7), resulting in 120 g/m^2-day. The benthic uptake rate of toluene in this site was estimated as 1.2 g/m^2-day in summer from the data previously reported [22]. The ratio of the benthic uptake rate of oxygen to that of toluene was 100, 30 times higher than the ratio that the stoichiometry of toluene oxidation would predict. This was not surprising for a biofilm that is mostly supported by sources of organic carbon other than toluene.

In October, the pseudo-first-order biodegradation rate constants (KX_f) were higher in the biofilms colonized over plant litter (300 hr^{-1}, Table 4.1) than those over gravel (13 and 99 hr^{-1}), although there were not enough data to show any conclusive results. This is consistent with the finding of Cohen et al. [6], who reported that the slurry samples made of plants and stream water from this site biodegraded toluene faster than material from any other surfaces. Although several researchers [30, 37] have reported the growth of biofilm on different surfaces, very few studies on the difference in the biodegradation capabilities of biofilms on different surfaces have been conducted (see [3]). Such studies were beyond the objectives of this work, but our results show that microorganisms in biofilms on different surfaces might have different biodegradation capabilities.

The product of the kinetic parameter, ϕ, and the biofilm thickness, L_f, is the argument of the hyperbolic function in equation (4.3). A small value of ϕL_f (≤ 0.5) yields the result that the value of the hyperbolic tangent function (ϕL_f) approximately equals the argument. Physically, this means that the microorganisms in the biofilm act like suspended microorganisms, the biofilm is fully penetrated, and diffusion within the biofilm is not limiting to the biodegradation rates. Biofilms in spring were fully penetrated (Table 4.1). In other seasons, the biofilms were shallow or deep (Table 4.1), following the criteria of Gantzer [24]. However, because of the possibility that a part of the depth of biofilms in summer and fall becomes anaerobic, ϕL_{ae} is relevant to determine the limiting factor within the aerobic layer. The ϕL_{ae} of most biofilms in summer and fall can be defined as shallow. If this becomes the case, toluene biodegradation could be limited in part by the absence of oxygen, although within the aerobic layer diffusion is a limiting factor.

The thickness of the diffusive layer (L) and the mass transport term (k_m) were calculated with two alternative equations (Table 4.2). The equation by Gantzer et al. [25] was obtained for sand-free gravel or cobble-lined streambed and the equation used by Kawashima and Suzuki [20] was based on a flat sediment streambed. Our site was more complex than the model streams of Gantzer et al. [25] and Kawashima and Suzuki [20]. However, both equations resulted in similar values of mass transfer coefficient (Table 4.2), and choice of one over the other did not make much difference in estimating overall biodegradation rates.

The thickness of the diffusive layer above the uppermost layer of streambed may be different from that of lower layers. However, in this study, we used the same value for all colonized surface. The equation from Gantzer et al. [25] was for a mean thickness of diffusive layer for all layers of gravel and cobbles in their model stream. Sensitivity analysis was conducted to estimate the magnitude of error which might have been associated with this approximation; when a order of magnitude higher value for the thickness of diffusive layer was assumed for the half of colonized area, the value of biodegradation rate constant changed by less than 30%.

The kinetic term, $D_f\phi \tanh(\phi L_f)$ (Table 4.1), was much smaller than the mass transfer term, k_m (Table 4.2), indicating that microbial kinetics were the most limiting factor. This is consistent with the finding of Cohen et al. [22], which showed that mass transport through a diffusive layer was not likely a limiting factor because of the turbulent nature of this stream. It is also consistent with the study of Kim et al. [22], which reported that higher stream velocity did not increase the biodegradation rates at this site, and suggested that mass transfer within the diffusive layer might not be limiting to biodegradation. Lewis and Gattie [2] showed a positive correlation of the biodegradation rate constant (by attached microorganisms) with the water velocity for different sites. In data from the same site, however, the biodegradation rate constant was not positively correlated with water velocity. Moreover, at water velocities higher than 300 m/h, they found the positive correlation of the rate constant with water velocity to be weaker. Gantzer et al. [38] showed that the streambed biofilm activity increased with the friction velocity. However, the velocity range they tested was only up to 144 m/h, and a plateau was starting to be reached at this velocity. At our site, the water velocity and friction velocity were usually higher than 200 m/h (Table 4.2), most likely high enough that mass transfer within the diffusive layer is not limiting the biodegradation rate.

The ratio, A_c/A_s was determined as 7 ± 3. The model stream of Gantzer et al. [25, 38] had a ratio of 6-7. The ratio was 6-16 for a gravel-lined section of the streambed at the study site of Pignatello et al. [3]. At our site, in the section where gravel dominated the stream bottom, only the top layer of stones was exposed to the overlying water, with the result that the ratio was as small as 3. However, the upper section of the reach was mostly covered by plant litter, which provided a larger colonized area for microorganisms, and the ratio was as large as 10. This is consistent with the study of Lewis et al. [8] which reported that leaf litter in the fall season provided a large surface area.

The ratio, A_c/A_s, in this site may also vary with seasons. The reported ratio was measured in the fall season. However, the stream bottom did not appear to vary greatly between seasons. Spatial heterogeneity probably contributes more to the uncertainty of the ratio than seasonal variation. However, in the spring of 1994, filamentous green algae were prevalent in the stream. Biofilms appeared to be attached to their surfaces, yet their surface area was not included in the measurement of A_c. This could have resulted in a higher ratio of A_c/A_s for the spring.

With this range of the ratio, seasonal average biodegradation rate constants were predicted under three possible scenarios and compared with experimentally determined *in-situ* biodegradation rate constants [22] (Fig. 4.2). The three scenarios considered were that 1) there was no oxygen limitation in the whole depth of the biofilm, 2) there was oxygen limitation in a part of the biofilm and the DO consumption rate of the biofilm was 0.5 g/m^3-sec, and 3) there was oxygen limitation but the DO consumption rate of the biofilm was taken as 1.4 g/m^3-sec.

In summer and fall, the predicted biodegradation rate constants matched the measured *in-situ* rates well, while the rate constant for spring underestimated the *in-situ* rate constant (Fig. 4.2). The underestimation of the rate constant for spring may have been due to the underestimation of the area ratio, A_c/A_s, with unaccounted colonized area discussed earlier.

The extent to which the oxygen limitation assumptions lowered the biodegradation rate constants in summer and fall was surprisingly small (in spring, the whole depth of the very thin biofilm is presumably supplied with oxygen, Fig. 4.2). Thus, the predicting capability of the biofilm kinetic model under the assumption that toluene is the only limiting substrate is remarkably robust.

The overall biodegradation rate constant was affected by the surface area ratio, A_c/A_s. Therefore, the uncertainty associated with the biodegradation rate constant mostly came from the spatial heterogeneity and measurement error associated with the ratio, A_c/A_s, in spring and summer (Table 4.3). This is consistent with the conclusion of Kawashima and Suzuki [20] that the BOD removal by attached microorganisms was mostly dependent on surface area ratio. The variability and uncertainty of microbial kinetics, KX_f, contributed nearly as much as area ratio to the variability of the overall biodegradation rate. On the other hand, variability of the thickness of biofilms was not relevant to the biodegradation rate constant when the biofilms became so thick that only a part of the biofilms could degrade toluene.

The overall uncertainty range in the predicted rate constants was determined by the variability of microbial kinetics and by the area ratio (Table 4.3). The uncertainty might be improved by dividing the whole reach into subreaches where microbial kinetics and area ratio are spatially less variable, estimating the rate constants for subreaches, and integrating the constants for the whole reach. The temperature correction for the biodegradation rate constants in spring and fall brings an additional uncertainty that is not quantified: the rule used, that a 10°C decrease in temperature halves KX_f, deserves further investigation.

Conclusion

Our study combined a culture experiment, which can conducted in a straightforward way in the laboratory, with a biofilm kinetic model, and successfully predicted the *in-situ* biodegradation rates of toluene in a stream. This suggests a workable way of estimating the biodegradation rates of a chemical in a stream where attached microorganisms are primarily responsible for the biodegradation. In our site, mass transfer within the diffusive layer did not appear to limit the biodegradation rate, while microbial kinetics did. Diffusion within the biofilm was also a limiting factor in the summer and fall, although it did not limit the biodegradation rates in the spring when the biofilms were thin. Although oxygen limitation in the biofilms in summer and fall may occur, the predicted biodegradation rate constants were not affected much by the limitation. Greater accuracy may be obtained by improvement in A_c measurement and by determination of KX_f at *in-situ* temperatures to avoid uncertainties of temperature correction. Role of oxygenation also deserves further investigation.

