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When Is It Best Not to Remediate?: Mid-Course Corrections for Super Fund

by

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Submitted to the Department of Civil and Environmental Engineering in
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ABSTRACT

This thesis examined, through a case study, one of cleanup goals at remediation sites set by the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA), better known as Superfund: *to reduce the mobility of contaminants*. Although containing the contaminants to source areas may be safe for public health in general, it can prohibit an inexpensive remediation alternative to allow the contaminants to flow with groundwater and be naturally discharged to surface water. This thesis investigated the natural discharge of volatile organic compounds (VOCs) from a Superfund site (Well G & H site, Woburn, Massachusetts) to the nearby Aberjona River as a remediation alternative. The results showed that the travel times of the center of mass of plumes from source areas to the Aberjona River ranged in the order of 100 years for most of VOCs. Considering the ineffectiveness and cost of pump-and-treat, which has been employed to remediate the site, and the existence of inexpensive drinking water source in the study site, it may be best not to remediate some source areas but to wait for the VOCs to be naturally discharged. This thesis also suggested that cleaning up groundwater watershed-wide rather than by each source area would be more adequate to utilize the natural discharge as a remediation alternative.

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I. Introduction

The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) with the Superfund Amendments and Reauthorization Act of 1986 (SARA), better known as Superfund, have grown to be one of the most controversial of all environmental laws. Under Superfund, the U.S. Environmental Protection Agency (EPA) is responsible for placing the most serious hazardous waste sites on the National Priorities List (NPL), for assessing the risks posed by the sites, and for selecting the most appropriate cleanup option for each site.

One of the most controversial issues in CERCLA and SARA is the cleanup standard. First, SARA requires EPA to choose a cleanup strategy that is "cost-effective", but also will result in a "permanent and significant decrease" in the volume, toxicity, and mobility of contaminants. The provision of "permanent" remedy has often called for more costly remedial actions such as treating and pumping contaminated groundwater than merely restricting the use of contaminated groundwater, resulting in the cleanup cost of all current and future NPL sites in the range of \$106 billion to \$463 billion (Probst et al., 1995). Even at this high cost, it has been questioned that it is ever going to be possible to clean contaminated groundwater due to our limited knowledge on heterogeneity of earth and interactions between contaminants and aquifer (Macdonald and Kavanaugh, 1994; Travis and Doty, 1990). Moreover, some have questioned about the benefit of the cleanup in light of the high cleanup cost (Gupta et al., 1995). Second, SARA requires that sites

be cleaned in accordance with any legally applicable or relevant and appropriate standards (ARARs or applicable or relevant and appropriate requirements), where such standards exist. The ARARs has often led EPA to set the cleanup standard of contaminated groundwater to drinking water standards defined by the Safe Drinking Water Act (SDWA). Many believe that the drinking water standards are not appropriate for groundwater remediation and the compliance with drinking water standards is unnecessarily stringent.

Facing the criticisms on the cleanup standards and the high cleanup cost, this thesis addressed the question, "What happens if we do nothing about contaminated groundwater?" Even without remedial actions, the aquifer can be cleaned by itself through natural processes such as discharge of contaminated groundwater to streams, sorption, volatilization, diffusion into fractures in bedrock, and biodegradation. Doing nothing, but waiting for the contaminated aquifer to clean itself, can be a remediation alternative yet at no cost in certain cases.

Although "do nothing" is considered as a remediation alternative by EPA in investigating NPL sites, it is not preferred because the goal of cleanup is often to decrease the mobility of contaminants as required by CERCLA. Natural cleansing would also take hundreds of years, much longer than a projected time of cleanup by remedial actions. Therefore, even attempts to estimate the time for the contaminated groundwater to be cleaned by the natural processes are rarely made, regardless of the urgency of the need of clean groundwater at a specific site.

In this thesis, I investigated the natural cleanup as a remediation alternative at

the Well G & H Superfund site in Woburn, Massachusetts, where remedial actions have begun to pump and treat groundwater contaminated with chlorinated volatile organic compounds since 1992. I also proposed the revisions in CERCLA for EPA to consider the natural cleansing ability of contaminated aquifer in making remediation decisions.

The objectives of this study were 1) to assess the time which may be taken for the aquifer to be naturally cleaned, 2) to compare the natural cleanup with remedial actions in view of the cost and the urgency of the need of clean groundwater at the site, and 3) to make recommendations in the revision of Superfund program.

II. Background

The Well G & H site

History: The well G & H had supplied drinking water to a part of the city of Woburn, Massachusetts from 1964 to 1969. In 1979, chlorinated volatile organic compounds were detected at concentrations ranging from 1 to 400 parts per billion in the well water and consequently the wells were shut down. Further investigation identified the contamination of groundwater in an area of east Woburn with the chlorinated volatile organic compounds. The well site was designated as a "Superfund" site in 1982. The site is located in the City of Woburn, approximately 10 miles north of the City of Boston, Massachusetts, and has an area of approximately 330 acres (Fig. 1). Five source areas of contamination, which are W.R. Grace & Company, Inc., Unifirst Corporation, Wildwood Conservation Corporation, Olympia Nominee Trust and New England Plastics Corporation, have been identified in the site (Fig. 2).

Geology: The depth to bedrock from land surface ranges from zero, where bedrock crops out at several locations along the east and west side of the valley to approximately 140 ft in the center of the Aberjona River valley. The bedrock valley is filled with glacial outwash deposits and alluvial sediments. Stratified sand and gravel deposits up to 140 ft thick form the most important aquifer in the study area. The unconsolidated valley fill deposits, in general, form three layers; the uppermost layer of sand, silt, clay, and peat layer, the middle layer of 10-50 ft thick coarse sands, and

the bottom layer of 20-50 ft thick coarse sands and gravel.

Contamination level: Maximum organic contaminant concentrations in groundwater at five source areas and central area ranged from 5 to 190,000 $\mu\text{g/L}$. Trichloroethylene (TCE), Perchloroethylene (PCE) and Dichloroethene (DCE) are common chlorinated volatile organic compounds in all six areas. The maximum organic contaminant concentrations in groundwater were summarized in Table 1.

Remediation Decision: There is no current human health risk from the contaminated groundwater since the water is not any longer supplied to public as drinking water. The risk that formed the basis for the determination of the remediation resulted from the scenario that the groundwater was supplied to future population as drinking water.

Cleanup Goal: Not only SARA has provisions of ARARs, but also the USEPA Groundwater Protection Strategy (August 1984) sets groundwater protection goals to be based on "the highest beneficial use to which groundwater having significant water resources value can presently be put". The groundwater aquifer at this site was used as a drinking water source before the well G & H were shut-off. Therefore, the cleanup goal at this site was set to achieve aquifer restoration to drinking water quality. EPA considers maximum contaminant levels (MCLs) defined by the Safe Drinking Water Act of 1974 to be ARARs. MCLs are available for most of the chemicals of concern in the groundwater except 1,1-dichloroethane, trans-1,2-

dichloroethene and tetrachloroethene (Table 1). The target levels used for 1,1-dichloroethene and tetrachloroethene are those for 1,2-dichloroethane and trichloroethene, respectively.

Remedial action: The USEPA evaluated five alternatives based on short-term effectiveness, long-term effectiveness, reduction of toxicity, mobility, or volume, implementability, cost, compliance with ARARs, overall protection of human health and the environment, and implementability. The five alternatives include no action, pump and treat at source areas, pump and treat at central area, pump at source areas and treat at central area, and pump and treat at southern boundary area. PRPs (primary responsible parties) at all source areas except Olympia Nominee Trust property have agreed to choose the pump and treat at source areas and pay for the cleanup. The remediation action has begun at W.R. Grace and Unifirst properties since 1992 and is to begin at Wildwood and New England Plastic in 1996. PRPs for Olympia Nominee Trust property have not been determined and the cleanup time has not yet been decided. Remedial actions have removed 16 kg of total VOCs from 1992 to 1994 at W.R. Grace site [GeoTrans, 1993, 1994] and 16 kg of TCE and 300 kg of tetrachloroethene for two years at Unifirst site [The Johnson Company, 1993, 1994]. The projected cleanup cost at this site is \$90 million over 30 years, assuming the discount rate to be 5%.

Fate of VOCs in Groundwater

Discharge to Streams

Discharge of solutes in groundwater to streams has been studied for a wide range of application: identifying stream flow generation, assessing ecological and human risk by potentially harmful chemicals, and calibrating and verifying groundwater flow model. For example, Genereux and Hemond (Genereux, 1991; Genereux and Hemond, 1990) determined the flux of ^{222}Rn to stream reaches to identify the origin of discharging groundwater. Phillips et al. (1991) determined the flux of boron, selenium, molybdenum, and total dissolved solids and Squillace and Thurman (1990) estimated the flux of atrazine and desethylatrazine.

Several researchers have reported the discharge of volatile organic compounds from contaminated groundwater to streams as well. Fusillo et al. (1991) measured the VOCs in the about-to-be-discharged water by using minipiezometers to collect samples of the ground water immediately beneath a streambed. Avery et al. (1991) determined the concentration of VOCs in the groundwater discharged to the Rock River in Illinois by using both well points driven into a river bottom and seepage meters. Vroblesky et al. (1991) showed the discharge of VOCs by collecting vapor of VOCs in bottom sediment.

In a previous study (Kim, 1995), the concentrations and total fluxes of VOCs in the groundwater discharging to streams were measured in the headwaters of the Aberjona watershed, which the Well G & H site is located within, 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. Measurements were made throughout 2 years, with spatial resolution ranging from tens to hundreds of meters. The fluxes of VOCs in the groundwater discharging to streams were shown to range from 5 g/yr of benzene to 43 kg/yr of trichloroethylene to 84 kg/yr of toluene. The total natural discharge rate of all identified VOCs from all tested sites in the Aberjona watershed was estimated to be 140 kg/yr (see Appendix for more detailed information).

Volatilization

Volatilization of VOC's from shallow unconfined aquifers, to some degree, must occur; just as gaseous radon diffuses from granitic bedrock to the surface due to a concentration gradient, so will these compounds. Swallow (1983) suggested that evaporative removal of an organic vapor from the water table could be a very important process, depending on the value on dispersion which is operative under field conditions. Indeed, soil venting, which allows VOCs to volatilize easily by venting, is one of the remediation techniques (Kerr Jr., 1990). Measurements of VOCs in soil gas are also used to detect groundwater contamination (Kerfoot, 1987).

Sorption

While other natural processes remove VOCs permanently from aquifer, sorption merely displaces the VOCs from groundwater to aquifer material. It has been

known that it is very difficult to remove the sorbed contaminants (Macdonald and Kavanaugh, 1994). Failure to clean up a contaminated site permanently often comes from the fact that sorbed contaminants respond too slowly to the cleanup actions. However, the sorption can dilute the concentration of VOCs in groundwater initially when the concentration of the VOCs in groundwater is high, and the sorbed VOCs are released slowly to flowing ground-water later with time. Therefore, sorption can be viewed as a natural process to attenuate the concentration of chemicals in groundwater.

Biodegradation

Some VOCs such as benzene, toluene and xylene are known to be biodegraded easily in groundwater, while chlorinated VOCs are known to be refractory. However, under anaerobic conditions, poly-halogenated VOCs are reductively biodegraded to less halogenated compounds. It has been shown that methanogenic bacteria can biodegrade chloroform, bromodichloromethane, and dibromochloromethane down to concentrations less than 0.1 ppb (Bouwer et al., 1981). Natural attenuation of contaminants through biodegradation has been paid attention as a remediation control (Lester and Mercer, 1995).

III. Problems with Remedial Actions at Well G&H site

Effectiveness of Pump-and-treat

The presence of tetrachloroethylene as a dense, non-aqueous phase liquid (DNAPL) which sinks to the bottom of the aquifer was detected at Unifirst site (Ebasco Services, 1989). The pump-and-treat employed for the remediation at this site has been known to have very little success in removing DNAPLs (Mackay and Cherry, 1989). The studied site has been also reported to have fractures in bedrock, where contaminants denser than water would diffuse (Ebasco Services, 1989), and pumping out the contaminants diffused into the fractures are very difficult (Mackay and Cherry, 1989). The presence of many fractures in bedrock and DNAPLs, therefore, makes the pump-and-treat incapable of cleaning up the contaminated groundwater but effective merely in containing plumes (Travis and Doty, 1990).

Drinking water standard

The aquifer of the studied site, the Aberjona River aquifer, is classified as Class I by the Commonwealth of Massachusetts, that means the groundwaters that are designated as a source of potable water supply. Under the EPA Groundwater Classification System, this aquifer is classified as Class IIB, which are aquifers that are potentially available for drinking water. Therefore, it is not reasonable to set the drinking water standard as its cleanup goal. However, the goal is not practical due to following reasons. First, in addition to technical problems with restoring the

contaminated groundwater to drinking water as discussed above, there are some hydrologic evidences that surface-water from the Aberjona River may be withdrawn in pumping groundwater at the site in dry seasons (Myette et al., 1987). Since the Aberjona River is contaminated with chemicals, including heavy metals and organic compounds, transported from upstream sources (GeoTrans, 1987), using groundwater from this site for drinking water may not be feasible until the Aberjona River is cleaned together. Second, it is questionable that the public would ever accept the use of the groundwater from this site for drinking water. The public has already expressed that they would never drink groundwater from this site (U.S. EPA, 1989b). Third, the need of groundwater from this particular area for drinking water is also not clear. Installing and maintaining new groundwater wells in this area may not be cost-saving for the residents of the city of Woburn in comparison to paying for water supplied from MWRA. The cleanup goal in this site may be, therefore, impractical.

IV. Natural Discharge as a Remediation Alternative

Travel Time of VOCs

The discharge of groundwater to the Aberjona River can be depicted as in Fig.3. Groundwater flow through saturated zone or fractures in bedrock and finally discharge to the Aberjona River. Immediately before the discharge to the Aberjona River, VOCs should flow through peat (Fig.3). Sophisticated modeling approaches with three-dimension or transient state have been employed to conduct the interaction between groundwater and surfacewater in this area (Reynolds, 1993; U.S. Geological Survery, 1989). However, in this study simply to illustrate the importance of natural discharge, it is assumed that the groundwater flow only horizontally up to the peat and then flow up vertically through the peat to the Aberjona River. Then, the time for a VOC to be discharged from a source area to the Aberjona River would be that:

$$t = t_h + t_p = \int \frac{nR}{q_h} dS + \int \frac{n_p R_p}{q_z} dz$$

$$= \frac{(n + K_{om} \cdot 2 f_{oc} \cdot \rho_s (1 - n))}{K_h} \sum \frac{(\Delta S_i)^2}{\Delta h_i} + \frac{(n_p + K_{om} \cdot 2 f_{oc,p} \cdot \rho_s (1 - n_p))}{K_p \frac{dh}{dz}} \cdot \Delta z$$

where t_h is the horizontal travel time of a VOC from a source area to the Aberjona River, t_p is the vertical travel time of the VOC through the peat to the Aberjona River, n is the porosity, R is the retardation factor, q is the specific discharge and S is the distance along a streamline of ground-water flow, the subscript, p indicates the parameters associated with the peat, z is the vertical direction of the peat depth, Δz is

the depth of the peat, and the overline indicates the average value. The subscript, i indicates each stream tube in Fig 5.

The retardation factor, R , is defined as (Freeze and Cherry, 1979):

$$R \equiv 1 + K_d \cdot \frac{\rho_b}{n}$$

where K_d is the distribution coefficient, ρ_b is the bulk density of the porous material, and n is the porosity. The distribution coefficient, K_d , can be estimated by (Schwarzenbach et al., 1993):

$$K_d = K_{om} \cdot f_{oc} \approx K_{om} \cdot (2 f_{oc})$$

where K_{oc} is the organic carbon/water partition coefficient, K_{om} is the organic matter/water partition coefficient, and f_{oc} is the fraction of organic carbon in soil. The organic matter/water partition coefficients, K_{om} in the unit of $[L \cdot kg^{-1} om]$, for chlorinated hydrocarbons can be estimated by (Schwarzenbach et al., 1993):

$$\log K_{om} = 0.88 \cdot \log K_{ow} - 0.27$$

where K_{ow} is the octanol/water partition coefficient $[L_{water}/L_{octanol}]$. The organic carbon content for site subsurface soil is uncertain but for glacial deposits and sands may range to as low as 0.1 percent. Researchers have reported that subsurface organic carbon contents are variable but may range from less than 0.1% to more than 0.5% depending on the soil (Karickhoff and Scott, 1979; Tedrow, 1986). However, the organic carbon content in the peat in the vicinity of the Aberjona Rive can be as high as 90%, and the average organic carbon content of 40% over the depth of 300 cm of

core taken from peat in the vicinity of the Aberjona River (Zeep, 1995). Therefore, the discharging VOCs can be retarded mostly in peat area due to this high organic carbon content.

The porosity (n) for sand and silt is in the range of 0.25-0.40 (Freeze and Cherry, 1979), and the bulk density (ρ_b) can be estimated by that $\rho_b = \rho_s(1-n)$ where ρ_s is the particle mass density and assumed to be 2.65 g/cm³ (Freeze and Cherry, 1979). The porosity in the peat was measured in the range from 0.4 to 0.9 (Zeep, 1995). Assuming the organic carbon content of 0.5% for subsurface soil and 40% for peat and the porosity of 0.25-0.40 for subsurface soil and 0.4-0.9 for peat, the retardation factors for VOCs found in the studied site can be estimated as shown in Table 2.

Previous field studies (Myette et al., 1987) suggested that the principal direction of ground-water flow on the western side of the Aberjona River valley is southeast on an average horizontal gradient of 0.005 ft/ft, and the direction of ground-water flow on the eastern side of the valley is southwest with an average horizontal gradient of 0.02 ft/ft. The hydraulic conductivity in this studies site has been also reported in the range of 20-200 ft/day (Brainard, 1980; Myette et al., 1987; U.S. Geological Survey, 1989). Among five source areas, the source plumes of Unifirst, W. R. Grace and New England Plastics are located on the eastern side of the Aberjona River and the sources plumes of Olympia and Wildwood are located on the western side of the Aberjona River (Fig. 4).

The thickness of the peat in the area was reported in the range from 2 to 7 ft

(Myette et al., 1987). It has been reported that the peat is a relatively loose, nearly saturated material which permits ground-water discharge to the river under normal conditions and induced infiltration of streamwater under pumping conditions (U.S. Geological Survey, 1987). The vertical hydraulic gradient in the peat area was reported in the ranges from 0.002 to 0.01 (Brainard, 1980). The hydraulic conductivities of the peat in the studied area are in the range from 0.03 to 30 ft/day as measured (Bialon, 1993; Zeep, 1995), higher than published estimates of the hydraulic conductivity for peat ranging from 0.001 to 0.1 ft/day (Siegel and Ericson, 1980). However, the groundwater modeling at this site conducted by others (Reynolds, 1993; U.S. Geological Survey, 1989) used 50 ft/day for the hydraulic conductivity of the peat on the basis of observed heads in the groundwater and surface-water. Six points in source areas (Fig. 5) were arbitrarily chosen to illustrate the range of travel times from the source areas to the Aberjona river as shown in Table 3.

Some VOCs with low retardation factors travel to the Aberjona River within 100 years, while others with high retardation factors travel to the river longer than 100 years (Table 3). Other study (U.S. Geological Survey, 1989) reported that the groundwater is discharged to the Aberjona River near this site as much as 0.27 ft³/sec (0.17 MG/day). Assuming that the estimated size of plumes for each source area (24 MG for W.R. Grace, 22 MG for Unifirst, 16 MG for Olympia, 126.5 MG for Wildwood, 3.7 for New England, 285 for Central Area (Ebasco Services, 1989)) is flushed out with the discharging groundwater, the flushing time is estimated to be 8

years. Including the travel time from the source areas to the Aberjona River and groundwater originated from areas other than the source areas, the flushing time would be much longer than 8 years. However, this estimation of 8 years shows that the flushing by discharging groundwater is quite possible and fast as shown in this study. However, it should be noted that the estimated travel time is for the center of the mass in plume and thus dispersion would make the flushing time of the whole volume of the plume longer than the estimated travel time. The accurate determination of flushing time can be obtained experimentally with more refinement of the model. It is worth determining the accurate amount of VOCs discharged to the Aberjona River experimentally using the in-stream tracer technique as used at other sites in the watershed by Kim (1995). The estimated travel time was determined under natural hydraulic conditions. This is not the case when the pump-and-treat is employed at source areas, since the hydraulic head at the plumes is lower than that of surroundings as pumped. It was not estimated how much the pumping at each source area would retard the natural travel of VOCs to the Aberjona River in this study and worthwhile being estimated in the future.

Uncertainties Associated with Travel Time

Hydraulic and geologic conditions of field sites are too complicated to allow us to estimate an accurate value for a travel time of a VOC in the field site. It is inevitable to include some uncertainties in the estimation, since field sites are generally highly heterogeneous and only random and representative measurements are

available. It is, therefore, very informative to analyze the uncertainties associated with the estimation of travel time, since the analysis can lead to identify the area where further refinement in measurements or more information are needed.

Following Kline (1985), the contribution by the uncertainty associated with each parameter was determined as shown in Table 4. The uncertainties associated with the value for K_{om} were not included in the error analysis, since the regression of the equation used was shown to be highly correlated with $R^2=0.97$ (Schwarzenbach et al., 1993). The analysis was conducted for the travel time of VOCs from the source point, A in Fig.5 to the Aberjona River. The error analysis for the travels times from all other source points showed results very similar to that shown in Table 4.

Heterogeneities associated with hydraulic conductivities contribute to the uncertainties most. This can be improved by employing an integrated value for the area rather than an average value as used in this study.

Comparison with Pump-and-Treat

The projected time of cleanup by pump-and-treat (30 years) is much shorter than the cleanup time by natural discharge for most of VOCs. However, the need and urgency of clean groundwater for drinking water should be considered in determining whether the natural cleanup takes too long time. It was reported that the Aberjona River could be withdrawn by pumping groundwater at this site in dry seasons (Myette et al., 1987) and the Aberjona River has been contaminated by upstream sources independent of the studied sites. Therefore, despite of the concern for the shortage of

drinking water supply in this area (U.S.EPA, 1989a), the cleanup of groundwater only at this site is unlikely to make the groundwater in this area drinkable. The present supply of drinking water by MWRA has been inexpensive for the residents of the city of Woburn and there are also no evidences that the city of Woburn would need the clean groundwater for drinking water in 30 years rather than after 1000 years.

The cost to monitor the transport of plumes would be minimal, in comparison to the cost of remediation which was estimated to be \$90 million. Superfund program as most environmental programs does not explicitly require the use of benefit/cost criteria for making remediation decisions. Usually, cost-effectiveness criteria are used to compare alternatives that produce similar environmental results. However, cost-effectiveness criteria are not as useful for comparing remediation and "no-action" alternatives. From an economic perspective, corrective action should be undertaken if the expected benefits exceed the costs. Benefit of having clean groundwater earlier by pump-and-treat than by natural discharge is very unclear to justify the cost at this site. Moreover, there were no attempts to measure the value of clean groundwater at this site in making decisions on remediation.

V. Changes to Superfund program

The need for changes to Superfund policy concerning aquifer restoration has been raised as issues on the Superfund debate (Anderson, 1990; Hazardous Waste Treatment Council, 1989; Lautenberg and Durenberger, 1989; Office of Technology Assessment, 1989). Specially, it has been indicated that the use of ARARs should be discontinued as cleanup goals and it should recognize that restoring aquifers to a pristine condition is not always necessary (Travis and Doty, 1990). However, most of recommendations still assume that the containment of plumes is always necessary. I recommend that the assumption should be reexamined for a more cost-effective Superfund policy. Also the strategy to clean up each source area should be reexamined as discussed below.

Exceptions of decreasing the mobility of contaminants

SARA requires EPA to choose remedial actions "which permanently and significantly reduces the volume, toxicity of mobility of the hazardous substances, pollutants, and contaminants over remedial actions not involving such treatment." (sec. 121. (b)). Complying the SARA and CERCLA, the EPA stated some of the cleanup objectives as stopping the introduction of contaminated groundwater from the source areas to the rest of the aquifer and reducing further migration of contaminated off-site.

Decreasing the mobility of contaminants would not allow the volatile organic

compounds to flow with groundwater and finally to discharge to streams. As shown in this study, volatile organic compounds can be naturally discharged to the Aberjona River without imposing any conceivable risks to human health and environment. The section of general rules of cleanup standard in SARA needs exceptions where allowing the mobility of contaminants can help natural cleanup of aquifer without imposing a further risk to human health and environment.

Watershed-wide approach

Even if groundwater is cleaned at source areas, contaminants from upstream sources in the Aberjona watershed is likely to contaminate groundwater in this site. At the upstream ends of the Aberjona River, there are many sources of contaminants including hazardous sites of Hemingway Transportation/Juniper Realty/Olympia Nominee Trust site, Piggeries site, M.D.C. and Woburn Aberjona Interceptor Sewers, Mystic River Sludge, Aberjona Auto Parts site, Whitney Barrel Company site, Brodie Industrial Trucks site and East Drainage Ditch. Without developing remedial strategies of cleaning up the Aberjona aquifer as a whole, the groundwater in the Well G & H area is not likely to be cleaned enough to be pumped for drinking water. Without watershed-wide approach on groundwater remediation, groundwater in this site cannot be used as drinking water because cleaning up source areas in this site cannot prohibit the contamination from upstream sources.

Current statue of Superfund does not prohibit the watershed-wide approach in theory. However, the liability approach of the Superfund, in which the parties that

generated or transported the hazardous materials at a site or that owned or operated the site are held as liable for cleanup of the site, does not give much incentives the responsible parties to develop remediation strategies on the whole affected watershed. Rather, the responsible parties tend to remediate their sites individually. In the Well G & H site, more investigation on the interaction between the Aberjona aquifer as a whole and the site of interest, such as defining the upgradient introduction of contaminants to the Aberjona River and refining the present understanding of the interaction of the Aberjona River and the aquifer systems on the site, was planned in the feasibility study of EPA (U.S.EPA, 1989a) but never conducted to develop a remediation strategy of the watershed. The groundwater in the Well G & H site is a part of a bigger hydraulic system, that is the Aberjona watershed which contains over 50 documented state-identified hazardous sites and one Superfund site (Industri-Plex site) besides this Well G & H site. This has been also raised as a question for the appropriateness of the present remedial actions for restoring the groundwater at the site to drinking water by others (GeoTrans, 1987). However, there are very little efforts to develop remediation strategies of the contaminated sites in the watershed with a watershed-wide approach.

VI. Conclusions

In this thesis, the natural discharge was assessed as a remediation alternative and it was estimated that, in the order of 100 years, the center of mass of VOC plumes could travel from the source areas to the Aberjona River. Further study in determining the accurate flushing time would be much needed. When there is an inexpensive substitute for drinking water and the mere existence of contaminated groundwater does not impose further risk on public health, "no-action" should be considered as a remediation alternative. In order to include the natural discharge as an option for remediation, the objective of cleanup of reducing the mobility of contaminants should be reexamined. With the watershedwide approach, it should be considered to allow the mobility of VOCs within the watershed and clean up the watershed as a whole for a more cost-effective cleanup strategy.