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Table 4.1. Biological Parameters of Biofilms

Experiment Date	Surface Type	Thickness of biofilm, L_f (μm)	Calculated thickness of aerobic layer in biofilm, L_{ae} (μm)[a]	KX_f (hr^{-1})	ϕL_f	Biofilm Type[b]	Kinetic Term, $D_f\phi\tanh(\phi L_f)$ (m/hr)
May. 94	Gravel	60	170	120	0.4	Fully penetrated	0.0068
May. 94	Gravel	38	170	280	0.4	Fully penetrated	0.010
June. 94	Leaf	180	140	530	2.4	Deep	0.037
Sep. 94	Leaf	1400	200	110	9.1	Deep	0.017
Sep. 94	Plant Stem	740	200	130	5.2	Deep	0.019
Oct. 94	Gravel	6100	200	13	13	Deep	0.0059
Oct. 94	Leaf	3500	200	300	37	Deep	0.029
Oct. 94	Gravel	280	200	99	2	Shallow	0.015
Spring		49±11	170	200±80	0.39±0.005		0.0084±0.0016
Summer		180	140	530	2.4		0.037
Fall		2400±2100	200	130±94	13±12		0.017±0.007

a. L_{ae} was calculated by taking k_{ae} as 1.4 g/m^3-sec in using the equation (4.14) and was corrected for stream water temperature.

b. A biofilm is defined to be deep when $\phi L_f \geq 2.2$, fully penetrated when $\phi L_f \leq 0.5$, and shallow when $0.5 < \phi L_f < 2.2$.

Table 4.2. Thickness of Diffusive Layer (L) and Mass Transfer Coefficient (k_m)

Season	Hydraulic Radius, R (cm)[a]	Stream Velocity, U (m/hr)[a]	Friction Velocity, U^* (m/hr)[b]	Thickness of Diffusive Layer, L (m)		Mass Transfer Coefficient, k_m (m/hr)	
				Ref. [25][c]	Ref. [20]	Ref. [25]	Ref. [20]
Spring	11	368	256	7.0×10^{-6}	3.2×10^{-5}	0.49	0.11
Summer	7	244	204	1.8×10^{-5}	3.5×10^{-5}	0.19	0.10
Fall	8	371	219	1.4×10^{-5}	3.2×10^{-5}	0.25	0.11
Winter	6	369	189	2.5×10^{-5}	3.2×10^{-5}	0.14	0.11

a. Data were taken from a previous study on this site [22].

b. Friction velocity was estimated from equation (4.11).

c. The thickness of diffusive layer was calculated from dividing the molecular diffusivity of toluene in water by the k_m estimated by equation (4.9).

Table 4.3. Predicted Biodegradation Rate Constant and Factors Contributing to Its Uncertainty

Season	biodegradation rate constant, $k_{streambed}$ (m/hr)	uncertainty level associated with biodegradation rate constant[a] (m/hr)					
		total uncertainty level	due to L_{ac}[b]	due to L_f	due to KX_f	due to k_m	due to A_c/A_s
Spring	3.0×10^{-2}	1.9×10^{-2}	*not applicable*	6.8×10^{-3}	1.2×10^{-2}	3.3×10^{-4}	1.3×10^{-2}
Summer	2.0×10^{-1}	8.8×10^{-2}	2.4×10^{-3}	NA[c]	NA[c]	1.3×10^{-2}	8.7×10^{-2}
Fall	5.5×10^{-2}	4.2×10^{-2}	8.8×10^{-3}	0	3.4×10^{-2}	1.3×10^{-3}	2.4×10^{-2}

a. The estimation of errors followed [39]. The uncertainty range of each parameter was taken as one standard deviation.

b. The error range of L_{ac} was taken as ±50 μm based on two values of k_{ac} used.

c. not available

Fig. 4.1. Substrate Concentration Profiles in a Biofilm

(source: [23])

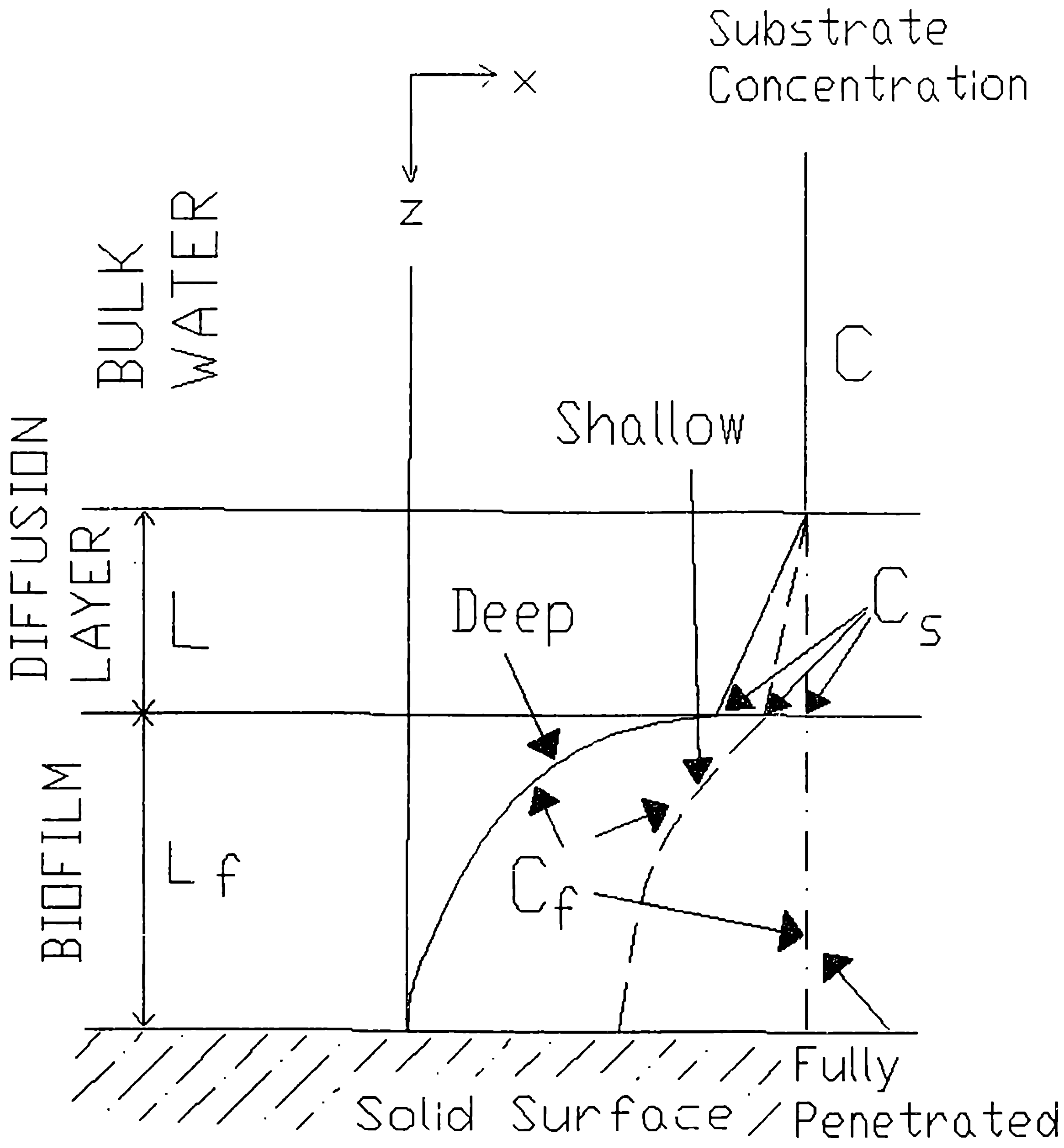
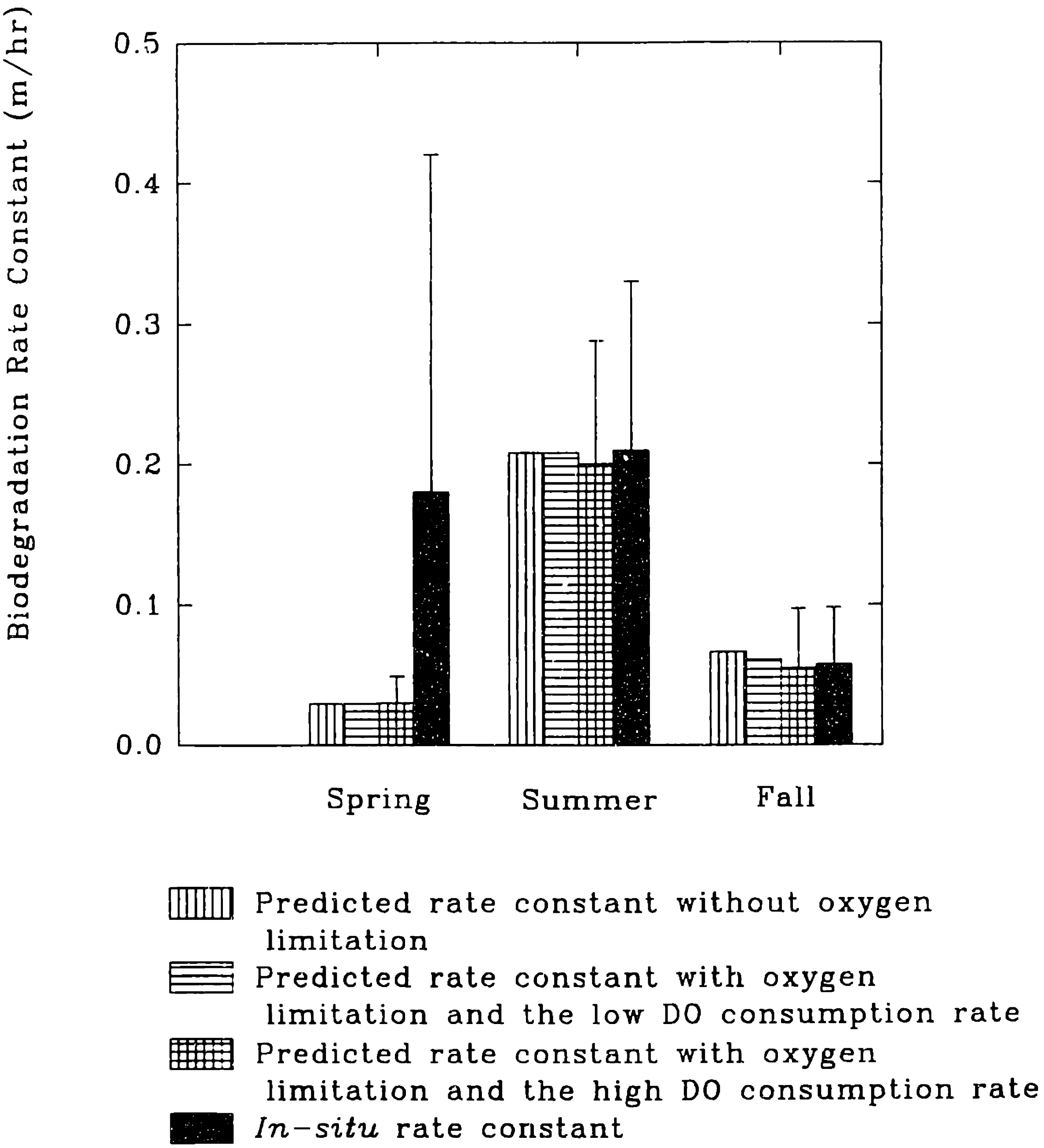


Fig. 4.2. ***In-Situ*** **and Predicted Biodegradation Rate Constant**
(The low DO consumption rate was taken as 0.5 g/m^3-sec given by Kawashima and Suzuki [40] and the high DO consumption rate as 1.4 g/m^3-sec obtained by experiments as explained in the method)



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Chapter 5. Future Research

Future works which can be extended from the study reported in this thesis are manyfolded-hydrology, biology, chemistry. I listed a few questions to be answered in the future. They are 1) how significant is the natural flushing of VOCs in a contaminated site with on-going remediation actions ? 2) can we enhance biotransformation of TCE and DCE in a natural stream ?

Assessment of Significance of Natural Flushing Rate of VOCs in a Contaminated Aquifer (the Well G & H area)

The natural flushing was shown to be potentially as effective as remediation in chapter 2. The Well G & H area is a Superfund site in the Aberjona watershed where remediation actions have begun. It was reported that the remediation of groundwater in this site removed total VOCs with the rate of 150-180 kg/yr for two years [1-4]. By studying the discharge of VOCs in a reach of the Aberjona River besides the well G & H area, the comparison of the natural flushing rate with the removal rate of VOCs by pump and treat system employed in this site can be more usefully demonstrated.

Field methodology similar to that reported in Chapter 1 can be employed for this study, but there is a limit in determining flowrates with the use of Mariotte bottle. The Mariotte bottle, a 50-L carboy bottle which maintains constant head, is used to inject a salt solution with a constant injection rate. While the Mariotte bottle is very easy to handle and maintain a constant injection rate, it can take only 50 L of salt solution, whose concentration is limited to 5 M due to the solubility of salt. There is a limit of flow rate that the injection of salt solution with the Mariotte bottle can show the noticeable increase of specific conductance in a stream and yet reach the steady state. The limit of the flow rate is around 50 L/s. The typical flowrates of the Aberjona river in the Well G & H area is 300 L/s.

Commonly, for a stream with high flowrate, the salt solution is injected with a pump from a tank which can hold a large amount of the solution. Alternatively, dye or other tracer such as Bromide and Lithium is used as a conservative solution because it can give noticeable increase of concentration with a relatively small amount injected. Each method has its own drawback. The injection of salt solution involves building a tank and running a pump, which can take lot of resources. The use of dye or Bromide or Lithium can arouse the issue of public health, depending on the area applied. The potential hazard of dye can make the dye not feasible to be injected to a certain stream.

A proposed technique is a dry salt injection. The constant injection of dry salt, if possible, doesn't need to carry water and a tank, yet can make possible to inject enough salt to a stream with high flowrate. The proposed scheme of the dry salt injector is shown in Fig. 5.1. Two galvanized pipes, whose diameters are 9 inches, are connected and one funnel (funnel 1) is inserted into the lower pipe and the other funnel (funnel 2) is connected to the end of the lower pipe. The salt is loaded into the upper pipe and the salt flows through the funnel 1 and is placed in the funnel 2. The funnel 2 can take only a constant amount of salt regardless of the amount of salt in the upper pipe, and thus it is maintained to have a constant injection rate as long as the upper pipe is not empty. An orifice made of a piece of plastic tubing is connected to the end of funnel 2; different sizes of the tubing can change the injection rate. The salt released from funnel 2 to funnel 3 is mixed with water supplied from upstream by a bilge pump to the bottom of the funnel 3. The salt solution made in funnel 3 overflows funnel 3 to the mixing tray and finally flows to the stream through a plastic tubing. Dissolving salts with stream water both in funnel 3 and in the mixing tray before injection minimizes the possibility of undissolved salt sinking to the bottom of the stream. This dry salt injector can hold 40 kg of salt at once and as high as 500 L/s of flowrate can be measured with the injector.

The dry salt injector was tested in two field sites: Montvale Avenue and Mishawam Road. Figure 5.2 shows the increase of specific conductance over time at a downstream measuring station with the continuous injection of dry salt by the dry salt injector. In the test at Mishawam Road site, the steady-state of specific conductance was observed by the injection of dry salt with the dry salt injector and the salt solution must have been injected with a constant rate. In the test at Montvale

Ave. site, the background specific conductance increased over time and it is believed to be due to road salting because it snowed the day before the experiment day and its morning. However, it was not very clear when the steady-state was reached, yet after around 35 minutes, the slope of specific conductance over time decreased. It is not clear that the increasing conductivity after 35 minutes is solely due to the increasing background or due to a inconstant injection of salt solution. A further refinement to maintain a constant injection rate of salt and dissolve all the salt before injection will be conducted. The flowrate estimated by the use of the dry salt injector was 470 L/s and it was comparable with the flowrate obtained by measuring velocities over cross-sectional area of the stream, 468 L/s.

The objective of this study would be to estimate the natural flushing rates of VOCs in a site with highly contaminated groundwater, to assess the importance of the natural flushing in comparison to artificial remediation, and to develop and apply a dry salt injector for the determination of high flowrates.

Enhanced Biodegradation of TCE and 1,2-DCE in a Natural Stream

TCE has been known to be resistant to biodegradation in most natural aerobic environments [5]. However, TCE and 1,2-DCE have been known to be biodegraded through cometabolism by methanotrophs in the laboratory microcosms [5-11]. This can be used to clean up water contaminated with TCE and 1,2-DCE. It is, however, difficult to conduct the test of biodegradability of such contaminants in the field because 1) many other transport and degradation processes occur, and 2) injecting such a chemical to a field site can contaminate the site. I am aware of only one study [12] which reported a field experiment of *in-situ* biodegradation of TCE. Semprini et al. (1990) showed that the *in-situ* biodegradation of TCE in groundwater after biostimulating the microflora in the aquifer with methane and oxygen in a field site.

The Sweetwater Brook in the Aberjona watershed, which was discussed in Chapter 1, have been found to be contaminated with TCE and DCE discharged from groundwater. The location where TCE and DCE were discharged was identified in the study reported in Chapter 1. This stream, therefore, can provide the field site to study the *in-situ* biodegradation of TCE and DCE without an intentional injection of TCE and DCE.

The proposed experiments is 1) to add methane to the stream for a period, 2) to measure the effect of a developing methane oxidizing community by doing mass balance, 3) to monitor the disappearance of TCE and 1,2-DCE in the stream, and 4) to estimate the biotransformation rate and volatilization rate by the use of in-stream tracer technique discussed in Chapter 2. Enumeration of methanotrophs will be performed before and after the field experiment.

The objective of this study is 1) to test biodegradability of TCE and DCE in a field site with biostimulation and 2) to estimate the relative significance of biodegradation of TCE and DCE with biostimulation in a stream.