Fig. 1. Site Location Map

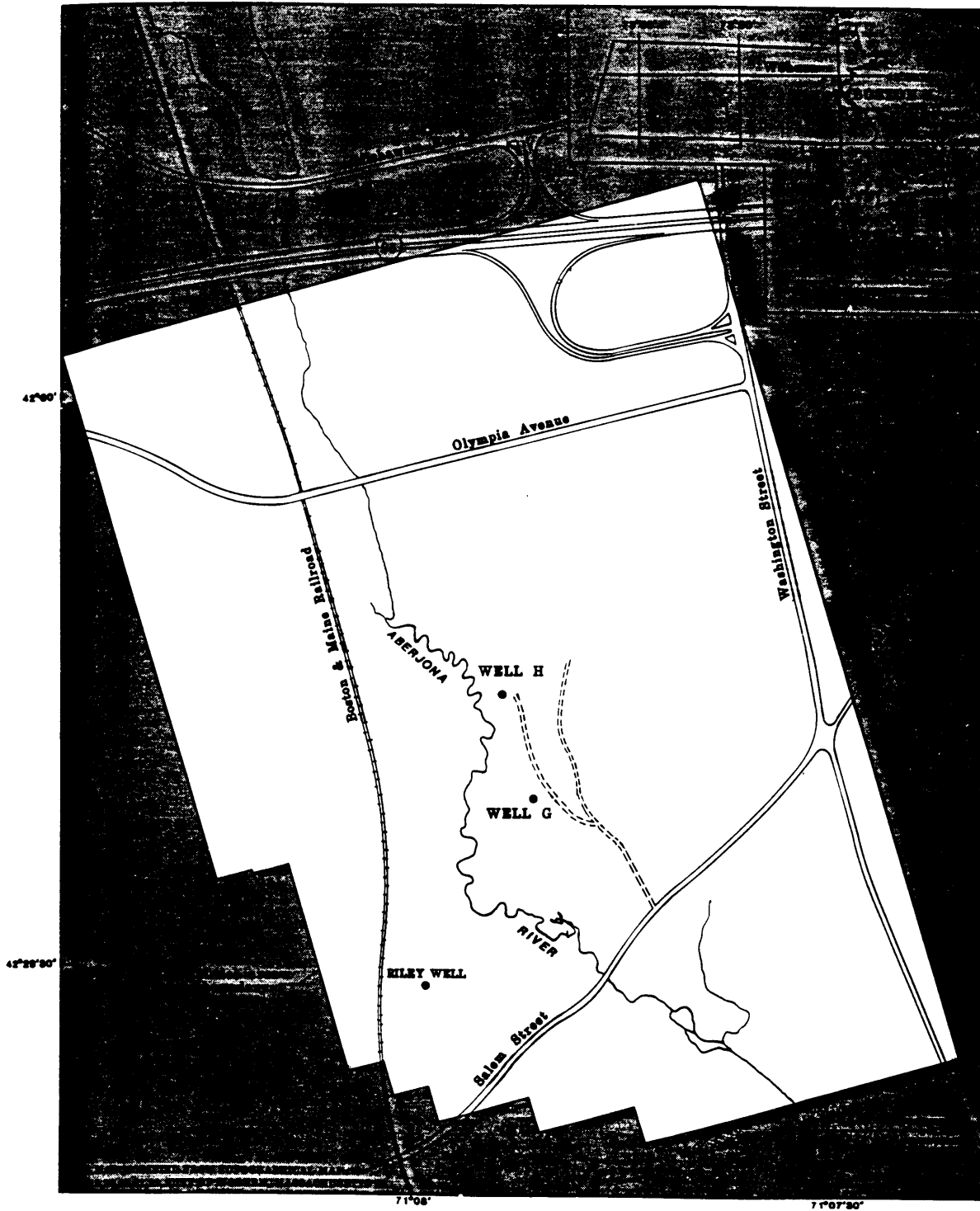


Fig. 2. Well G & H Site (source: Ebasco Services, 1989)

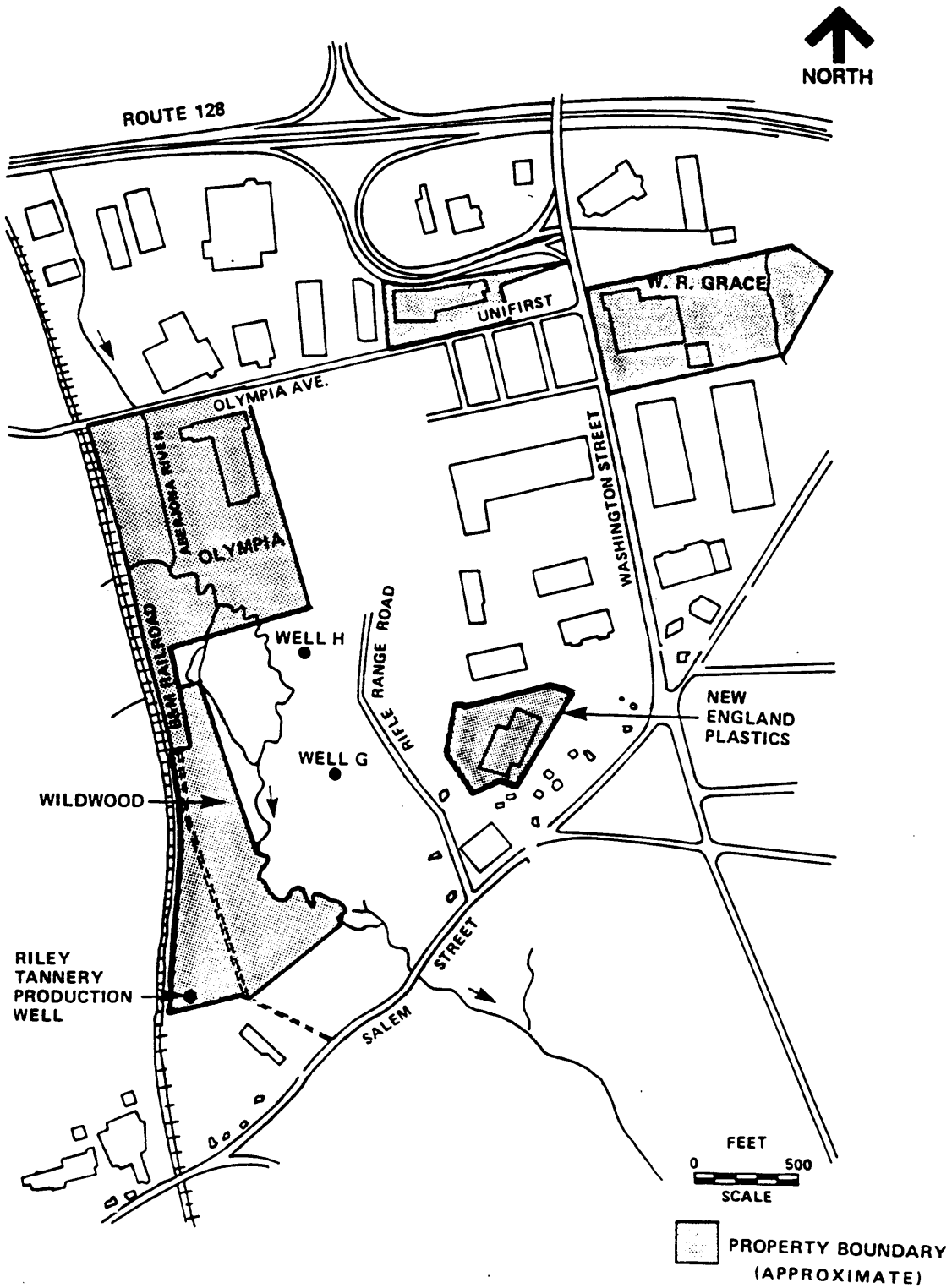


Fig. 3. A Representative Geologic Section and Ground-Water Discharge to Aberjona River (source: Myette et al., 1987)

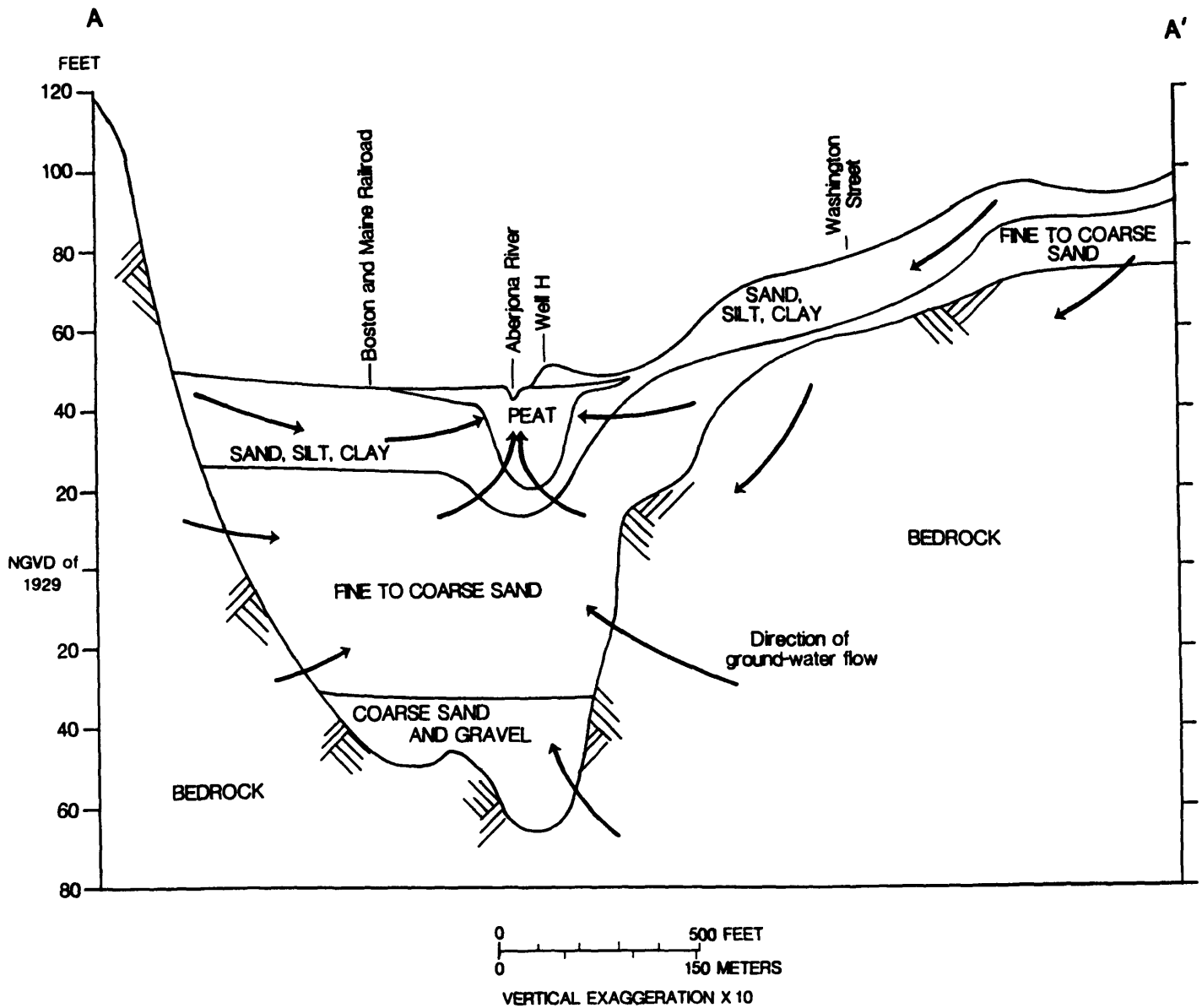


Fig. 4. Location of Source Plumes at the Wells G&H Site (source: Ebasco Services, 1989)