Fig. 5.1. Dry Salt Injector

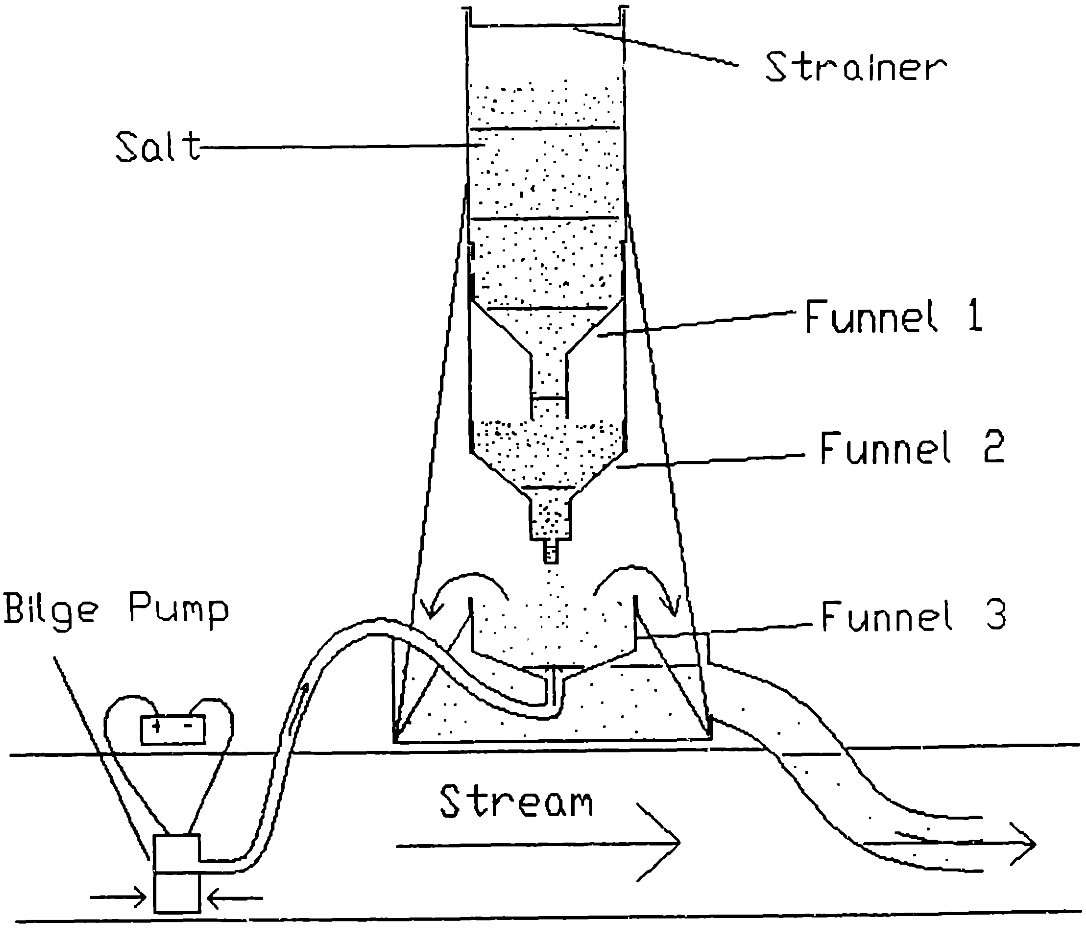
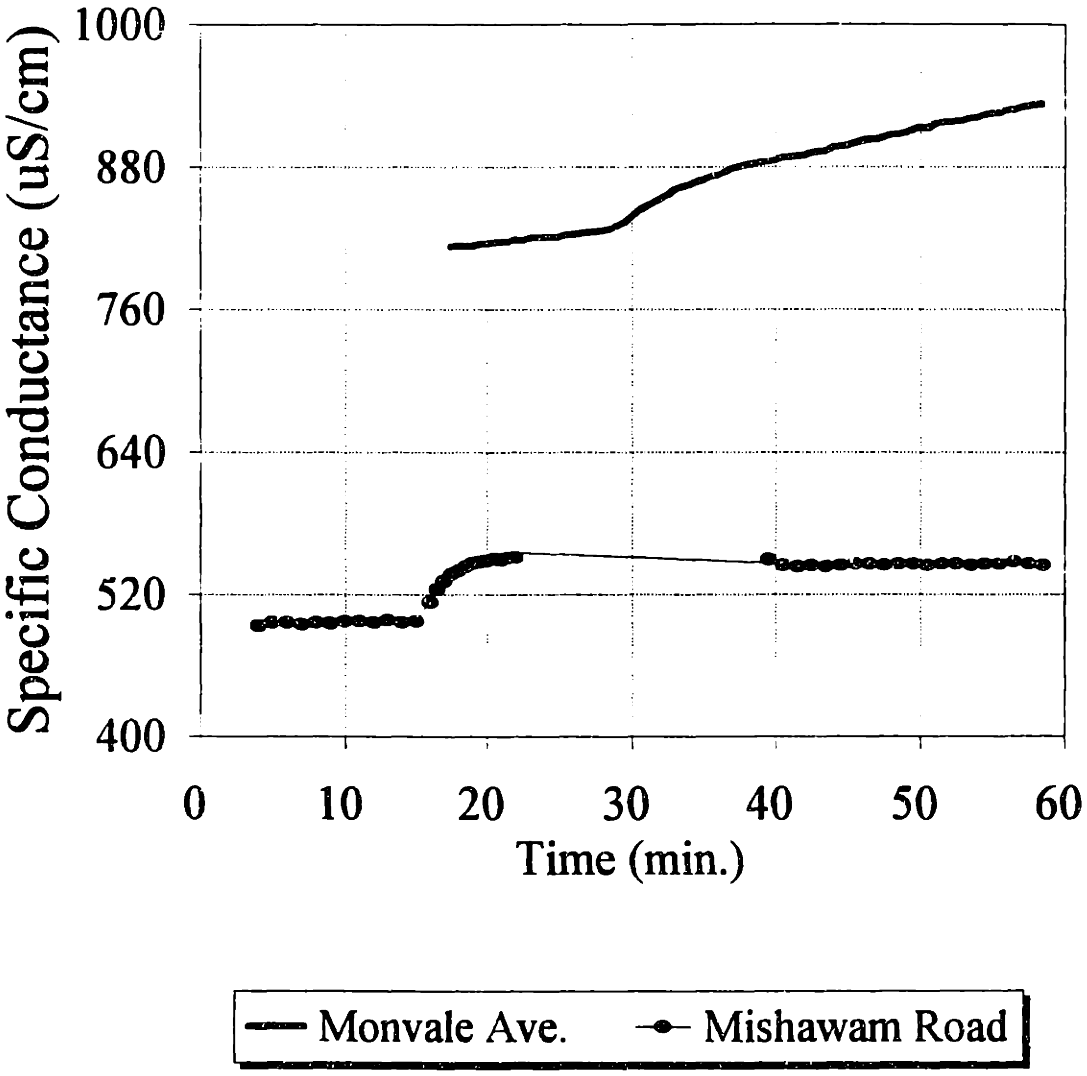


Fig. 5.2. Result of Use of Dry Salt Injector in Two Streams with High Flow Rate



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Appendix A. Propagated error analysis

Kline [1] suggested one way to calculate the propagated error as follows:

$$W_R=\sqrt{(\frac{\partial R}{\partial x_1}W_{x_1})^2+(\frac{\partial R}{\partial x_2}W_{x_2})^2+.......+(\frac{\partial R}{\partial x_n}W_{x_n})^2} \tag{A-1}$$

where R is a result computed from n measurands, x_1, x_2, ..., x_n and W is an certainty associated with the subscript indicating the variable.