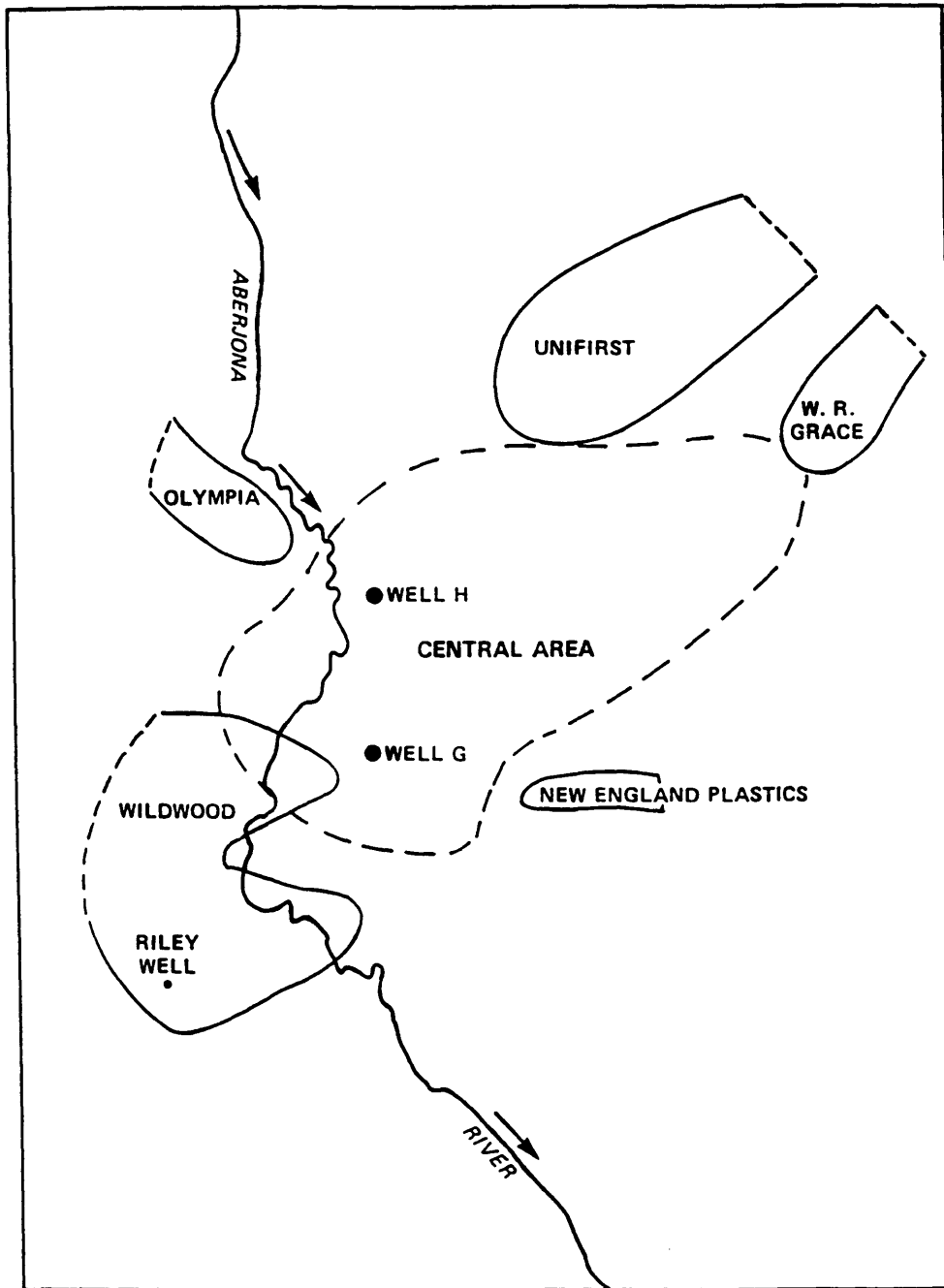


Fig. 5. Travel Path of VOCs from Source Areas to the Aberjona River

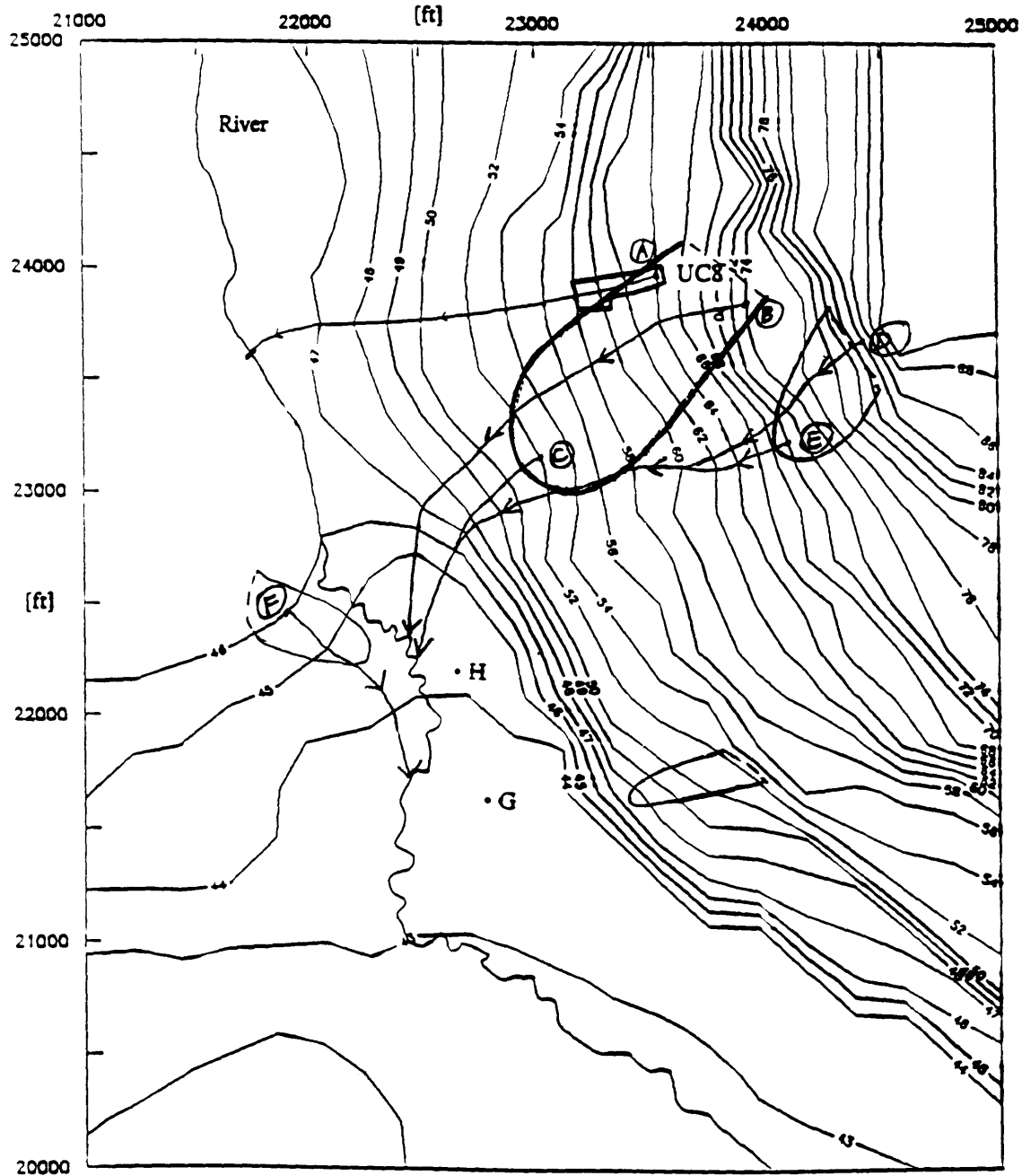


Table 1. Contamination Level of Volatile Organic Compounds and Cleanup Goal ($\mu\text{g/L}$) (source: Ebasco Services, 1989)

VOCs	Cleanup Goal*	Wildwood	Olympia	Unifirst	W.R. Grace	N.E. Plastics	Central Area
Chloroform	100	6000	-	5	-	1	10
TCE	5	190000	3400	684	2800	59	180
PCE	5	11000	45	20000	83	330	790
Methylene Chloride	-	800	7	25	3	9400	3
Vinyl Chloride	2	73			3600		
1,1,1-TCA	200	2800	2	1700		26	150
Ethylbenzene	680**	1000	5		350		
Toluene	2000**			400	3600		8
Total Xylene	440**	6800	170		630	6	
1,1-DCE	7	4508	23	700	7300	11	28

* Safe Drinking Water Act Maximum Contaminant Levels (MCLs)

** Safe Drinking Water Act Maximum Contaminant Level Goals (MCLGs)

Table 2. Retardation Factor of VOCs

VOCs	Retardation Factor	
	Subsurface Soil (n=0.25-0.40)	Peat (n=0.4-0.9)
Chloroform	2-3	7-86
Trichloroethene	4-7	18-230
Tetrachloroethene	8-16	44-590
Methylene Chloride	1	2-19
Vinyl Chloride	1	1-7
1,1,1-Trichloroethane	4-8	21-260
Ethylbenzene	14-26	76-1000
Toluene	6-11	30-400
o-Xylene	13-25	71-950
m-Xylene	14-28	81-1100

Table 3. Travel time of VOCs from source area to the Aberjona River

	Unifirst			W.R. Grace		Olympia
	A	B	C	D	E	F
Chloroform	15-25	30-50	10-20	5-15	10-20	10-20
Trichloroethylene	30-50	50-90	20-40	10-30	20-40	20-40
Perchloroethylene	60-110	100-190	40-80	30-70	50-90	50-90
Methylene Chloride	10-16	10-20	5-8	2-4	5-8	5-8
Vinyl Chloride	10-15	10-20	3-5	1-2	4-7	4-7
1,1,1-TCA	30-60	50-90	20-40	10-30	20-40	20-40
Ethyl Benzene	100-190	170-320	70-140	50-110	80-150	80-150
Toluene	40-80	70-130	30-60	20-50	30-60	30-60
<i>o</i> -Xylene	100-190	160-300	60-130	50-110	70-140	70-140
<i>m</i> -Xylene	100-260	200-360	70-140	60-140	80-160	80-160

Table 4. Contribution by each parameter for the uncertainties of the estimation of the travel time

	by n	by f_{oc}	by K_h	by n_p	by K_p	by $f_{oc,p}$	by Δz
Chloroform	3	14	37	10	15	12	8
Trichloroethylene	0	17	29	12	18	14	10
Perchloroethylene	2	17	25	13	18	15	10
Methylene Chloride	12	7	57	5	8	6	5
Vinyl Chloride	18	3	68	2	4	3	2
1,1,1-Trichloroethane	1	17	28	12	18	14	10
Ethyl Benzene	2	18	24	13	18	15	10
Toluene	1	17	26	13	18	14	10
<i>o</i> -Xylene	2	18	24	13	18	15	10
<i>m</i> -Xylene	2	18	24	13	18	15	10

VII. References

Anderson, G. D., What Needs To Be Done: A Policy Perspective on Ground Water and Soil Remediation, in *Ground Water and Soil Contamination Remediation: Toward Compatible Science, Policy, and Public Perception*, edited by Water Science and Technology Board, Commission on Engineering and Technical Systems, E. Commision on Geosciences and Resources., and National Research Council, p. 261, National Academy Press, Washington, D.C., 1990.

Avery, C., D. Yeskis, and W. Bolen, Interaction of ground water with the Rock River near Byron, Illinois. Abstracts of American Geophysical Union Fall Meeting December 9-13, 1991.

Bialon, J. L., *Characterization of the Physical and Engineering Properties of the Aberjona Wetland Sediment*, M.S. Thesis, M.I.T.(Cambridge), 1993.

Bouwer, E. J., B. E. Rittmann, and P. L. McCarty, Anaerobic Degradation of Halogenated 1- and 2-carbon Organic Compounds, *Environ. Sci. Technol.*, 15, 596-599, 1981.

Brainard, E. C., *Groundwater Modeling of the Aberjona Basin*, M.S. Thesis, M.I.T., 1980.

Ebasco Services, I., Feasibility Study Report, Wells G&H Site, Woburn, Massachusetts. EPA Work Assignment Number: 132-1L46, EPA Contract Number: 68-01-7250.

Freeze, R. A., and J. A. Cherry, *Groundwater*, Prentice-Hall,inc., Englewood Cliffs,NJ, 1979.

Fusillo, T., B. Sargent, R. Waler, T. Imbrigiotta, and W. Ellis Jr., Investigation of the discharge of groundwater containing volatile organic compounds into a stream at Picatinny Arsenal, New Jersey. Abstracts of American Geophysical Union Fall Meeting December 9-13, 1991.

Genereux, D. P., *Field studies of streamflow generation using natural and injected tracers on bickford and walker branch watersheds*, Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, 1991.

Genereux, D. P., and H. F. Hemond, Naturally occurring radon 222 as a Tracer for streamflow generation:steady state methodology and field example, *Water Resour. Res.*, 26, 3065-3075, 1990.

GeoTrans, inc, Wells G&H Site Remedial Investigation Report, Part 1, Woburn, Massachusetts. Prepared for W.R. Grace & Co.

GeoTrans, inc, W.R.Grace Remedial Action, Well G & H Site, Woburn, Massachusetts, Annual Report for September 1992-September 1993. Prepared for W.R. Grace & Co.-CONN.

GeoTrans, inc, W.R.Grace Remedial Action, Well G & H Site, Woburn, Massachusetts, Annual Report for October 1, 1993-September 30, 1994. Prepared for W.R.Grace & Co.-CONN.

Gupta, S., G. V. Houtven, and M. L. Cropper, Do Benefits and Costs Matter in Environmental Regulation? An Analysis of EPA Decisions under Superfund, in *Analyzing Superfund: Economics, Science, and Law*, edited by R. L. Revesz, and R. B. Stewart, p. 263, Resources for the Future, Washington,DC, 1995. (N)

Hazardous Waste Treatment Council, Right Train, Wrong Track: Failed Leadership in the Superfund Cleanup Program. Washington, DC. June.

Karickhoff, sd, and T. Scott, Sorption of hydrophobic pollutants on natural sediments, *Wat. Res.*, 13, 241-248, 1979.

Kerfoot, H. B., Soil-Gas Measurement for Detection of Groundwater Contamination by Volatile Organic Compounds, *Environ. Sci. Technol.*, 21, 1022-1024, 1987.

Kerr Jr., J. M., Investigation and remediation of VOCs in soil and groundwater, *Environ. Sci. Technol.*, 24, 172-173, 1990.

Kim, H., *Discharge of volatile organic compounds from a contaminated aquifer and their fate in a stream*, Ph.D. Dissertation, Massachusetts Institute of Technology (Cambridge), 1995.

Kline, S. J., The purpose of uncertainty analysis, *J. Fluids Eng.*, 107, 153-160, 1985.

Lautenberg, F. R., and D. Durenberger, *Cleaning Up the Nation's Cleanup Program. Report to Senate Subcommittee on Superfund, Ocean, and Water Protection, U.S. Congress, Washington, DC, May.*

Lester, B. H., and J. W. Mercer, *Comparative Evaluation of Groundwater Biodegradation Models: Summary of the API Workshop. Proceedings of the 1995 Petroleum Hydrocarbons and Organics Chemicals in Ground Water, Nov.29-Dec.1, Houston, Texas.*

Macdonald, J. A., and M. C. Kavanaugh, *Restoring contaminated groundwater:an achievable goal?*, *Environ. Sci. Technol.*, 28, 362A-368A, 1994.

Mackay, D. M., and J. A. Cherry, *Groundwater contamination: Pump-and-treat*

remediation, *Environ. Sci. Technol.*, 23, 630-636, 1989.

Myette, C. F., J. C. Olimpio, and D. G. Johnson, Area of Influence and Zone of Contribution to Superfund-Site Wells G and H, Woburn, Massachusetts. U.S.G.S., Water-Resources Investigations Report 87-4100, 1987. (N)

Office of Technology Assessment, Coming Clean: Superfund Problems Can Be Solved. U.S.Congress, October.

Phillips, S. P., S. Beard, and R. J. Gilliom, Estimation of the quantity and quality of groundwater inflow to the San Joaquin River, California, *EOS, Transactions of the American Geophysical Union*, 72(44), 168, 1991.

Probst, K. N., D. Fullerton, R. E. Litan, and P. R. Portney, *Footing the Bill for Superfund Cleanups: Who Pays and How?*, Resources for the Future, Washington,DC, 1995.

Reynolds, J. E., *Three-Dimensional, Transient Groundwater Modeling of the Aberjona Watershed*, M.S. Thesis, M.I.T.(Cambridge), 1993.

Schwarzenbach, R. P., P. M. Gschwend, and D. M. Imboden, *Environmental organic chemistry*, John Wiley & Sons, Inc., New York, 1993.

Siegel, D. I., and D. W. Ericson, Hydrology and water quality of the Copper-Nickel area, northeastern Minnesota. U.S. Geological Survey Water-Resources Investigations Report 80-739.

Squillace, P. J., and E. M. Thurman, Sources of atrazine and desethylatrazine in a selected reach of the Cedar River, Iowa, during baseflow conditions, *EOS, Transactions of the American Geophysical Union*, 71(43), 1341, 1990.

Swallow, J. A., *Volatilization of Organic Compounds from Shallow Phreatic Aquifers*, M.S. Thesis, M.I.T. (Cambridge), 1983.

Tedrow, *Soils of New Jersey*, Krieger Publishing Company, Malabar, Florida, 1986.

The Johnson Company, I., Year 1 Annual Report: Groundwater Extraction and Treatment System for the UniFirst Site. Prepared for UniFirst Corporation, Submitted to U.S.Environmental Protection Agency Region I.

The Johnson Company, I., Year 2 Annual Report: Groundwater Extraction and Treatment System For The UniFirst Site. Prepared for UniFirst Corporation, Submitted to U.S.Environmental Protection Agency Region I.

Travis, C. C., and C. B. Doty, Can contaminated aquifers at Superfund sites be

remediated?, *Environ. Sci. Technol.*, 24, 1464-1466, 1990.

U.S.EPA, Wells G & H, Record of Decision.

U.S. EPA, Wells G&H Site Responsiveness Summary, Woburn, Massachusetts.

U.S. Geological Survey, Hydrogeology and Simulation of Ground-Water Flow at Superfund-Site Wells G and H, Woburn, Massachusetts. Prepared in cooperation with the U.S.Environmental Protection Agency Waste Management Division, Region I.

< Map format undefined - will use Standard: >

U.S.Geological Survey (1987): Reading, Massachusetts. U.S.Department of the Interior. 7.5x15 minute series (topographic). Map 42071-E1-TM-025. Scale 1:25000.

Vroblesky, D. A., M. M. Lorah, and S. P. Trimble, Mapping zones of contaminated ground water discharge using creek-bottom-sediment vapor samplers, Aberdeen Proving Ground, Maryland, *Ground Water*, 29, 7-12, 1991.

Zeep, P., Personal communication. Doctoral Candidate, Department of Civil and Environmental Engineering, M.I.T.

APPENDIX

Natural Discharge of VOCs from a Contaminated Aquifer to Surface Waters

Heekyung Kim and Harold F. Hemond

To be submitted to *Water Resources Research* or *Water Research*.

Abstract

Although volatile organic compounds (VOCs) can be naturally discharged from a contaminated aquifer and thus the natural discharge has the potential to clean the contaminated aquifer at no cost, little attention has been paid in the past to estimating the importance of natural discharge in the cleanup. In this paper, the concentrations and total fluxes of VOCs in the groundwater discharging to streams were measured in the headwaters of the heavily industrialized Aberjona watershed eastern in Massachusetts 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. Measurements were made throughout 2 years, with spatial resolution ranging from tens to hundreds of meters. Concentrations in the inflow as low as $0.05 \mu\text{g/L}$ of benzene could be reliably detected in East Drainage Ditch; the largest inflow observed was $2200 \mu\text{g/L}$ of trichloroethylene in Sweetwater Brook. The total natural discharge rate of all identified VOCs from all tested sites was estimated to be 140 kg/yr . This amount was of similar magnitude to the mass of VOCs removed by on-going remediation efforts at two locations in a Superfund site in the watershed, suggesting that the natural discharge rates of contaminated aquifers under natural gradient conditions should be considered in developing remediation strategies at hazardous sites.

Introduction

Volatile organic compounds (VOCs) are widely distributed and problematic contaminants in groundwater. Although the remediation of groundwater contaminated with VOCs is often mandated, the inherent complexities of the Earth's subsurface and the characteristics of the contaminants can make remediation exceedingly difficult and costly [Macdonald and Kavanaugh, 1994]. In determining the remediation, natural attenuation process such biodegradation has begun to be paid attention as a part of remediation strategies [Lester and Mercer, 1995]. However, the natural discharge of contaminants from an aquifer has not been quantified and the significance of their natural discharge in cleaning a contaminated aquifer has not been investigated enough.

Since groundwater is often discharged to surfacewater, VOCs in the groundwater are naturally discharged from some contaminated aquifers. Remediation alternatives such as the pump-and-treat systems, commonly used to clean contaminated groundwater in the United States, might or might not improve on this natural rate, and in some cases could arguably retard the natural discharge of VOCs by altering the natural head difference between the groundwater and streams. Therefore, quantitative estimates of natural discharge rate of VOCs from a contaminated aquifer are important to sound remediation plans.

In this work, we investigated the natural discharge 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.1). Chemical wastes have been discharged into the Aberjona watershed for over 150 years, and chemical contamination has been documented at over 50 sites. Two Superfund sites have been designated in the watershed. Although arsenic and other inorganic contaminants dominate some sites, contamination of groundwater with VOCs has been a major concern. Pump-and-treat systems have been employed at two locations in one Superfund site (Well G & H area) since 1993. The objectives of this work were to identify locations on the upper watershed where the discharge of contaminated groundwater occurs, to measure discharge rates of contaminants under natural gradient conditions, and to compare the natural discharge in relationship to the results of remediation efforts.

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. [Lee and Cherry, 1978; Lee and Hynes, 1978] 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. [1991] 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. [1991] 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, Vroblecky et al. [1991] used vapor samplers composed of activated carbon fused to a ferromagnetic wire 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 very local studies, 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 uncertainty in total flux if inferences about a reach of stream must be made 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 desired reaches of stream.

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 (e.g. coarse gravel). The use of in-stream tracer techniques to measure inflows of naturally-occurring substances is described by Genereux and Hemond [1990], who used introduced tracers to determine levels of ^{222}Rn , an indicator of hydrologic flow path, entering streams 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 [Genereux and Hemond, 1990]:

$$\frac{dC}{dx} = \frac{q}{Q} C_q - \left(\frac{q}{Q} + \frac{k_v}{U} \right) C \quad (1)$$

where C is concentration of a VOC in the stream [$\mu\text{g/L}$], 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 [$\mu\text{g/L}$], 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}].

Mass balance for the injected conservative tracer enables the determination of q . Incorporation of q into mass balance of the volatile tracer then permits the determination of k_v . Knowing the ratio of the volatilization rate of a volatile organic compound to that of the volatile tracer, and measuring the volatilization rate of the tracer in a stream, gives an estimate of the volatilization rate of the volatile organic compound. This in turn permits calculation of C_q , the lateral inflow concentration of the compound. It is convenient, but not essential, that the volatile tracer has a gas exchange coefficient similar 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 [Smith et

al., 1980; Tsivoglou et al., 1965]. Thus k_v for the volatile tracer provides a good basis for estimating k_v of the compound of interest [Smith et al., 1980; Tsivoglou et al., 1965].

Methods

Study Sites

The streams studied were in the upper portion of the Aberjona River watershed (Fig.1). 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 selected, after reconnaissance, for the presence of elevated concentrations of VOCs (Fig.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 1.

Tracer Methodology

Genereux and Hemond [1990] present derivation of expressions from which the flowrates, the lateral inflow rate, and the concentration of a volatile chemical in water entering a reach of stream are determined from concentration measurements of stream water together with measurements of two introduced tracers. The results are:

$$Q_i = \frac{Q_{inj} C_{inj}}{\alpha S_i} \quad (2)$$

$$Q_{ij} = \frac{C_{inj} Q_{inj}}{\alpha \Delta x_{ij}} \left(\frac{1}{S_j} - \frac{1}{S_i} \right) \quad (3)$$

$$C_{ij}^x = \frac{S_i C_j^x - S_j C_i^x + \frac{1}{4} (S_j + S_i) (C_j^x + C_i^x) \lambda^x \ln \left(\frac{G_i S_j}{G_j S_i} \right)}{S_i - S_j} \quad (4)$$

where Q_i is the flowrate at the i^{th} 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 factor relating the conductivity reading to the concentration of salt in solution [M/ μ S], S_i is the increase in specific conductivity at station i after the injection of salt solution [μ S], q_{ij} is groundwater lateral inflow between station i and j [L/m-s], Δx_{ij} is distance between the i^{th} and j^{th} station [m], C_{ij}^x is concentration of a VOC, x , in the inflow between station i and j [μ g/L], C_j^x is the concentration of a VOC, x , found at station j [μ g/L], G_i is concentration of propane at station i [μ g/L], and λ^x is the ratio of the volatilization rate constant of the VOC of concern, x , to that of the volatile tracer.

Field Methodology

Continuous stream reaches from several tens to 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 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 adequate transverse mixing.

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 for these purposes in the streams studied [Kim et al., 1995]. It was confirmed in the same study that the attenuation of trichloroethylene concentration due to volatilization was well predicted

in a stream using the propane gas as a tracer.

Background conductivity was measured at all stations for about 10 minutes before the injection of tracers began, using a portable conductivity meter (Amber Science Digital Conductivity Meter, model 604). After the injection of tracers began, the conductivities were measured every 30 seconds until a steady state was attained. Water samples were then taken at each station in 300-mL BOD bottles, preserved with 2.4 ml of 3.5 % mercuric chloride solution.

In general, the ratio of the volatilization rate constant of a VOC of interest to that of propane, λ , is not unity. To estimate λ , we used ratios from Smith et al. [1980] where possible; otherwise, we calculated the ratio on the basis of 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.

Finally, the concentration of VOCs in the lateral inflow was calculated by Eqn (3). The errors associated with estimates of inflow rates were calculated conservatively, as presented elsewhere [Kim, 1995].

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). VOCs were 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, He 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 system 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. Reproducibility was examined by analyzing triplicate standards and shown to be better than $\pm 5\%$.

Results

Sweetwater Brook

Hydraulics. The Sweetwater Brook site was divided into either 3 or 5 reaches for each experiment, and studied over a 2-year period. Typical baseflow between 66 m and 550 m downstream from SWBK 2950 was approximately 60 L/s in spring, and

about half this value in summer and fall. Only one datum, 46 L/s, was obtained 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.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, between 217 m and 283 m from SWBK 2950 (data not shown).

VOCs. Trichloroethylene (TCE) was the VOC of highest concentration at the Sweetwater Brook site, ranging from 10 to 40 $\mu\text{g/L}$. 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 this study, the concentration of TCE at 66 m increased steadily from 0.1 $\mu\text{g/L}$ on 6/3/91 to 33 $\mu\text{g/L}$ on 11/14/92. It became evident that there was not only inflow of TCE between 66 m and 116 m, but there was a long-term trend toward increasing inflow between 33 m and 66 m.

The concentrations of VOCs in lateral inflow between 33 m and 66 m were not determined until April, 1992, after which they reached values as high as 2200 $\mu\text{g/L}$ for TCE (Fig.4a) and 200 $\mu\text{g/L}$ for 1,2-DCE (Fig.4b). The concentrations of TCE and 1,2-DCE in the lateral inflow of the reach between 66 m and 116 m ranged

up to 460 $\mu\text{g/L}$ (Fig.4a) and 49 $\mu\text{g/L}$ (Fig.4b), respectively. This finding is consistent with earlier observations of TCE in this stream in the range of concentration of 10 to 150 $\mu\text{g/L}$ [Ecology and Environment, 1980]. There was no detectable influx 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

Reach I is the furthest upstream among the studied reaches in the East Drainage Ditch, also known as the New Boston Drainway. The lateral inflow was very low, only 0.011 L/s/m; VOC concentrations in the inflow were 23 $\mu\text{g/L}$ of 1,1,1-trichloroethane and 12 $\mu\text{g/L}$ of trichloroethylene (Fig.7b). Toluene was not found in East Drainage Ditch I.

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. Measured flow varied from 5 L/s to 42 L/s; the average of flowrates measured in spring, summer, fall and winter months were 23, 9, 15 and 15 L/s, respectively.

The reach between 0 to 134 m typically showed the highest lateral inflow rates among the three reaches (Fig.5), from undetectable (10/27/91 and 5/30/92) to 0.053 L/s/m (5/3/92). When treated as 3 subreaches on 9/28/91, most of the inflow (0.025

L/s/m) occurred between 44 and 88 m; inflow between 0 m and 44 m was 0.014 L/s/m and inflow between 88 m and 133 m was 0.0023 L/s/m.

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.5). In the last downstream reach (266 m to 400 m downstream from EDDW 4800), the inflows ranged 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, including 1,1-dichloroethane (DCA), 1,2-dichloroethene (DCE), 1,1,1-trichloroethane (TCA), carbon tetrachloride (CCl₄), 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 [Kim et al., 1995]. 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 ranged from 0.5 to 13 µg/L and from less than 0.05 to 3.1 µg/L, respectively.

In all experiments, inflow to the subreach furthest upstream (0 to 133 m downstream from EDDW 4800) contained the highest levels of chlorinated VOCs, including DCA, DCE, TCA, CCl₄ and TCE (Fig.6). The most abundant were TCE and 1,2-DCE. Despite the high levels of toluene at this site, inflow of toluene could not be demonstrated; the major toluene source lies upstream (but below East Drainage Ditch I).

Only two experiments, on 7/3/90 and 7/19/92, showed VOCs in the lateral inflow to the second subreach (Fig.6). Only one experiment, on 3/1/92, showed the

inflow of a VOC (TCA) in the furthest downstream reach.

East Drainage Ditch III

East Drainage Ditch III showed the highest hydraulic inflow, 0.27 L/s/m, measured anywhere in the stream (Fig.7a). This portion of the East Drainage Ditch had low concentrations of VOCs in the inflow, 2.2 $\mu\text{g/L}$ of trichloroethylene and 0.05 $\mu\text{g/L}$ of benzene on the date measurements were made (Fig.7a).

Aberjona River

The Aberjona River site is directly downstream of the Industriplex Superfund site. This site showed a small lateral inflow (0.009 L/s/m), containing only 2.3 $\mu\text{g/L}$ of 1,1,1-trichloroethane (Fig.7c), even though some of the groundwater in the nearby Industriplex site is more highly contaminated with VOCs [Roux Associates et al., 1991].

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.7e).

Landfill Creek II

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.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.7d). Benzene and chlorobenzene were found in the inflow to the upstream subreach but no inflow of VOCs was found in the downstream subreach (Fig.7d). There was no measurable inflow in the whole reach on 9/25/90.

Discussion

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. The spatial variability was higher than expected, since the sites studied appear relatively homogeneous in their geological characteristics [Brainard, 1990]. Although there are few data with which to compare this spatial variability elsewhere, a high degree of heterogeneity in lateral inflow has been also found at Walker Branch [Ellins et al., 1990; Genereux, 1991; Huff et al., 1982; Lee and Hynes, 1978], where the geological setting appears to be much more heterogeneous than the Aberjona Valley.