The above equation is applied to calculate the errors associated with ΔQ_{ij} and C_{ij}^x. The results are as follows:

1. ΔQ_{ij}

$$\Delta Q_{ij}=\frac{C_{inj}Q_{inj}}{\alpha}(\frac{1}{S_j}-\frac{1}{S_i}) \tag{A-2}$$

$$W_{\Delta Q_{ij}}=\sqrt{(\frac{\partial\Delta Q_{ij}}{\partial S_i}W_{S_i})^2+(\frac{\partial\Delta Q_{ij}}{\partial S_j}W_{S_j})^2+(\frac{\partial\Delta Q_{ij}}{\alpha}W_{\alpha})^2} \tag{A-3}$$

$$W_{\Delta Q_{ij}}=C_{inj}Q_{inj}\sqrt{[\frac{W_{S_i}}{\alpha S_i^2}]^2+[\frac{W_{S_j}}{\alpha S_j^2}]^2+[\frac{W_{\alpha}}{\alpha^2}(\frac{1}{S_j}-\frac{1}{S_i})]^2} \tag{A-4}$$

2. C_{ij}^x

By dividing the numerator and the denominator of Eqn. (A-4) by S_j,

$$C_{ij}^x=\frac{C_j^x\frac{S_i}{S_j}-C_i^x+\frac{1}{4}(1+\frac{S_i}{S_j})(C_j^x+C_i^x){k^P}_{ij}\tau_{ij}\lambda^x}{\frac{S_i}{S_j}-1} \tag{A-5}$$

Then,

$$k^{p}_{ij}\tau_{ij}=\ln(\frac{G_iS_j}{G_jS_i}) \tag{A-6}$$

Eqn. (A-5) becomes that

$$C^x_{ij}=\frac{C^x_j-\frac{S_j}{S_i}C^x_i+\frac{1}{4}(\frac{S_j}{S_i}+1)(C^x_j+C^x_i)\ln(\frac{G_iS_j}{G_jS_i})\lambda^x}{1-\frac{S_j}{S_i}} \tag{A-7}$$

Then, A and B are defined as followings:

$$A_{ij}=\frac{G_i}{G_j} \tag{A-8}$$

$$B_{ij}=\frac{S_i}{S_j} \tag{A-9}$$

By combining Eqn. (A-7) with Eqn. (A-8) and (A-9),

$$C^x_{ij}=\frac{C^x_jB_{ij}-C^x_i+\frac{1}{4}(1+B_{ij})(C^x_j+C^x_i)\ln(\frac{A_{ij}}{B_{ij}})\lambda^x}{B_{ij}-1} \tag{A-10}$$

Now, the variables are A_{ij}, B_{ij}, C_j^x, C_i^x, and λ^x.
Partial derivatives of C_{ij}^x with respect to each variables are obtained as followings:

$$\frac{\partial C^x_{ij}}{\partial A_{ij}}=\frac{(1+B_{ij})(C^x_i+C^x_j)\lambda^x}{4A_{ij}(B_{ij}-1)} \tag{A-11}$$

$$\frac{\partial C_{ij}^{x}}{\partial B_{ij}}=\frac{4C_{j}^{x}B_{ij}-4C_{i}^{x}+(C_{i}^{x}+C_{j}^{x})\lambda^{x}(2B_{ij}\ln A_{ij}-2B_{ij}\ln B_{ij}-B_{ij}+\frac{1}{B_{ij}}}{4(B_{ij}-1)^{2}} \qquad \text{(A-12)}$$

$$\frac{\partial C_{ij}^{x}}{\partial C_{i}^{x}}=\frac{-1+\frac{1}{4}(1+B_{ij})\lambda^{x}\ln(\frac{A_{ij}}{B_{ij}})}{B_{ij}-1} \qquad \text{(A-13)}$$

$$\frac{\partial C_{ij}^{x}}{\partial C_{j}^{x}}=\frac{B_{ij}+\frac{1}{4}(1+B_{ij})\lambda^{x}\ln(\frac{A_{ij}}{B_{ij}})}{B_{ij}-1} \qquad \text{(A-14)}$$

$$\frac{\partial C_{ij}^{x}}{\partial \lambda^{x}}=\frac{(1+B_{ij})(C_{i}^{x}+C_{j}^{x})\ln(\frac{A_{ij}}{B_{ij}})}{4(B_{ij}-1)} \qquad \text{(A-15)}$$

Then, the propagated error of $C_{i,}^{x}$ is as followings:

$$W_{C_{ij}^{x}}=\sqrt{(\frac{\partial C_{ij}^{x}}{\partial A_{ij}}W_{A_{ij}})^{2}+(\frac{\partial C_{ij}^{x}}{\partial B_{ij}}W_{B_{ij}})^{2}+(\frac{\partial C_{ij}^{x}}{\partial C_{i}}W_{C_{i}})^{2}+(\frac{\partial C_{ij}^{x}}{\partial C_{j}}W_{C_{j}})^{2}+(\frac{\partial C_{ij}^{x}}{\partial \lambda^{x}}W_{\lambda^{x}})^{2}}$$

(A-16)

3. C_{exp}^{x}

The concentration of a VOC, x, at downstream is calculated from the concentration at upstream and the volatilization rate constant of propane as followings:

$$C^x_{j,\mathrm{exp}} = C^x_i \left(\frac{G_j}{G_i}\right)^{\lambda^x} \left(\frac{S_i}{S_j}\right)^{\lambda^x-1} \tag{A-17}$$

By combining Eqn. (A-17) with Eqn. (A-8) and (A-9),

$$C^x_{j,\mathrm{exp}} = C^x_i \frac{B_{ij}^{\lambda^x-1}}{A_{ij}^{\lambda^x}} \tag{A-18}$$

$$\frac{\partial C^x_{j,\mathrm{exp}}}{\partial C^x_i} = \frac{B_{ij}^{\lambda^x-1}}{A_{ij}^{\lambda^x}} \tag{A-19}$$

$$\frac{\partial C^x_{j,\mathrm{exp}}}{\partial A_{ij}} = C^x_i(-\lambda^x)\frac{B_{ij}^{\lambda^x-1}}{A_{ij}^{\lambda^x+1}} \tag{A-20}$$

$$\frac{\partial C^x_{j,\mathrm{exp}}}{\partial \lambda^x} = \frac{C^x_i}{B_{ij}}\left(\frac{B_{ij}}{A_{ij}}\right)^{\lambda^x}\ln\left(\frac{B_{ij}}{A_{ij}}\right) \tag{A-21}$$

$$\frac{\partial C^{x}_{j,\exp}}{\partial B_{ij}}=C^{x}_{i}(\lambda^{x}-1)\frac{B^{\lambda^{x}-2}_{ij}}{A^{\lambda^{x}}_{ij}} \tag{A-22}$$

Then, the propagated error of $C_{j,\exp}{}^{x}$ is that:

$$W_{C^{x}_{j,\exp}}=\sqrt{\left(\frac{\partial C^{x}_{j,\exp}}{\partial C^{x}_{i}}W_{C^{x}_{i}}\right)^{2}+\left(\frac{\partial C^{x}_{j,\exp}}{\partial A_{ij}}W_{A_{ij}}\right)^{2}+\left(\frac{\partial C^{x}_{j,\exp}}{\partial \lambda^{x}}W^{x}_{\lambda}\right)^{2}+\left(\frac{\partial C^{x}_{j,\exp}}{\partial B_{ij}}W_{B_{ij}}\right)^{2}}$$

(A-23)

α= Response factor of conductivity meter to the concentration of NaCl solution [M/(μS/cm)]
τ_{ij}= Travel time of a tracer from a upstream station, i, to a downstream station, j
λ^x= Ratio of volatilization rate constants of a VOC, x, to propane
A_{ij}= G_i/G_j
B_{ij}= S_i/S_j
C= Concentration of a chemical in a stream
C_{ij}^x= Concentration of a VOC, x, in the inflow of the reach between a upstream station, i, and a downstream station, j
C_{inj}= Concentration of NaCl solution injected to a stream
C_j^x= Concentration of a VOC, x, found at a downstream station, j
C_q= Concentration of a chemical in the inflow
G_i= Concentration of propane at a upstream station, i
k^p_{ij}= Volatilization rate constant of propane in the reach between a upstream station, i, and a downstream station, j
k_v= Volatilization rate constant [per unit time]
$Q_{(i)}$= Volumetric streamflow (at the i^{th} station) [volume per unit time]
q= Rate of inflow of water to a stream channel per unit length of channel [volume per unit time per unit length of channel]
Q_{inj}=Injection rate of NaCl solution to a stream [L/s]
R = a result computed from n measurands, x_1, ..., x_n
S_i=Conductivity increased to steady-state from background at a upstream station, i
S_j= Conductivity increased to steady-state from background at a downstream station, j
U = Flow velocity
W_R= an uncertainty with a variable, R
x = lateral distance
Δx_{ij}= lateral distance between the i^{th} and j^{th} station
ΔQ_{ij}= Inflow rate between a upstream station, i, and a downstream station, j [volume per unit time]

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Appendix B. *In-situ* oxygen measurement in sediments

In-situ oxygen profile in the sediment was measured, using an oxygen microelectrode. The oxygen microelectrode was made from approximately 1 cm of 0.100 mm-diameter platinum wire, crimped and soldered to a coaxial cable. The platinum wire was insulated on the sides by glass (a disposable glass pipet tip was used). The insulated platinum wire was inserted in a 16G-stainless steel tubing and attached to it with epoxy resin. The resulting electrode was ground to a smooth, planar, circular surface at the tip, using a piece of fine sand paper and grinding powder. The resulting electrode assembly was sufficiently stiff and strong to be manually inserted into sediments. An Ag/AgCl microelectrode (MI-401, Microelectrodes, Inc.) was used as an anode. The measuring circuitry for the oxygen microelectrode was made by following a circuit diagram used by Reimers et al.[1]. The circuit diagram is presented in Fig. B.1. The oxygen concentration in bulk water is measured with both the microelectrode in the field and Winkler titration [2] in the laboratory, and used as a calibration point.