Relation of VOC discharge to groundwater contamination

The discharge of VOCs via groundwater inflow to a stream necessarily indicates the contamination of nearby groundwater. It is therefore of interest to compare the VOC discharges located in this study with occurrences of groundwater

contamination previously known to exist. The East Drainage Ditch, among the experiment sites in this study, passes through a highly industrialized area and industries which are located adjacent to the ditch includes: Raffi & Swanson, Inc., Olin Corp. (formerly National Polychemical and Stepan Chemical), E.C. Whitney & Sons, Inc., Whitney Barrel Co., New England Pigments and Resins (formerly International Minerals Corporation), Former Stauffer Chemical Company Site, Woburn Steel Drum, and Ritter Trucking Company.

This study showed the discharge of TCA and TCE at East Drainage Ditch I at concentration of 10 $\mu\text{g/L}$ and 25 $\mu\text{g/L}$, respectively (Fig.8). Altevoigt [Altevoigt, 1994] also detected TCA in soil gas alongside this stream. Groundwater near the East Drainage Ditch I (Olin Chemical in Fig.8) has been shown to be contaminated with TCA (6 $\mu\text{g/L}$ average from over 70 monitoring wells, 22 $\mu\text{g/L}$ maximum), TCE (20 $\mu\text{g/L}$ average, 460 $\mu\text{g/L}$ maximum), benzene (11 $\mu\text{g/L}$ average, 120 $\mu\text{g/L}$ maximum) and toluene (300 $\mu\text{g/L}$ average, 12000 $\mu\text{g/L}$ maximum) [Olin Corporation, 1993]. A previous study [Ecology and Environment, 1982] also reported the Raffi & Swanson as a likely source of VOCs including toluene and 1,1,1-TCA in the East Drainage Ditch.

Toluene was found in this study to be discharged to the reach between East Drainage Ditch I and II (Fig.8). Groundwater in the southern part of the nearby Industri-Plex Superfund site (Fig.8) has been found to be contaminated with benzene (48 mg/L) and toluene (29 mg/L) [Roux Associates et al., 1991]. However, the source of toluene in this stream may not be related to the Industri-Plex site, because

the hydraulic gradient in this area is from northeast to southwest; thus the source of toluene discharged into this stream is suggested to lie north of the Industri-Plex site. Also, benzene was found at a much lower level (in the range of 1 $\mu\text{g/L}$) in this stream relative to toluene ($> 100 \mu\text{g/L}$), unlike groundwater in the Industri-Plex site. However, groundwater in a nearby state-identified hazardous waste site (Ritter Trucking Company site in Fig.8) was shown to be more significantly contaminated with toluene (1300 $\mu\text{g/L}$, [Toxic Systems Management, 1985]) than with benzene (200 $\mu\text{g/L}$, [Toxic Systems Management, 1985]).

The discharge of DCE and TCE to Sweetwater Brook was consistent with contamination reported in nearby groundwater [Ecology and Environment, 1981a]. The concentration of TCE in the inflow has changed along with that of DCE over the course of the experiments, suggesting that the source of TCE may be related to the source of DCE. The concentration of DCE to TCE in the inflow (approximately 0.1) was somewhat higher than the ratio of the concentration of DCE to TCE in a nearby monitoring well (0.04, estimated from 90 $\mu\text{g/L}$ of DCE and 2300 $\mu\text{g/L}$ of TCE, [Ecology and Environment, 1981b]). It has been reported that TCE can be biodegraded to DCE under methanogenic conditions [Vogel and McCarty, 1985], and some researchers have reported the ratio of DCE to TCE to be higher in the streambed-water samples than in ground water samples, as a result of the dechlorination of TCE [Fusillo et al., 1991]. However, at this site the difference was small and could also be due to spatial heterogeneity or different retardation factors for TCE and DCE.

Overall, TCA was the most 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 [Goldberg-Zoino and Associates, 1986; Hidell-Eyster Technical Services, 1986; TGG Environmental, 1989; Toxic Systems Management, 1985].

A significant amount of VOCs in the upstream end of the Aberjona watershed was shown to be naturally discharged and contaminate the East Drainage Ditch in this study. This finding is consistent with the recommendation of a previous study [GeoTrans, 1987] that the contamination of the upstream of the Aberjona River by the natural discharge might contaminate the remediation site (the Well G & H Superfund site) located at the downstream of the Aberjona River and thus, without considering the entire upstream end of the Aberjona River, EPA could not adequately evaluate the remedial alternatives for the remediation site.

Comparison of natural discharge from the aquifer and remedial efforts

The total of the estimated natural discharge rates of VOCs in the studied sites ranged from 5 g/yr of benzene to 40 kg/yr of TCE to 80 kg/yr of toluene (Fig.8). Most of the latter was toluene discharged from groundwater to within 100 m upstream from EDDW 4800. TCE removal by natural discharging at the Sweetwater Brook site approximated 90 kg over 2 years in our study.

For comparison, at Well G & H Superfund site remedial action has removed 16 kg of total VOCs from groundwater over two years at one location (W.R. Grace site, [GeoTrans, 1993, 1994]) and 16 kg of TCE and 300 kg of tetrachloroethene from groundwater for two years at another location [Unifirst site, The Johnson Company, 1993, 1994].

Conclusion

This study show that natural discharge is quantitatively significant in removing VOCs from the aquifer. Such information could be useful in planning aquifer cleanup. For example, it is possible that a pump and treat system improperly located, could actually retard aquifer cleanup by slowing down the natural discharge rate (e.g. by reversing the head difference between streams and groundwater). This study has also shown that the discharge of VOCs from groundwater to streams can be a practical tool to indicate contamination of groundwater. Determining the significance of natural discharging in cleaning contaminated groundwater, could help determine if employing any given remediation system would significantly augment or possibly delay the natural discharging at a contaminated site. It is recommended to consider natural flushing measurements for surveying for groundwater contamination on a watershed-wide basis as well as making decisions regarding remediation.

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References

Altevogt, A. S., *Soil Gas Analysis as a Predictor of VOC Concentrations in Groundwater and Stream Inflow*, MS Thesis, Massachusetts Institute of Technology, 1994.

Avery, C., D. Yeskis, and W. Bolen, Interaction of ground water with the Rock River near Byron, Illinois. Abstracts of American Geophysical Union Fall Meeting December 9-13, 1991.

Brainard, E., *Groundwater Modeling of the Aberjona Basin*, M.S. Thesis, Massachusetts Institute of Technology, 1990.

Durant, J. L., *Industrial History, Matagenicity, and Hydrologic Transport of Pollutants in the Aberjona Watershed*, M.S. Thesis, Massachusetts Institute of Technology, 1991.

Ecology and Environment, inc., Field Investigation of Uncontrolled Hazardous Waste Sites. FIT project, TDD #F1-8005-01E-05.

Ecology and Environment, inc., Field Investigations of Uncontrolled Hazardous Waste Sites. Inventory and Analysis of Existing Well Data for East and North

Woburn, Massachusetts, TOO No. F1-8010-03.

Ecology and Environment, inc., Preliminary Investigation of Surface and Groundwater Contamination in the Sweetwater Brook Watershed, Stoneham and Woburn, Massachusetts. TDD No. F1-8109-01.

Ecology and Environment, inc., Preliminary Investigation of Surface Water Contamination at the East Drainage Ditch, 1982.

Ellins, K. K., A. Roman-Mas, and R. Lee, Using ^{222}Rn to examine groundwater/surface discharge interaction in the Rio Grande De Manati, Puerto Rico, *J. Hydrol.*, 115, 319-341, 1990.

Fusillo, T., B. Sargent, R. Waler, T. Imbrigiotta, and W. Ellis Jr., Investigation of the discharge of groundwater containing volatile organic compounds into a stream at Picatinny Arsenal, New Jersey. Abstracts of American Geophysical Union Fall Meeting December 9-13, 1991.

Genereux, D. P., *Field studies of streamflow generation using natural and injected tracers on bickford and walker branch watersheds*, Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, 1991.

Genereux, D. P., and H. F. Hemond, Naturally occurring radon 222 as a Tracer for streamflow generation: steady state methodology and field example, *Water Resour. Res.*, 26, 3065-3075, 1990.

GeoTrans, inc., Wells G&H Site Remedial Investigation Report, Part 1, Woburn, Massachusetts. Prepared for W.R. Grace & Co.

GeoTrans, inc., W.R. Grace Remedial Action, Well G & H Site, Woburn, Massachusetts, Annual Report for September 1992-September 1993. Prepared for W.R. Grace & Co.-CONN.

GeoTrans, inc., W.R. Grace Remedial Action, Well G & H Site, Woburn, Massachusetts, Annual Report for October 1, 1993-September 30, 1994. Prepared for W.R. Grace & Co.-CONN.

Goldberg-Zoino and Associates, inc., Site Assessment Report, 3C Company, 181 New Boston Street, Woburn, Massachusetts. Prepared for Robert Weaver Jr. & Associates, Boston, Massachusetts.

Hayduk, W., and H. Laudie, Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions, *AIChE J.*, 20, 611-615, 1974.

Hidell-Eyster Technical Services, inc., Addendum to Environmental Site Assessment for Land Located at 11 Sixth Road, Woburn, Massachusetts. (Project #05-8682).

Huff, D. D., R. V. O'Neill, W. R. Emanuel, J. W. Elwood, and J. D. Newbold, Flow variability and hillslope hydrology, *Earth Surface Processes and Landforms*, 7, 91-94, 1982.

Kim, H., *Discharge of volatile organic compounds from a contaminated aquifer and their fate in a stream*, Ph.D. Dissertation, Massachusetts Institute of Technology (Cambridge), 1995.

Kim, H., H. F. Hemond, L. R. Krumholz, and B. A. Cohen, *In-situ* biodegradation of toluene in a contaminated stream: Part 1. field studies, *Environ. Sci. Technol.*, 29, 108-116, 1995.

Lee, D. R., and J. A. Cherry, A field exercise on groundwater flow using seepage meters and mini-piezometers, *Journal of Geological Education*, 27, 6-10, 1978.

Lee, D. R., and H. B. N. Hynes, Identification of groundwater discharge zones in a reach of hillman creek in southern Ontario, *Water Poll. Res. Canada*, 13, 121-133, 1978.

Lester, B. H., and J. W. Mercer, Comparative Evaluation of Groundwater Biodegradation Models: Summary of the API Workshop. Proceedings of the 1995 Petroleum Hydrocarbons and Organics Chemicals in Ground Water, Nov.29-Dec.1, Houston, Texas.

Macdonald, J. A., and M. C. Kavanaugh, Restoring contaminated groundwater:an achievable goal?, *Environ. Sci. Technol.*, 28, 362A-368A, 1994.

Olin Corporation, Comprehensive Site Assessment Phase II Field Investigation Report, Volume III. Wilmington Facility.

Roux Associates, inc., Environmental Science and Engineering, and PTI Environmental Services, Remedial Investigation, Ground-water/Surface-water Investigation Plan. Prepared for Industri-Plex Site Remedial Trust, 36 Commerce Way, Woburn, Massachusetts.

Schwarzenbach, R. P., P. M. Gschwend, and D. M. Imboden, *Environmental organic chemistry*, John Wiley & Sons, Inc., New York, 1993.

Smith, J. H., D. C. Bomberger Jr., and D. L. Haynes, Prediction of the volatilization rates of high-volatility chemicals from natural water bodies, *Environ. Sci. Technol.*, 14, 1332-1337, 1980.

TGG Environmental, inc., Environmental Studies, Tank/Soil Removal, 856 Woburn Street, Wilmington, Massachusetts. Prepared for Vanson Corporation, North Andover, Massachusetts.

The Johnson Company, inc., Year 1 Annual Report: Groundwater Extraction and Treatment System for the UniFirst Site. Prepared for UniFirst Corporation, Submitted to U.S.Environmental Protection Agency Region I.

The Johnson Company, inc., Year 2 Annual Report: Groundwater Extraction and Treatment System For The UniFirst Site. Prepared for UniFirst Corporation, Submitted to U.S.Environmental Protection Agency Region I.

Toxic Systems Management, inc., Site Report relative to hazardous materials for property located at 856 Woburn Street, Wilmington, Massachuesetts. Reported to DEQE, Northeast Regional Office, Woburn, MA.

Tsivoglou, E. C., R. L. O'Connell, C. M. Walter, P. J. Godsil, and G. S. Logsdon, Tracer measurements of atmospheric reaeration-1. laboratory studies, *J. Wat. Pollut. Control Fed.*, 37, 1343-1362, 1965.

Vogel, T. M., and P. L. McCarty, Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under

methanogenic conditions, *Appl. Environ. Microbiol.*, 49, 1080-1083, 1985.

Vroblesky, D. A., M. M. Lorah, and S. P. Trimble, Mapping zones of contaminated ground water discharge using creek-bottom-sediment vapor samplers, Aberdeen Proving Ground, Maryland, *Ground Water*, 29, 7-12, 1991.

Table A1. Characteristics of Study Sites

Studied Stream		Experiment Date	Length of Reach (m)	Sum of Concentration Ranges of Identified VOCs ($\mu\text{g/L}$)	Characteristics
East Drainage Ditch (EDDW 4800 ^a)	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.
	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 A2. 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	$0.92 \pm 0.30^{b,d}$
tetrachloroethylene	0.72 ± 0.13^a
trichloroethylene	0.79 ± 0.21^a
1,1,1-trichloroethane	$0.92 \pm 0.14^{b,d}$
benzene	0.78 ± 0.04^a
toluene	$0.86 \pm 0.05^{c,d}$
chlorobenzene	$0.73 \pm 0.04^{b,d}$
ethylbenzene	$0.62 \pm 0.05^{b,d}$

a. taken from [Smith et al., 1980].

b. calculated from molecular diffusion coefficients; molecular diffusion coefficients based on [Schwarzenbach et al., 1993].

c. calculated from molecular diffusion coefficients; molecular diffusion coefficients based on [Hayduk and Laudie, 1974].

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. A1. Study Site Location Map
 (source: [Durant, 1991])

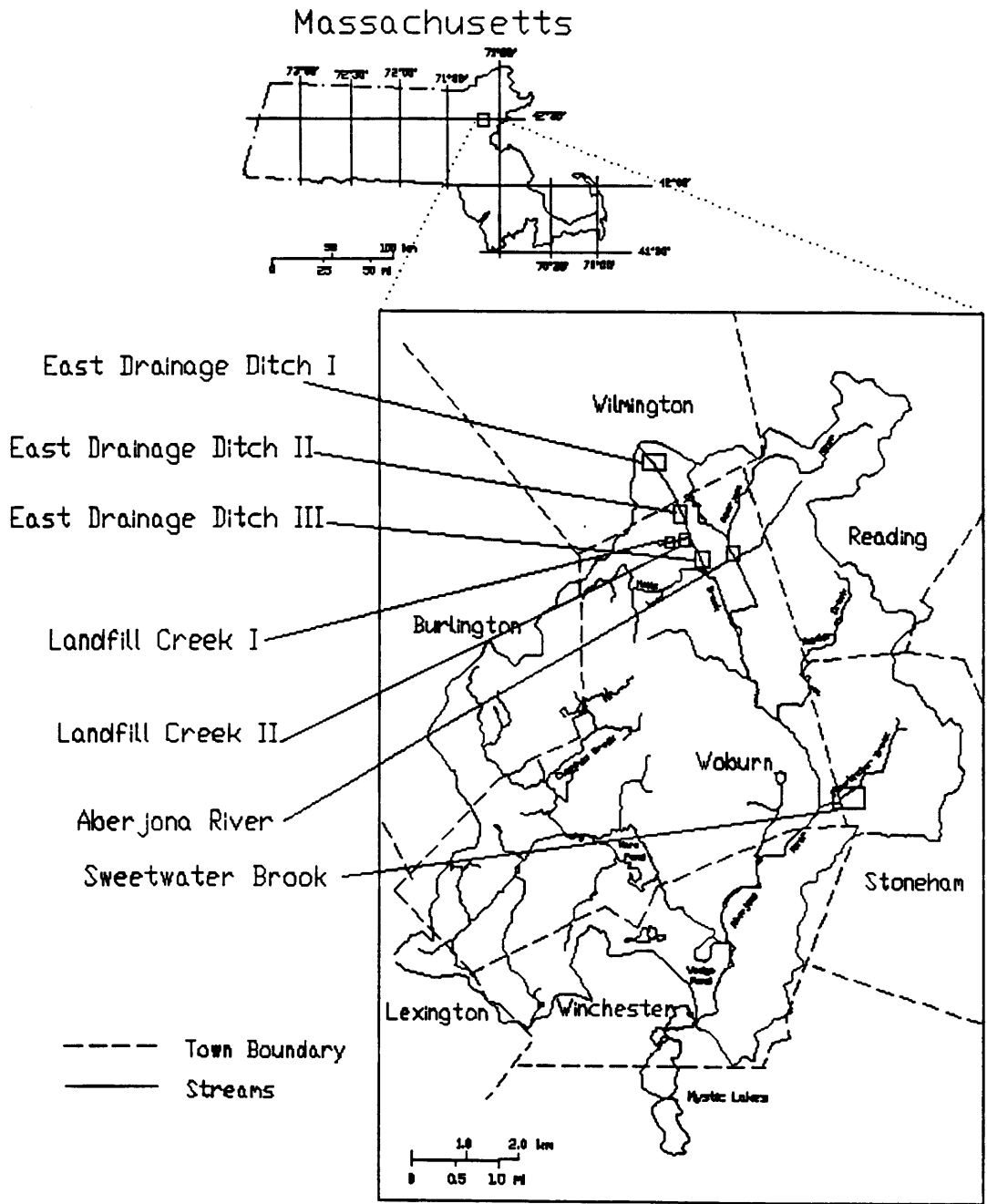


Fig. A2. Volatile Organic Compounds in Surfacewater and Groundwater^a
 a: Groundwater data were obtained from [Ecology and Environment, 1981a].

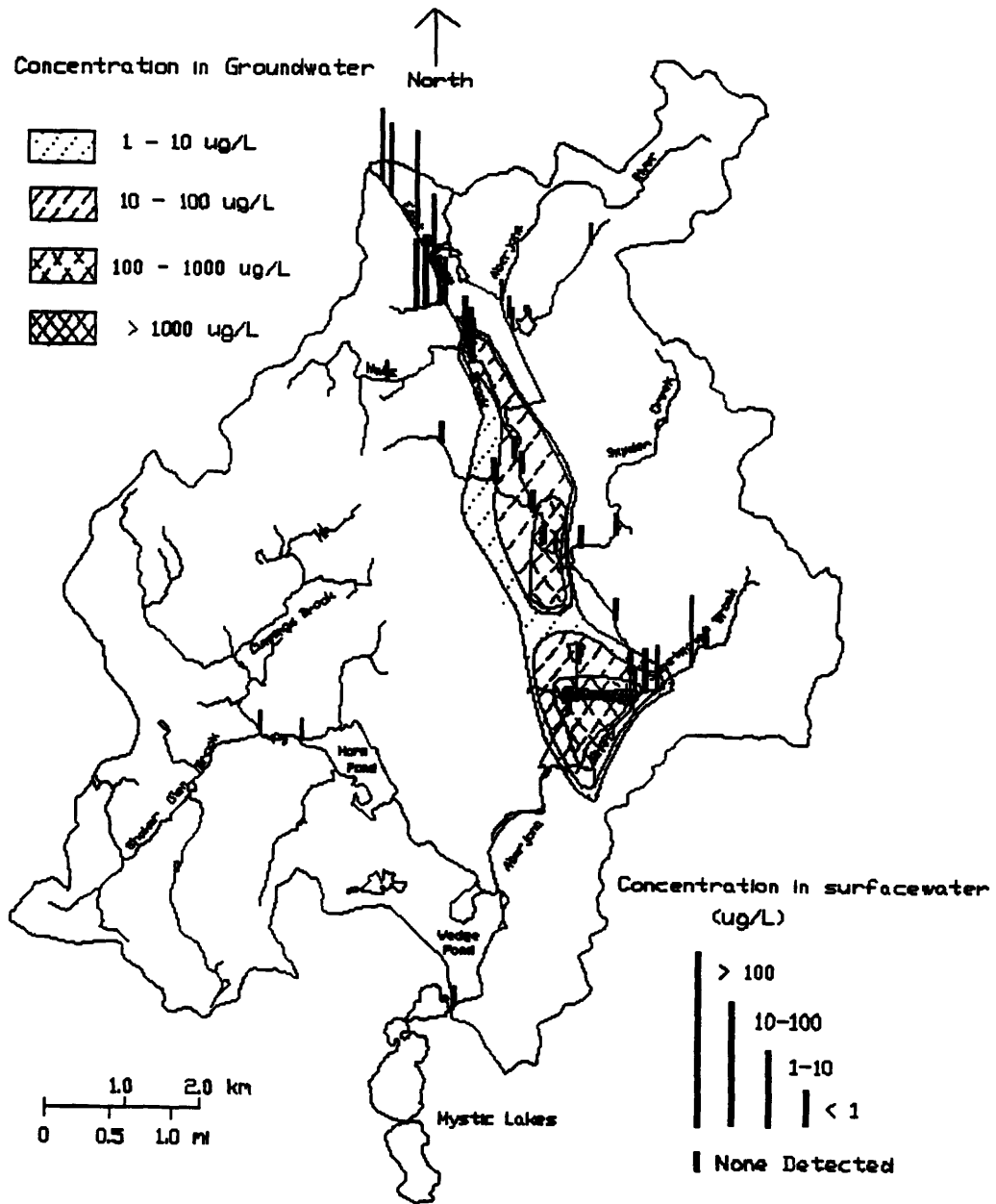


Fig. A3. Lateral Inflow at Sweetwater Brook

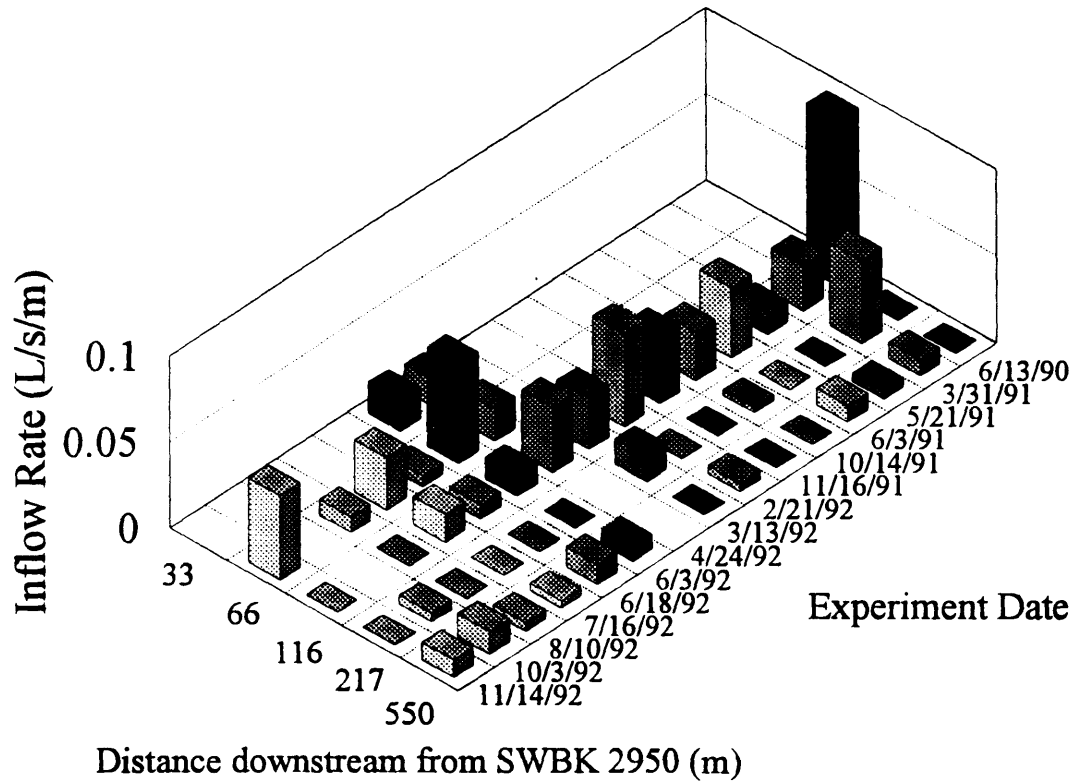
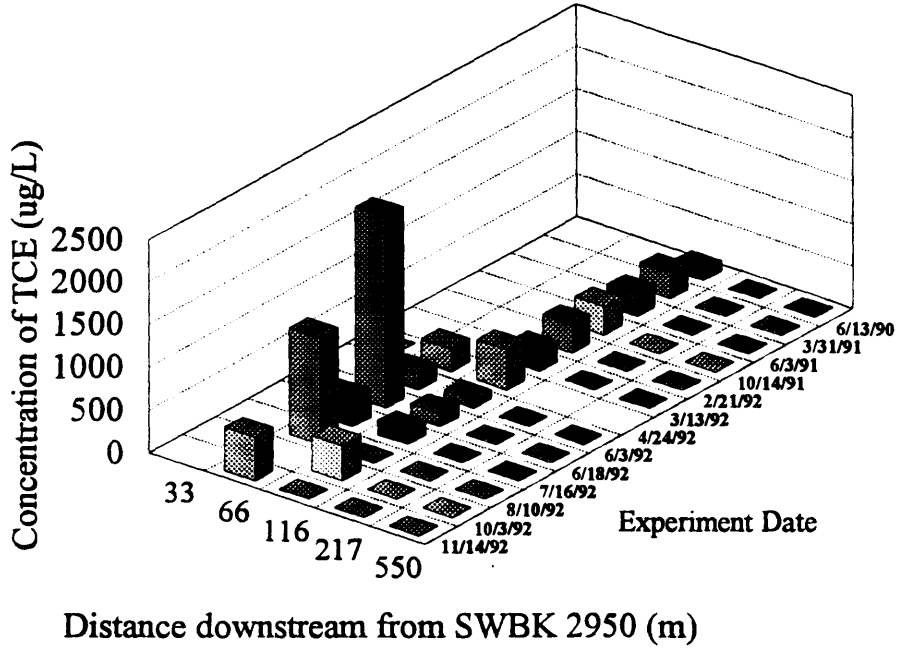


Fig. A4. VOCs in the Inflow at Sweetwater Brook

(a)



(b)