The voltage reading from current generated by the presence of oxygen with the depth of sediment is shown in Fig. B.2. It is shown that, to 2 mm of depth, it reads the current which indicates the presence of oxygen.

Fig. B.1. Circuit Diagram For Oxygen Meter
(source: [1])

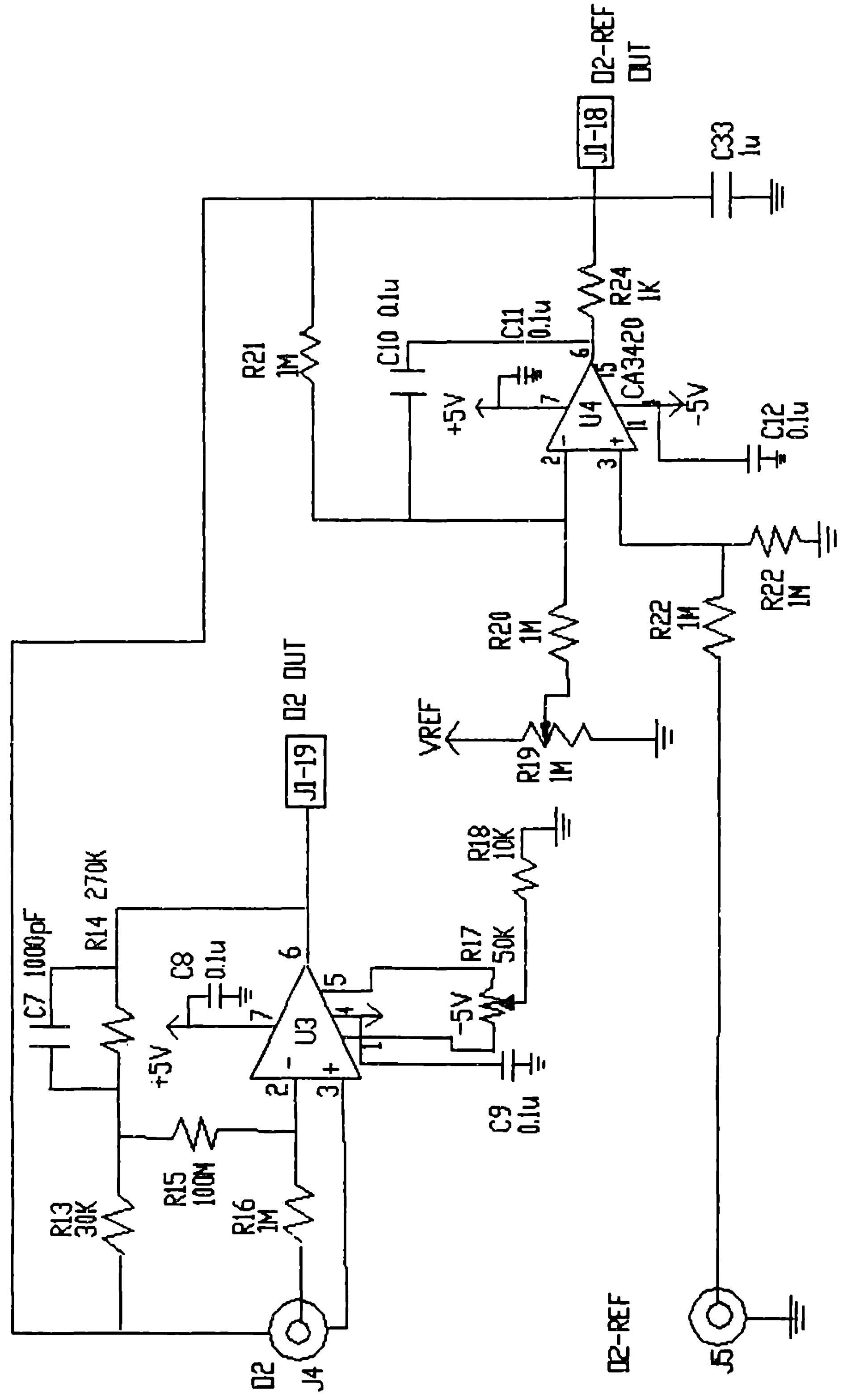
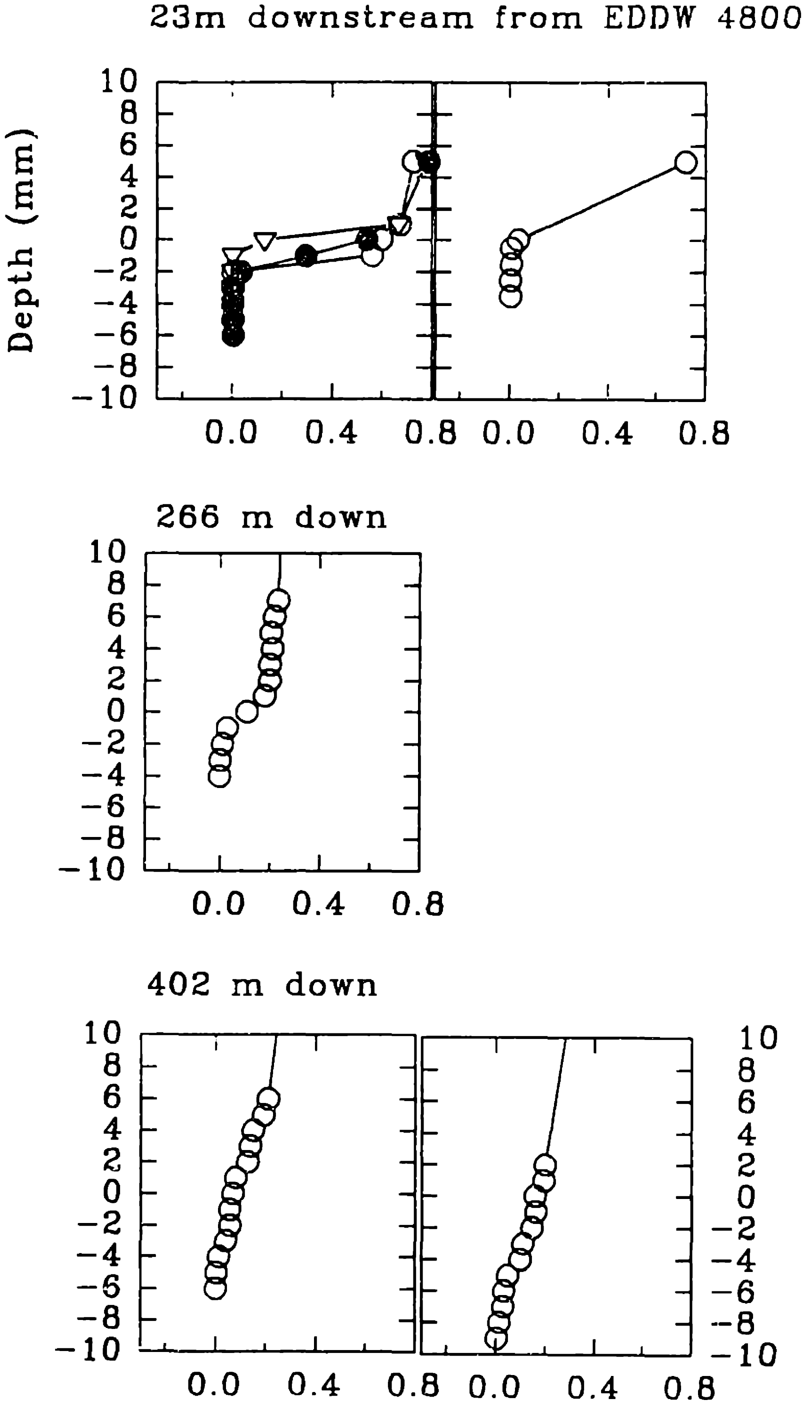


Fig. B.2. Oxygen in Stream Sediment


23m downstream from EDDW 4800

266 m down

402 m down

Voltage converted from current generated by the presence of oxygen

References

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Appendix C. Gas Exchange Coefficient in Small Streams

Gas exchange coefficients of propane in two streams were obtained by in-stream tracer techniques described in Chapter 2 and 3 of this thesis. From the gas exchange coefficients of propane, gas exchange coefficients of oxygen were calculated from the relationship of k(propane)/k(oxygen)=0.72 over a wide range of mixing conditions [1]. The measured gas exchange coefficients for 14 experiments in the East Drainage Ditch II were then compared with the values which could be predicted from 16 equations (Table C.1) among the equations that Parker and Gay [2] compiled to predict the gas exchange coefficient of oxygen. The equations as transcribed from Parker and Gay [2] require stream velocity (u) in ft/s and stream depth (d) in ft to give the gas exchange coefficient of oxygen (k) in day^{-1}. Froude number (N) was calculated as in Parker and Gay [2]: $N=u/(gd)^{0.5}$ where g is the gravitational acceleration. Channel slope (w) was taken as 0.0047 [3]. The gas exchange coefficients of oxygen predicted from the equations and those measured on each experiment date in the East Drainage Ditch were plotted in Fig.C.1.

Table C.1. Equations for Predicting Gas Exchange Coefficient of Oxygen, k_{O2} (day^{-1}).

Equation No.	Reference	k_{o2}
1	[4]	$\frac{116.6(1+N^2)(uw)^{0.375}}{d\sqrt{0.9+N}}\coth\frac{4.1(uw)^{0.125}}{\sqrt{0.9+N}}$
2	[5]	$\frac{12.81\sqrt{u}}{d^{1.5}}$
3	[6]	$\frac{234.5(uw)^{0.404}}{d^{0.66}}$
4	[7]	$\frac{336.8\sqrt{uw}}{d}$
5	[8]	$\frac{48.39(1+0.17N^2)(uw)^{0.375}}{d}$
6	[9]	$\frac{106.16u^{0.413}w^{0.273}}{d^{1.408}}$

7	[10]	$\frac{0.03453u^{2.695}}{d^{3.085}w^{0.823}}$
8	[11]	$\frac{7.61u}{d^{1.33}}$
9	[12]	$\frac{23.23u^{0.73}}{d^{1.75}}$
10	[12]	$\frac{21.74u^{0.67}}{d^{1.85}}$
11	[10]	$\frac{11.57u^{0.969}}{d^{1.673}}$
12	[13]	$\frac{8.62u}{d^{1.5}}$

13	[14]	$10.92(u/d)^{0.85}$
14	[15]	$\frac{6.87u^{0.703}}{d^{1.054}}$
15	[16]	$\frac{4.67u^{0.6}}{d^{1.4}}$
16	[9]	$\frac{20.19u^{0.607}}{d^{1.689}}$

Table C.2. Gas Exchange Coefficients of Propane (k_v) in East Drainage Ditch II

Exp. No.	Experiment Date	Water Temperature (°C)	Average Flowrate (L/s)	Stream Velocity (m/min)	Stream Depth (cm)	k_v (hr^{-1})
1	3/1/92	1.0	12.8	5.2	12	0.32
2	3/29/92	10.5	22.3	7.9	14	0.34
3	5/3/92	15.3	40.6	7.9	26	0.12
4	5/30/92	18.0	14.5	3.6	20	0.48
5	6/28/92	20.0	10.2	4.2	12	0.62
6	7/3/90	14.5	10.8	4.4	15	0.80
7	7/19/92	22.5	6.9	3.7	9	0.86
8	8/15/92	18.0	7.5	4.0	9	0.61
9	9/20/92	15.0	4.7	3.3	7	0.47
10	9/28/91	14.5	26.0	10.6	15	0.92
11	11/7/92	7.0	8.3	2.9	15	0.26
12	11/25/90	8.0	19.7	8.0	15	0.51
13	12/8/91	7.3	18.0	5.8	15	0.19
14	1/29/92	3.8	12.4	6.5	10	0.27

Fig. C.1. Gas Exchange Coefficients of Oxygen in East Drainage Ditch II

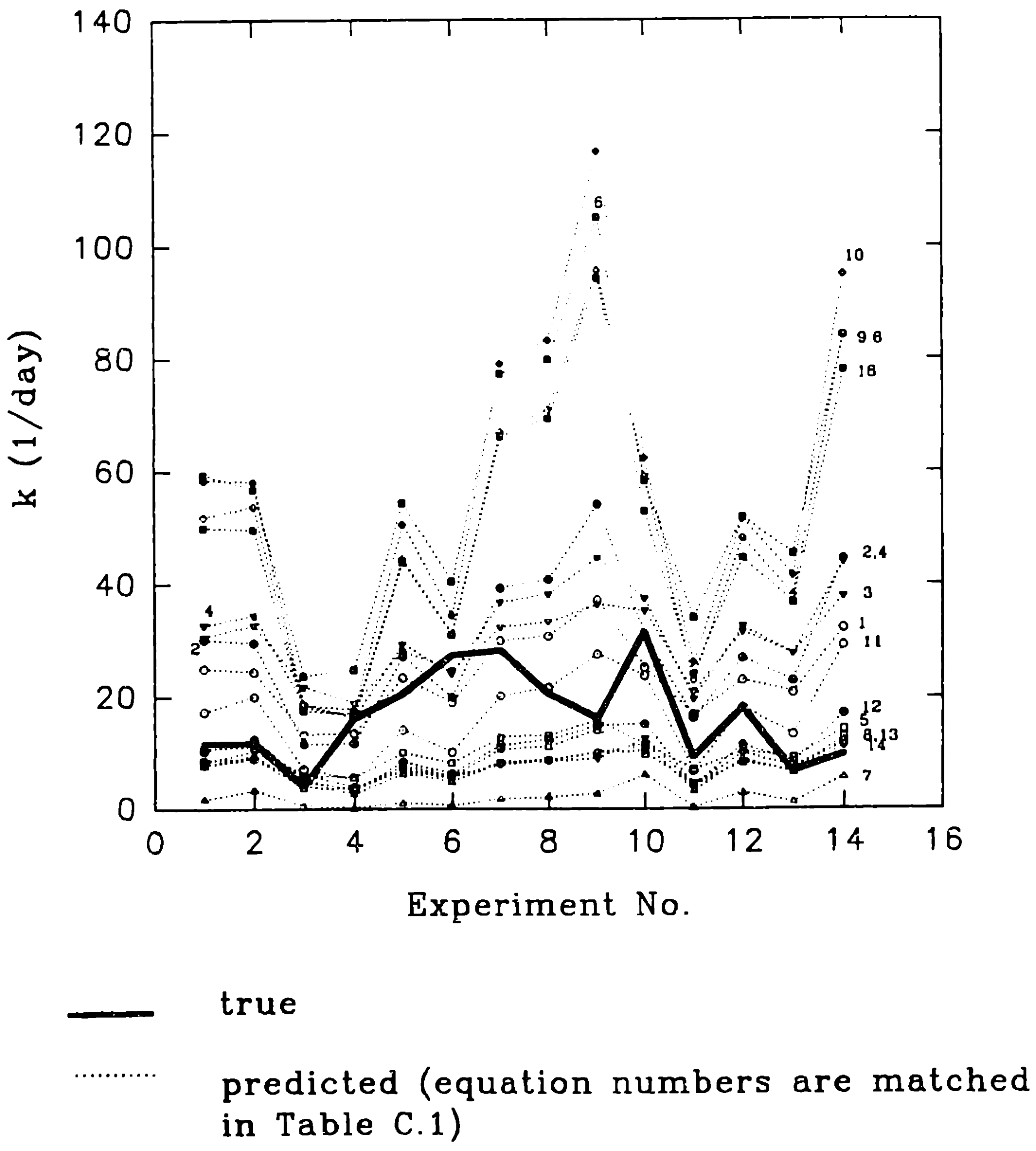

Table C.3. Gas Exchange Coefficients of Propane (k_v) in Sweetwater Brook

Experimet Date	Water Temperature (°C)	Average Flowrate (L/s)	Stream Velocity (m/min)	k_v (hr^{-1})
6/13/90	13	40.4	9.5	0.64
3/31/91	11	66.9	13.1	0.31
6/3/91		26.5	6.1	0.60
10/14/91		22.1	7.8	0.67
2/21/92	6	45.8	8.2	0.57
3/13/92	6	78.4	12.4	0.74
6/3/92	16	39.1	7.5	0.49
6/18/92	17	32.9	5.5	0.82
7/16/92		24.4	5.4	0.48
8/10/92	19	22.4	4.5	0.17
10/3/92	16	22.6	4.6	0.21
11/14/92	9	25.3	4.0	0.13

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Appendix D. Typical Chromatogram from a Stream Water Sample

Not all peaks in a chromatogram obtained from stream water samples were identified. In order to determine the fraction of identified volatile organic compounds among the total volatile organic compounds, two chromatograms from water samples in the experiment sites were shown (Fig.D.1 and 2);one from the East Drainage Ditch II and the other from the Landfill Creek I. The analytical method was described in the method section of the chapter 2 and 3 in this thesis. Propane, intentionally injected (see Chapter 2 for the method), was shown in both chromatograms and it was excluded in determining the fraction of the unidentified peak areas.

The identified peaks in the chromatogram shown in Fig.D.1 and 2 were summarized in Table D.1. In the water sample taken from the East Drainage Ditch, the total area of peaks from the chromatogram is 3.4×10^7 and the area of identified peaks is 3.0×10^7, yielding 12% of area of total peaks unidentified. On the other hand, only 30% of peak areas (excluding the peak of propane) were identified in the chromatogram obtained from the water sample taken from the Landfill Creek.

Fig. D.1. Chromatogram of a Sample from the East Drainage Ditch II
(The sample was taken from the 3rd station (EDDW 4070) on March 29, 1992.)