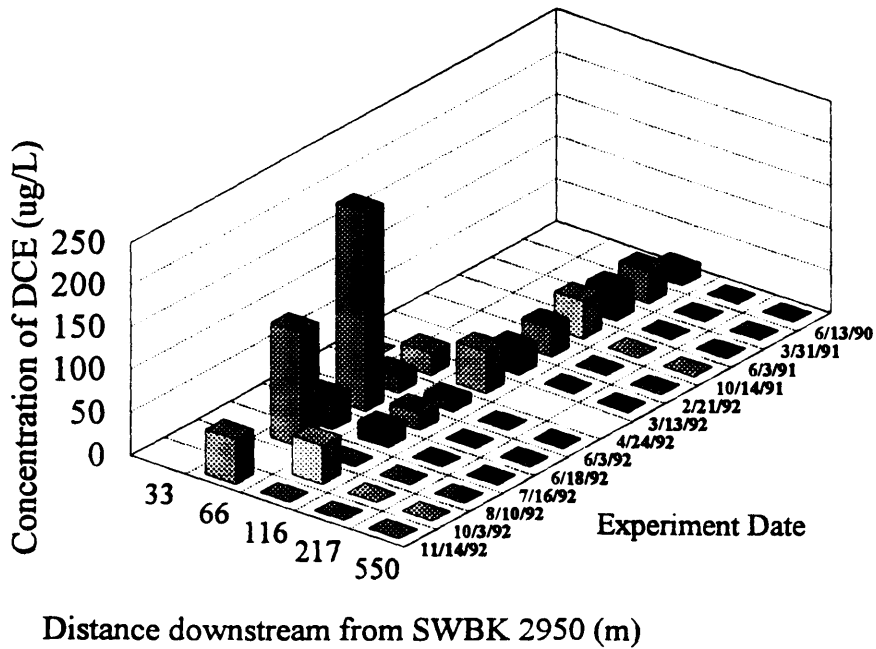


Fig. A5. Lateral Inflow at East Drainage Ditch II

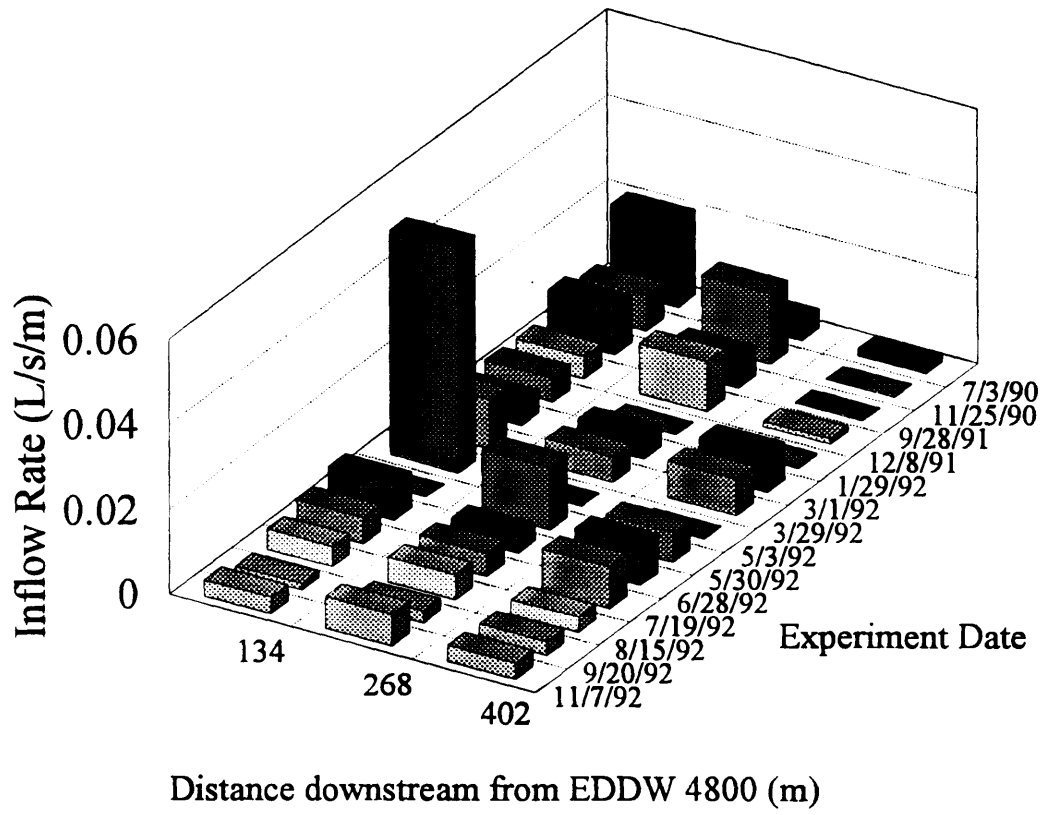


Fig. A6. VOCs in the Inflow at East Drainage Ditch II

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=CCl₄, e=TCE.

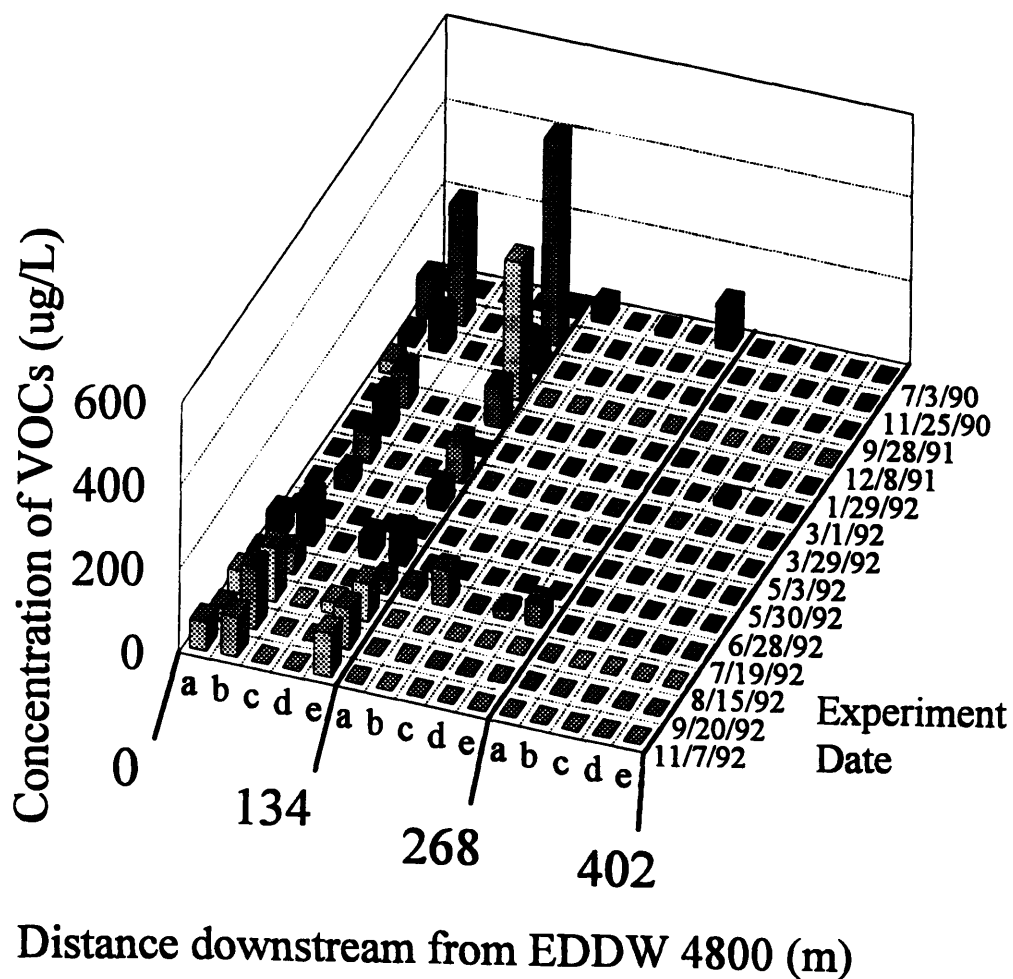


Fig. A7. Lateral Inflow and Discharge of VOCs at (a) East Drainage Ditch I, (b) East Drainage Ditch III, (c) Aberjona River, (d) Landfill Creek I, and (e) Landfill Creek II

(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 (e) is 2.4 $\mu\text{g/L}$ not 13 $\mu\text{g/L}$.)

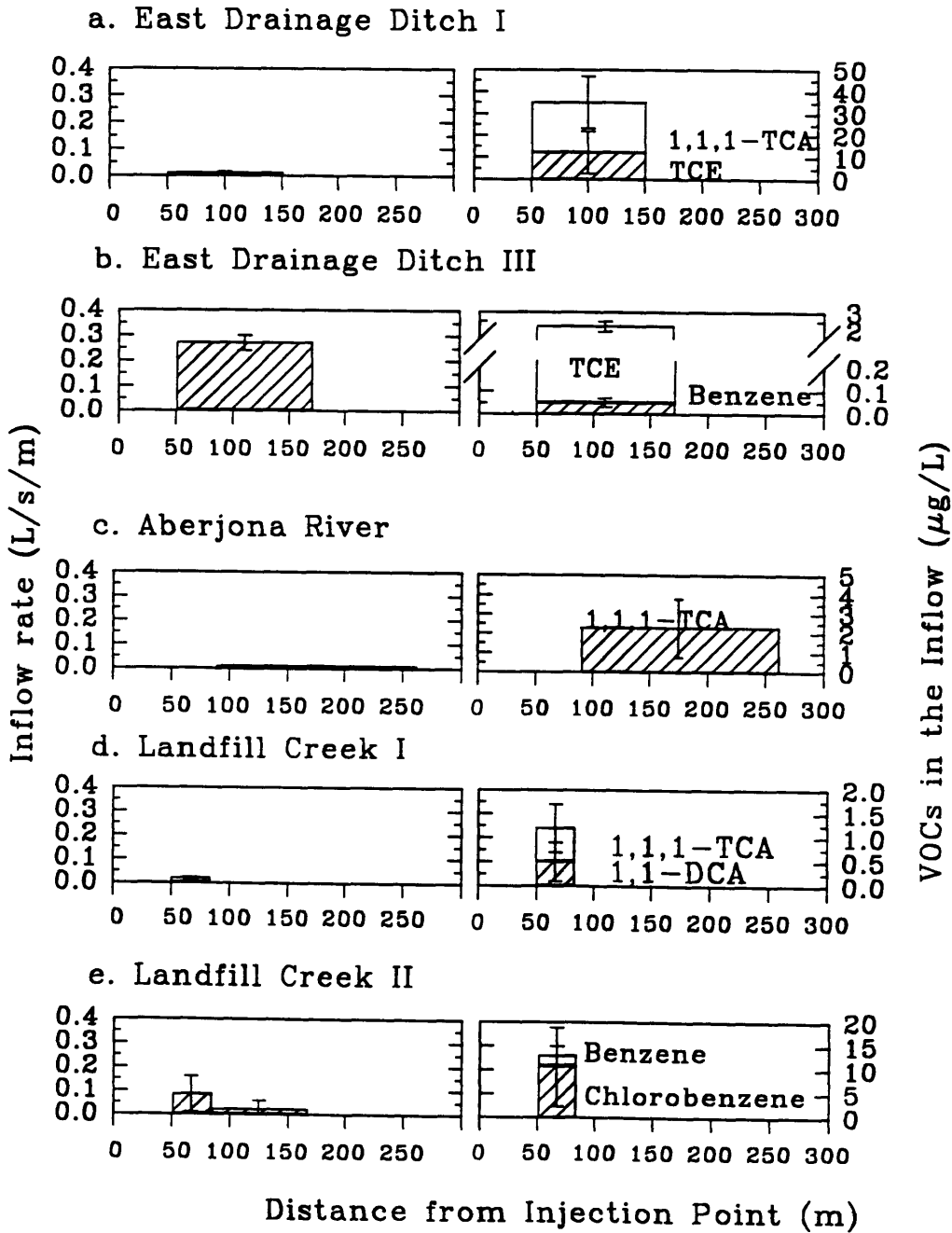
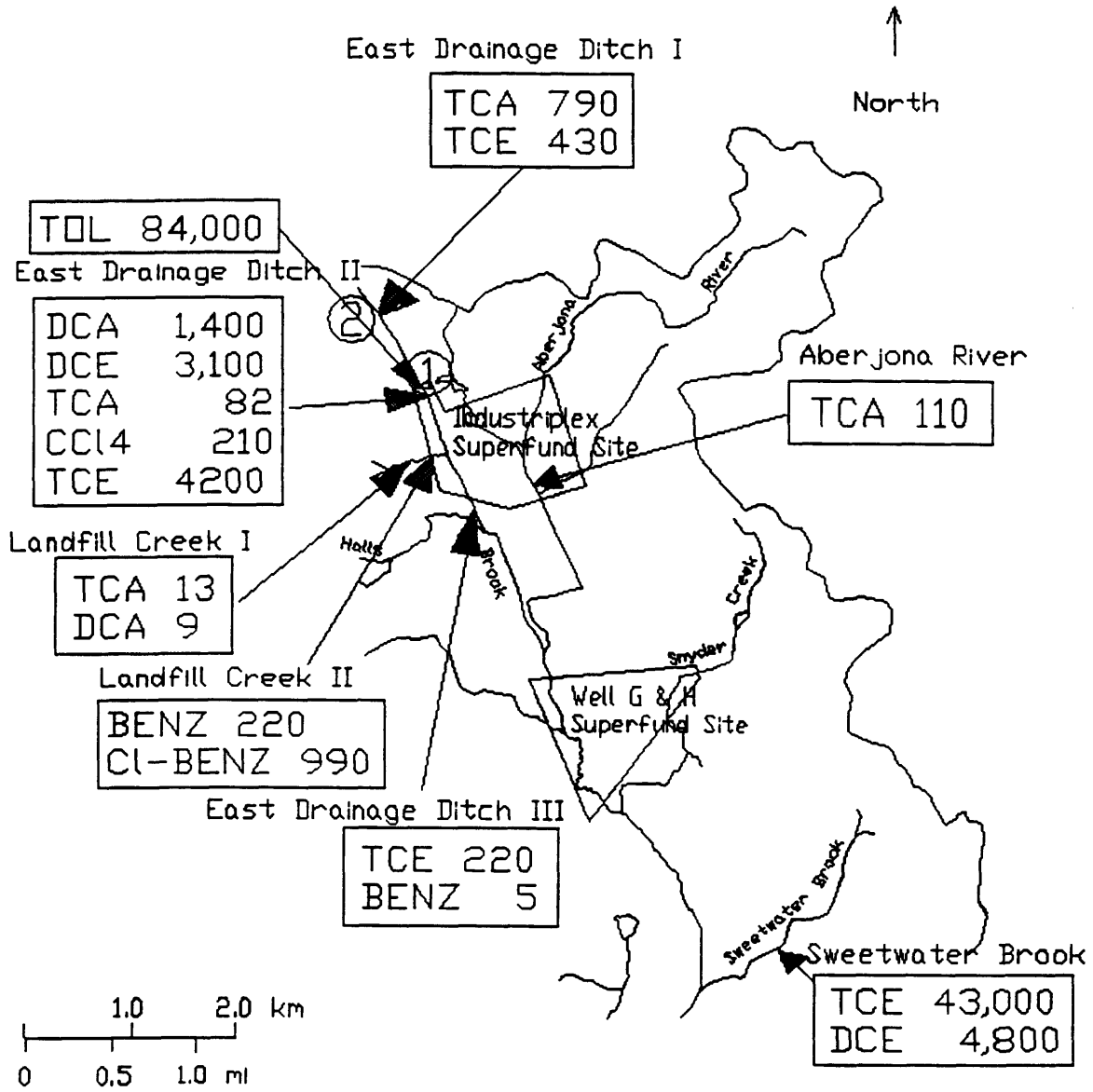


Fig. A8. Natural Discharging Rates of VOCs (g/yr)



○ = State-confirmed hazardous sites
 1 = Ritter Trucking Company, Wilmington
 2 = Olin Chemicals, Wilmington