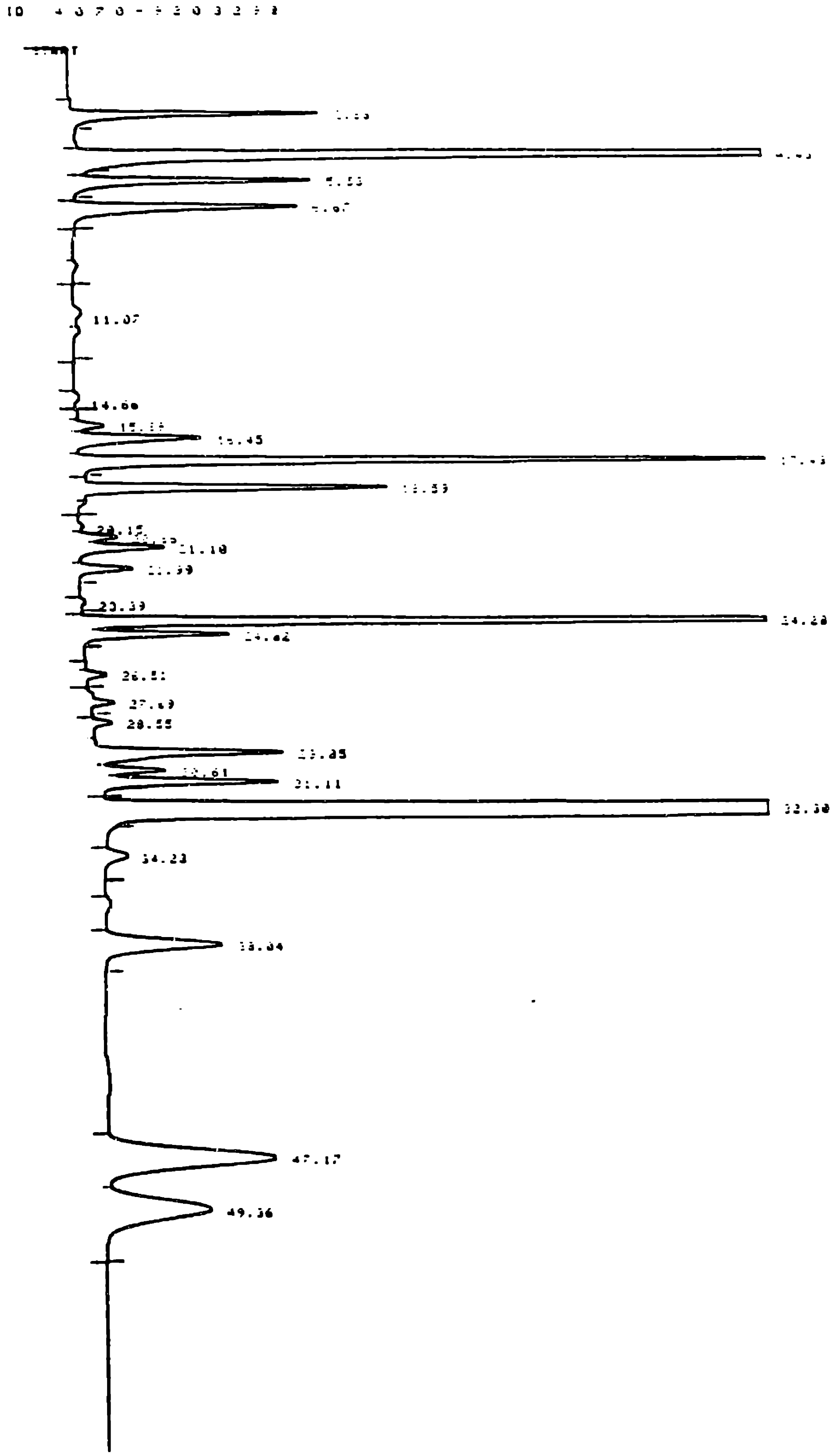

Fig. D.2. Chromatogram of a Sample from the Landfill Creek
(The sample was taken from the confluence of the Landfill Creek and the East Drainage Ditch (Fig. 2.1) on Oct.16,1990)

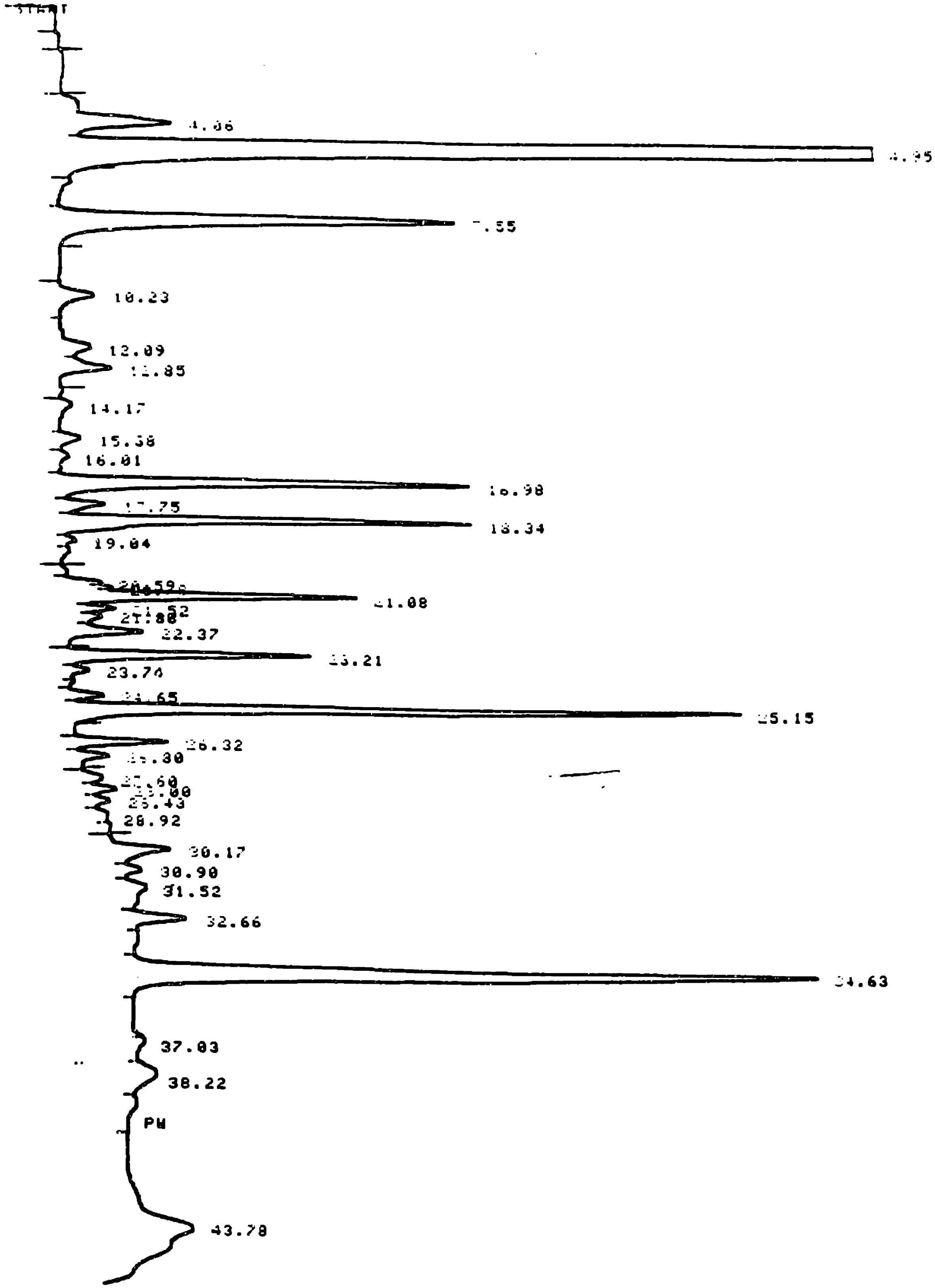

Table D.1. Identified Peaks in the Chromatograms

Chromatogram	Retention Time (min.)[a]	Corresponding VOC	Concentration ($\mu g/L$)
From the East Drainage Ditch (Fig. D.1)	4.43	propane injected	Not quantified
	16.45	1,1-dichloroethane	3.3
	17.43	1,2-dichloroethene	14.4
	20.66	1,1,1-trichloroethane	1.3
	21.10	carbon tetrachloride	6.9
	24.28	trichloroethylene	21.5
	24.82	benzene	0.6
	32.30	toluene	84.2
From the Landfill Creek (Fig. D.2)	4.95	propane injected	Not quantified
	21.08	1,1,1-trichloroethane	2.0
	25.15	benzene	0.6
	34.63	chlorobenzene	1.9

a. The retention times of VOCs varied with time, but stayed the same within a day. Two samples were analyzed in different date and the retention time of a VOC in one chromatogram is not the same as that of the VOC in the other. The retention times of VOCs were obtained by analyzing a standard sample with samples to be analyzed in the same day.